

Photochemistry of Organic Molecules

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A WORD TO THE USER

ACS AUDIO COURSES are instructional units on subjects of significant interest that are suitable for both individual study and group use.

The ACS AUDIO COURSE on "Photochemistry of Organic Molecules," by Professor Nicholas J. Turro of Columbia University, is designed to enable the listener to gain a broad view of the field of organic photochemistry, to be able to read critically and intelligently articles on photochemical processes, and to be able to apply principles put forth to practical situations. No mathematical background is required, but a background in undergraduate-level organic and physical chemistry is assumed.

This volume is the reference manual that is integrated with the audiotape of "Photochemistry of Organic Molecules." The two together--the tape and manual--comprise the ACS AUDIO COURSE; neither is complete without the other. Because the lecturer refers constantly to the manual, each listener should have a copy of the manual as he listens, so he may follow these references.

This manual was not written to be a self-sufficient textbook. It was designed, rather, to be used as a workbook while listening to the tape. The listener is urged to take notes with the expectation that this activity will reinforce the learning process. The product is a personally annotated volume which should serve as an authoritative and up to date introduction to the subject.

Your comments and suggestions have proved to be exceptionally valuable guides for improving our educational programs. We hope you will continue to send them to us.

Department of Educational Activities
American Chemical Society

OUTLINE

1. The Nature and Behavior of Electronically Excited Molecules

- 1.0 Electronic excitation
- 1.1 Electronically excited states
- 1.2 Electronic structure
- 1.3 Spin effects
- 1.4 Energetics
- 1.5 Energy diagrams
- 1.6 Nuclear structure
- 1.7 Dynamics
- 1.8 Reactivity and efficiency
- 1.9 Summary
- 1.10 Problems
- 1.11 Answers to problems

2. Mechanisms of Electronic Excitation and Deexcitation

- 2.0 Goal
- 2.1 Radiative processes
- 2.2 Theory of absorption and emission
- 2.3 Classical interaction of light and molecules
- 2.4 How do molecules absorb and emit light?
- 2.5 Quantitative connection between E and K_e
- 2.6 Methods of estimating K_e and E
- 2.7 Energetic, dynamic and structural information from absorption and emission spectra
- 2.8 Empirical rules for assigning electronic configurations
- 2.9 Examples of information from absorption and emission spectra
- 2.10 Calculation of rate constants for electronic deexcitation
- 2.11 Summary
- 2.12 Problems
- 2.13 Answers to problems

3. Electronic Energy Transfer

- 3.0 Energy transfer
- 3.1 $D^* + A \xrightarrow[\text{ET}]{K} D + A^*$
- 3.2 Requirements to be competitive with K_D

3. (continued)

- 3.3 The resonance mechanism
- 3.4 Measurement of K_{ET}
- 3.5 The exchange mechanism
- 3.6 Intramolecular energy transfer
- 3.7 Uses of resonance energy transfer
- 3.8 Uses of exchange transfer
- 3.9 Triplet sensitizers
- 3.10 Impurity quenching
- 3.11 Summary
- 3.12 Problems
- 3.13 Answer to problems

4. Photochemical Dynamics

- 4.1 Efficiency, reactivity and chemical yield
- 4.2 Phenomenological description of dynamic quantities
- 4.3 Rate processes: unimolecular
- 4.4 Rate processes: bimolecular
- 4.5 Sensitization and quenching
- 4.6 Uses of sensitization and quenching
- 4.7 Experimental techniques
- 4.8 Summary
- 4.9 Problems
- 4.10 Answers to problems

5. Pericyclic Reactions: A Useful Basis for Classification and Mechanistic Analysis

- 5.1 Pericyclic reactions
- 5.2 Cycloaddition and cycloelimination reactions
- 5.3 Selection rules for cycloaddition reactions
- 5.4 Electrocyclic reactions
- 5.5 Selection rules
- 5.6 Sigmatropic reactions
- 5.7 Selection rules
- 5.8 Cheletropic reactions
- 5.9 Summary
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6. Photochemistry of Alkenes and Polyenes

- 6.1 General considerations
- 6.2 Model for electronically excited states
- 6.3 Energetics and dynamics
- 6.4 Primary photochemical processes
- 6.5 cis-trans-Isomerization
- 6.6 Hydrogen abstraction
- 6.7 Cycloaddition and cycloelimination
- 6.8 Electrocyclic reactions
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- 7.4 Primary photochemical processes
- 7.5 cis-trans-Isomerization
- 7.6 Hydrogen abstraction
- 7.7 Cycloaddition and cycloelimination
- 7.8 Electrocyclic reactions
- 7.9 Sigmatropic rearrangements
- 7.10 Miscellaneous reactions
- 7.11 Summary of reactions of aromatic hydrocarbons
- 7.12 Problems
- 7.13 Answers to problems

8. Photochemistry of Carbonyl Compounds

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- 8.2 Model for electronically excited states
- 8.3 Energetics and dynamics
- 8.4 Primary photochemical processes
- 8.5 α -Cleavage reactions
- 8.6 Hydrogen abstraction
- 8.7 Cycloaddition
- 8.8 Summary
- 8.9 Problems
- 8.10 Answers to problems

9. Photochemistry of Conjugated Enones and Related Compounds

- 9.1 General considerations
- 9.2 Model for electronically excited states
- 9.3 Energetics and dynamics
- 9.4 Primary photochemical processes
- 9.5 cis-trans-Isomerization
- 9.6 Hydrogen abstraction
- 9.7 Cycloadditions and cycloeliminations

9. (continued)

- 9.8 Electrocyclic reactions
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- 9.10 Summary
- 9.11 Problems
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10. Photochemistry of Some Unsaturated Nitrogen Chromophores and Photochemical Oxidations

- 10.0 Unsaturated nitrogen chromophores
- 10.1 Examples of photoreactions of unsaturated nitrogen chromophores
- 10.2 Singlet oxygen chemistry
- 10.3 Problems
- 10.4 Answers to problems

CHAPTER 1
THE NATURE AND BEHAVIOR OF
ELECTRONICALLY EXCITED MOLECULES

1.0 ELECTRONIC EXCITATION: ELECTRONIC TRANSITIONS

A. Concept of electronic excitation



B. Concept of electronically excited states

C. Configuration to approximate states. ($n, \pi^*; \pi, \pi^*$; charge transfer)

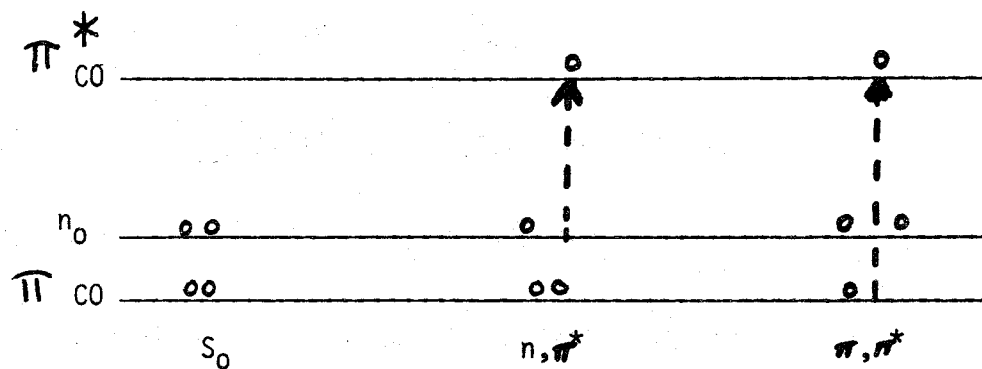
D. Singlets and triplets (S_0, T_1, S_1)

1.1 ELECTRONICALLY EXCITED STATES: ELECTRONIC ISOMERS

- A. Electronic structure (configuration): n, π^* and π, π^*
- B. Multiplicity (S_1 and T_1)
- C. Energy relative to S_0 : E_1 and E_3
- D. Nuclear structure
- E. Dynamics: physical and chemical: k
- F. Reactivity (k) versus efficiency (ϕ)

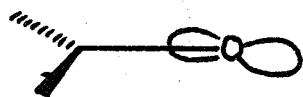
1.2 ELECTRONIC STRUCTURE: ELECTRONIC CONFIGURATIONS RESULTING FROM ELECTRONIC TRANSITIONS

A. n, π^* and π, π^* transitions: orbitals

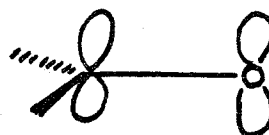


(2)

B. n, π^* and π, π^* configurations



n -ORBITAL



π^* -ORBITAL

1.3 SPIN EFFECTS: SINGLET AND TRIPLET STATES

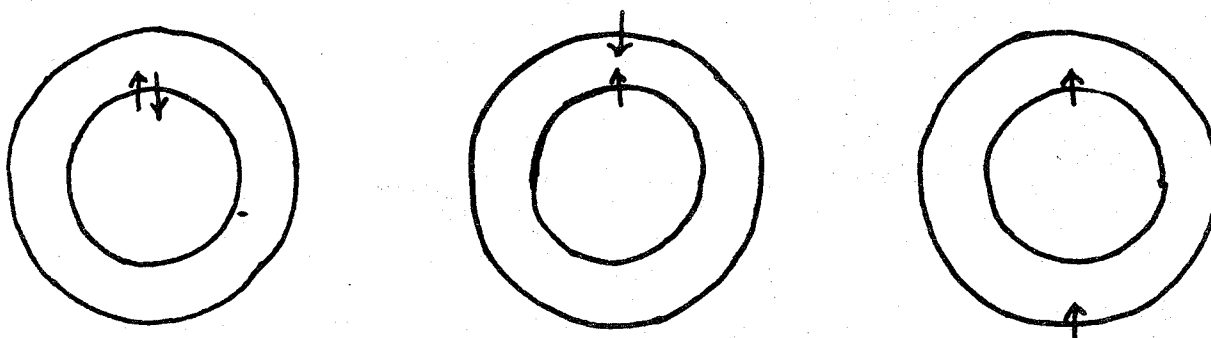
$$S_1 = (\pi)^2 (n)^1 (\pi^*)^1 \equiv {}^1(n, \pi^*) \quad (3)$$

$$T_1 = (\pi)^2 (n)^1 (\pi^*)^1 \equiv {}^3(n, \pi^*) \quad (4)$$

$$S_2 = (\pi)^1 (n)^2 (\pi^*)^1 \equiv {}^1(\pi, \pi^*) \quad (5)$$

$$T_2 = (\pi)^1 (n)^2 (\pi^*)^1 \equiv {}^3(\pi, \pi^*) \quad (6)$$

A. Can a difference in spin create a difference in chemistry?



1. Electron-electron repulsion is lower in T_1 than in S_1 . Electrons "see" less of each other in T_1 . Energy of T_1 is lower than energy of S_1 .
2. Electronic distributions of S_1 and T_1 are different.

1.4 ENERGETICS

A. Energy interconversions

$$\Delta E = E^* - E^0 = h\nu \quad (7)$$

$$\lambda(\text{\AA}) = 10^{-8} \text{ cm} = 0.1 \text{ nm} \quad (8)$$

$$E(\text{kcal/mole}) = \frac{2.86 \times 10^5}{\lambda(\text{\AA})} = \frac{2.86 \times 10^4}{\lambda(\text{nm})} \quad (9)$$

B. Examples (Table 1-1 on p. 11)

"Photochemical region" = 200 nm to 700 nm

| (nm) | E(kcal/mole) |
|------|--------------|
| 200 | 143 |
| 300 | 95 |
| 400 | 71 |
| 500 | 57 |
| 600 | 48 |
| 700 | 41 |

C. Note wide variations in E_1 (singlet energies) and E_3 (triplet energy) values.

Table 1-1

Dynamic and Energetic Data for Some Organic Molecules at 25°C.^{a,b,c}

| MOLECULE | E ₁ | E ₃ | k _F | k _{IC} | k _{ST} | k _P | k _{TS} |
|--------------------|----------------|----------------|-----------------|-----------------|------------------|------------------|-----------------|
| Benzene | 115 | 85 | 10 ⁶ | 10 ⁶ | 10 ⁷ | 10 ⁻¹ | 10 ⁶ |
| Napthalene | 90 | 61 | 10 ⁶ | 10 ⁶ | 10 ⁷ | 10 ⁻¹ | 10 ⁴ |
| 1-Fluoronapthalene | 89 | 60 | 10 ⁶ | 10 ⁶ | 10 ⁷ | 1 | ? |
| 1-Chloronapthalene | 89 | 59 | 10 ⁶ | 10 ⁶ | 10 ⁸ | 10 | ? |
| 1-Bromonapthalene | 89 | 59 | 10 ⁶ | 10 ⁶ | 10 ⁹ | 50 | ? |
| 1-Iodonapthalene | 89 | 59 | 10 ⁶ | 10 ⁶ | 10 ¹⁰ | 500 | ? |
| Anthracene | 76 | 42 | 10 ⁸ | 10 ⁷ | 10 ⁸ | 10 ⁻¹ | 10 ⁴ |
| Benzophenone | 75 | 69 | 10 ⁶ | ? | 10 ¹⁰ | 100 | 10 ⁵ |
| Biacetyl | 62 | 56 | 10 ⁵ | 10 ⁷ | 10 ⁸ | 100 | 10 ⁴ |
| Acetone | 84 | 78 | 10 ⁵ | 10 ⁷ | 10 ⁸ | 100 | 10 ⁶ |

(a) E₁ and E₃ are in kcal/mole.

(b) k's are in units of sec⁻¹. Order of magnitude values only.

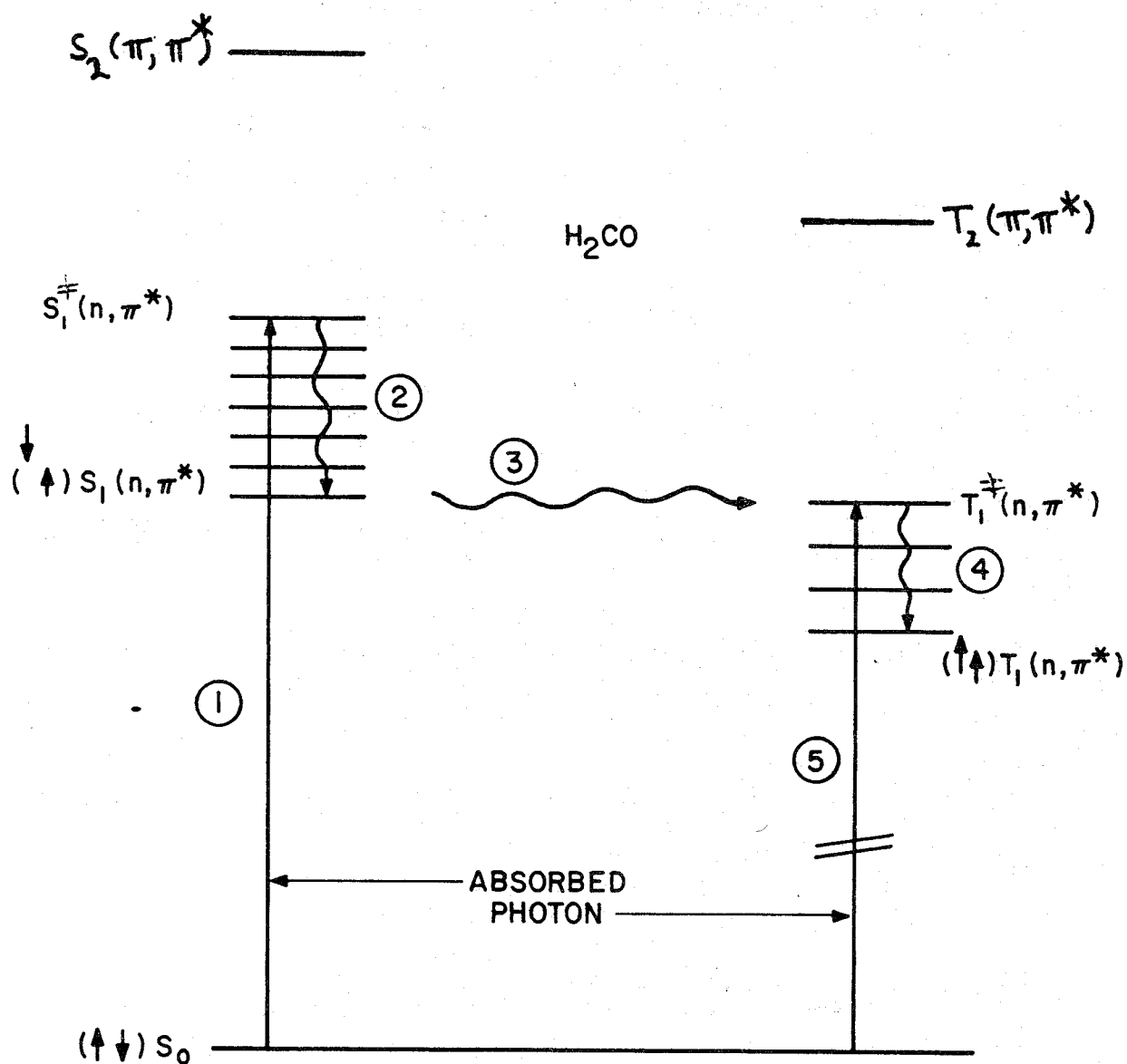
(c) These values will be somewhat solvent dependent and refer to a non-polar environment.

1.5 ENERGY DIAGRAMS: A KEY INTELLECTUAL BASIS FOR UNDERSTANDING ELECTRONICALLY EXCITED ORGANIC MOLECULES

A. Paths of electronic excitation (Fig. 1-1 on p. 13)

| <u>Process</u> | <u>Name</u> | <u>Typical Rate (sec⁻¹)</u> |
|--|------------------------|--|
| (1) $S_0 + h\nu \longrightarrow S_1^*$ | Absorption | 10^{15} |
| (2) $S_1^* \longrightarrow S_1 + \Delta$ | Vibrational Relaxation | $10^{11}-10^{12}$ (k_V) |
| (3) $S_1 \longrightarrow T_1^*$ | Intersystem Crossing | 10^6-10^{10} (k_{ST}) |
| (4) $T_1^* \longrightarrow T_1 + \Delta$ | Vibrational Relaxation | $10^{11}-10^{12}$ (k_V) |
| (5) $S_0 + h\nu \longrightarrow T_1^*$ | Absorption | 10^{15} |

Figure 1-1
Paths of Electronic Excitation



Absorption of light to excite S_2 is also possible, but is not shown. Should S_2 be excited by light, then the radiationless internal conversion process $S_2 \rightarrow S_1$ would rapidly populate S_1 .

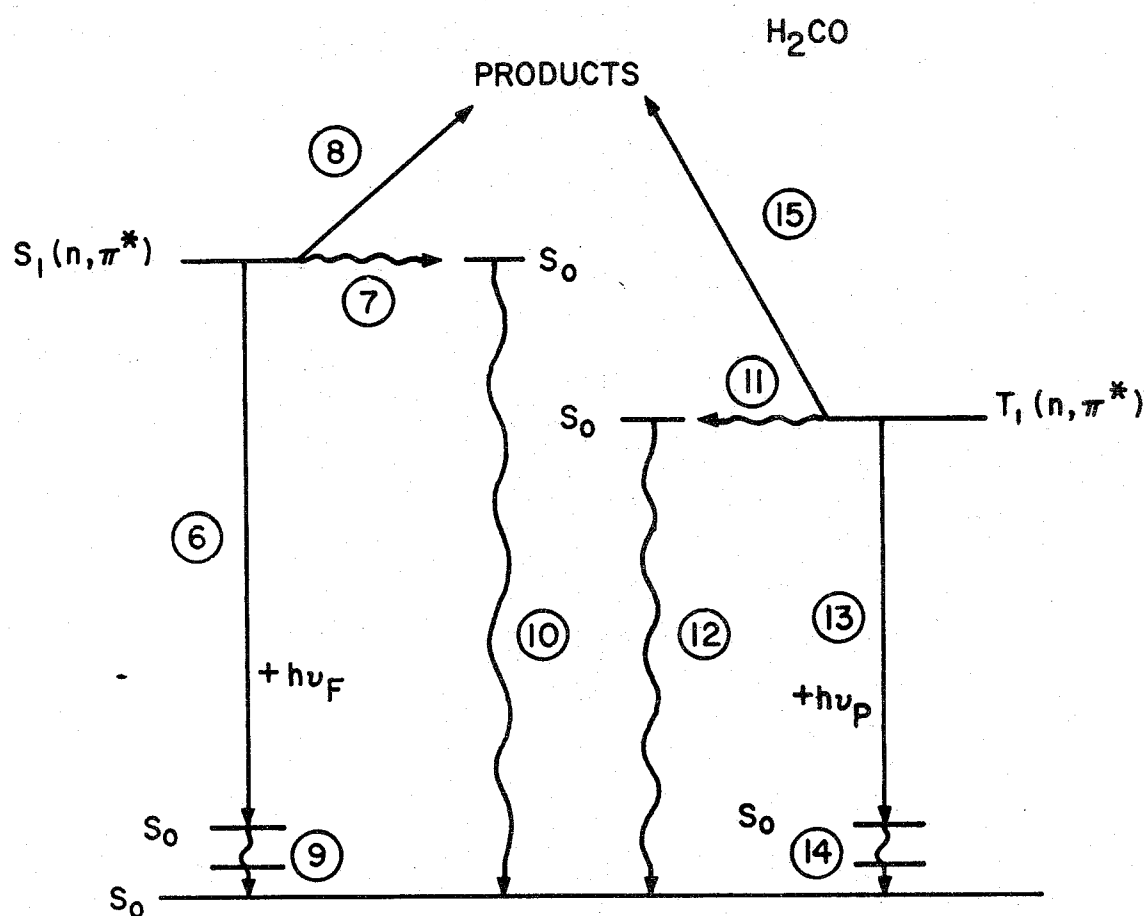
1.5 (continued)

B. Paths of electronic deexcitation (Figure 1-2 on p. 15)

| <u>Process</u> | | | <u>Name</u> | <u>Typical Rate (sec⁻¹)</u> |
|----------------|-----------------------------|---------------------|------------------------|--|
| (6) | $S_1 \longrightarrow$ | $S_0^* + h\nu_F$ | Fluorescence | $10^5 - 10^9 (k_F)$ |
| (7) | $S_1 \longrightarrow$ | $S_0^* + \Delta$ | Internal Conversion | $10^5 - 10^{10} (k_K)$ |
| (8) | $S_1 \longrightarrow$ | Products | Photoreaction | $10^2 - 10^{10} (k_R^1)$ |
| (9) | $S_0^* \longrightarrow$ | $S_0 + \Delta$ | Vibrational Relaxation | $10^{11} - 10^{12} (k_V)$ |
| (10) | $S_0^{***} \longrightarrow$ | $S_0 + \Delta$ | Vibrational Relaxation | $10^{11} - 10^{12} (k_V)$ |
| (11) | $T_1 \longrightarrow$ | $S_0^{**} + \Delta$ | Intersystem Crossing | $10^{-2} - 10^6 (k_{TS})$ |
| (12) | $S_0^{**} \longrightarrow$ | $S_0 + \Delta$ | Vibrational Relaxation | $10^{11} - 10^{12} (k_V)$ |
| (13) | $T_1 \longrightarrow$ | $S_0^* + h\nu_P$ | Phosphorescence | $10^{-2} - 10^3 (k_P)$ |
| (14) | $S_0^* \longrightarrow$ | $S_0 + \Delta$ | Vibrational Relaxation | $10^{11} - 10^{12} (k_V)$ |
| (15) | $T_1 \longrightarrow$ | Products | Photoreaction | $10^2 - 10^{10} (k_R^3)$ |

Figure 1-2

Paths of Electronic Deexcitation

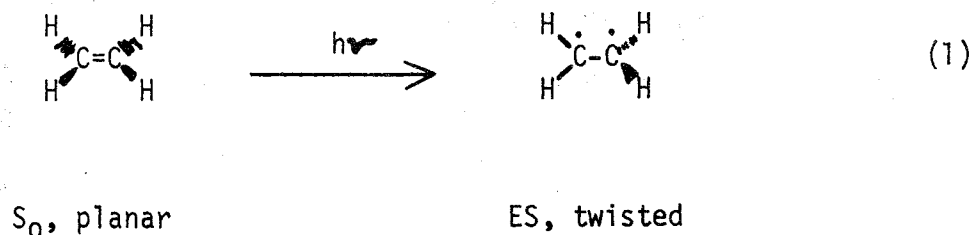


Paths of electronic deexcitation. Note that, in general, several paths are available for deexcitation of S_1 and T_1 .

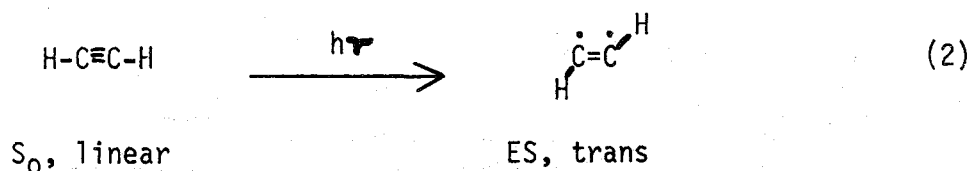
1.6 NUCLEAR STRUCTURE: EXAMPLES

- A. Formaldehyde (Figure 1-3 on p. 17)
- B. Electronic jumps (electronic transitions)
- C. Franck-Condon Principle; Franck-Condon state
- D. Importance of vibrational relaxation and internal conversion to S_1 : Kasha's Rule
- E. Nuclear geometries of S_1 and T_1 are generally different from that of S_0 .
- F. Electronic structures of S_1 and T_1 are always different from that of S_0 .
- G. Other examples:

1. Ethylene



2. Acetylene

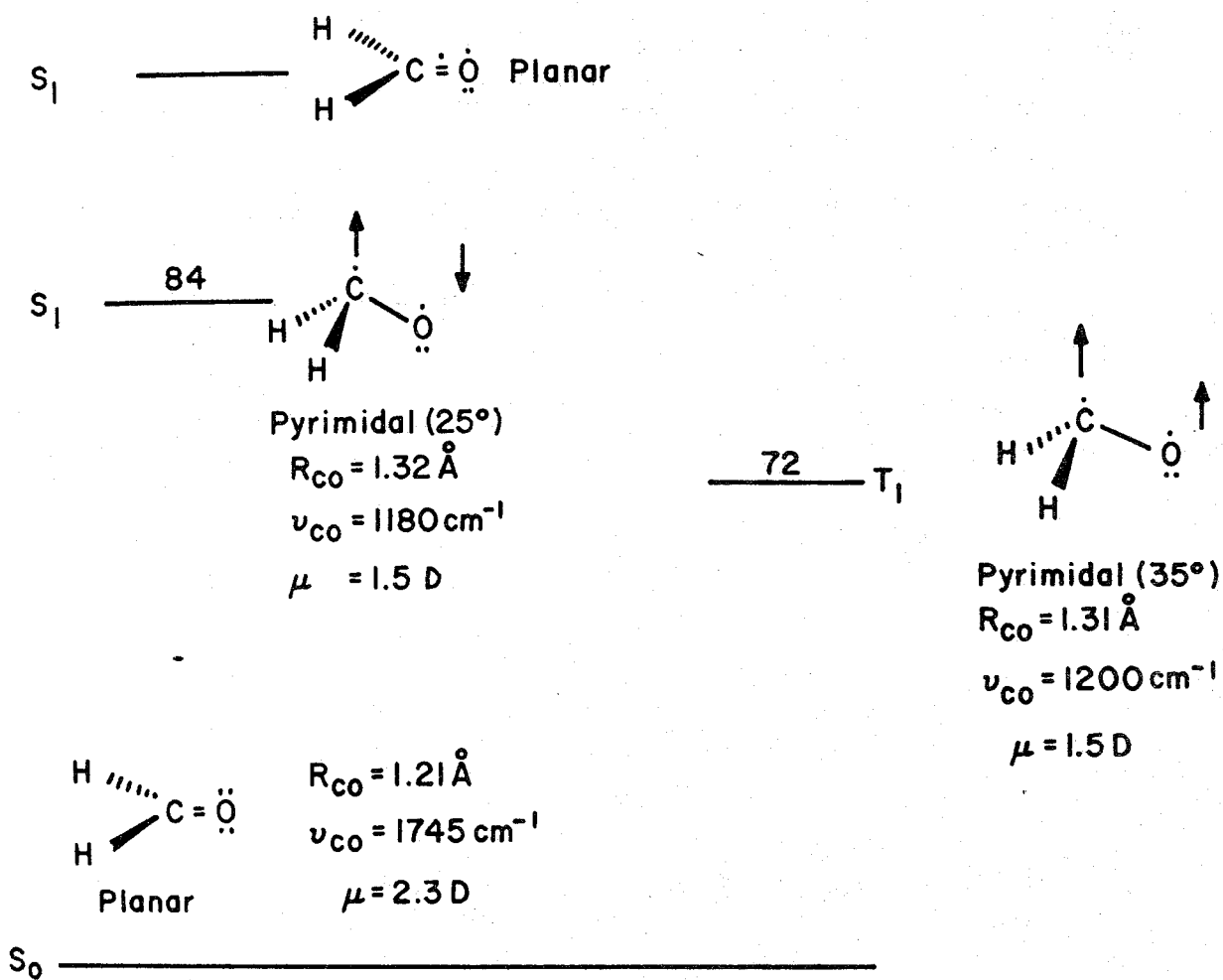


1.7 DYNAMICS

- A. Questions: what do structure-dynamic relations depend upon?
- B. Examples (Table 1-1 on p. 11)
- C. Note wide variations in rates as a function of structure.

Figure 1-3

Energy Diagram of Formaldehyde



An energy diagram for formaldehyde, depicting structures, configurations and energetics

1.8 REACTIVITY AND EFFICIENCY

- A. Reactivity depends mainly upon configuration (electronic structure), then upon energetics.



- B. Efficiency depends only on competing rates, not absolute rate constants.

$$\phi = \frac{k}{\sum \text{all } k\text{'s}}$$

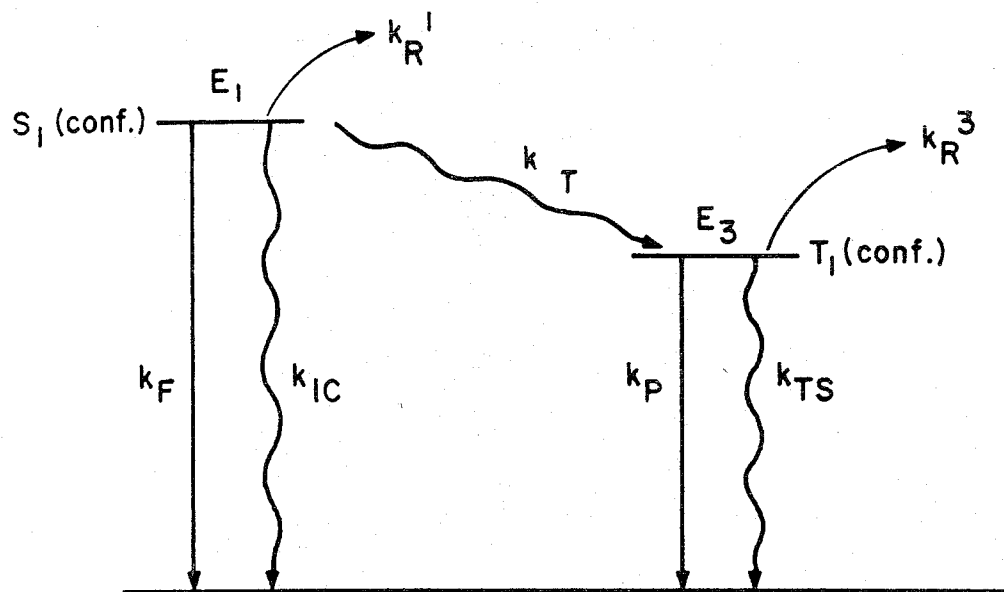
1.9 SUMMARY

- A. A shorthand energy diagram (Figure 1-4 on p. 19)

- B. Key ideas

1. Absorption of light (How does it happen?)
2. Vibrational relaxation (Always very fast)
3. Internal conversion to S_1 (Always very fast)
4. Intersystem crossing S_1 to T_1 (Structure dependent)
5. Fluorescence
6. Phosphorescence
7. Franck-Condon principle
8. Orbitals - Configurations - States
9. Singlets and triplets

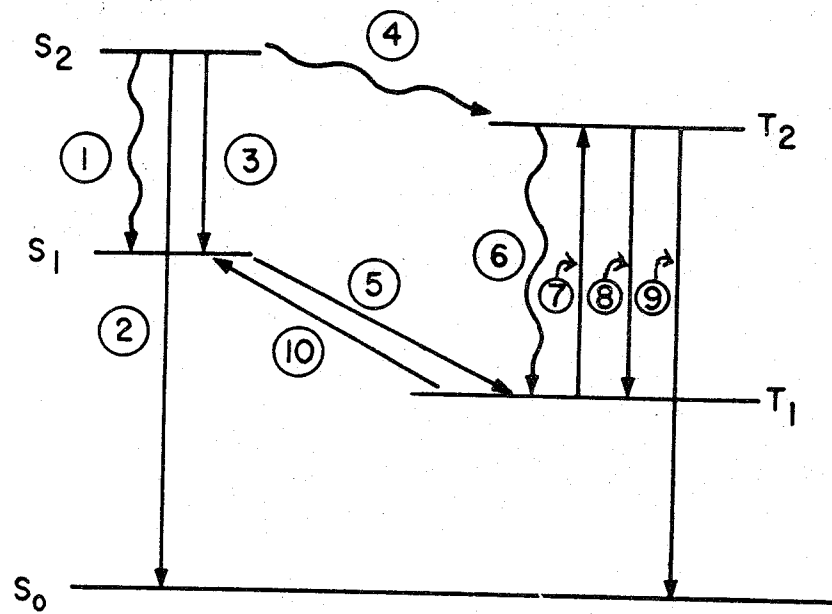
Figure 1-4
A Shorthand Energy Diagram



1.10 PROBLEMS

- A. In general, the internal conversion process ($S_1 \rightarrow S_0$) does not compete effectively with intersystem crossing ($S_1 \rightarrow T_1$) even though the latter process is "spin forbidden." Suggest a rationale for this observation.
- B. Classify each process (1-10) in Figure 1-5 as one of the processes 1-15 listed in section 1.5.
- C. From the data given in Table 1-1, draw energy diagrams for (a) naphthalene and (b) benzophenone. Include the state energies, configurations and dynamics. Would you expect comparable types of photochemical processes for benzophenone and for naphthalene?

Figure 1-5



1.11 ANSWERS TO PROBLEMS

A. Discussed on the tape (Side 1).

B. Process 1: internal conversion, $S_2 \rightsquigarrow S_1$, followed by vibrational relaxation (the whole process is really two steps, an electronic interconversion, followed by vibrational relaxation)

Process 2: fluorescence, $S_2 \longrightarrow S_0 + h\nu$. Radiative transition between states of the same spin

Process 3: fluorescence, $S_2 \longrightarrow S_1 + h\nu$. Emissions from S_2 are exceedingly rare, thus hardly any examples of process 2 or process 3 are known.

Process 4: intersystem crossing, $S_2 \rightsquigarrow T_2$. A conceivable, but rarely documented process

Process 5: phosphorescence, $S_1 \longrightarrow T_1 + h\nu$. Has not been observed

Process 6: internal conversion, $T_2 \rightsquigarrow T_1$

Process 7: allowed absorption, $T_1 + h\nu \longrightarrow T_2$. No spin change occurs since both the initial and final states are triplets.

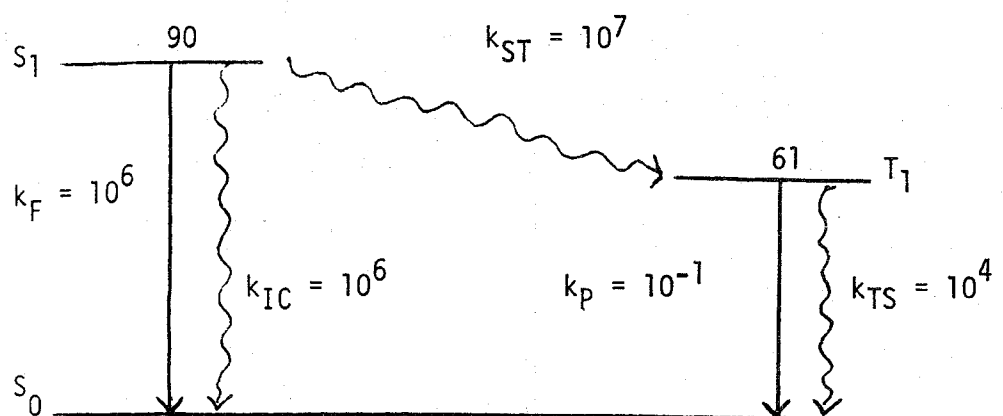
Process 8: fluorescence, $T_2 \longrightarrow T_1 + h\nu$. Known for molecules possessing triplet ground states, e.g., diphenyl methylene

Process 9: phosphorescence, $T_2 \longrightarrow S_0 + h\nu$. Unknown since process 6 is so much faster

Process 10: forbidden absorption, $T_1 + h\nu \longrightarrow S_1$. Not known, but should be observable in the near infrared for long-lived triplets. Experimentally, this region presents technical problems with respect to sensitivity of detection.

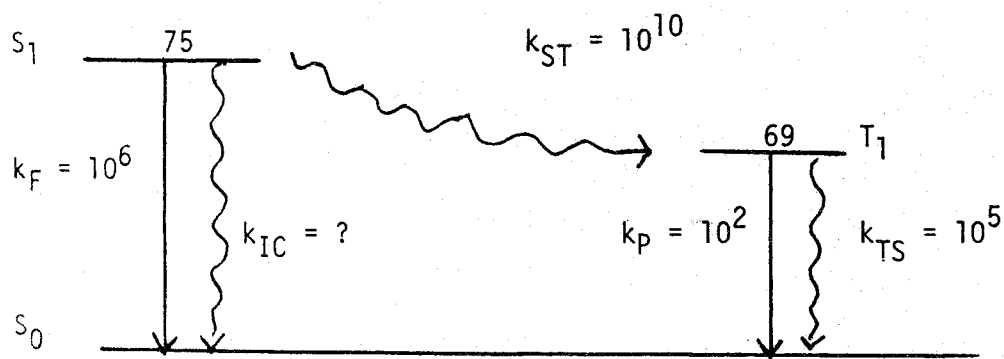
1.11 (continued)

c. a NAPHTHALENE (ENERGIES IN KCAL/MOLE, RATE IN SEC^{-1})



c. b

BENZOPHENONE



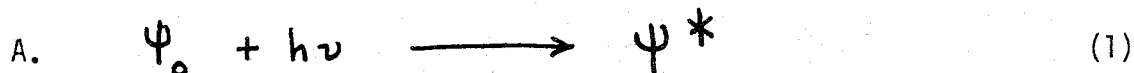
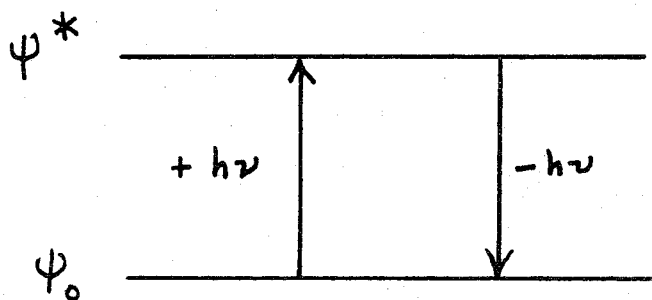
CHAPTER 2

MECHANISMS OF ELECTRONIC EXCITATION AND DEEXCITATION

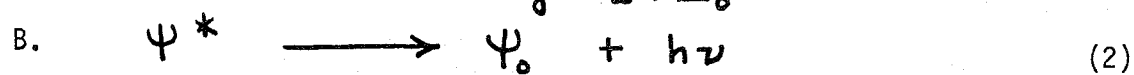
2.0 GOAL: UNDERSTANDING PHOTODYNAMICS: RADIATIVE AND RADIATIONLESS PROCESSES:

Rev.: "Molecular Photochemistry," Chapters 2, 3 and 4.

2.1 RADIATIVE PROCESSES: ABSORPTION AND EMISSION



$$\epsilon = K \log I_a / I_0$$



$$k_e = 1/\tau_e$$

2.2 THEORY OF ABSORPTION AND EMISSION

- A. Relationship of $E(I_a)$ and $k_e(1/\tau_e)$ to theoretical quantities
- B. General solution: calculate value of a "matrix element" $\langle \psi_0 | H | \psi^* \rangle$
- C. If $E^* - E_0 = h\nu$, then $\langle \psi_0 | H | \psi^* \rangle^2$ measures the probability of
 $\psi_0 + h\nu \rightleftharpoons \psi^*$
- D. Must identify ψ_0 and ψ^* with an orbital configuration
- E. Must identify H with a reasonable "perturbation" which will cause transition
 $\psi_0 \rightleftharpoons \psi^*$

2.3 CLASSICAL INTERACTION OF LIGHT AND MOLECULES

- A. Electromagnetic wave
- B. Electric and magnetic forces

$$F \text{ (on electron)} = eE + e\left[\frac{vH}{c}\right] \quad (3)$$

$$v = \frac{c}{\lambda} \quad (4)$$

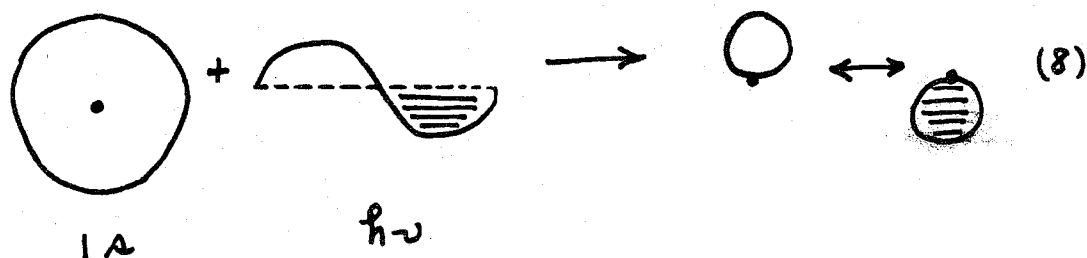
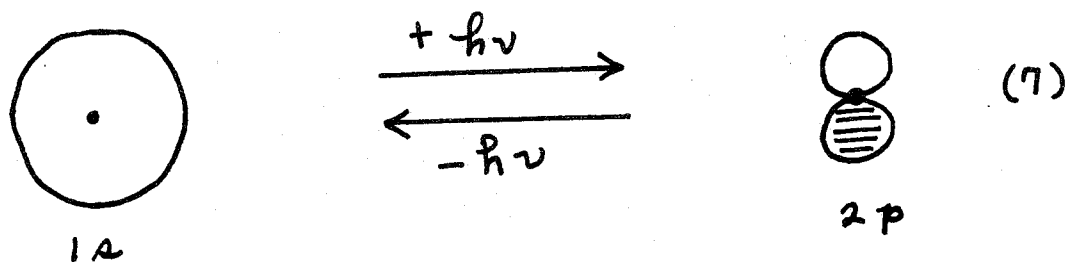
- C. Conclusions: $v \sim 10^{15} - 10^{16} \text{ sec}^{-1}$, comparable to frequency of electron in an orbital and only the electric part of the wave interacts with electrons

2.4 HOW DO MOLECULES ABSORB AND EMIT LIGHT?

$$\epsilon \propto \langle \psi_0 | H | \psi^* \rangle^2 \quad (5)$$

$$k_e \propto \langle \psi_0 | H | \psi^* \rangle^2 \quad (6)$$

- A. Electric field of light corresponds to H
- B. H causes ψ_0 (electrons) to oscillate
- C. The "shape" of ψ_0 becomes like that of ψ^*
- D. The energy of the light wave is "used up" (absorbed) in "shaping" ψ^*
- E. Key interaction between light and a molecule is that of an electric field acting on the negatively charged electrons.



2.5 QUANTITATIVE CONNECTION BETWEEN E AND k_e

$$k_e \sim 10^{-9} \tau_{\text{max}}^{-1} E_{\text{max}} \Delta \nu_{\text{max}} \quad (9)$$

- A. Example. The absorption maximum of acetone in cyclohexane is about 15 and is located at 280 nm. The half-width of the band extends from 250 nm to 310 nm. Calculate the radiative lifetime of acetone fluorescence. Repeat the calculation for a molecule which has the same absorption maximum and half-width as acetone but has $\epsilon_{\text{max}} = 10,000$.
- B. Problem. The radiative lifetime of benzophenone phosphorescence is 10^{-2} sec. Assume that the absorption is 400 nm and has a band half-width of 1000 cm^{-1} ; calculate E_{max} for the $S_0 \rightarrow T_1$ absorption of benzophenone. Many aromatic hydrocarbons have an inherent radiative phosphorescence lifetime of about 10 sec. Calculate the maximum extinction coefficient for the $S_0 \rightarrow T_1$ for such hydrocarbons.

/FOR $S_0 \rightarrow T_1$

D. Nuclear (or vibrational) part

1. Franck-Condon Principle

2. Example: Franck-Condon absorption (Figure 5-2 on p. 32)

3. Problem: If the equilibrium geometry of the ground state is different, do you expect an intense 0,0 absorption band?

2.6 METHODS OF ESTIMATING k_e and E

A. Estimate magnitude of $\langle \psi_0 | H | \psi^* \rangle$

B. Break each ψ up into component parts

$$\psi \sim \phi_0 \times \delta \quad (11)$$

$$\langle \psi_0 | H | \psi^* \rangle \sim \langle \phi_0 | H | \phi^* \rangle \langle x_0 | x^* \rangle \langle \delta | \delta^* \rangle \quad (12)$$

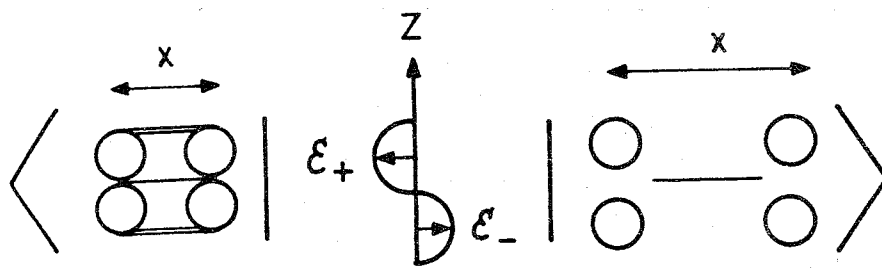
C. Electronic part is analogous to the magnitude of the "dipole" induced by the electric field of the light wave.

1. Symmetry of ϕ_0 and ϕ^*
2. Spatial overlap of ϕ_0 and ϕ^*
3. Problem. Why are n, π^* transitions usually weak ($E \sim 10 - 100$) while π, π^* transitions are generally strong ($E > 1000$)? See Figure 2-1 on p. 31.

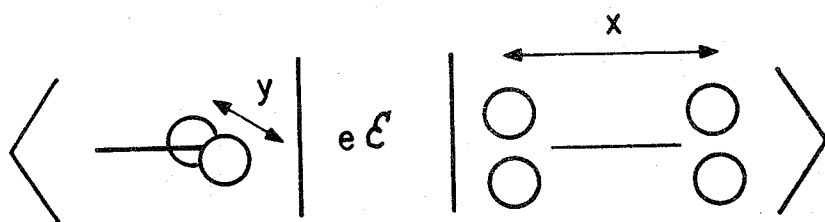
D. Nuclear (or vibrational) part

1. Franck-Condon Principle
2. Example: Franck-Condon absorption (Figure 2-2 on p. 32)
3. Problem: If the equilibrium geometry of the ground state is very different, do you expect an intense 0,0 absorption band?

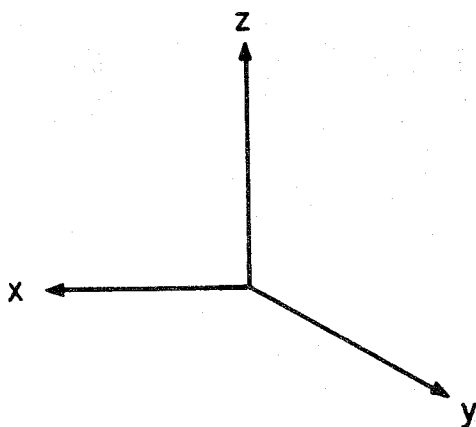
Figure 2-1



$$\langle \pi | e\mathcal{E} | \pi^* \rangle \neq 0$$



$$\langle n | e\mathcal{E} | \pi^* \rangle \sim 0$$



2.6 D. (continued)

4. Radiationless processes; intersystem crossing (Figure 2-3 below)

Figure 2-2 →
Franck-Condon Absorption

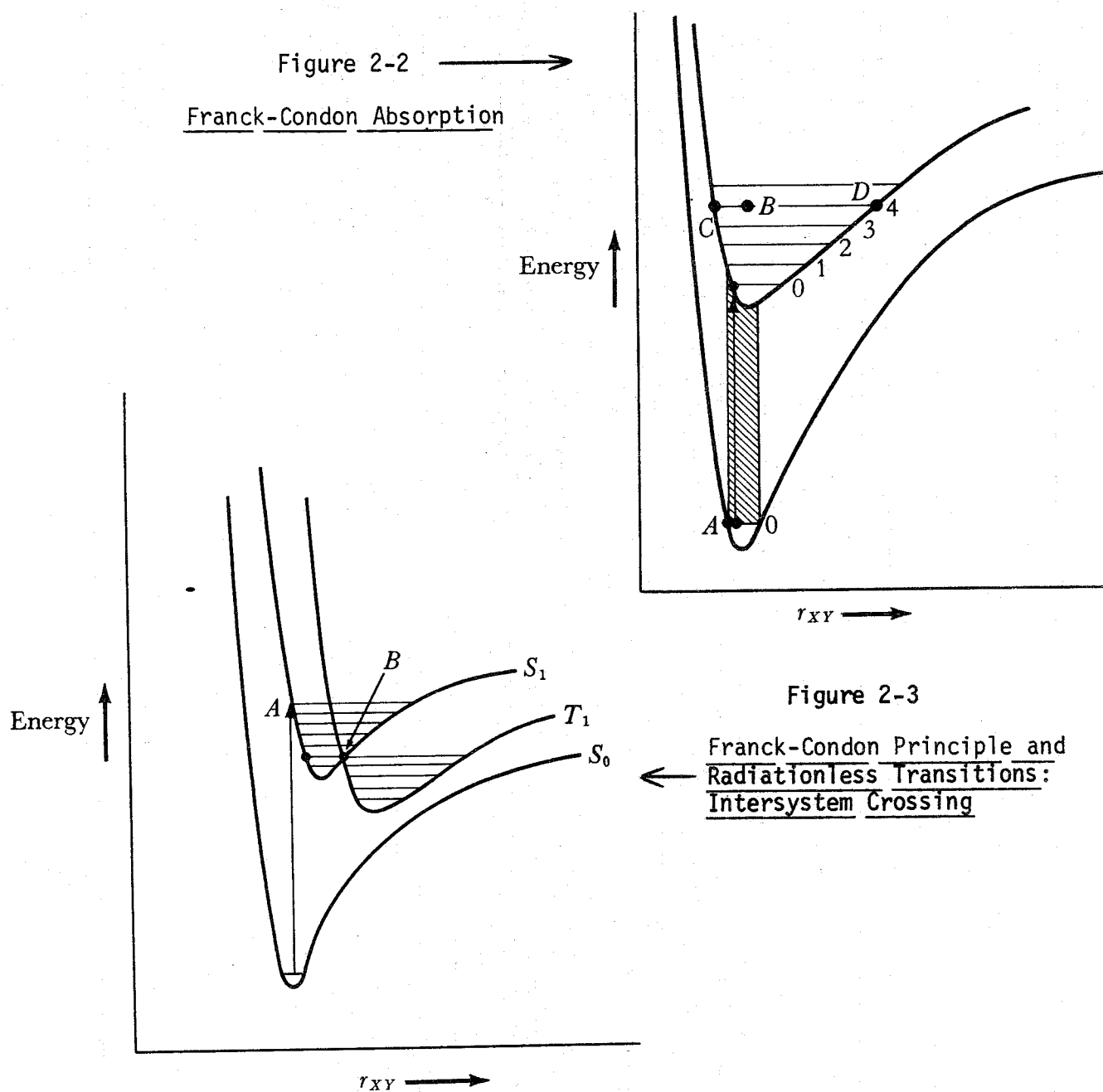
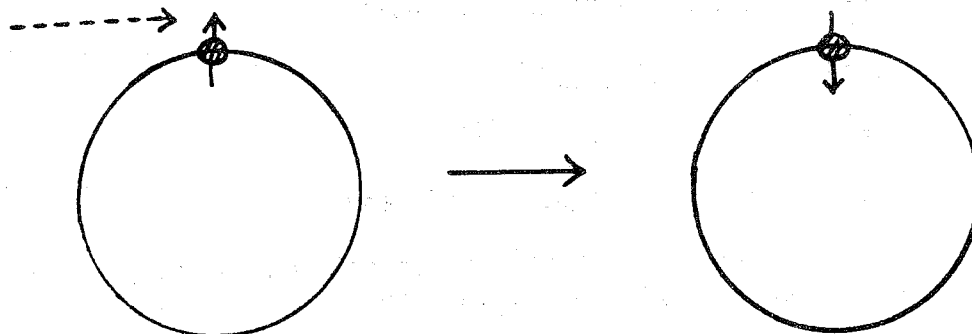


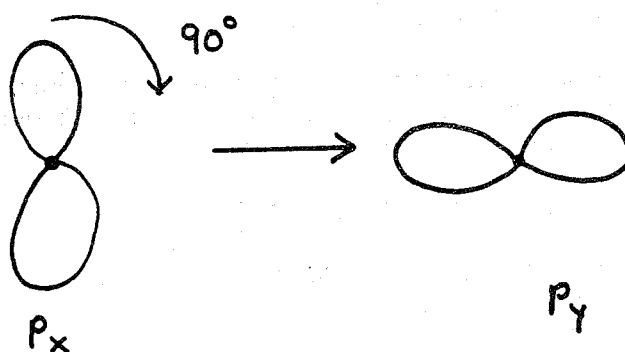
Figure 2-3
← Franck-Condon Principle and
Radiationless Transitions:
Intersystem Crossing

E. The electronic spin component

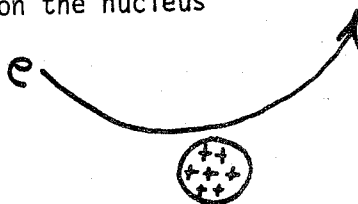
1. No singlet-triplet transitions allowed in the first approximation
2. Need a magnetic interaction to put a "torque" on the magnetic moment of the spin



3. Angular momentum change (s-character)



Charge on the nucleus



4. Examples:

- (a) $n \rightarrow \pi^*$ transitions, $k_p \sim 10^2 \text{ sec}^{-1}$ but $\pi \rightarrow \pi^*$ transitions $k_p \sim 10^{-1} \text{ sec}^{-1}$
- (b) Heavy atom effect: Chapter 1, Table 1-1 for naphthalene, $k_p \sim 10^{-1} \text{ sec}^{-1}$, but for 1-iodonaphthalene, $k_p \sim 10^2 \text{ sec}^{-1}$
- (c) Oxygen perturbation of $S_0 \rightarrow T_1$ absorption

5. Problem. The phosphorescence rate of aromatic hydrocarbons increases in heavy atom solvents such as ethyl iodide, but the phosphorescence rate of benzophenone is not affected by heavy atom solvents. Explain the basis for these differing observations.

2.7 ENERGETIC, DYNAMIC AND STRUCTURAL INFORMATION FROM ABSORPTION AND EMISSION SPECTRA

A. Routinely available experimental data:

1. Absorption spectrum:

- (a) intensity of bands (ϵ)
- (b) vibrational structure of bands
- (c) solvent and substituent effects on intensity, shape and position of absorption bands
- (d) lowest energy vibration of a band (0,0 band)

2. Emission spectrum:

- (a) efficiency of fluorescence and phosphorescence (ϕ_F and ϕ_P)
- (b) vibrational structure of bands
- (c) lifetime of fluorescence and phosphorescence; solvent and substituent effects on the emission efficiencies, shapes, positions and lifetimes of various bands

B. Information from absorption and emission spectra

1. Information on energetics: absorption yields E_1 , E_2 , etc. Emission yields E_1 and E_3 .
2. Information on dynamics: absorption yields k_F (eq. 9) and k_P (less useful). Emission yields k_S , k_T , k_{ST} (k_S and k_T are the rates of decay by all processes of S_1 and T_1 , respectively)
3. Information on structure: absorption yields major electronic configuration of singlets. Not useful for triplets. Consider E_{max} , E_1 , substituent solvent effects and structure of the band. Emission yields major electronic configurations of emitting states S_1 and T_1 . Consider τ_S , τ_P , E_1 , E_3 vibrational structure.

2.8 EMPIRICAL RULES FOR ASSIGNING ELECTRONIC CONFIGURATIONS

A. n, π^* States

1. Absorption

- (a) $E_{\max} \sim 10-100$
- (b) E_{\max} blue-shifted by increasing solvent polarity
- (c) E_{\max} blue-shifted by electron donating groups

2. Emission

- (a) ϕ_F usually small
- (b) ϕ_P occasionally high
- (c) $\tau_P \lesssim 10^{-2}$ sec,
- (d) Vibrational structure

B. π, π^* States

1. Absorption

- (a) $E_{\max} \sim 1000-10,000$
- (b) E_{\max} red-shifted as solvent polarity is increased
- (c) E_{\max} red-shifted by electron donating groups

2. Emission

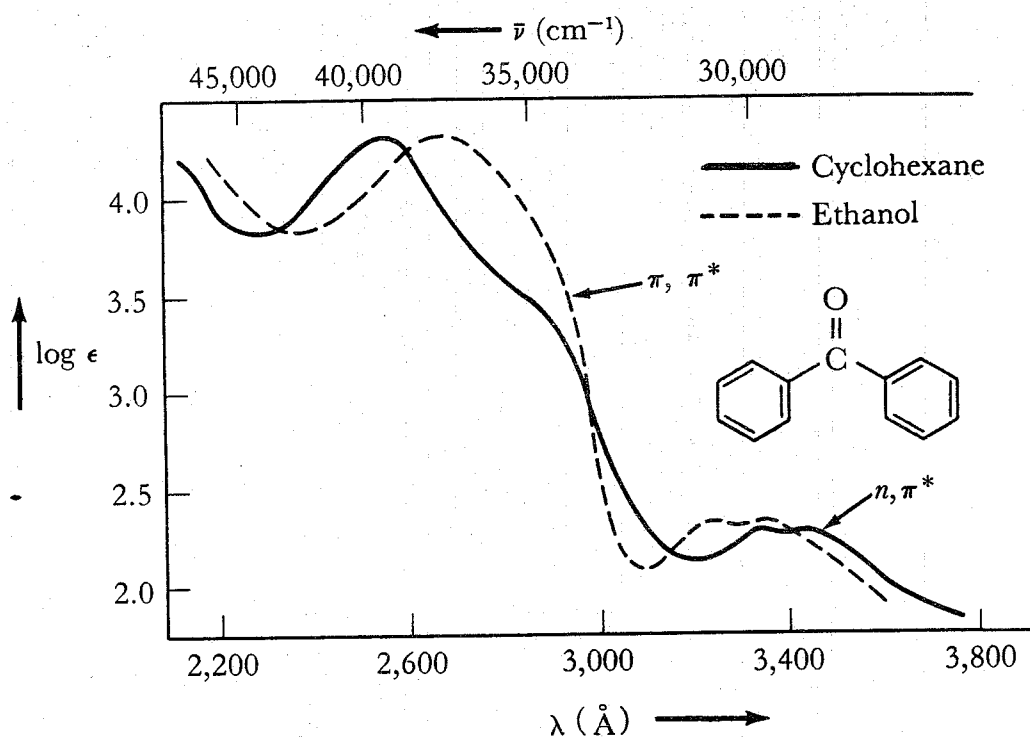
- (a) ϕ_F variable but often greater than 0.1
- (b) ϕ_P rarely high
- (c) $\tau_F \sim 10^{-8}$ sec
- (d) $\tau_P \gtrsim 10^{-1}$ sec
- (e) Vibrational structure

2.9 EXAMPLES OF INFORMATION FROM ABSORPTION AND EMISSION SPECTRA

A. Benzophenone: a classic example of S_1 (n, π^*) and T_1 (n, π^*) states

Figure 2-4

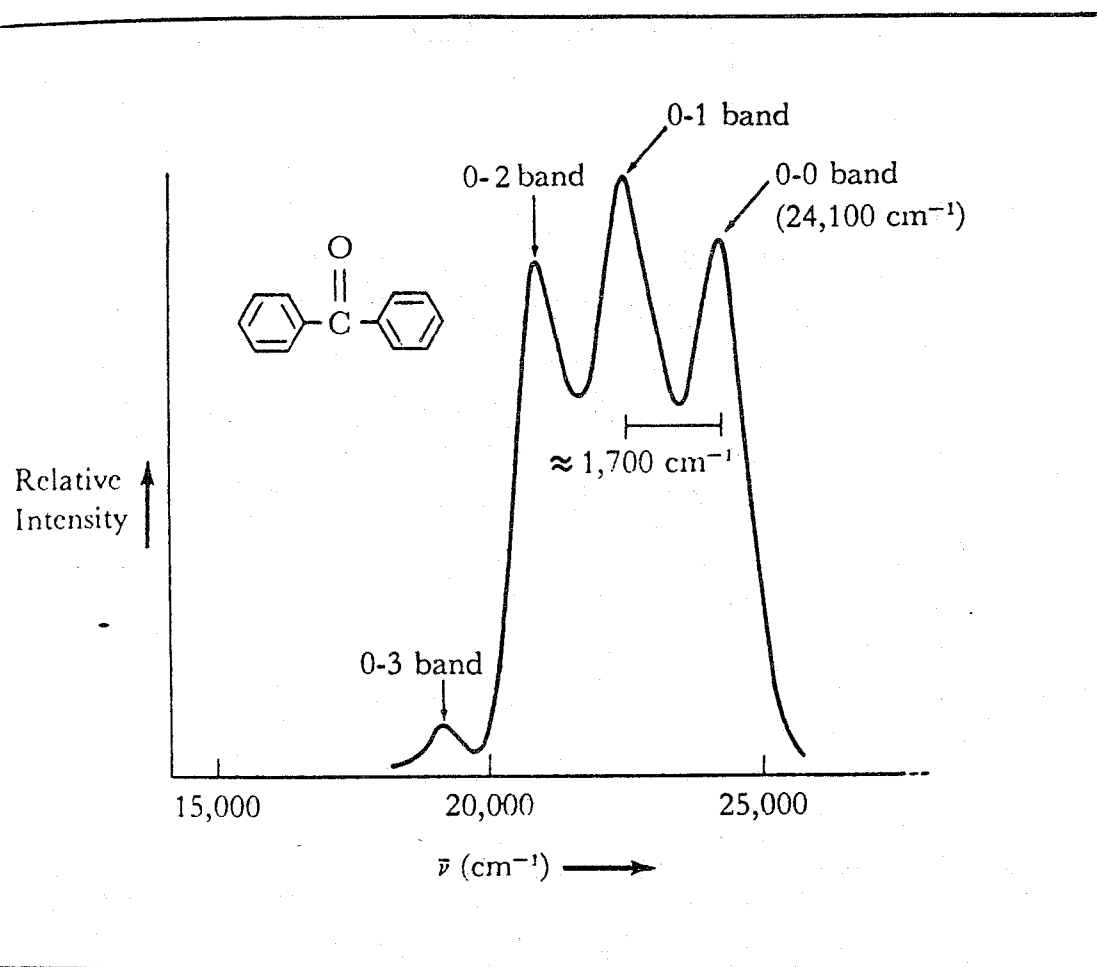
Absorption Spectrum of Benzophenone



2.9 A. (continued)

Figure 2-5

Emission Spectrum of Benzophenone

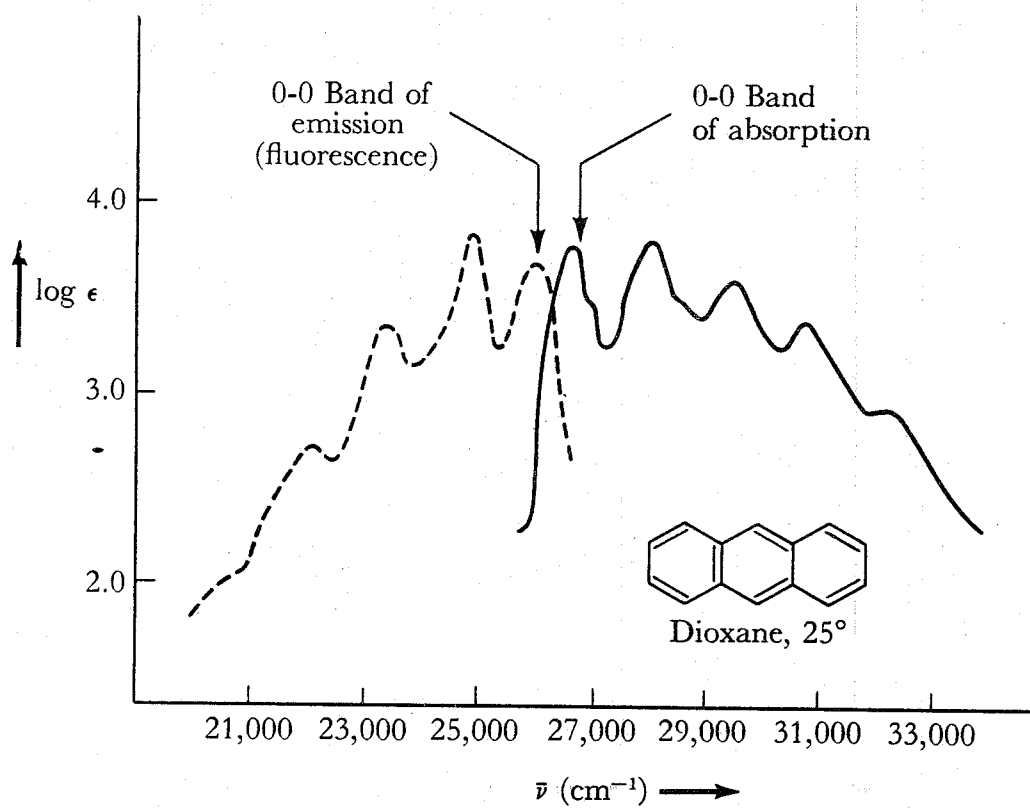


2.9 (continued)

B. Anthracene: a classic example of S_1 (π, π^*) and T_1 (π, π^*) states

Figure 2-6

Absorption and Emission Spectrum of Anthracene



2.10 CALCULATION OF RATE CONSTANTS FOR ELECTRONIC DEEXCITATION

$$\phi_F = \frac{k_F}{k_S} \quad (13)$$

$$\begin{aligned} k_S &= \text{total rate of deactivation of } S_1 = k_F + k_D^1 \\ k_S &= 1/\tau_S \text{ where } \tau_S \text{ is the measured rate of decay of } S_1 \\ \phi_P &= \phi_{ST} \left(\frac{k_D}{k_T} \right) \\ k_T &= \text{total rate of deactivation of } T_1 \\ k_T &= 1/\tau_T \text{ where } \tau_T \text{ is the measured rate of decay of } T_1 \end{aligned} \quad (14)$$

2.11 SUMMARY

A. Absorption and emission

1. Structure: electronic and nuclear configuration of S_1 and T_1
2. Energetics: electronic excitation energy of S_1 and T_1
3. Dynamics: rates of deactivation of S_1 and T_1
4. Efficiencies: relative rates or probabilities

B. Theory

1. Decomposition of state into electronic, nuclear and spin parts
2. Probabilities of configurational changes
3. Franck-Condon principle
4. Spin flipping

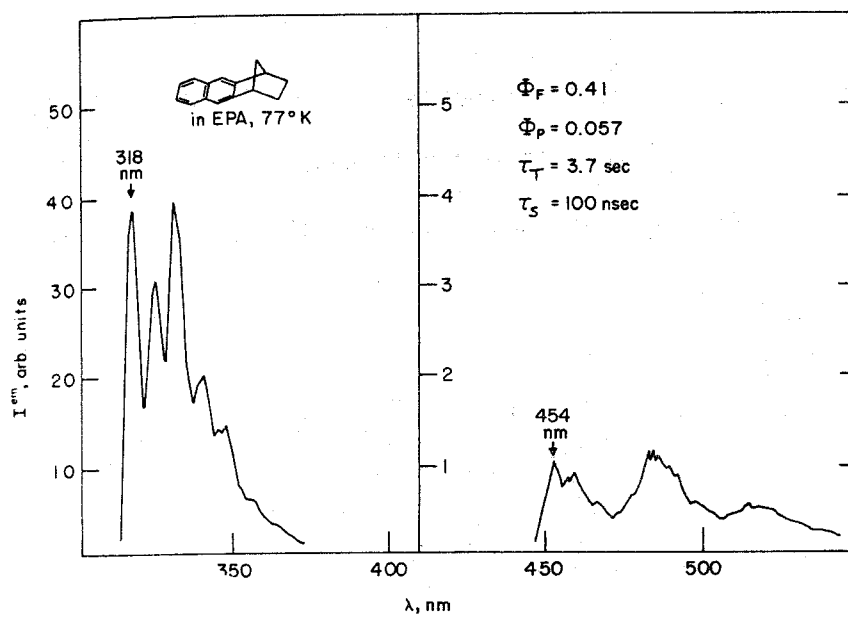
2.12 PROBLEMS

- A. Suppose a molecule shows the following emission properties at 77°K: $\phi_F = 0.10$, $\phi_P = 0.20$, $\tau_S = 10^{-9}$ sec, $\tau_T = 1$ sec and $\phi_{ST} = 0.90$. Calculate k_F and k_P , the inherent rate constants for fluorescence and phosphorescence, from these data.
- B. The singlet absorption spectrum of anthracene is approximately a "mirror image" of its fluorescence spectrum (Figure 2-6). Rationalize this observation on the basis of the Franck-Condon principle.
- C. The radiationless process $S_1 \rightarrow T_1$ and the radiative process $T_1 \rightarrow S_0 + h\nu$ are "forbidden" according to the principles of quantum mechanics. Yet benzophenone undergoes $S_1 \rightarrow T_1$ crossing and emission of phosphorescence both with an efficiency of essentially 1.00. How does one understand these apparent "violations" of quantum mechanical principles?
- D. $\text{CH}_3\text{COCH}=\text{CH}_2$ in hexane shows two absorption maxima in the ultraviolet region
- one with $E_{\text{max}} \sim 10,000$, $\lambda_{\text{max}} \sim 240$ nm and
 - one with $E_{\text{max}} \sim 100$, $\lambda_{\text{max}} \sim 340$ nm.

Assign configurations to the states produced by each absorption. Predict the direction of shift of each maximum (higher or lower wavelengths) if the spectrum of $\text{CH}_3\text{COCH}=\text{CH}_2$ is taken in methanol.

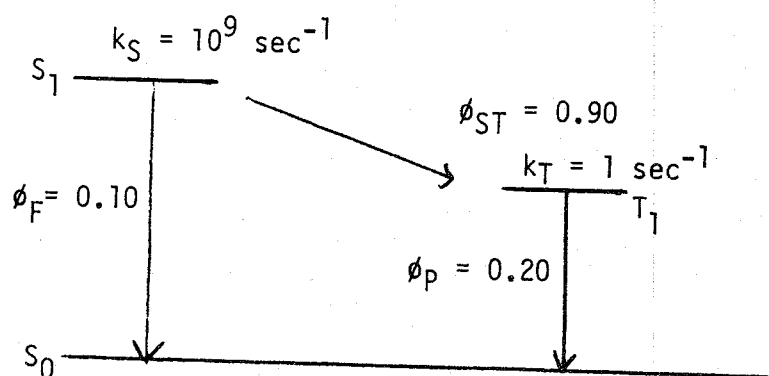
- E. Figures 2-7 and 2-8 are emission spectra taken at 77°K in a hydrocarbon solvent.
- Calculate E_1 and E_3 for the two compounds.
 - Why are the measured values of emission yields and lifetimes so different for the two compounds?
 - Calculate k_{ST} , k_F and k_P for these compounds (assume that no internal conversion occurs from S_1).

Figure 2-7



2.13 ANSWERS TO PROBLEMS

- A. The energy diagram for the hypothetical molecule should be written down immediately in order to simplify the visualization of what's happening. Now, the important thing to do is to



deconvolute the kinetic information contained by k_S and k_T .

First, k_S is the rate of deactivation of S_1 by all paths, i.e., fluorescence, intersystem crossing, internal conversions, reactions, etc. Similarly, k_T is the rate of deactivation of T_1 by all paths. Let us define k_F = inherent rate of fluorescence, k_{DS} = all other paths for deactivation of S_1 . Similarly for deactivation of T_1 , let k_P = inherent rate of phosphorescence, k_{TS} = rate of intersystem crossing to S_0 and k_{DT} = all other paths for deactivation of T_1 .

From equation 2-13 for S_1 we have

$$\phi_F = k_F/k_S = k_F/(k_F + k_{ST} + k_{DS})$$

(continued)

2.13 A. (continued)

Similarly, we have

$$\phi_{ST} = k_{ST}/k_S = k_{ST}/(k_F + k_{ST} + k_{DS})$$

$$\text{and } \phi_P = \phi_{ST} k_P/k_T = \phi_{ST} k_P/(k_P + k_{TS} + k_{DT})$$

We may now calculate k_F and k_{ST} as

$$k_F = \phi_F k_S = (0.10)(10^9) = 10^8 \text{ sec}^{-1}$$

$$k_{ST} = \phi_{ST} k_S = (0.90)(10^9) = 9 \times 10^8 \text{ sec}^{-1}$$

Since $\phi_F + \phi_{ST} = 1.00$, there must be no other paths for deactivation of S_1 , i.e., $k_F + k_{ST} \gg k_{DS}$.

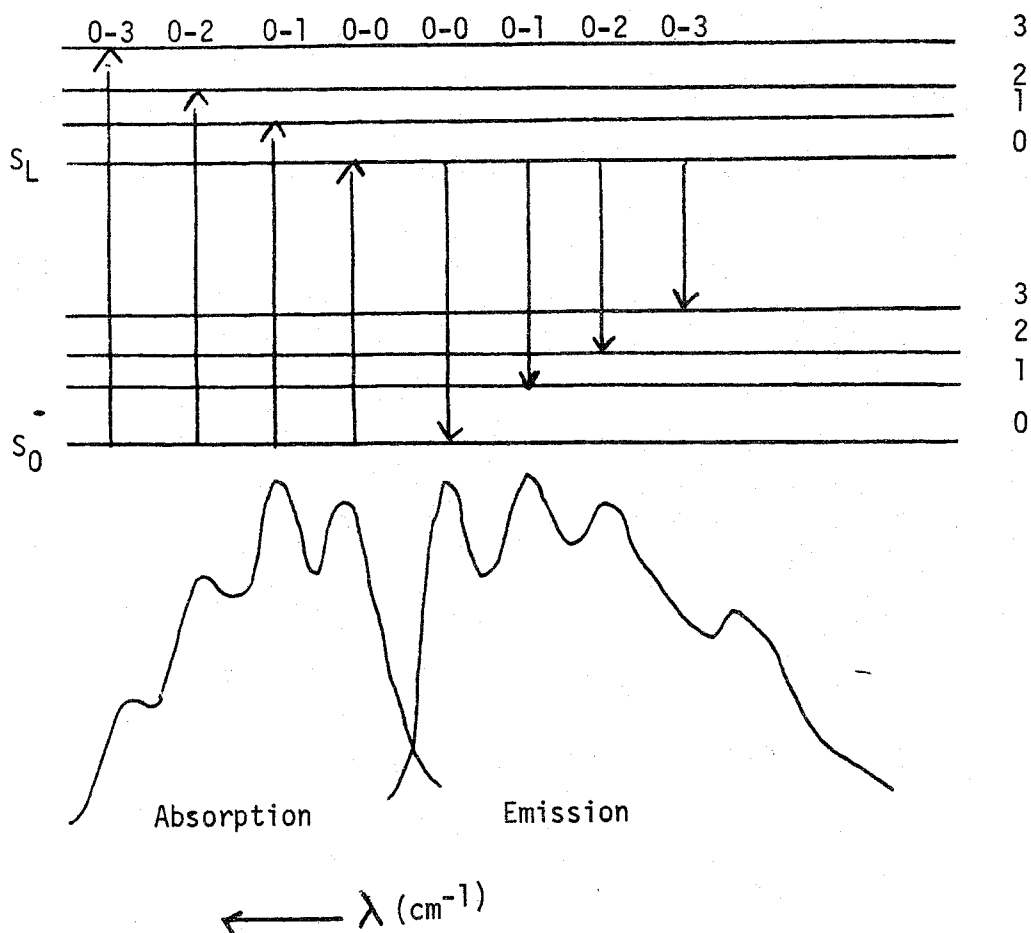
Next, we may calculate k_P from equation 2-14

$$k_P = \phi_P k_T / \phi_{ST} = 0.20 (1) / 0.90 = 0.22 \text{ sec}^{-1}$$

Finally, notice that since only $0.20/0.90 \times 100 = 22\%$ of the triplets actually emit, $k_{TS} + k_{DT}$ must be comparable to and indeed greater than k_P .

2.13 (continued)

B. Consider the figure below which depicts the vibrational levels of S_1 and S_0 . Remember emission only takes place from S_1 . If the molecule has similar vibrational possibilities in S_0 and S_1 , then the transition probabilities of the various vibrational transitions $S_0 \rightarrow S_1$ ($v = 0, 1, 2$, etc.) should be similar to those for $S_1 \rightarrow S_0$ ($v = 0, 1, 2$, etc.) since the Franck-Condon for both kinds of transitions should be similar, i.e., $S_0 \rightarrow S_1$ ($v = 2$) compared to $S_1 \rightarrow S_0$ ($v = 2$)



Notice that this approximation would predict exact coincidence of the 0-0 vibrational transitions of absorption and emission. They are not exactly coincident because the emitting excited state has a slightly different shape relative to S_0 .

2.13 (continued)

- C. "Forbiddenness" is only a relative term and has experimental meaning only when compared to an "allowed" process. The word derives from the fact that in the first approximations made in quantum mechanics, nuclear motion is frozen, magnetic fields and electron-electron repulsions are ignored. In this approximation forbiddenness means exactly zero probability. In real life, however, molecules vibrate, electron-electron repulsions exist and magnetic effects operate. Thus, we can use the term forbiddenness only in a relative fashion, i.e., the molecule has a "memory" of the zero order approximation and processes which are forbidden occur with a lower probability (or at a slower rate) than the corresponding "allowed" processes. Our problem in using the "forbidden-allowed" terminology thus becomes one of deciding on comparing the appropriate processes.

Now, the $S_1 \rightsquigarrow T_1$ intersystem crossing is an electronic transition between excited states of different spin. The corresponding "allowed" process would be the $S_2 \rightsquigarrow S_1$, an internal conversion between excited states of the same spin. The latter processes have rates of the order 10^{12} - 10^{11} sec^{-1} . In benzophenone the rate for $S_1 \rightsquigarrow T_1$ is estimated to be 10^{10} sec^{-1} . However, this "forbidden" radiationless process competes only with the allowed radiative process $S_1 \longrightarrow S_0 + h\nu$. The latter occurs with a rate of only about 10^5 sec^{-1} . Thus, ϕ_{ST} is essentially unity.

(continued)

2.13 C. (continued)

The forbidden $T_1 \longrightarrow S_0 + h\nu$ process occurs competitively with $T_1 \rightsquigarrow S_0$, also a forbidden process. As it turns out, the latter is slower than the radiative process, so the emission wins out in the competition.

2.13 D. We routinely identify weak, $\epsilon \lesssim 100$, absorption maxima with n, π^* transitions, since these are "forbidden" in the zero approximation. The more intense, $\epsilon > 1000$ absorption maxima are associated with π, π^* transitions. Thus, we expect that the strong band at 240 nm in $\text{CH}_3\text{COCH}=\text{CH}_2$ is due to a π, π^* transition and will suffer a red shift (move to longer wavelengths) with increasing solvent polarity. The weak band at 320 nm is assigned to a n, π^* transition and should suffer a blue shift (move to shorter wavelengths) with increasing solvent polarity.

2.13 (continued)

E. (1) The 0-0 band (the highest energy vibration for fluorescence and phosphorescence) is defined as the E_1 and E_3 , respectively. We identify these bands by simple inspection and take the first distinct maximum we see. In Figure 2-7 the first fluorescence maximum is at 318 nm (we know it is the fluorescence because it occurs at higher energy and, incidentally, is the mirror image of the molecule's absorption spectrum). The energy conversion equation on p. 10 allows us to calculate E_1 as $2.86 \times 10^4 / 454 \text{ nm} = 63 \text{ kcal/mole}$. For the molecule in Figure 2-8, $E_1 = 2.86 \times 10^4 / 316 = 90.5 \text{ kcal/mole}$.

(2) The measured yields and lifetimes are so different for the hydrocarbon and the bromo compound because the latter atoms assist spin-orbital coupling, i.e., any processes which involve a spin flip - should be better for the bromo compound (Br) relative to the hydrocarbon (HC). Thus, $S_1 \rightsquigarrow T_1$ and $T_1 \rightarrow S_0 + h\nu$ are expected to be faster for the bromo compound than for the hydrocarbon. Also ϕ_F decreases and ϕ_P increases for the bromo compound.

(continued)

2.13 E. (continued)

(3) In order to calculate k_{ST} , k_F and k_P we make use of equations 2-13 and 2-14. Since we assume no internal conversion from

S_1 , then $\phi_{ST} = 1 - \phi_F$ and

$$\phi_{ST}(HC) = 0.59$$

$$\phi_{ST}(Br) = 0.996$$

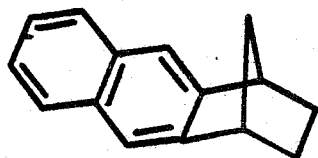
The key equations are:

$$k_F = \phi_F / \tau_S$$

$$k_{ST} = \phi_{ST} / \tau_S$$

$$k_P = \phi_P / \tau_T \phi_{ST}$$

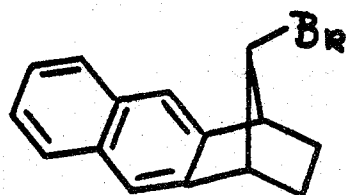
Plugging in the experimental values for these quantities we have:



$$k_F = 4.1 \times 10^6 \text{ sec}^{-1}$$

$$k_{ST} = 5.9 \times 10^6 \text{ sec}^{-1}$$

$$k_P = 0.026 \text{ sec}^{-1}$$



$$k_F = 4.0 \times 10^6 \text{ sec}^{-1}$$

$$k_{ST} = 1.0 \times 10^9 \text{ sec}^{-1}$$

$$k_P = 5.1 \text{ sec}^{-1}$$

CHAPTER 3

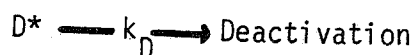
ELECTRONIC ENERGY TRANSFER

3.0 ENERGY TRANSFER: A RADIATIONLESS, ONE-STEP TRANSFER OF ELECTRONIC EXCITATION ENERGY FROM A DONOR, D*, TO A QUALIFIED ACCEPTOR

Rev: "Energy Transfer and Organic Photochemistry," Chapter 2



(1)



(2)

D = Donor (sensitizer)

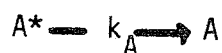
A = Acceptor (quencher)

3.2 REQUIREMENTS TO BE COMPETITIVE WITH k_D

A. Conservation of energy

1. $E(D^*) > E(A^*)$ Exothermic

2. Irreversible



(3)



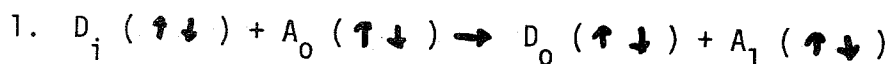
(4)

if exothermic, reversibility is not important and

$E_a^{ET} = E_a^{-ET} + [\Delta H = E(A^*) - E(D^*)]$

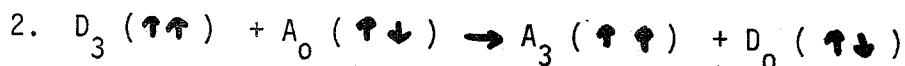
(5)

B. Conservation of spin: total spin should remain constant



(6)

$\Delta S = 0$, singlet-singlet transfer allowed (spin)



(7)

$\Delta S = 0$, triplet-triplet transfer allowed (spin)

3.2 (continued)

C. Mechanisms for excitation energy transfer

1. The "golden rule" for rates

$$\Psi_i \neq \Psi_f$$

$$\text{RATE} \propto \rho \frac{|\langle \Psi_i | H_p | \Psi_f \rangle|^2}{|E_f - E_i|} \quad (8)$$

$$\frac{1}{\Delta E} \propto \frac{\Delta E}{\hbar}$$

2. The nature of H_p

a. Electronic perturbations

b. $H_p = H_c$ (coulombic) + H_e (exchange)

(9)

c. $k_{ET} \propto \frac{\rho}{\Delta E} \{ |\langle \Psi_i | H_c | \Psi_f \rangle|^2 + |\langle \Psi_i | H_e | \Psi_f \rangle|^2 \}$ (10)

3. The coulombic term

$$H_c \propto \frac{q_A q_B}{R^4} \quad (11)$$

4. The exchange term

$$H_e = e^2/R \quad (12)$$

3.3 (continued)

B. Pulsating dipole is set up; coupling depends on resonances available; size of dipole of D^* , A^* .



D. Coupling allows equilibrium. What makes it irreversible? $E(D^*) > E(A^*)$. Figure 1

E. Forster: Worked out the theory and related resonances and dipole strengths to measurable quantities

1. $k_e = 1/\tau_e \propto E$ Einstein (14)

2. $k_e, E \propto I$ (generated by excitation)

3.

$$\propto \frac{1}{R^6} \left(\frac{f_D \epsilon_A}{R^6} \right) \quad (15)$$

\uparrow DIPOLE STRENGTH OF D^* \uparrow FALL OFF OF DIPOLE-DIPOLE INTERACTIONS
 \nwarrow EFFECTIVE INTERACTIONS OF D^* AND A

4. $\epsilon_{\max}^A \sim 10,000$: $1/\tau^{D^*} \sim 10^8$; $k_{ET}(\max) \sim 10^{11} \text{ M}^{-1} \text{ sec}^{-1}$
for $R \sim 50 \text{ \AA}$

$\epsilon_{\max}^A \sim 10$: $1/\tau^{D^*} \sim 10^5$; $k_{ET}(\max) \sim 10^5 \text{ M}^{-1} \text{ sec}^{-1}$
for $R \sim 50 \text{ \AA}$

3.4 MEASUREMENT OF k_{ET}

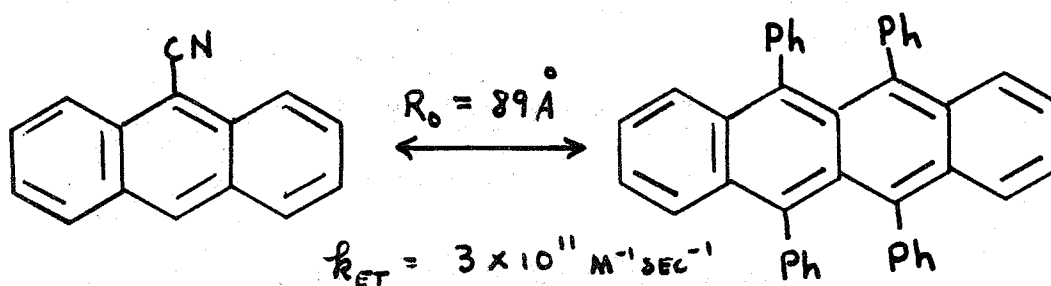
A. Convenient to define R_0 as distance for which

B. $1/\tau^{D*} = k_{ET}[A]$ (16)

Rate of deactivation = rate of energy transfer of D^* .

At this point $k_{ET} = (1/\tau^{D*})/[A]$.

C. Example: Intermolecular

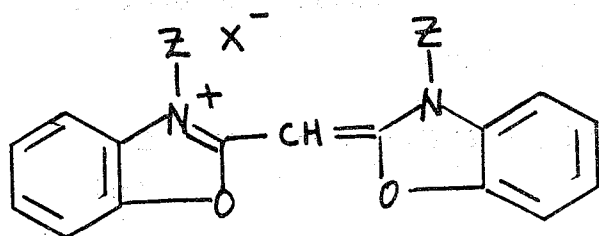


1. $k_{diff} \approx 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$
2. Proof: $k_{ET} > k_{diff}$ demonstrates long range transfer
3. $k_{ET} (\text{measured}) = k_{ET} (\text{calc.})!$
4. Kuhn (see Figure 3-1 on p.55)

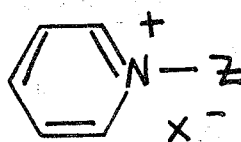
Figure 3-1

Example of Long-Range Interaction

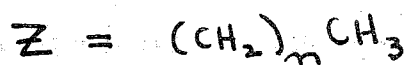
(a)



\equiv

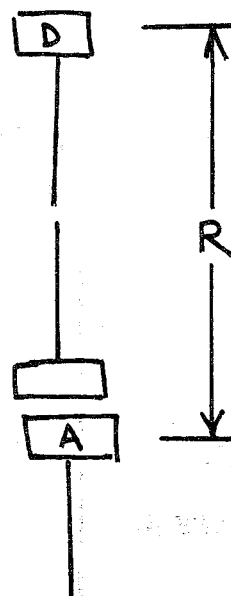


\equiv



= FATTY ACID

(b)



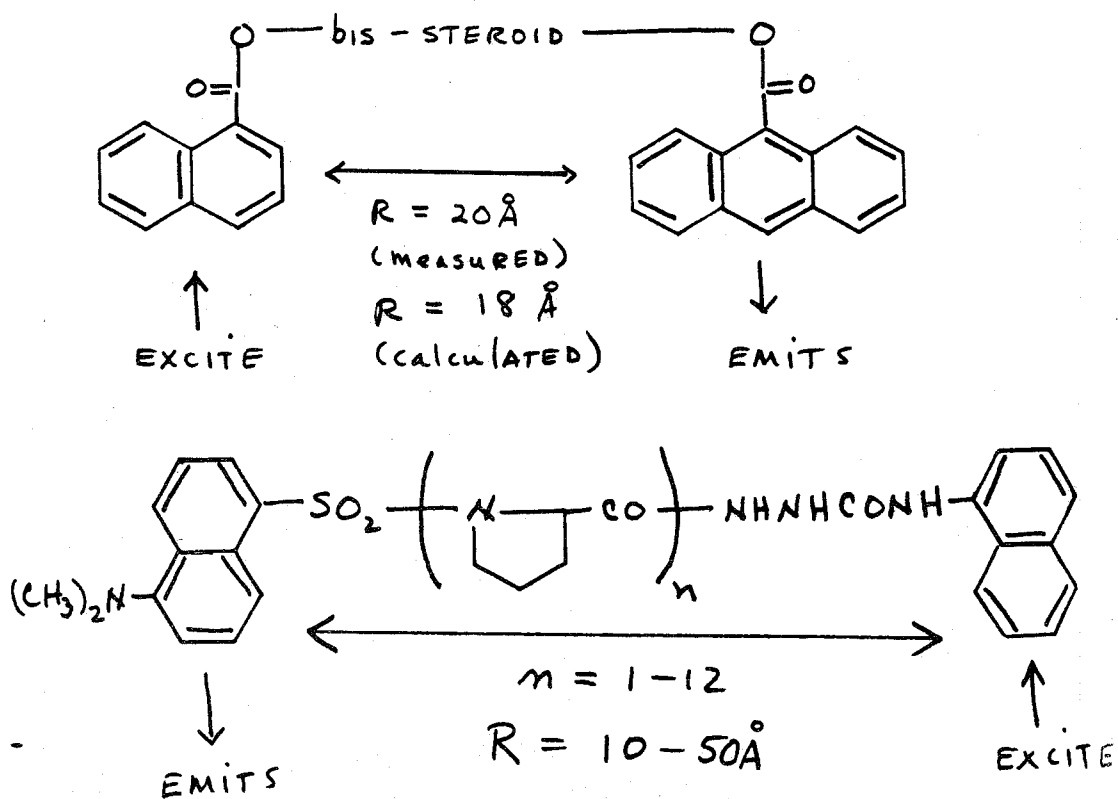
(c) % ENERGY TRANSFER = $f(R)$

$R_0 \sim 50 \text{ \AA}$

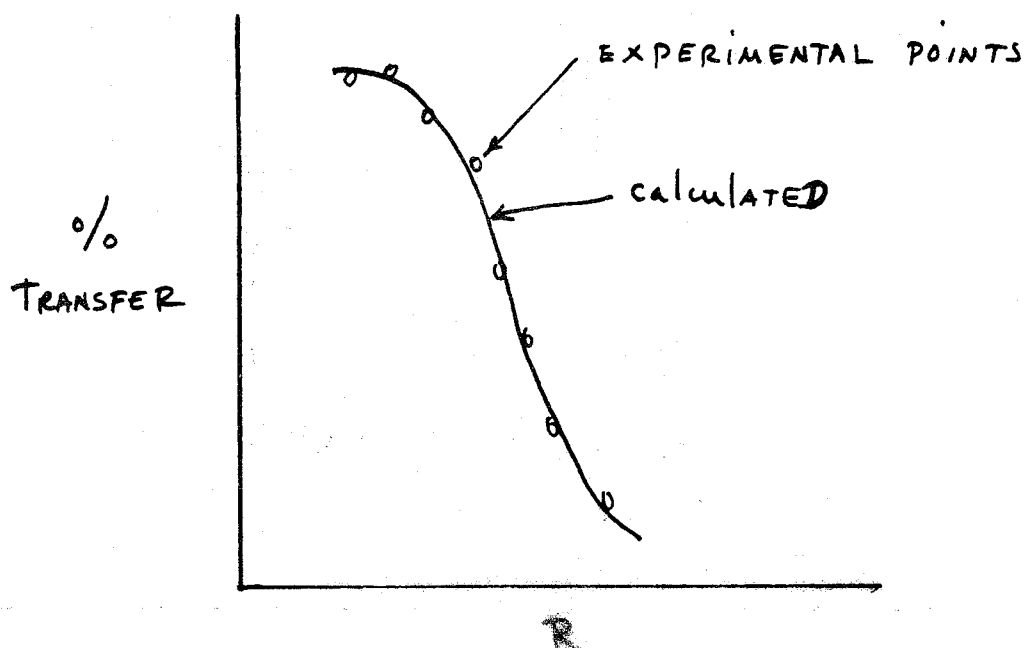
3.4 (continued)

D. Intramolecular tests: Non-conjugated chromophores

1. Molecules with fixed distances

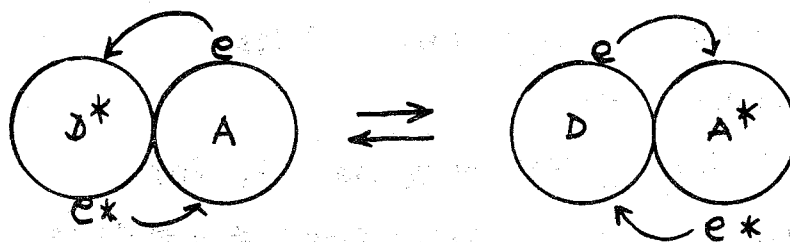


2. Test of Forster theory



3.5 THE EXCHANGE MECHANISM

A. Electrons on D^* and A exchange during a collision



1. $k_{ET} \propto \exp(-R)$

R = separation of D^* and A

2. k_{ET} depends only on exchange-size of orbitals of D^* and A.

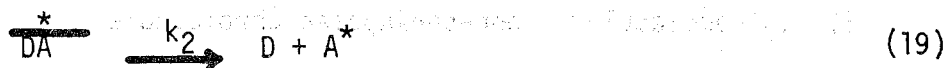
B. Diffusion of D^* and A together (collision) required for exchange

1. Debye Theory

$$k_{diff} = \frac{8RT}{3000\eta} \quad \eta = \text{viscosity} \quad (17)$$

$$\begin{aligned} k_{diff}^{calc} &= 5 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1} \text{ C}_6\text{H}_6 \\ &= 2 \times 10^{10} \text{ M}^{-1} \text{ sec}^{-1} \text{ hexane} \end{aligned}$$

2. Diffusion, collision, cage effects



3. In general, if $E(D^*) > E(A^*)$

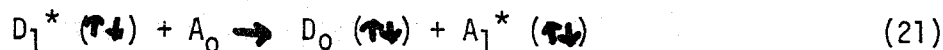
$$k_2 > k_{-1}$$

i.e., energy transfer is effectively irreversible.

3.5 (continued)

C. Types of exchange transfer

1. Singlet-singlet ($\uparrow\downarrow$)

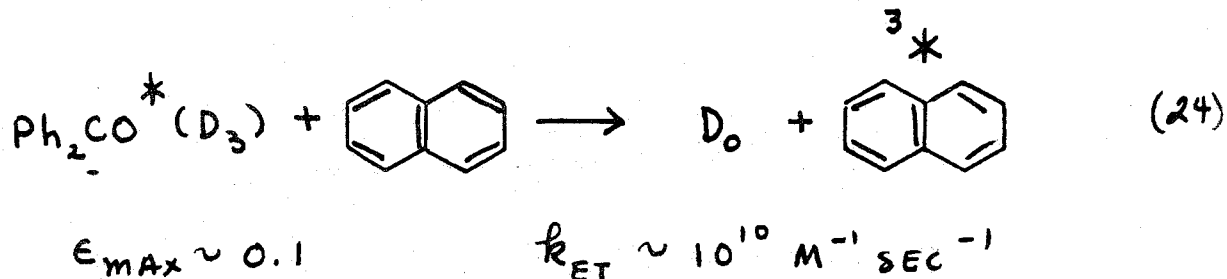
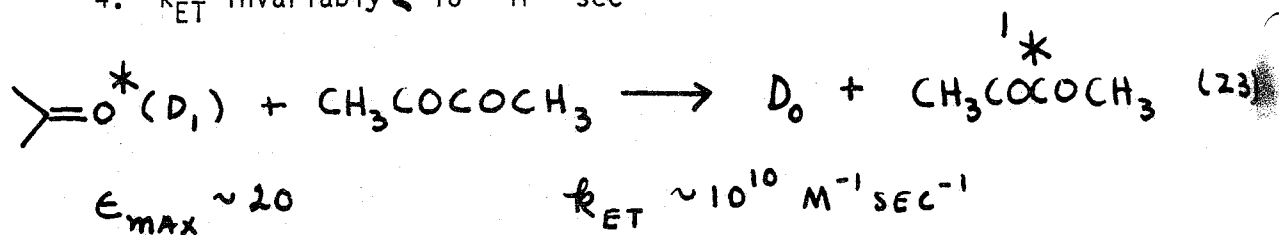


2. Triplet-triplet



3. Occurs rather than resonance when $\epsilon(D \rightarrow D^*)$ is weak (< 1000)

4. k_{ET} invariably $< 10^{10} \text{ M}^{-1} \text{ sec}^{-1}$

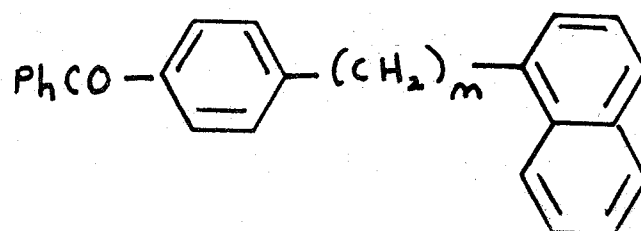


D. General rules: intermolecular

1. $k_{ET} \sim k_{\text{diff}}$, if $E(D^*) > E(A^*)$
2. Independent of electronic structure of D^* and A

E. Intramolecular: non-conjugated chromophore

1.

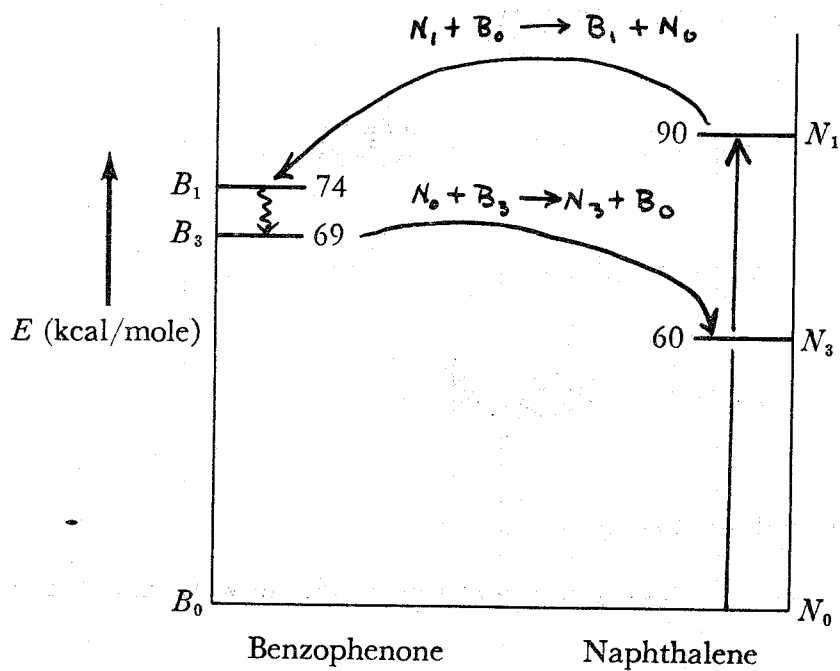


3.5 E. (continued)

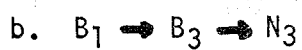
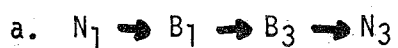
2.

Figure 3-2

Energy Levels of Benzophenone and Naphthalene



3. Indirect population of N_3



c. $\phi_{ST}(N) = 0.6$

$\phi_{ST}(N \rightarrow B) = 1.0$

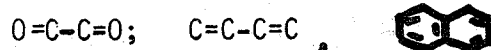
3.6 INTRAMOLECULAR ENERGY TRANSFER: CONJUGATED CHROMOPHORE

A. Strong and weak coupled chromophore

1. Unit chromophore



2. Strong interactions



3. Weak interactions



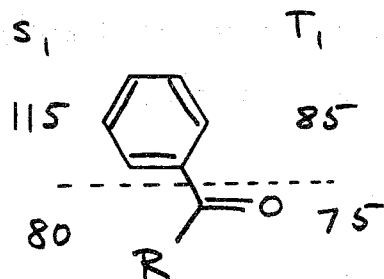
B. Concept of energy sinks

1. Lowest energy chromophore winds up with excitation

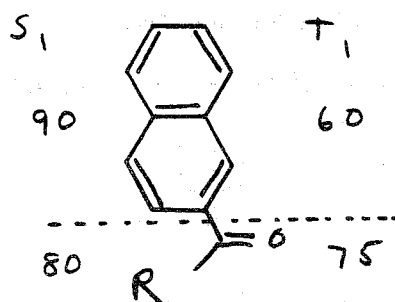
| 2. A — B | | IF | THEN |
|----------|-------|-------------------|-------------|
| A_1 | B_1 | $E_1(A) > E_1(B)$ | $S_1 = B_1$ |
| A_3 | B_3 | $E_1(B) > E_1(A)$ | $S_1 = A_1$ |
| | | $E_3(A) > E_3(B)$ | $T_1 = B_3$ |
| | | $E_3(B) > E_3(A)$ | $T_1 = A_3$ |

3.6 (continued)

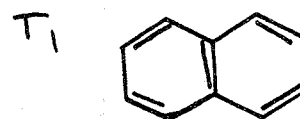
C. Examples



S_1 and T_1 on $C=O$



S_1 $C=O$



3.7 USES OF RESONANCE ENERGY TRANSFER: WIDE RANGE OF APPLICATIONS TO MOLECULAR SPECTROSCOPY, PHOTOCHEMISTRY, PHOTOBIOLOGY

A. Theory "well understood" via Forster treatment

1. Useful in estimating distances between interacting chromophores
2. May be important in excitation "hopping" from molecule to molecule
3. May be the mechanism of "self-quenching."

B. Difficult to find system that meets requirements since selective excitation of D_1 is required and since $E(A_1) > E(D_1)$

C. Mainly applicable to $D_1 + A \rightarrow A_1 + D$, but $D_3 + A_0 \rightarrow A_1 + D_0$ is known, although usually very inefficient

3.8 USES OF EXCHANGE TRANSFER

A. Theory less well developed

1. Appears to be diffusion controlled if $E(D^*) > E(A^*)$
2. $D_3 + A_0 \rightarrow A_3 + D_0$, very important (25)
3. $D_1 + A_0 \rightarrow A_1 + D_0$ (26)
4. $D_3 + A_0 \rightarrow A_1 + D_0$ (27)
5. No apparent structural dependence

B. Very useful in understanding mechanisms

1. Stern-Volmer quenching (Chapter 5) - kinetics

$$\frac{\phi}{\phi_q} = 1 + k_q \tau_{D^*} [A] = 1 + \frac{k_q [A]}{k_D} \quad (28)$$

- a. Lifetime of D_3 and D_1 if $k_q = k_{ET}$, since $k_{ET} = k_{diff}$
- b. k_q if τ_{D^*} is known
2. Standard method of sorting out singlet and triplet mechanism

C. Helpful in directing photochemical syntheses

3.9 TRIPLET SENSITIZERS

A. Desirable properties

1. $D_0 \rightarrow D_1$ at long λ
2. $E(D_3)$ as high as possible
3. $\phi_{ST} \sim 1$
4. k_D^3 long as possible
5. Chemically non-reactive

B. Tables of E_1 and E_3 values (see p. 63)

1. Values $\pm 1-2$ kcal/mole
2. Derived from 77°K emission
3. May be solvent dependent

TABLE 3-1

Table of Singlet (E_1) and Triplet (E_3) Energies
Of Organic Molecules. Values are in kcal/mole.

| <u>MOLECULE</u> | E_1 | E_3 |
|--------------------|-------|-------|
| Ethylene | ~ 120 | 85 |
| Benzene | 115 | 85 |
| Anisol | ~ 100 | 81 |
| Benzonitrile | ~ 100 | 77 |
| Acetophenone | 80 | 74 |
| Diphenylamine | 89 | 71 |
| Benzophenone | 74 | 69 |
| Triphenylene | 82 | 67 |
| Biphenyl | ~ 100 | 65 |
| Anthraquinone | 68 | 62 |
| Naphthalene | 90 | 61 |
| 2-Acetonaphthone | 77 | 59 |
| 1,3-Pentadiene | 100 | 57 |
| 1-Acetonaphthone | ~ 80 | 56 |
| Biacetyl | 64 | 55 |
| 1,3-Cyclohexadiene | 75 | 54 |
| Pyrene | 77 | 48 |
| Anthracene | 72 | 42 |
| Perylene | 64 | 36 |
| Tetracene | 61 | 29 |

3.10 IMPURITY QUENCHING

A. Oxygen



2. If $k_q = 10^{10}$, then rate of O_2 quenching = $10^{10} [O_2]$

3. $[O_2] \sim 10^{-3} M$ in organic solvents, then rate of quenching
 $= 10^{10}(10^{-3}) \sim 10^7 \text{ sec}^{-1}$

B. Other low energy impurities

C. A handy list of E_1 and E_3 values

3.11 SUMMARY

- Energy transfer as a method of indirect excitation (sensitization)
- Energy transfer as a method of deexcitation (quenching)
- Very important in photochemical systems
- Diffusion control quenching
- Energy sink concept

3.12 PROBLEMS

- Calculate the minimum lifetime τ_{D^*} required for oxygen to quench 99% of D^* , if k_q is $10^{10} M^{-1} \text{ sec}^{-1}$ (i.e., diffusion controlled) at a concentration of $O_2 = 10^{-3} M$.

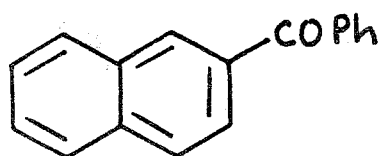
3.12 (continued)

- B. Use the concept of "excitation energy sinks" (section 3.6) to decide on which chromophore excitation (in S_1 and T_1) resides for the following molecules (see Table 1-1, Chapter 1).

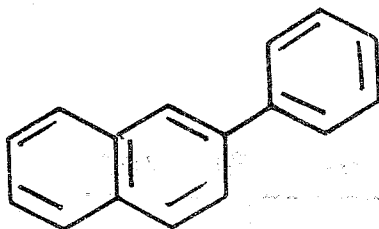
1.



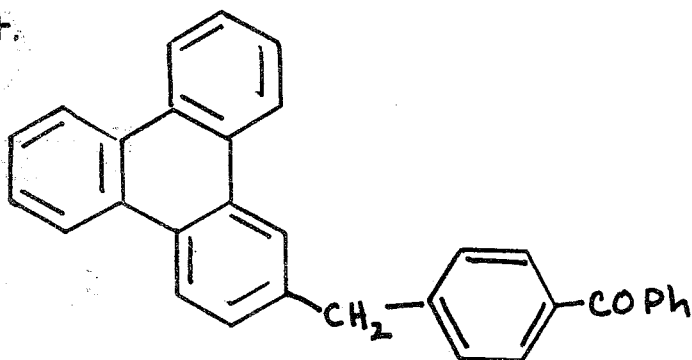
2.



3.

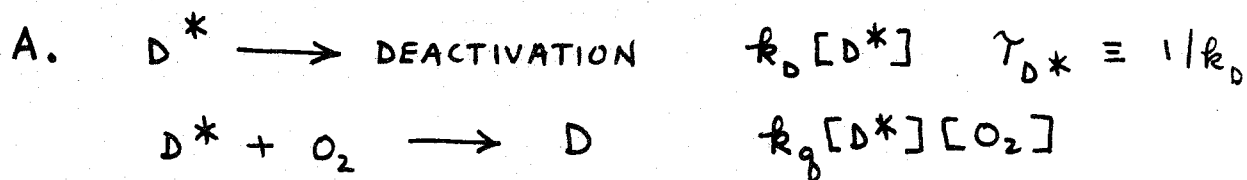


4.



- C. Should the efficiency of energy transfer by the resonance mechanism depend more on the radiative lifetime of the donor (transition dipole of the donor) or on the absorption coefficient corresponding to the transition $A \rightarrow A^*$? Explain your reasoning.
- D. Should the rate constant of energy transfer by the resonance mechanism depend on the radiative lifetime of the acceptor? On the absorption coefficient of the donor?
- E. Why is the simple observation of diffusion controlled quenching of an electronically excited donor insufficient evidence to establish that energy transfer from donor to quencher is occurring? Suggest a measurement which would establish whether energy transfer actually occurred.

3.13 ANSWERS TO THE PROBLEMS

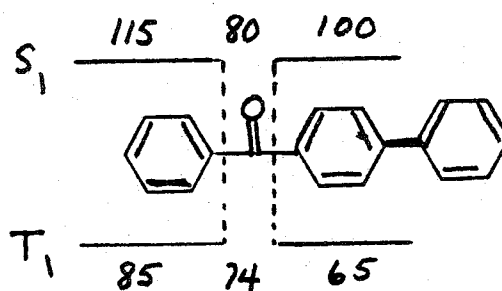


$$99 k_D = k_q [O_2] = 99 / \tau_{D^*}$$

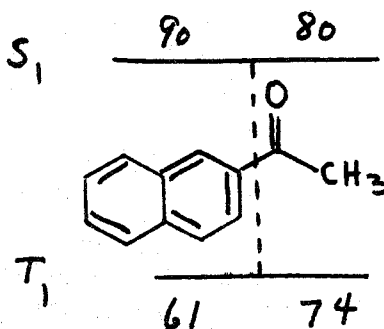
$$\tau_{D^*} = 99 / (10^{10} \times 10^{-3}) = 9.9 \times 10^{-7}$$

B.

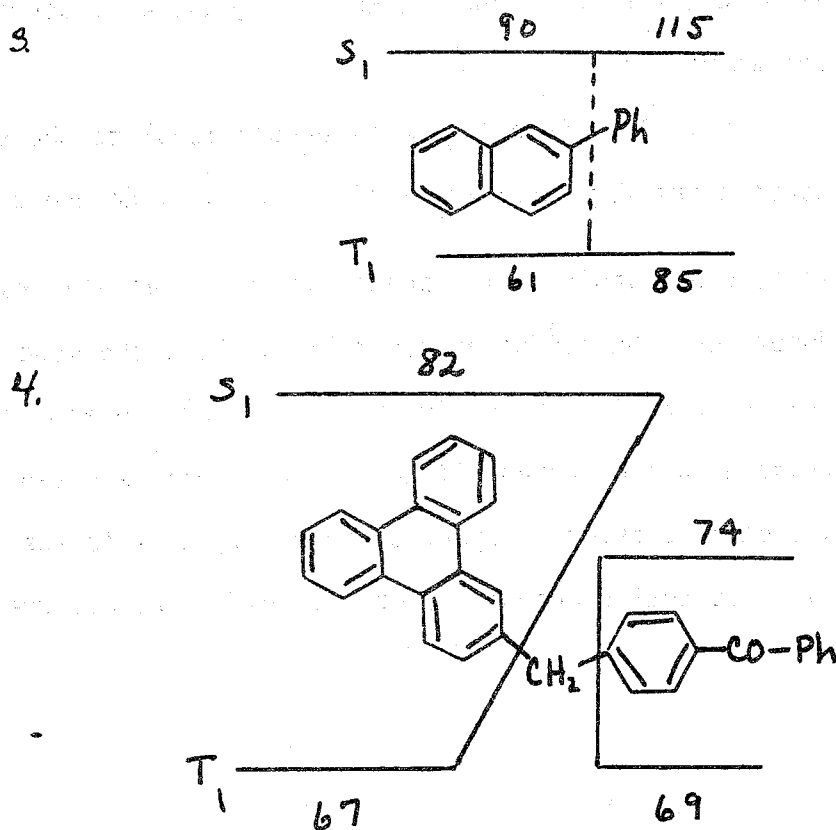
1.



2.



3.13 B. (continued)



C. To answer this question we must examine the theoretical expression for resonance transfer, equation 15. According to the expression, the rate will be directly proportional to both quantities. Although the rate will be slower for transfer with weakly absorbing donors, their corresponding lifetimes will be longer; thus, the efficiency of transfer will be roughly independent of the donor radiative lifetime.

3.13 (continued)

- D. Equation 15 does not show an explicit dependence on the radiative lifetime of the acceptor. However, since the radiative rate of A^* is directly proportional to ϵ_A (14), k_{ET} will depend on the radiative lifetime of A^* .

Similarly, since $1/\tau_{D^*}$ is proportional to the extinction coefficient for donor absorption, k_{ET} will depend on the latter.

- E. It is conceivable that a photoreaction of an electronically excited donor could be diffusion controlled. Thus, the mere observation of quenching would not suffice to "prove" that electronic energy transfer had occurred. If an electronically excited state of the acceptor is detected spectroscopically, this is the best kind of evidence that electronic energy transfer has occurred.

CHAPTER 4

PHOTOCHEMICAL DYNAMICS

4.1 EFFICIENCY, REACTIVITY AND CHEMICAL YIELD

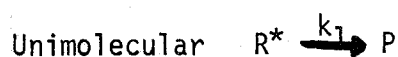
Rate constant, k = reactivity

Quantum yield, ϕ = efficiency

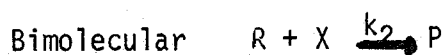
Chemical yield, % = relative efficiency

4.2 PHENOMENOLOGICAL DESCRIPTION OF DYNAMIC QUANTITIES

A. Reactivity: rate constant for process of interest



$$-\frac{d[R^*]}{dt} = k_1[R^*] = \frac{d[P]}{dt} \quad (1)$$



$$-\frac{d[R^*]}{dt} = -\frac{d[X]}{dt} = k_2[R^*][X] = \frac{d[P]}{dt} \quad (2)$$

k_1 and k_2 are measures of reactivity toward formation of P.

B. Efficiency: probability of a process relative to all processes assigned probability of 1

$$\phi = \frac{\text{molecules undergoing process}}{\text{photons absorbed by system}} \quad (3)$$

$$\phi = \frac{\text{molecules/time}}{\text{photons absorbed/time}} \quad (4)$$

$$I_a = \text{photons/time-volume} \quad (5)$$

$$\phi_1 = \frac{k_1[R^*]}{I_a} = \frac{k_1[R^*]}{\text{all deactivation of } R^*} \quad (6)$$

$$\phi_2 = \frac{k_2[R^*][X]}{I_a} = \frac{k_2[R^*][X]}{\text{all deactivation of } R^*} \quad (7)$$

4.2 (continued)

C. Chemical yield: efficiency of process of interest relative to efficiencies of all irreversible chemical processes

$$\% \text{ yield} = \frac{\phi}{\sum \phi_i} \quad (8)$$

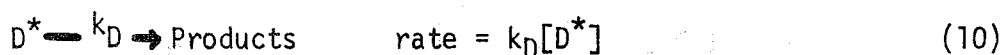
$$\sum \phi_i = \phi + \text{all other (irreversible chemical) processes} \quad (9)$$

D. Conclusion

1. If we know all the k 's (reactivity), we know ϕ and % yield
2. If we know all the ϕ 's, we know % yield, but not k 's
3. % yield is not a useful dynamic parameter, in general

4.3 RATE PROCESSES: UNIMOLECULAR

A. Unimolecular decay



$$\text{Rate Law: } -\frac{d[D^*]}{dt} = k_D[D^*] \quad (11)$$

$$\ln \frac{[D^*]}{[D^*]_{t=0}} = -k_D t \quad (12)$$

$$\tau_D(\text{sec}) \equiv 1/k_D(\text{sec}^{-1}) \quad (13)$$

B. Experimental determination of $[D^*]/[D^*]_0$

$$\frac{I}{I_0} = \exp(-k_D t) \quad (14)$$

4.3 (continued)

C. Examples: naphthalene in a micelle (Figure 1)

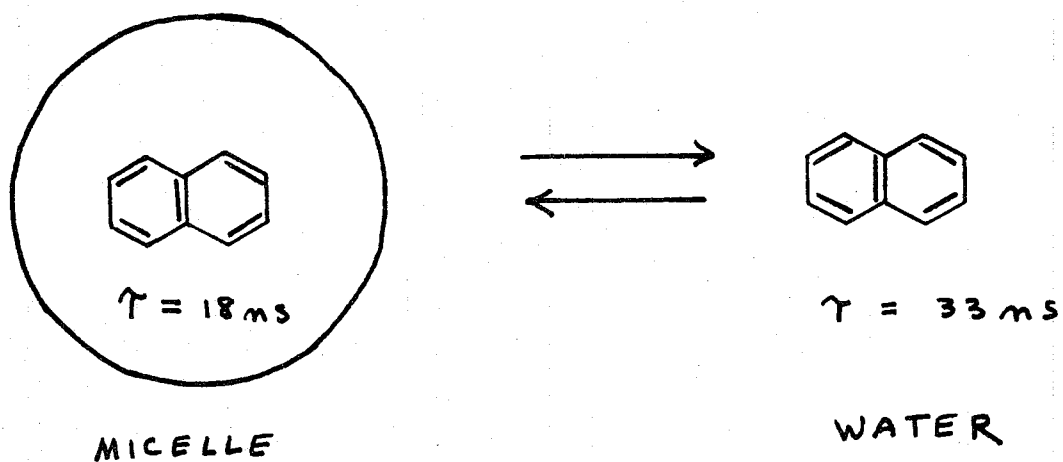
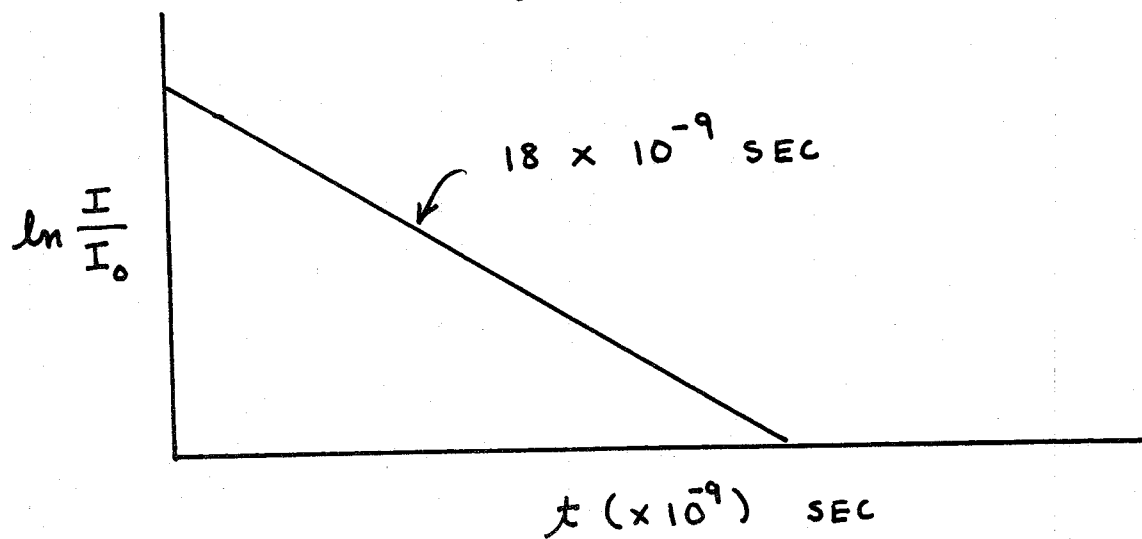
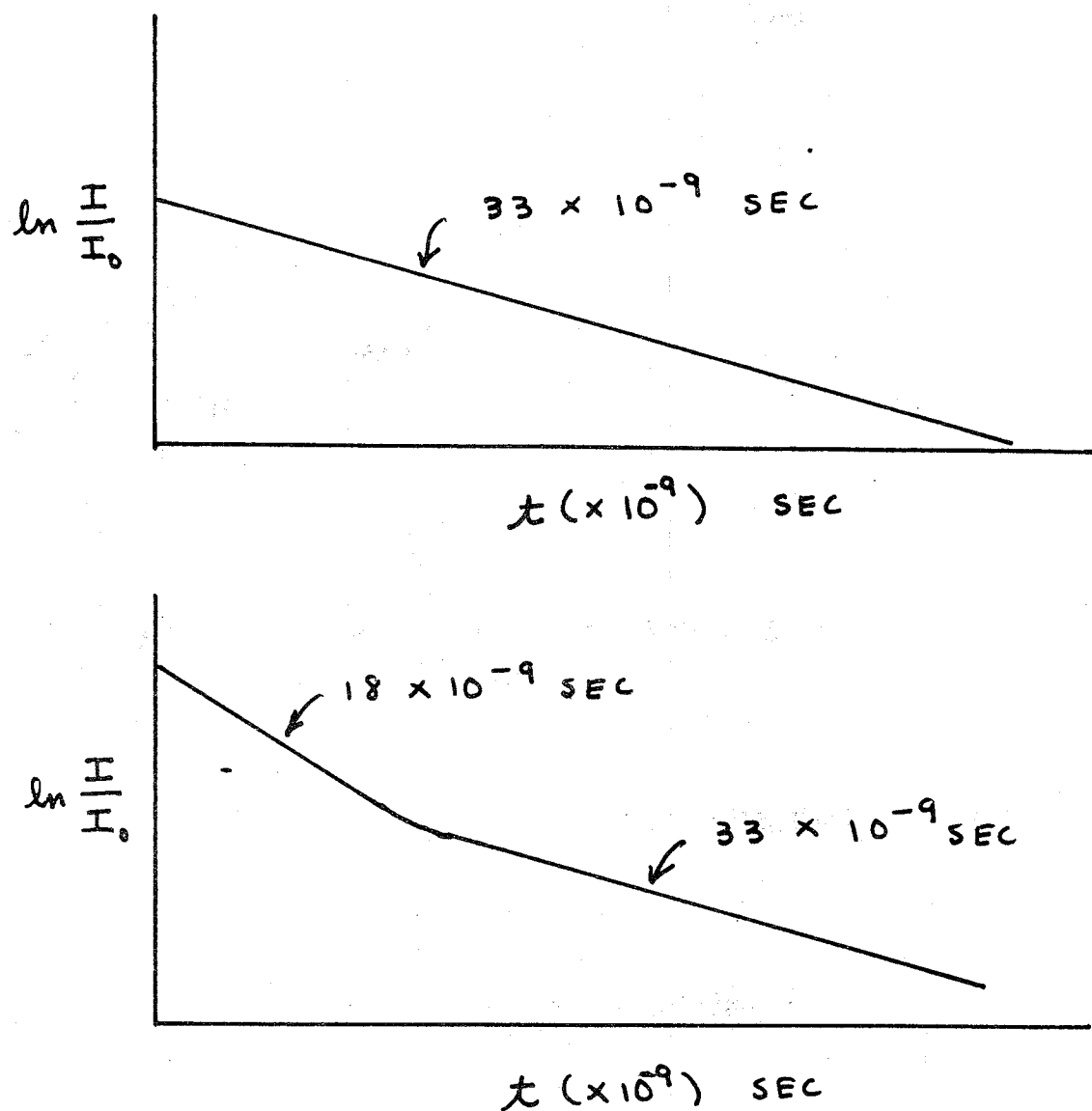


Figure 4-1



4.3 Figure 4-1 (continued)



D. Other experimental methods

1. Phosphorescence decay ($T_1 \rightarrow S_0 + h\nu$)
2. Triplet-triplet absorption ($T_1 + h\nu \rightarrow T_n$)

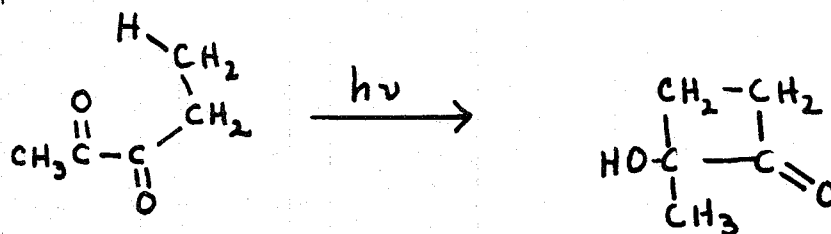
4.3 (continued)

E. Extraction of rate constants from unimolecular decay rates

$$\phi = \rho \frac{k_r}{k_D} \quad (16)$$

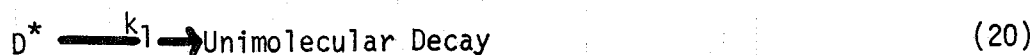
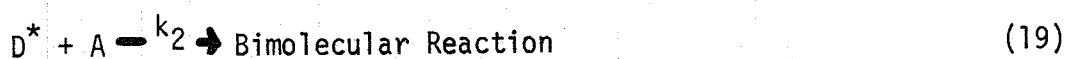
$$k_r = \phi \rho k_D \quad (17)$$

F. Example



Measured values: $k_D = 5 \times 10^6 \text{ sec}^{-1}$; $\phi = 0.1$; $\rho = 1.0$
 $k_r = 5 \times 10^5 \text{ sec}^{-1}$

4.4 RATE PROCESSES: BIMOLECULAR



A.

$$\phi_2 = \rho \frac{k_2[D^*][A]}{k_2[D^*][A] + k_1[D^*]} = \frac{k_2[A]}{k_2[A] + k_1} \quad (21)$$

B.

$$\frac{1}{\phi_2} = \frac{1}{\rho} + \frac{k_1}{\rho k_2[A]} \quad (22)$$

4.4 (continued)

C. Example (Figure 4-2)

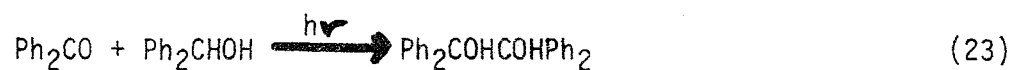
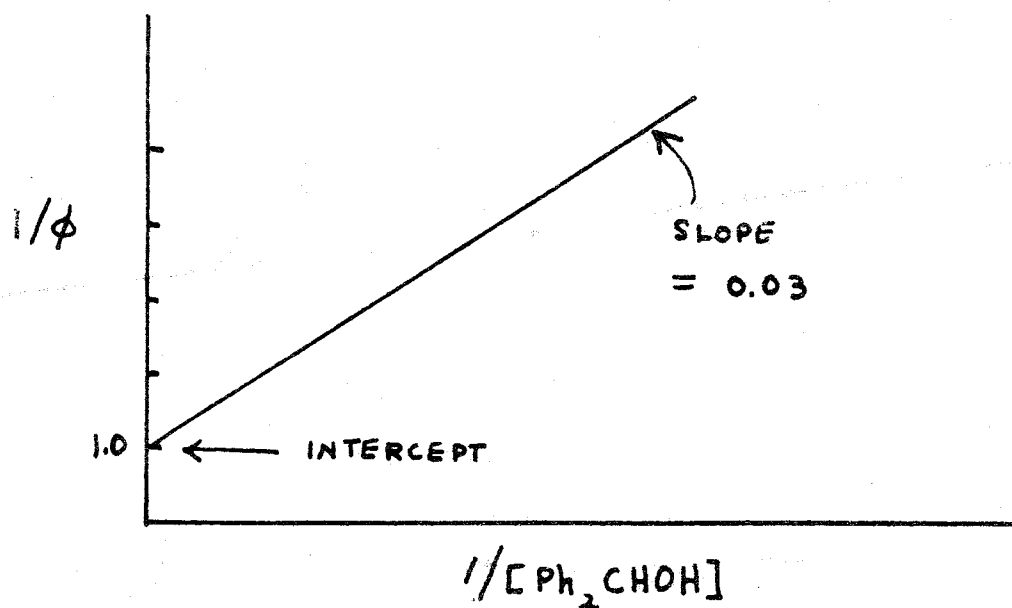


Figure 4-2

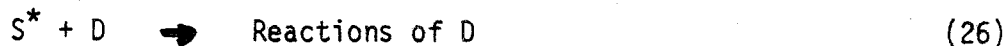


1. Conclude $k_1/k_2 = 0.03 \text{ M}$
2. From direct phosphorescence decay measurement,
 $k_1 = 10^4 \text{ sec}^{-1}$

$$k_2 = 3 \times 10^5 \text{ M}^{-1} \text{ sec}^{-1}$$

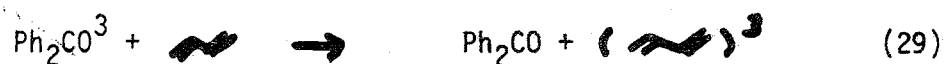
(24)

4.5 SENSITIZATION AND QUENCHING



B. Mechanisms

1. Physical: energy transfer

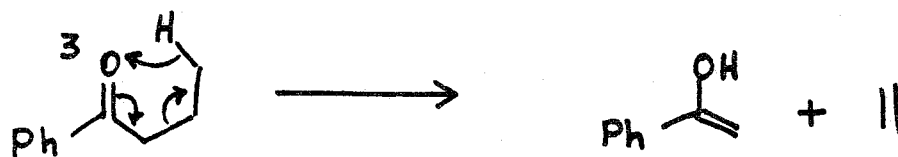


2. Chemical: intermediates



D. Mechanisms

1. Physical: energy transfer and exciplex formation



2. Chemical: intermediates

4.6 USES OF SENSITIZATION AND QUENCHING

A. Sorting out of S_1 and T_1

B. Criteria

Triplet sensitization by energy transfer

Triplet quenching by energy transfer

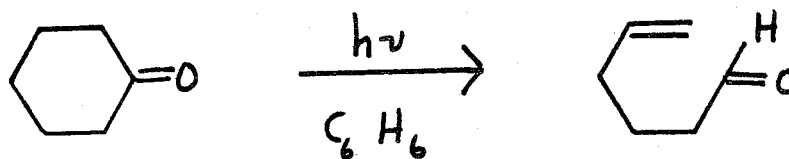
C. Stern-Volmer kinetics

$$\frac{\phi^0}{\phi} = 1 + \frac{k_q[Q]}{k_1 + k_2[A]} \quad (37)$$

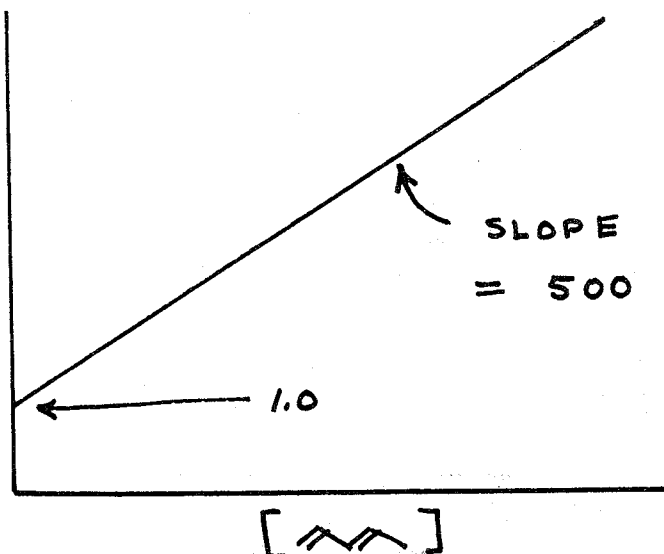


D. Example

Figure 4-3



ϕ^0/ϕ



1. Conclude $k_q/k_D = k_q\tau_D = 500 \text{ M}^{-1}$
2. $k_q \sim 5 \times 10^9 \text{ M}^{-1} \text{ sec}^{-1}$
3. Conclude $k_D = 10^7 \text{ sec}^{-1}$
4. Fluorescence not quenched
5. Conclude triplet only reacts

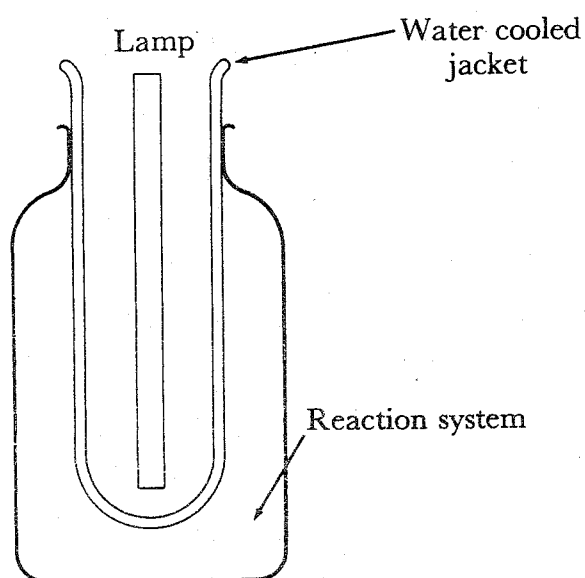
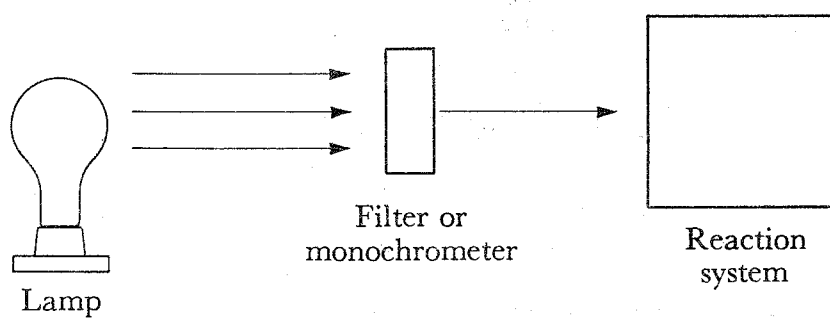
4.7 EXPERIMENTAL TECHNIQUES.

Rev: Calvert and J.N. Pitts, "Photochemistry," Wiley, 1966, Ch. 7.

A.

Figure 4-4

Generation, Control and Measurement of Light

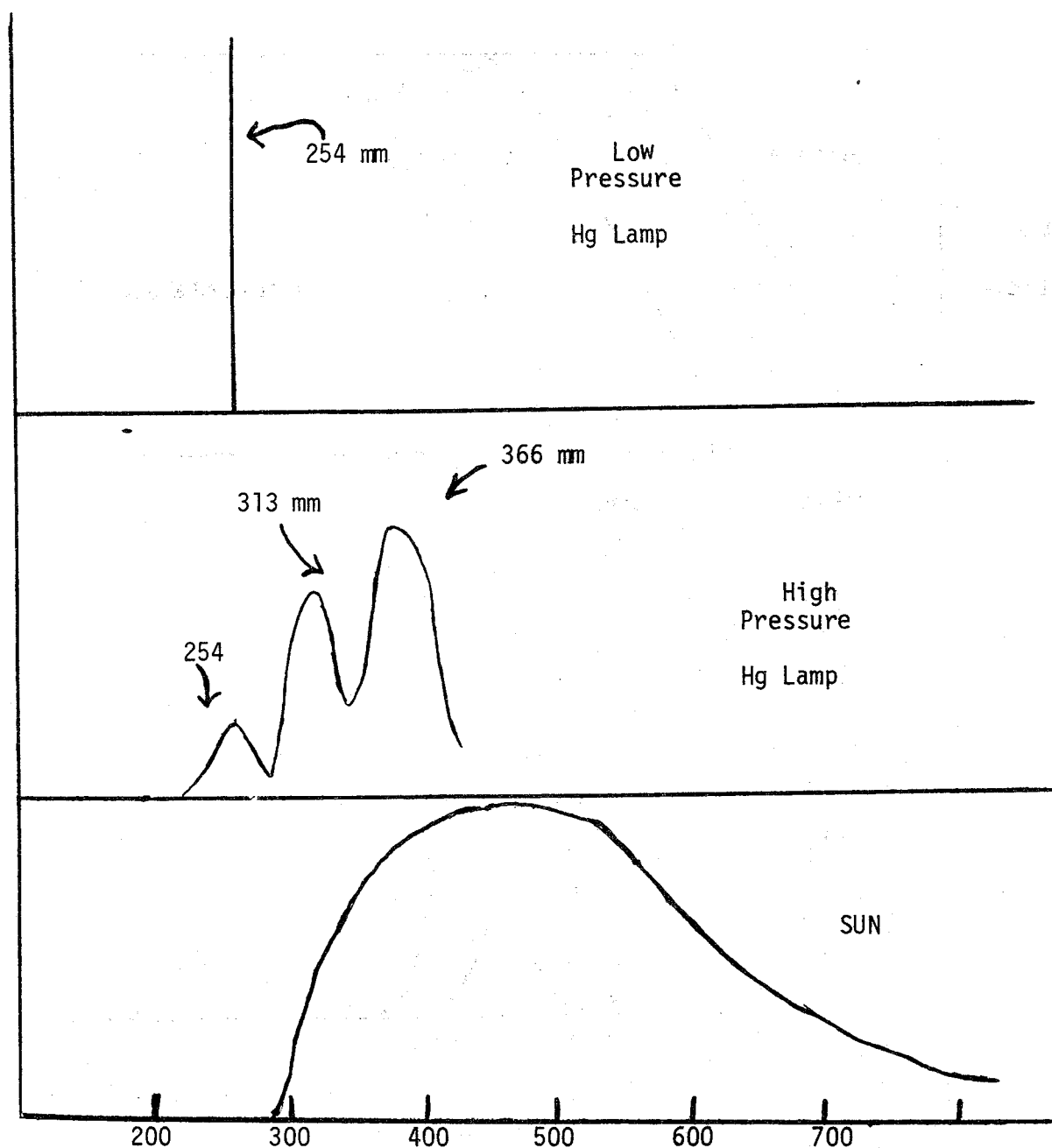


4.7 (continued)

B. Sources of ultraviolet and visible light

1. Low pressure mercury lamps
(254 nm and 578 nm)
2. High pressure mercury lamps
(254 nm, 313 nm, 366 nm, 405 nm)
3. Sunlight

Figure 4-5



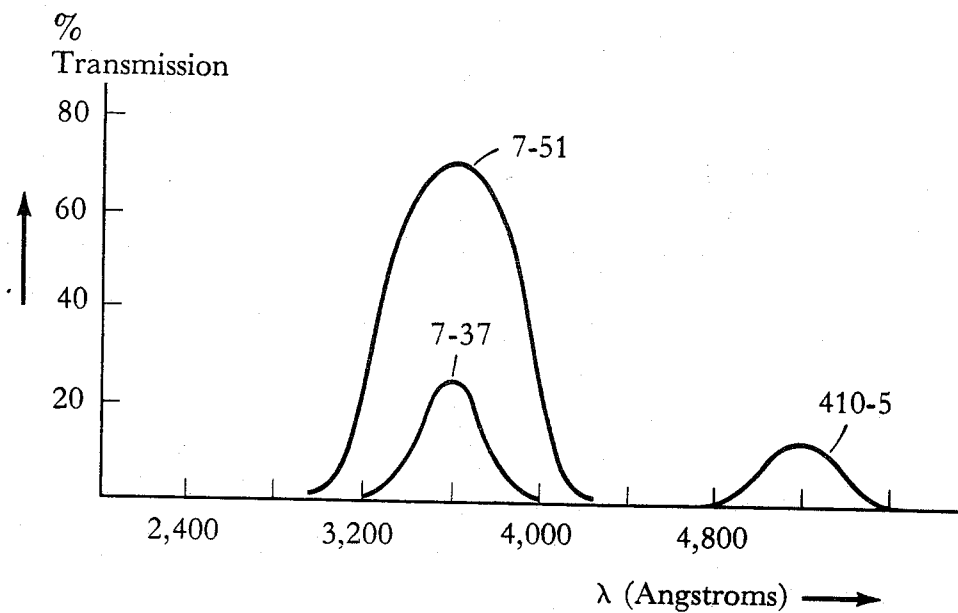
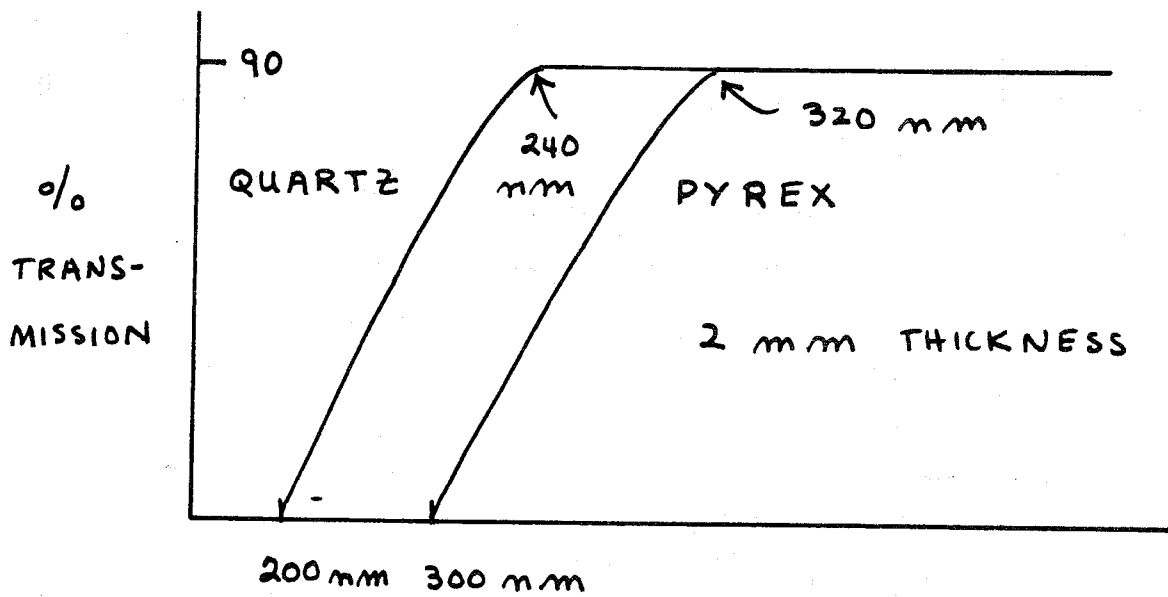
4.7 (continued)

C. Control of light

1. Filters: glass (Figure 4-6)

2. Monochrometers

Figure 4-6



4.7 (continued)

D. Measurement of light

1. Phototubes
2. Chemical actinometry

E. General considerations

1. Emission of lamp
2. Absorption of sample
3. Transmission of intervening environment
4. Absorption of intermediates or products
5. Quenching effects

4.8 SUMMARY

A. Differentiation of reactivity, efficiency, yield

1. Reactivity given by k , a molecular parameter
2. Efficiency given by ϕ , a probability dependent on reaction conditions
3. Yield given by ratio of probability process to all other (irreversible) processes

B. Kinetic expressions

1. Unimolecular

$$\frac{P}{P_0} = \exp(-k_d t)$$

2. Bimolecular

$$\frac{1}{\phi} = \frac{1}{\phi_0} + \frac{k_1}{\phi_0 k_2 [A]}$$

3. Stern-Volmer quenching

$$\frac{\phi_0}{\phi} = 1 + \frac{k_q [Q]}{k_D}$$

4. No need to measure ϕ , ρ

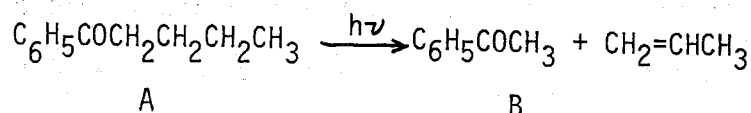
5. Independent of ϕ_D^*

4.9 PROBLEMS

- A. Figure 4-7 plots the relative intensity I/I_0 of fluorescence emission of a cyclohexane solution of norcamphor at room temperature in the presence of a fixed concentration of biacetyl (a diffusion control quencher of norcamphor singlets). For cyclohexane k_{dif} is known to be $10^{10} \text{ M}^{-1} \text{ sec}^{-1}$ at 25°C . The scale on the right side plots $\ln I/I_0$ and the scale on the left plots raw data I/I_0 . (a) Calculate the fluorescence lifetime of norcamphor from both plots (the fluorescence lifetime of norcamphor in cyclohexane at 25°C in the absence of quencher is $5.5 \times 10^{-9} \text{ sec}$). (b) Calculate the concentration of biacetyl required to reduce the fluorescence lifetime to the observed value.

- B. The viscosity of cyclohexane at 300°C is approximately 10 millipoise. Calculate k_{dif} for cyclohexane.

- C. Butyrophenone, A, undergoes the following photoreaction:

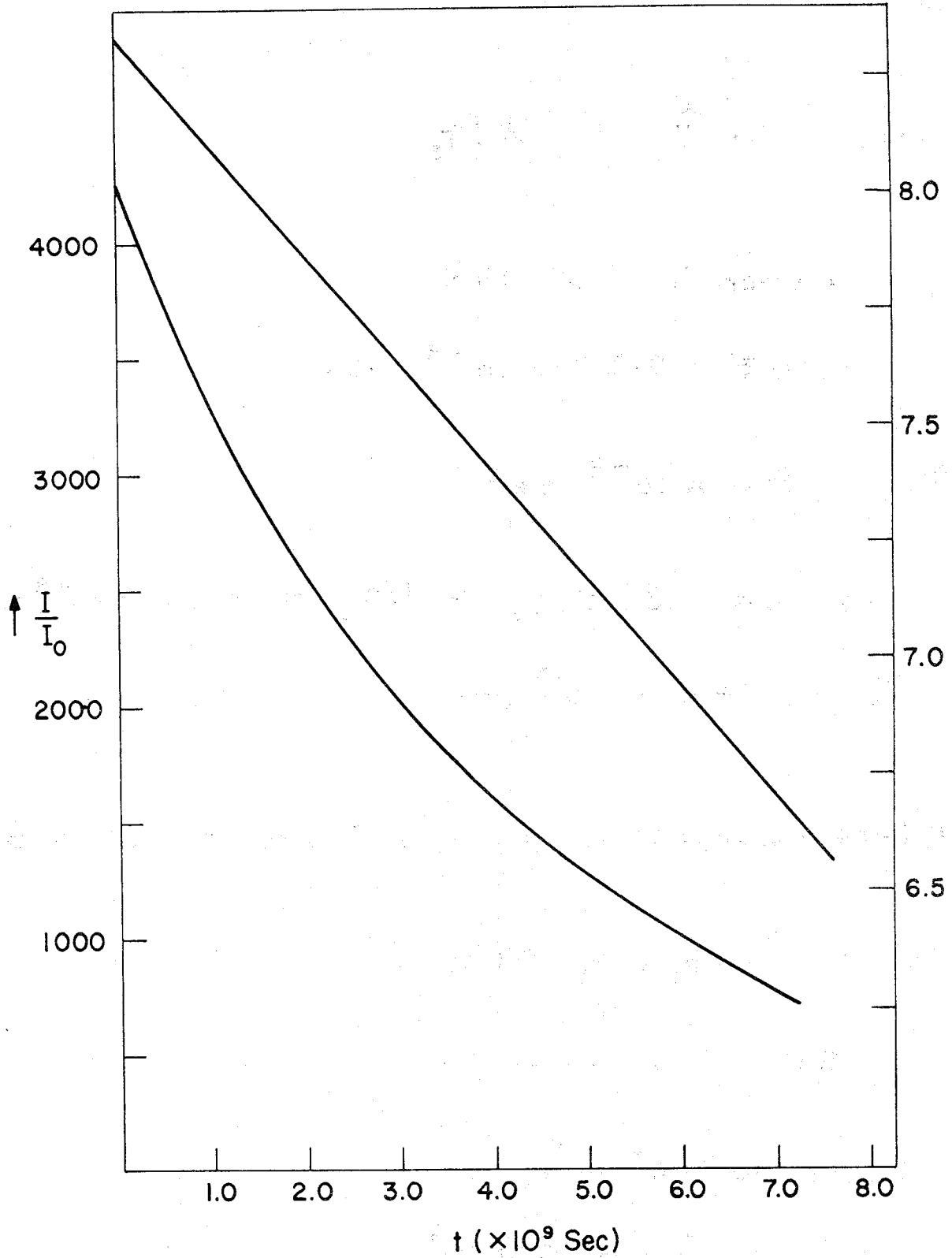


In tert-butanol, the quantum yield for acetophenone (B) formation (ϕ_p) is 1.0. The reaction is known to proceed exclusively from triplet A. Addition of 1,3-pentadiene (a diffusion control quencher of triplet (A) quenches formation of B at 300°C according to the equation

$$\frac{\phi_p^0}{\phi_p} = 1 + 40 [\text{diene}]$$

Calculate the rate constant for triplet reaction of A if the viscosity of tert-butanol is 5×10^{-3} poise at 300°C .

Figure 4-7



4.10 Answers to the Problems

A.

$$E_q(14) \quad \ln \frac{I}{I_0} = t/\tau_s$$

$$\begin{aligned} \tau_s &= t(4000) - t(1480) \\ &= (4.3 - 0.3) \times 10^{-9} \text{ SEC} \end{aligned}$$

$$\tau_s = 4.0 \times 10^{-9} \text{ SEC}$$

$$\text{SLOPE OF } \ln I/I_0 = 1/\tau_s = 0.25 \times 10^{+9} \text{ SEC}^{-1}$$

$$\tau_s = 4.0 \times 10^{-9} \text{ SEC}$$

$$\tau_s^0(\text{NORCAMPHOR}) = 5.5 \times 10^{-9} \text{ SEC} = 1/\tau_s = k_s$$

$$\tau_s^B = 1/(k_s + k_q[B])$$

$$k_q[B] = 1/\tau_s^B - 1/\tau_s$$

$$k_q = 10^{10} \text{ M}^{-1} \text{ SEC}$$

$$[B] = \frac{(2.5 - 1.8) \times 10^8}{10^{10}} = 5 \times 10^{-3} \text{ M}$$

4.10 (continued)

B.

$$\begin{aligned}k_{DIF} &= 2.2 \times 10^7 / 10 \times 10^{-3} \\&= 2.2 \times 10^9 \text{ M}^{-1} \text{ SEC}^{-1}\end{aligned}$$

C.

$$\frac{\phi^0}{\phi} = 1 + \frac{k_{ET}}{k_D} [Q] = 1 + k_{ET} \tau_D [Q]$$

$$\phi_P = 1.0 \quad \therefore \quad \phi_{ST} = 1.0$$

$$\begin{aligned}k_{ET} &= k_{DIF} = 2.2 \times 10^7 / 5 \times 10^{-3} \\&= 4.4 \times 10^9 \text{ M}^{-1} \text{ SEC}^{-1}\end{aligned}$$

$$k_{ET} / k_D = 40$$

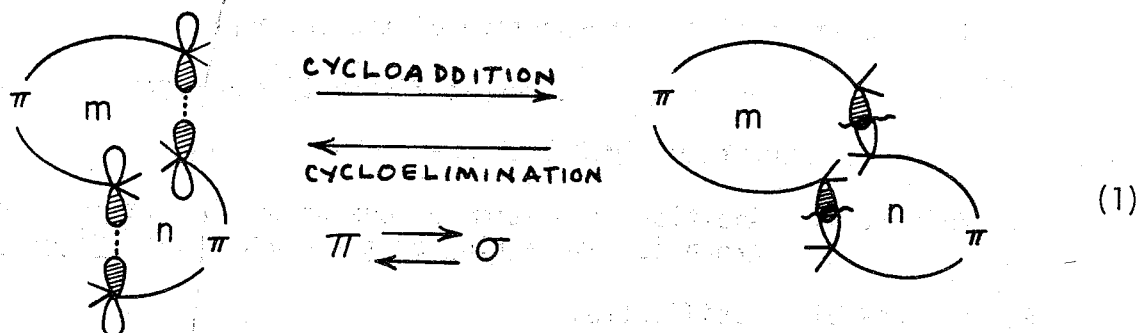
$$k_D = 4.4 \times 10^9 / 40 = 1.1 \times 10^8 \text{ SEC}^{-1}$$

CHAPTER 5
PERICYCLIC REACTIONS: A USEFUL BASIS FOR CLASSIFICATION
AND MECHANISTIC ANALYSIS

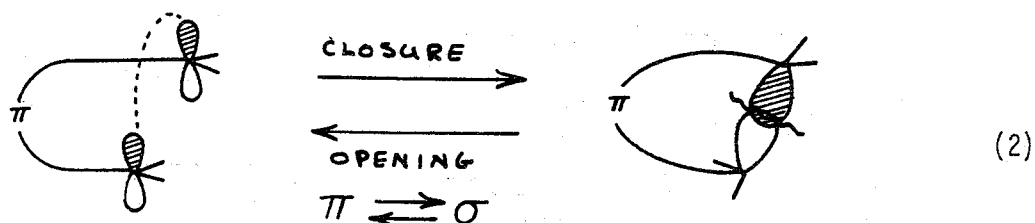
5.1 PERICYCLIC REACTIONS: CONCERTED REACTIONS INVOLVING A CYCLIC ARRAY OF INTERACTING ORBITALS. Rev: R.B. Woodward and R. Hoffman, "The Conservation of Orbital Symmetry," Academic Press, 1970; R.E. Lehr and A.P. Marchand, "Orbital Symmetry: A Problem Solving Approach," Academic Press, 1972.

A. Classification

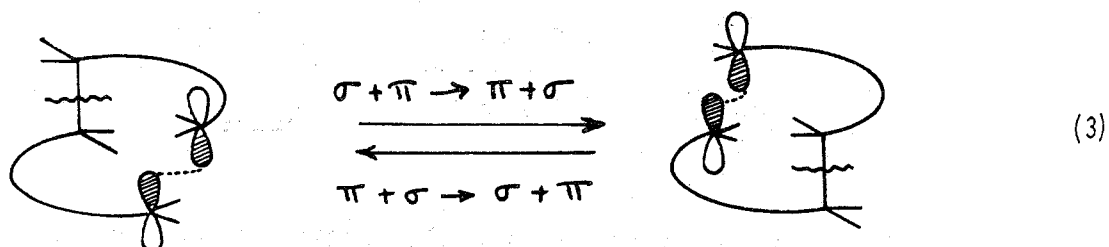
1. Cycloaddition and cycloelimination



2. Electrocyclic closures and openings

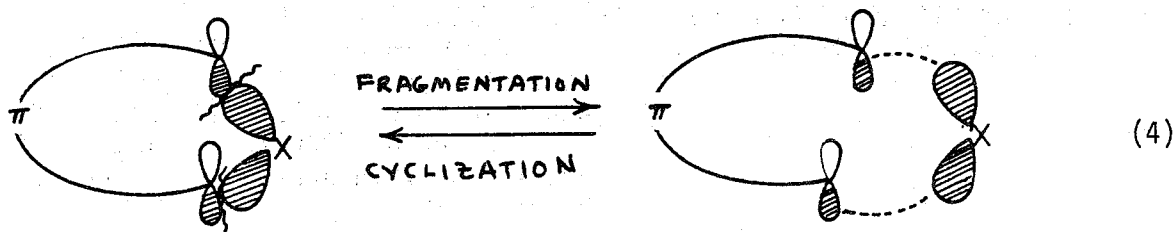


3. Sigmatropic rearrangements



5.1 A. (continued)

4. Cheletropic fragmentations and cyclizations



B. Unifying feature: closed cycle of interacting orbitals

C. Usefulness

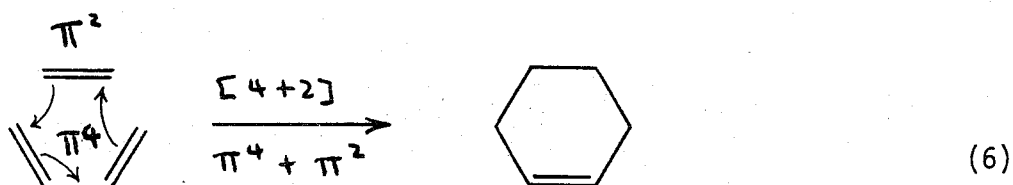
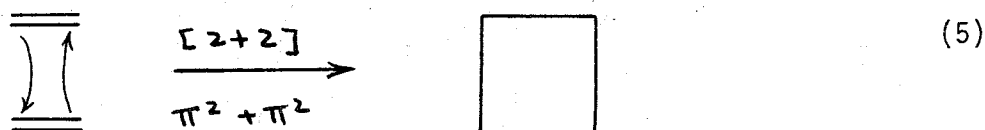
1. Classification, irrespective of mechanism
2. Stereoselectivity, stereospecificity if concerted

5.2 CYCLOADDITION AND CYCLOELIMINATION REACTIONS.

A. Definition: Addition of m atoms of one group to n atoms of another group to make a ring of $m + n$ atoms (and vice-versa).

B. Methods of classification

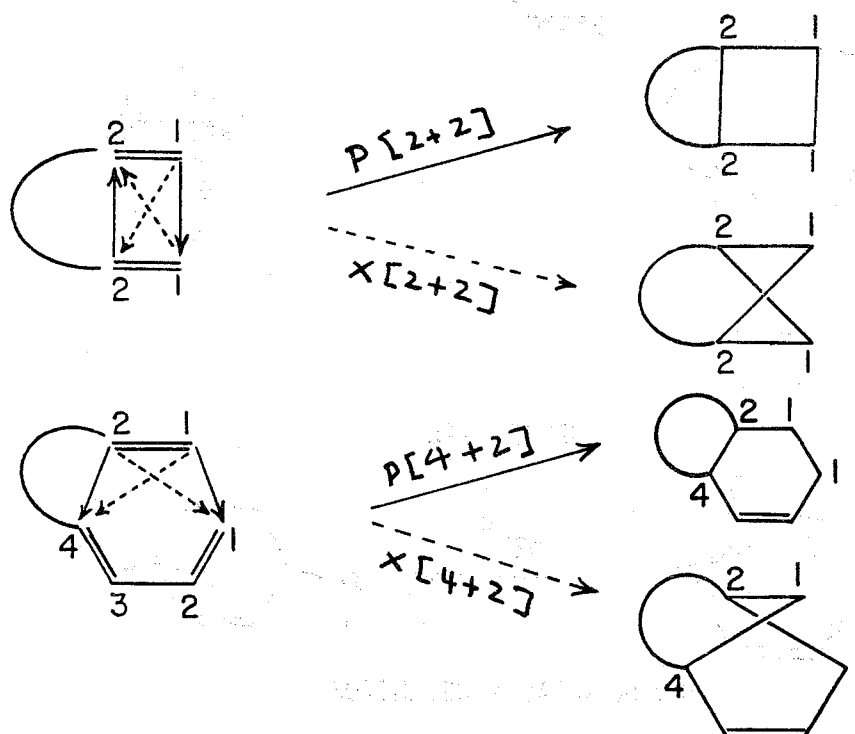
1. Number of atoms participating [$m + n$]
2. Number and types of electrons [π or σ]
3. Stereoselectivity [P or X]
4. Stereospecificity [a or s]



5. Counting "participating electrons": arrow convention

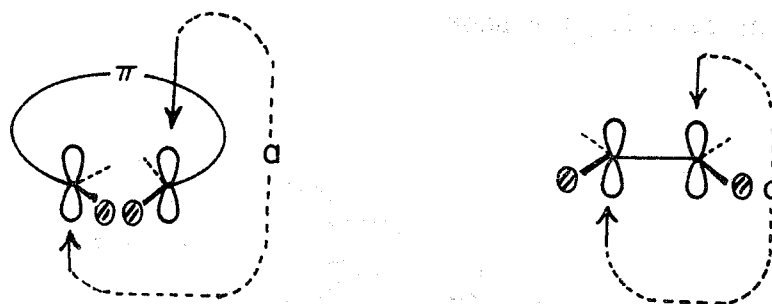
5.2 (continued)

C. Parallel and cross additions



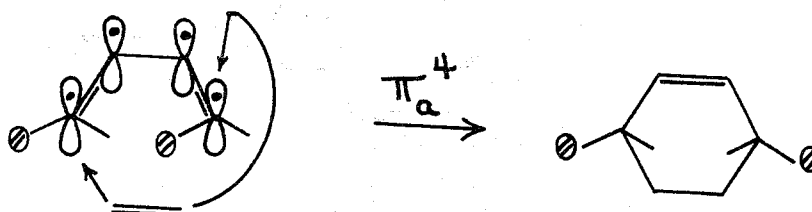
D. Suprafacial and antarafacial additions

1. Antarafacial: New bonding on opposite sides (faces) of a system



(11)

ANTARAFACIAL

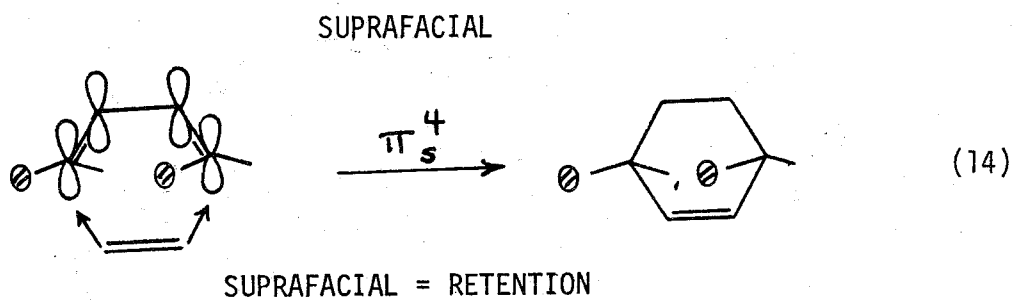


(12)

ANTARAFACIAL = INVERSION

5.2 D. (continued)

2. Suprafacial: New bonding on the same side (face) of the system

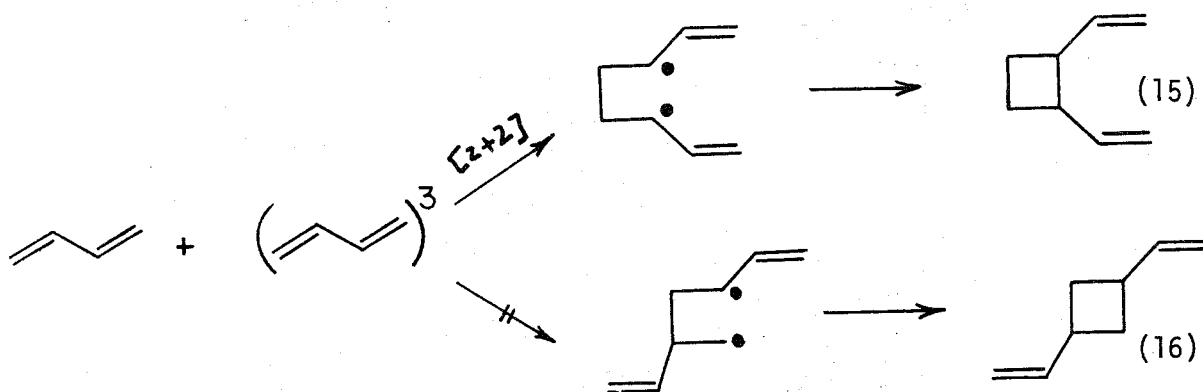


5.3 SELECTION RULES FOR CYCLOADDITION REACTIONS

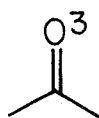
A. Multistep (Ionic or radical)

1. Stereoselectivity determined most stable intermediates and structural effects
2. Stereospecificity poor

B. Examples



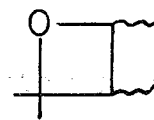
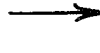
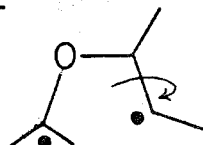
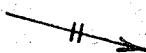
5.3 B. (continued)



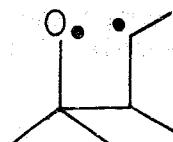
+



[2+2]



(17)



(18)

C. Concerted

1. Stereoselectivity determined by best overlap of participating bonds and structural effects.
2. Orbital symmetry rules.

Table 5-1

Rules for $m + n$ Cycloadditions

Number of electrons
($m + n$)

Δ (thermal)

$h\nu$ (photochemical)

$4q$

$m_s + n_a \text{ OR } m_a + n_s$

$m_s + n_s \text{ OR } m_a + n_a$

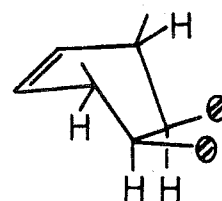
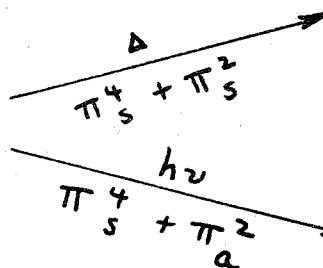
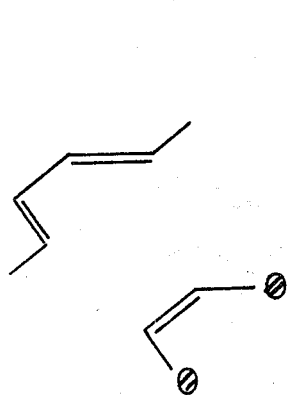
$4q + 2$

$m_s + n_s \text{ OR } m_a + n_a$

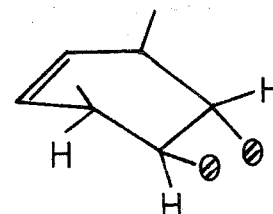
$m_s + n_a \text{ OR } m_a + n_s$

3. Important result for photochemistry: $4q$ systems can be $m_s + n_s$

4. Example: $(m + n) = (4 + 2)$.



(19)

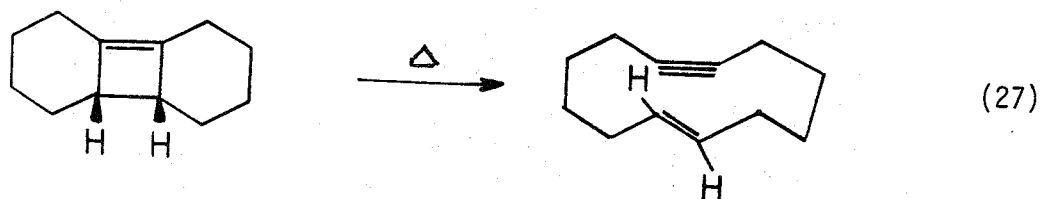
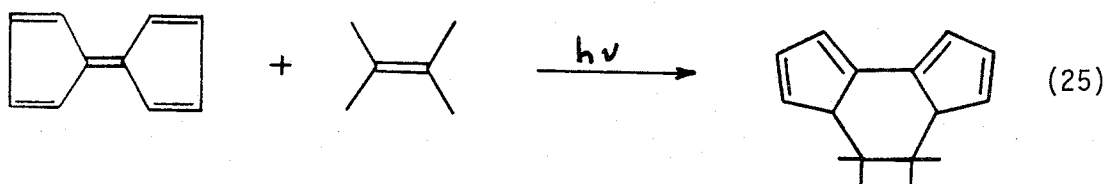
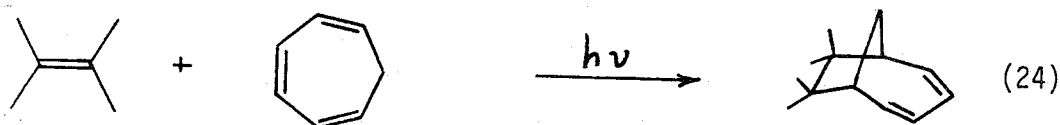
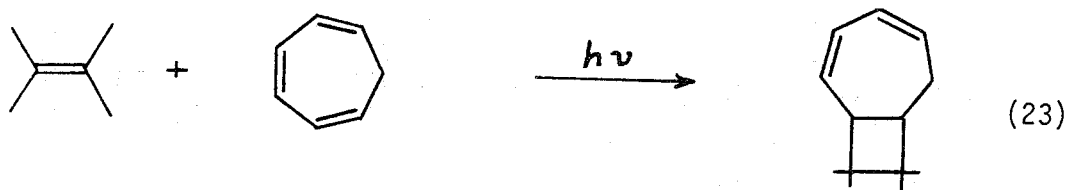
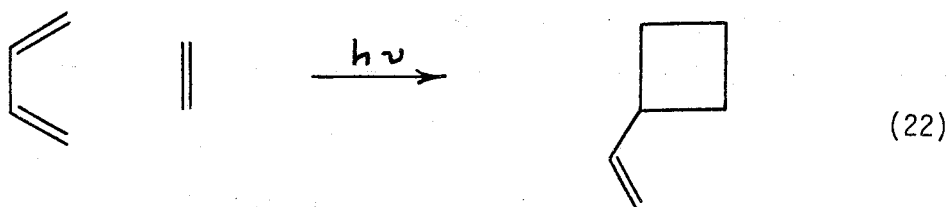
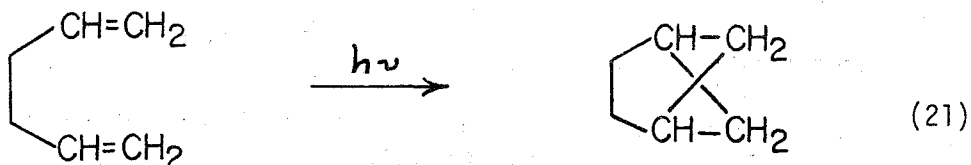


(20)

5.3 (continued)

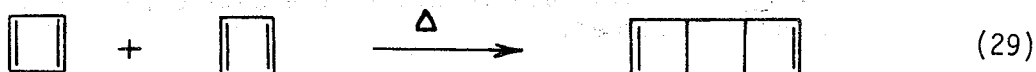
D. Problems.

Classify the following reactions with respect to pertinent number of atoms, number and types of electrons, stereospecificity (a or s) and stereoselectivity (x or p).



(continued)

5.3 D. (continued)



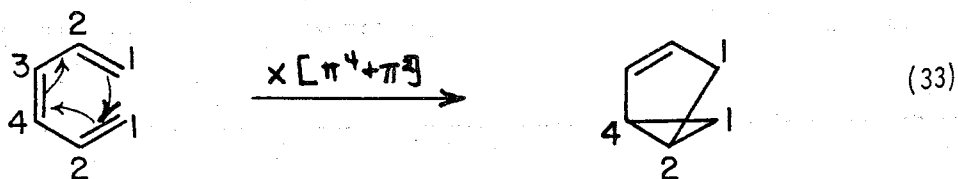
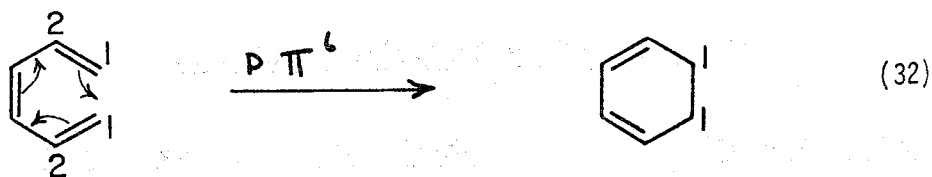
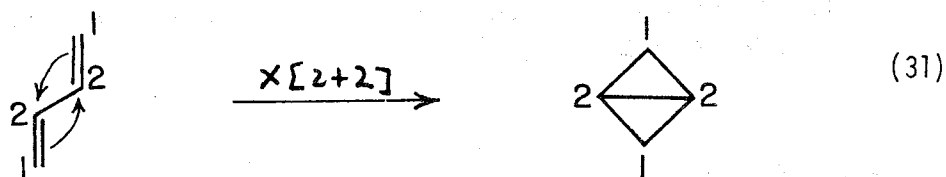
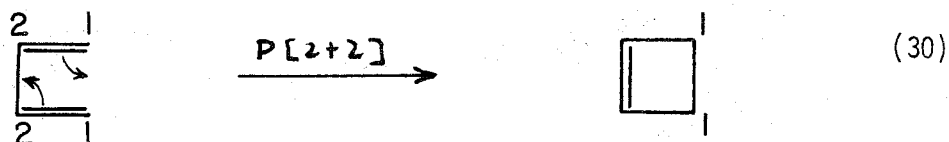
5.4 ELECTROCYCLIC REACTIONS.

A. Definition: Pericyclic reaction in which a sigma bond is formed between the termini of a linear system of conjugated π electrons (and vice-versa).

B. Classification.

1. Number of electrons
2. Stereoselectivity
3. Stereospecificity

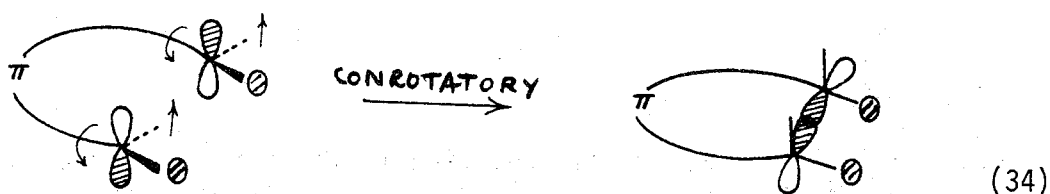
C. Examples: Compare to cycloadditions.



5.4 (continued)

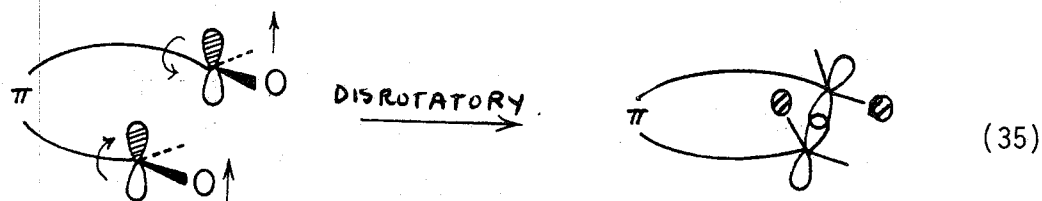
D. Stereoselectivity

1. Conrotation: p-orbitals rotate in the same direction when the sigma bond is formed.



2. Conrotation = inversion at one reacting center (comparable to π_a).

3. Disrotation: p-orbitals rotate in opposite directions when the sigma bond is formed.



4. Disrotation = retention at both reacting centers. (comparable to $\pi_s + \pi_s$).

5.5 SELECTION RULES.

A.

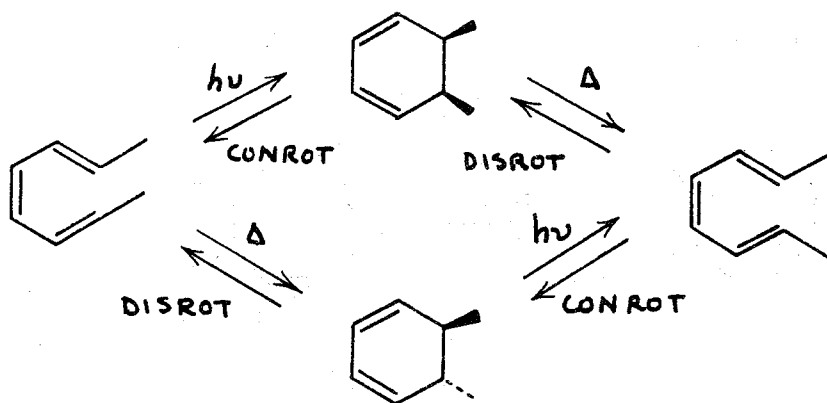
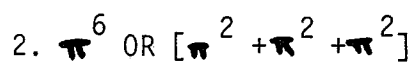
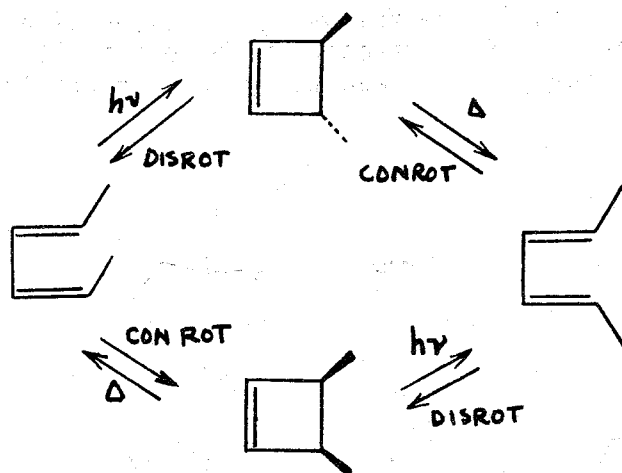
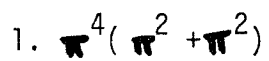
TABLE 5-2

Rules for π^h Electrocyclic Reactions.

| <u>Number of electrons</u> | <u>Δ (thermal)</u> | <u>$h\nu$ (photochemical)</u> |
|----------------------------|--------------------------------------|--|
| $4q$ | conrotatory | disrotatory |
| $4q + 2$ | disrotatory | conrotatory |

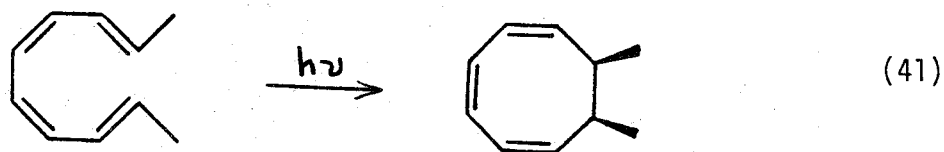
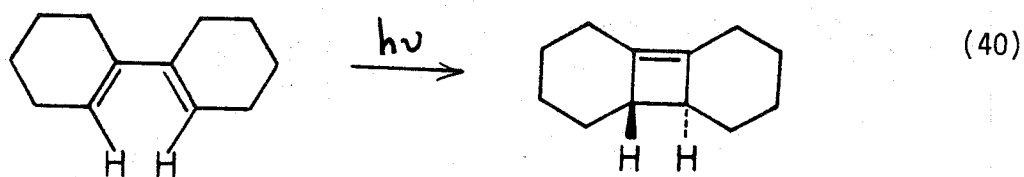
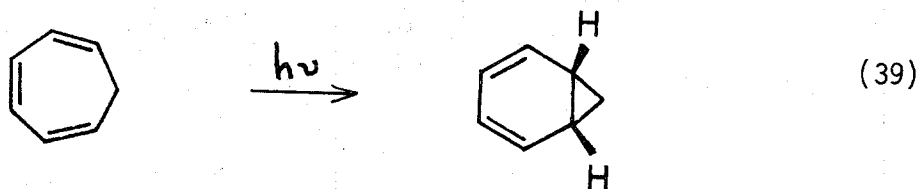
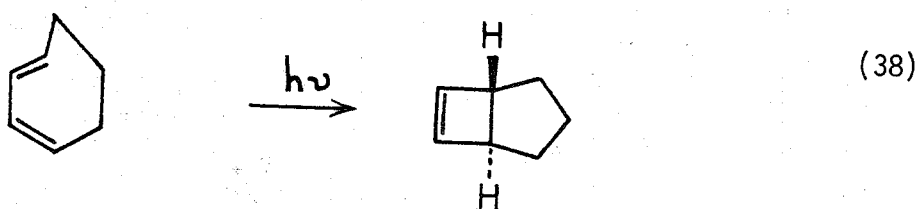
5.5 (continued)

B. Examples



5.5 (continued)

C. Problems. Classify the following reactions with respect to the pertinent number of electrons, stereoselectivity, stereospecificity, and whether they are allowed to occur concertedly.



5.6 SIGMATROPIC REACTIONS

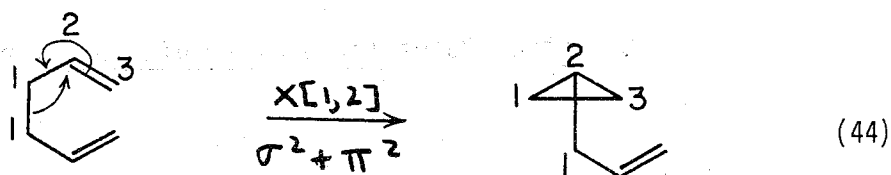
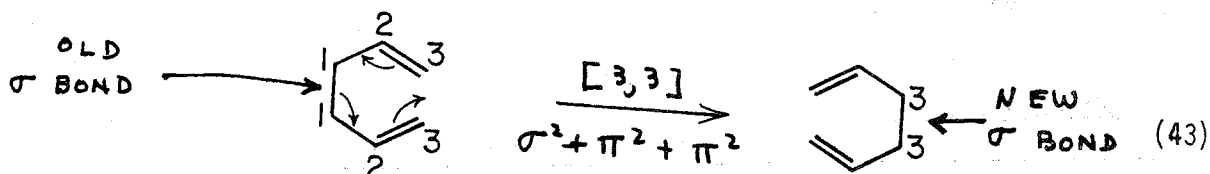
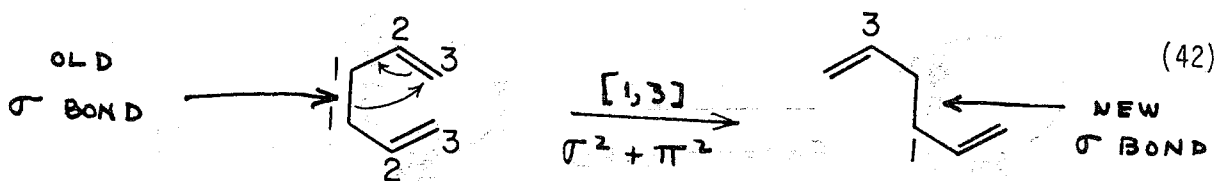
A. Definition: Migration of a sigma bond, flanked by one or more π bonds, to a new position along the π system

B. Classification:

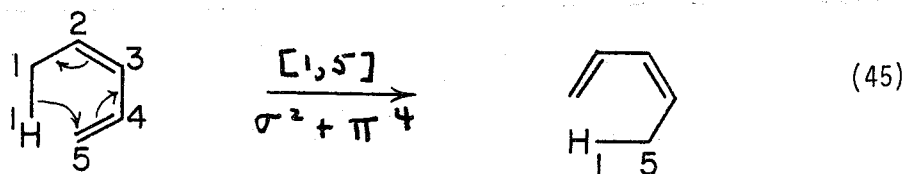
1. Number of electrons
2. Stereoselectivity (i,j notation)
3. Stereospecificity (suprafacial, antarafacial)

C. Examples

1. Consider old σ bond (label 1,1) and new σ bond (i and j atoms away from the old one).

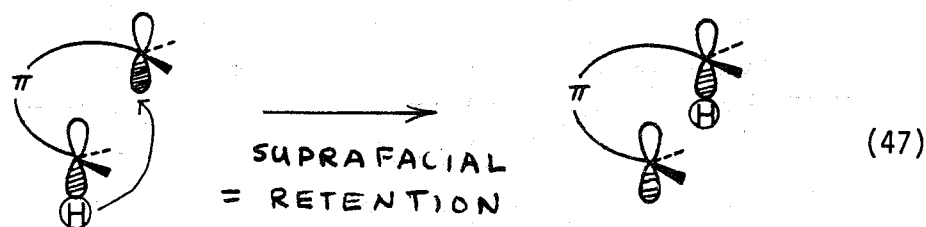
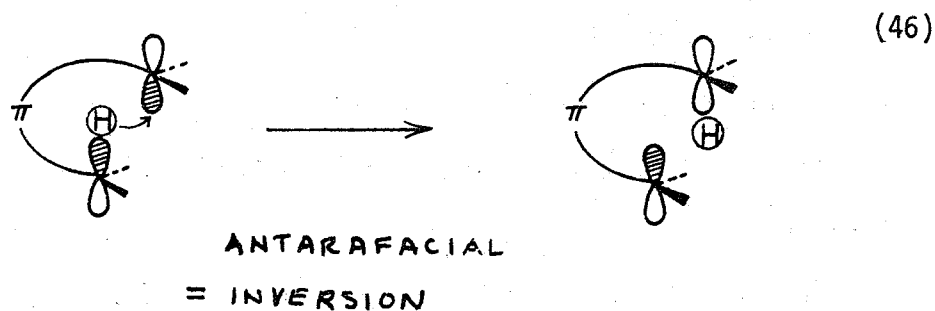


2. Hydrogen shifts always $[1,j]$



5.6 (continued)

D. Stereospecificity



5.7 SELECTION RULES

A.

Table 5-3

Selection Rules for Sigmatropic Reactions.

Number of electrons

Δ (thermal)

$h\nu$ (photochemical)

4q

a-s

a-a or s-s

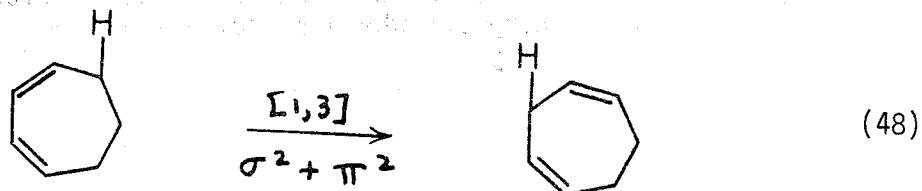
4q + 2

a-a or s-s

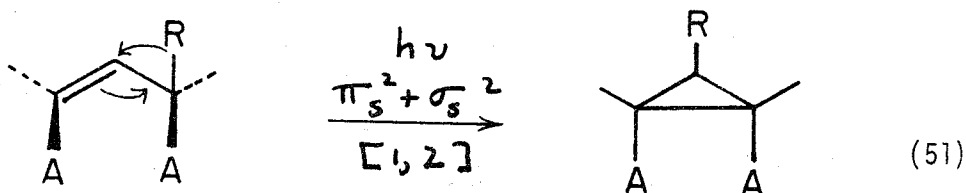
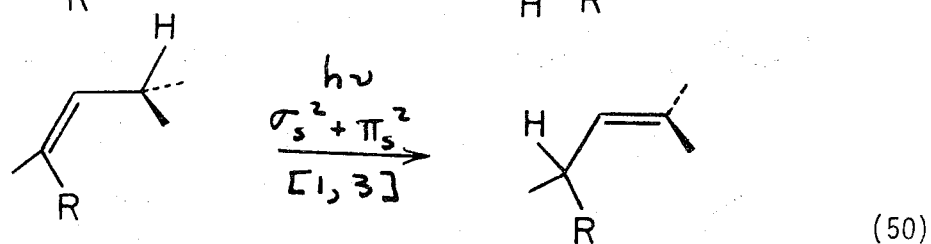
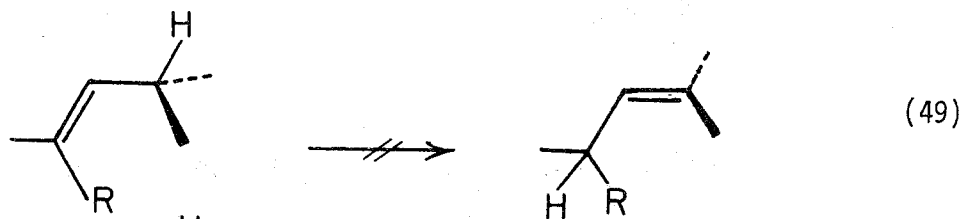
a-s

5.7 (continued)

B. Examples

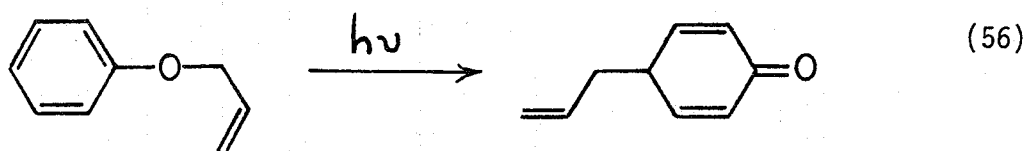
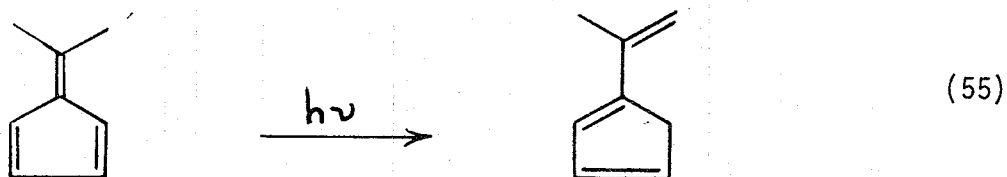
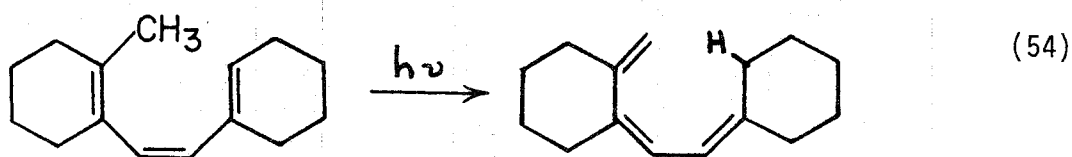
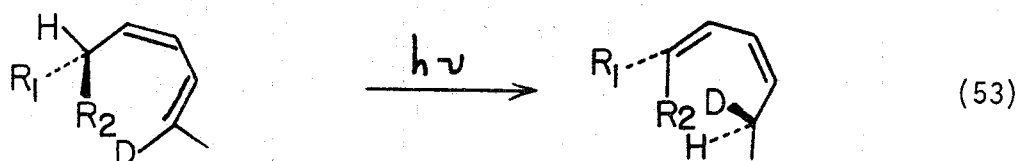
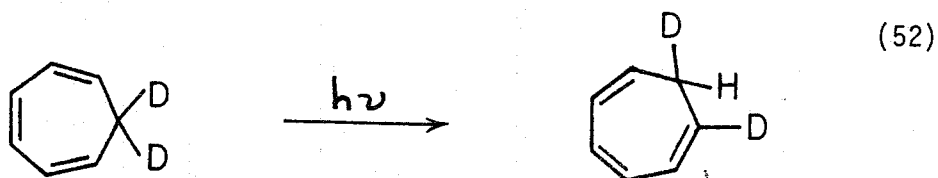


4 electrons: Must be s on H, therefore, a on carbon; thermally, s on carbon photochemically. a is impossible in small and medium rings.



C. Problems.

1. Classify the following reactions with respect to the pertinent number of electrons, stereoselectivity, stereospecificity and whether they are allowed to occur concertedly.



5.8 CHELETROPIC REACTIONS

A. Definition: Two sigma bonds which terminate at a single atom are made or broken.

B. Examples



5.9 SUMMARY

A. Cycloadditions and cycloelimination

1. $\pi_s^2 + \pi_s^2$ common

2. $\pi_s^2 + \pi_a^4$, $\pi_a^2 + \pi_s^4$ rare

3. P and X additions.

4. Selection rules may not always apply.

B. Electrocyclic closures and openings

1. Many examples follow the "rules".

2. Analogous to cycloadditions: conrotatory = antarafacial = inversion; disrotatory = suprafacial = retention.

C. Sigmatropic

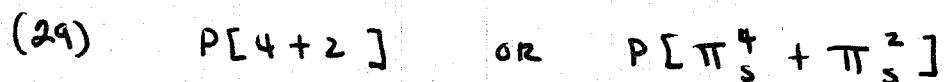
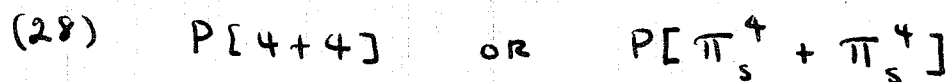
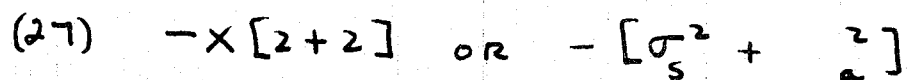
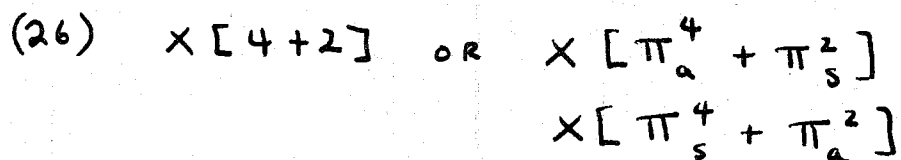
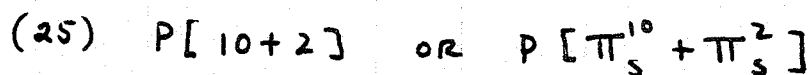
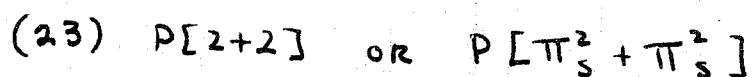
1. Suprafacial favored in small and medium ring compounds

2. Suprafacial favored for small i, j values

D. Pericyclic reactions usually singlet reactions

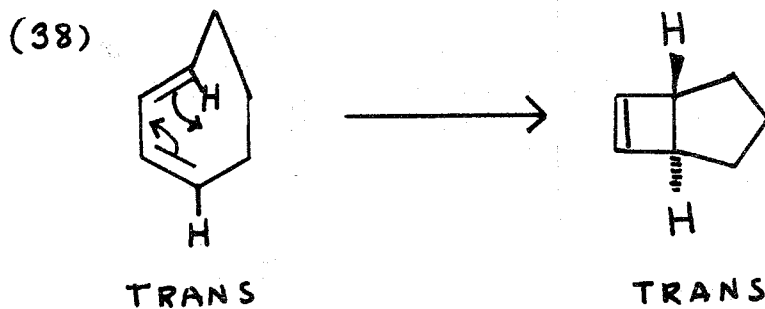
5.10 ANSWERS TO THE PROBLEMS

Cycloaddition reactions (5.3 D)

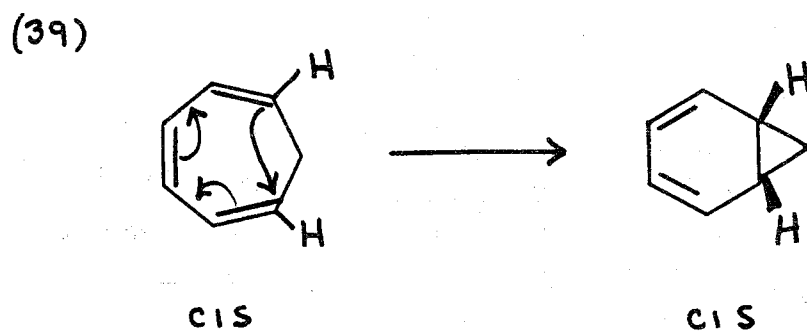


5.10 (continued)

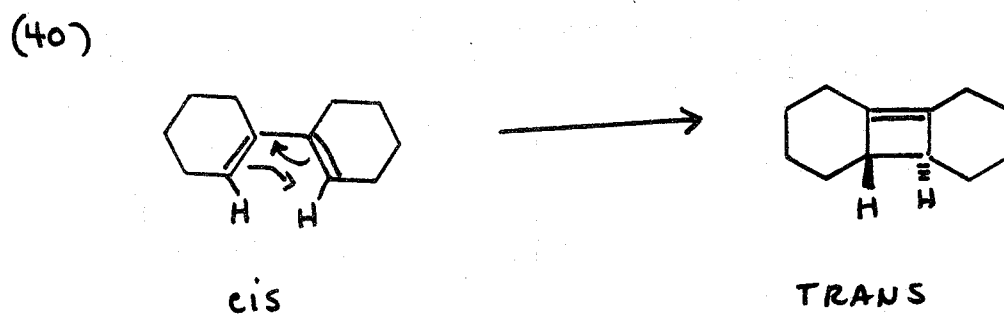
Electrocyclic reactions (5.5 C)



$P[\pi^4]$ DISROT = RET $h\nu$ allowed



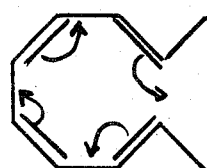
$P[\pi^6]$ DISROT = RET $h\nu$ FORBIDDEN



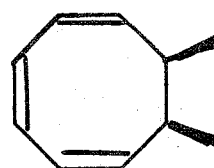
$P[\pi^4]$ CONROT = INVER $h\nu$ FORBIDDEN

5.10 (continued)

(41)



cis



cis

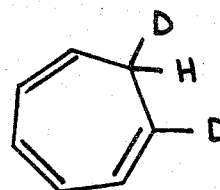
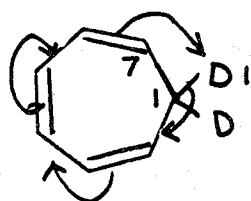
$P[\pi^8]$

DISROT = RET

$h\nu$ ALLOWED

Sigmatropic reactions (5.7C)

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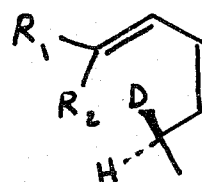
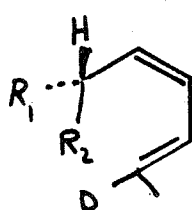


$[1,7]$

$\sigma_s^2 + \pi_s^6$

$h\nu$ ALLOWED

(53)

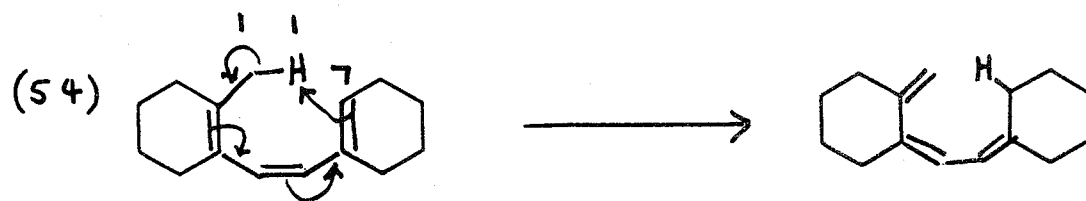


$[1,5]$

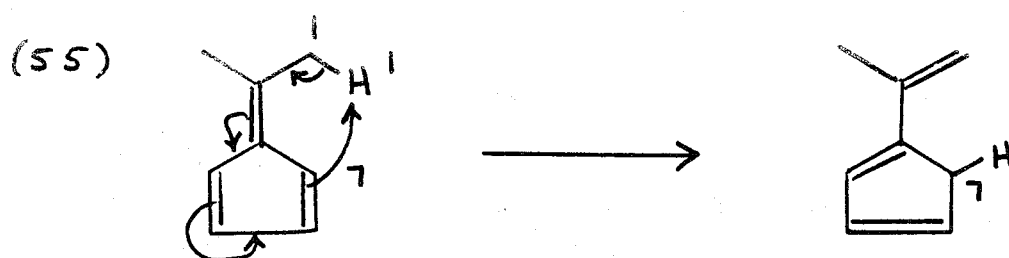
$\sigma_s^2 + \pi_a^4$

$h\nu$ ALLOWED

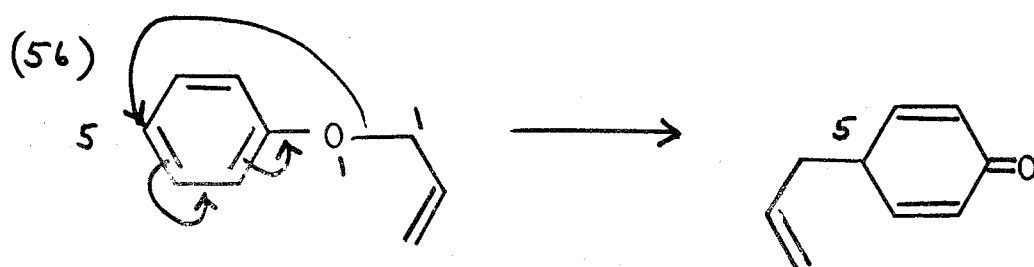
5.10 (continued)



$[1,7] \quad \sigma_s^2 + \pi_s^6 \quad h\nu \text{ ALLOWED}$



$[1,7] \quad \sigma_s^2 + \pi_s^6 \quad h\nu \text{ ALLOWED}$



$[1,5] \quad \sigma_s^2 + \pi_a^4 \quad h\nu \text{ ALLOWED}$

CHAPTER 6
PHOTOCHEMISTRY OF ALKENES AND POLYENES

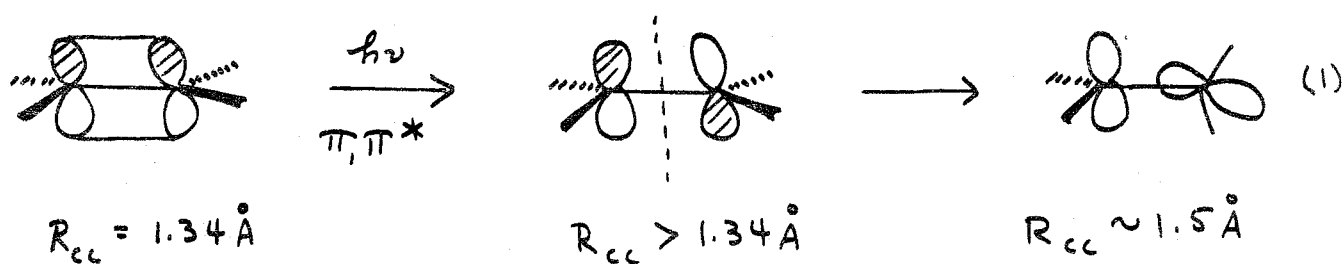
6.1 GENERAL CONSIDERATIONS

Rev.: Chem. Rev., 69, 639 (1969); Org. Photochem., 1, 197 (1968);
Fortschrit. Chem. Forschung, 11, 216 (1969); J. Chem. Ed.,
46, 7 (1969).

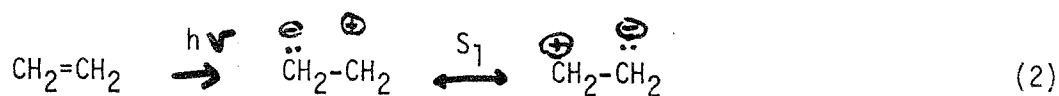
- A. Model for electronically excited states of ethylenes and conjugated polyenes
- B. Energetics and dynamics of the electronically excited states of ethylenes and polyenes
- C. Primary photochemical processes of ethylenes and conjugated polyenes

6.2 MODEL FOR ELECTRONICALLY EXCITED STATES

- A. $\pi \rightarrow \pi^*$
- B. Orbital description

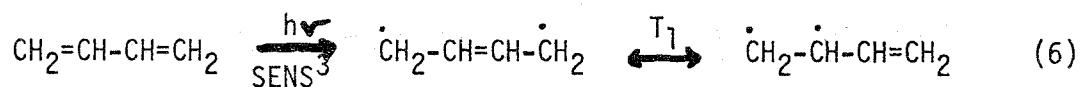
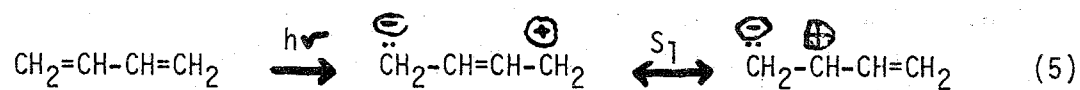


- C. Valence bond description



6.2 (continued)

F. Valence bond description



G. Ground state model

1. Reactive ethylenes and polyenes
2. Carbon radicals

H. Summary

1. S_1 polarizable, reduced bond order
2. T_1 radical-like, reduced bond order
3. Tendency of both S_1 and T_1 to change shape and twist

6.3 ENERGETICS AND DYNAMICS

A. Energetics

1. Emission rare
2. Energetics from perturbed $S_0 \rightarrow T_1$ absorption
3. Large S_1 - T_1 gap

Table 6-1

Singlet (E_1) and Triplet (E_3) Energies for Some Ethylenes
and Conjugated Polyenes*

| <u>Molecule</u> | E_1 | E_3 |
|---|-------|-------|
| $\text{CH}_2=\text{CH}_2$ | 120 | 82 |
| $\text{CH}_2=\text{C}(\text{CH}_3)_2$ | 95 | 81 |
| <u>trans</u> - $\text{CH}_3\text{CH}=\text{CHCH}_3$ | 95 | 81 |
| <u>cis</u> - $\text{CH}_3\text{CH}=\text{CHCH}_3$ | 95 | 78 |
| $(\text{CH}_3)_2\text{C}=\text{C}(\text{CH}_3)_2$ | 86 | 76 |
| <u>cis</u> - $\text{CHCl}=\text{CHCl}$ | - | 76 |
| Norbornene | - | 74 |
| <u>trans</u> - $\text{CHCl}=\text{CHCl}$ | - | 72 |
| $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}_2$ | 80 | 60 |
| $\text{CH}_2=\text{CCH}_3-\text{CCH}_3=\text{CH}_2$ | 80 | 60 |
| 1,3-Cyclohexadiene | 75 | 54 |
| 1,3,5-Hexatriene | 70 | 48 |

*Kcal/Mole

6.3 (continued)

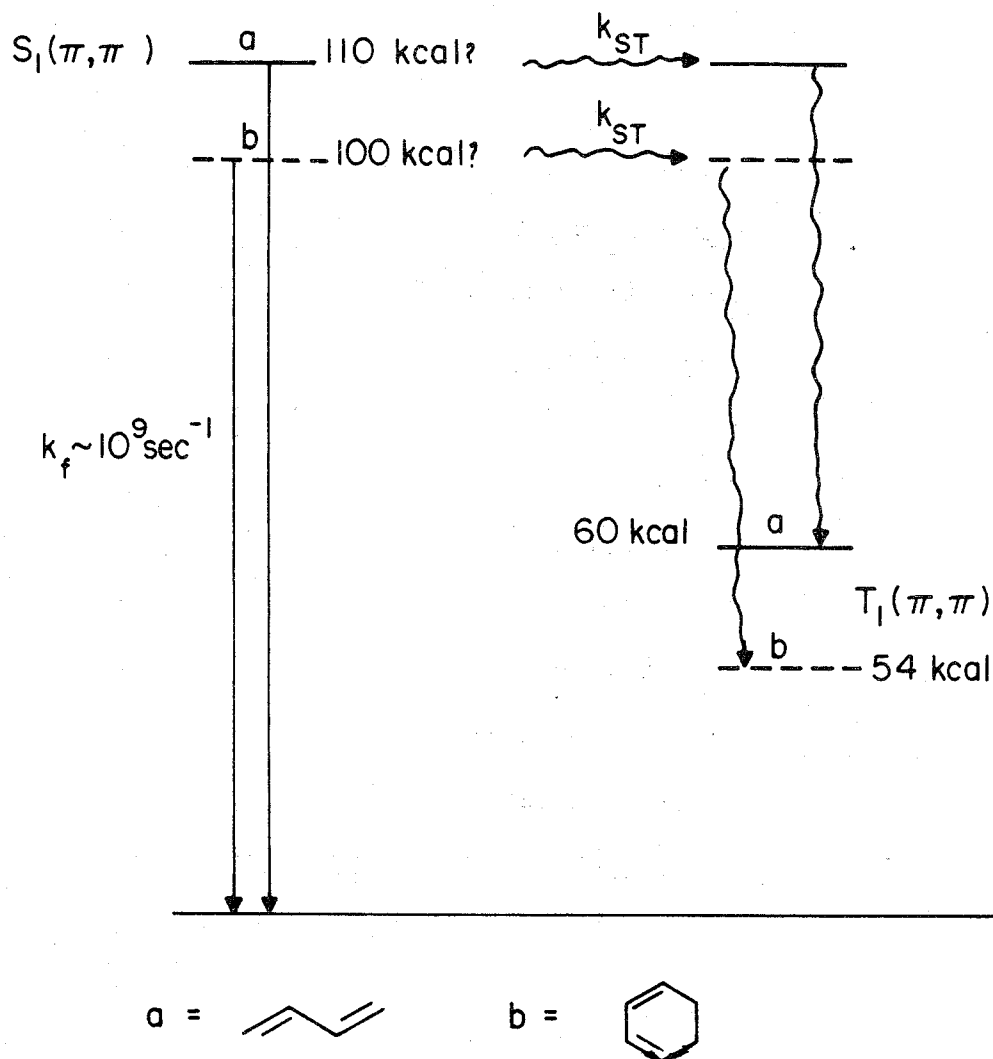
B. Dynamics

1. $k_F(\text{calc.}) \sim 10^9 \text{ sec}^{-1}$
2. $\phi_F \ll 0.01$; conclude $k_D^1 \gg 10^{10} \text{ sec}^{-1}$
3. Triplets: little information
4. General: S_1 and T_1 short-lived, rapid torsional modes and bonding

C. Energy diagram

1. $\phi_{ST} \ll 0.01$
2. Data crude

Figure 6-1



6.4 PRIMARY PHOTOCHEMICAL PROCESSES

A. cis-trans-Isomerization

1. Expected because of reduced bond order in S_1 and T_1
2. Very general
3. Special effects in small or medium rings

B. Hydrogen abstraction

1. Equivalent to C=C reduction
2. Probably radical-like in character

C. Cycloadditions and cycloeliminations

1. Review selection rules and terminology: Chapter 5
2. S_1 likely to be pericyclic; T_1 likely to be "biradical-like"

D. Electrocyclic closures and openings

1. Review selection rules and terminology: Chapter 5
2. S_1 likely to be pericyclic; T_1 likely to undergo other reactions

E. Sigmatropic rearrangements

1. Review selection rules and terminology: Chapter 5
2. S_1 likely to be pericyclic; T_1 likely to undergo other reactions

F. Miscellaneous reactions

1. Cheletropic
2. Fragmentations - weak bonds
3. Additions and rearrangements

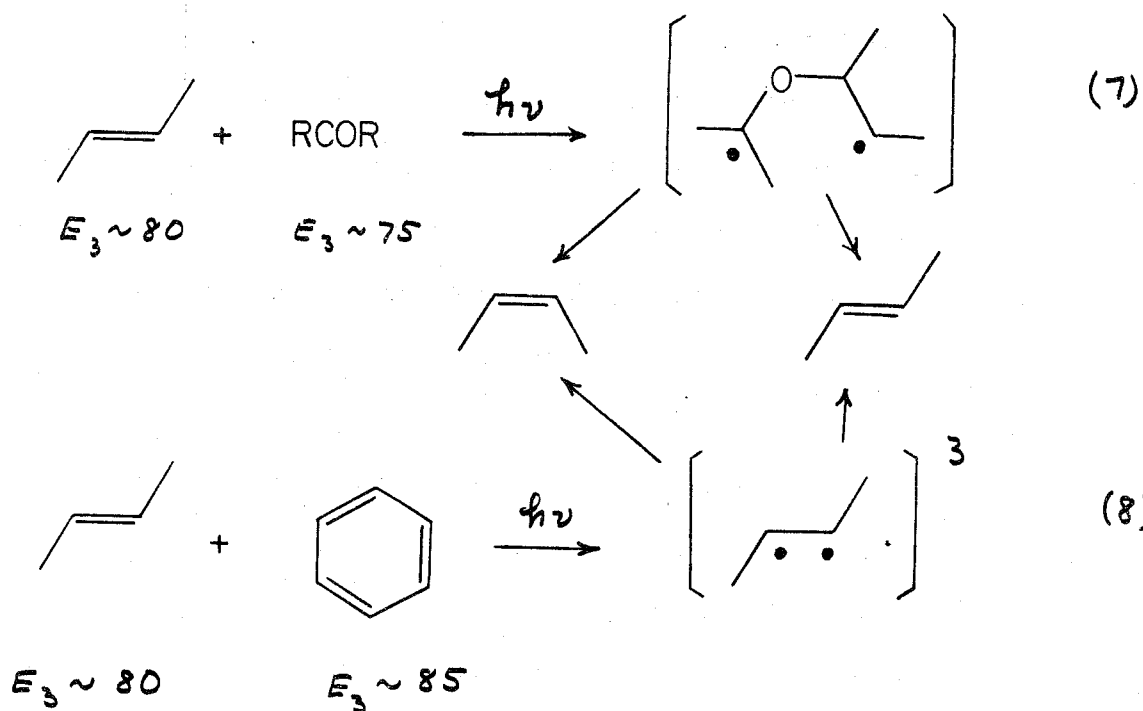
G. Writing mechanisms

1. S_1 - pericyclic
2. T_1 - biradical
3. Twist motion rapid
4. T_1 - must be sensitized

6.5 cis-trans-ISOMERIZATION

A. Acyclic

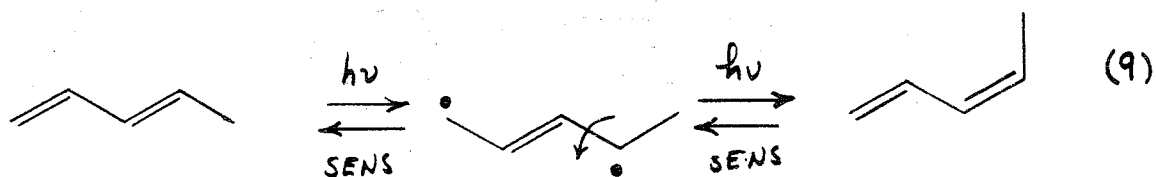
Ref.: Fortschrit. Chem. Forschung, 11, 216 (1969);
Prog. Reaction Kinetics, 2, 166 (1964)



1. Sensitization may be "chemical" (eq. 7) or "physical" (eq. 8)
2. Side reactions: ketones add and abstract hydrogen atoms; benzene adds (singlet); triplet alkene may undergo other reactions.

6.5 A. (continued)

3. May be useful synthetically



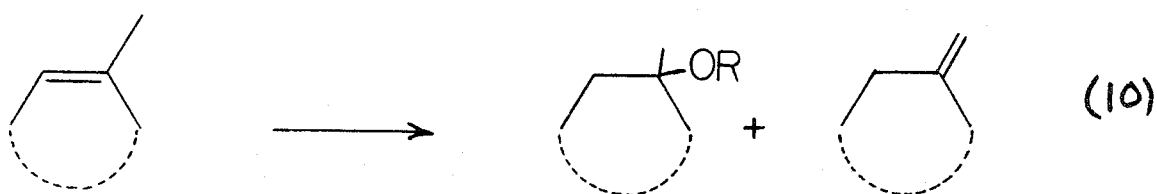
4. Photostationary mixtures are set up

5. Photostationary mixture depends on E_3 sensitizer

6. "Chemical" spectroscopy: determine $E_3(\text{SENS})$, determine $\phi_{\text{ST}}(\text{SENS})$

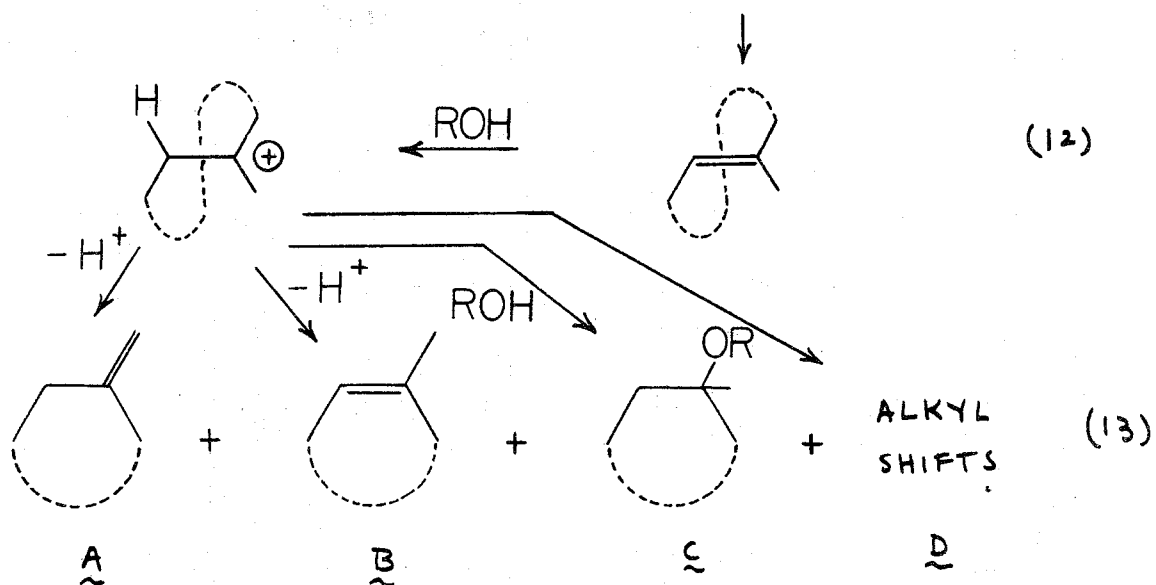
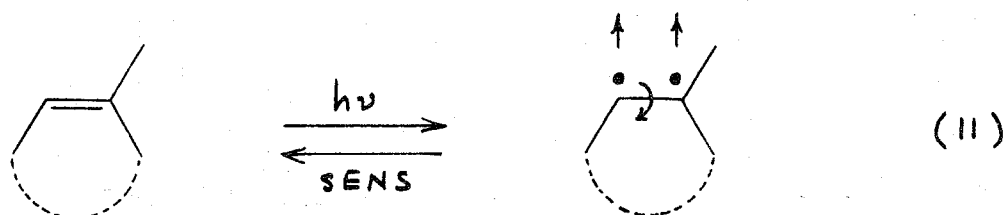
B. Cyclic

Ref.: Science, 170, 137 (1970); Accounts Chem. Res., 2, 33 (1969)

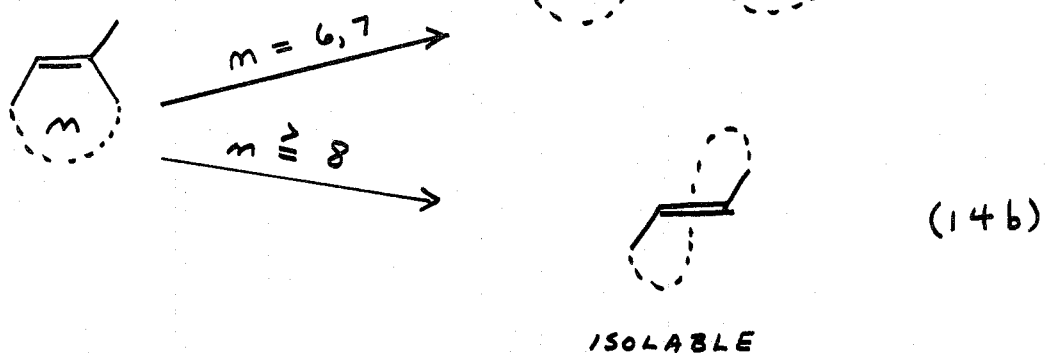
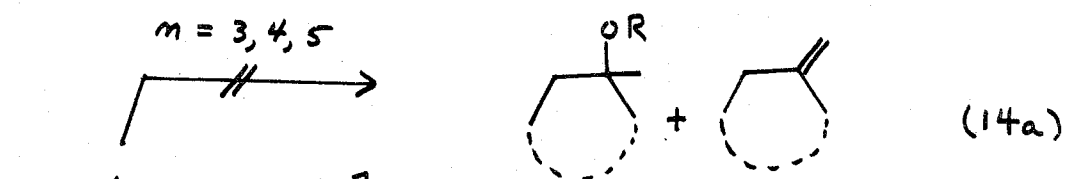


6.5 B. (continued)

1. Production of strained, reactive trans-cycloalkenes

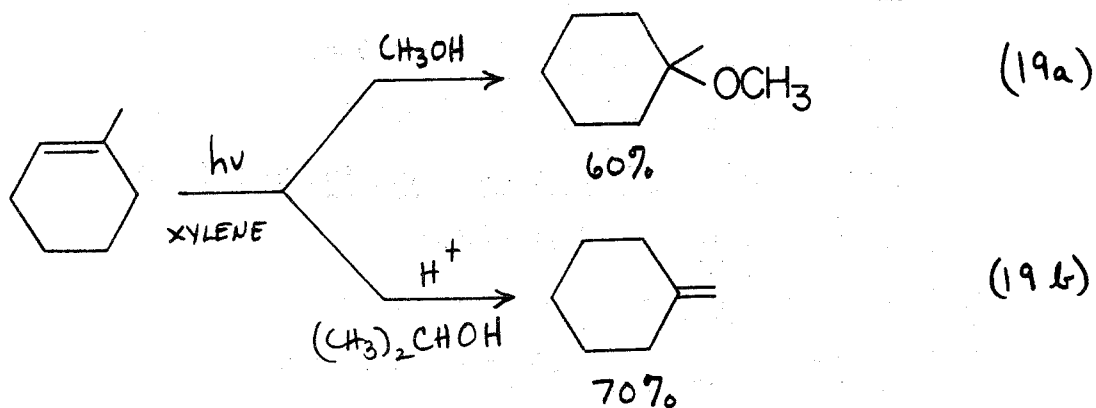
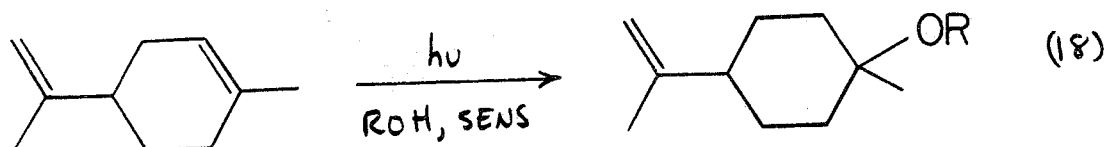
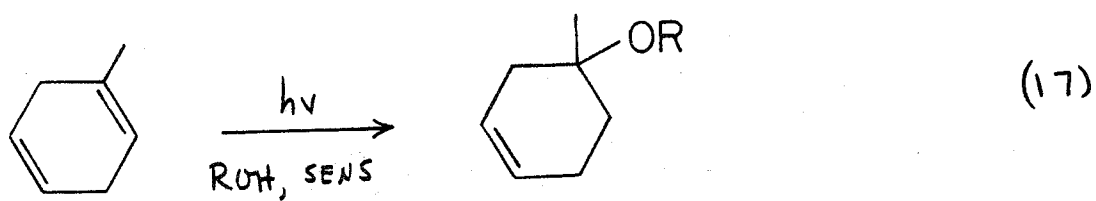
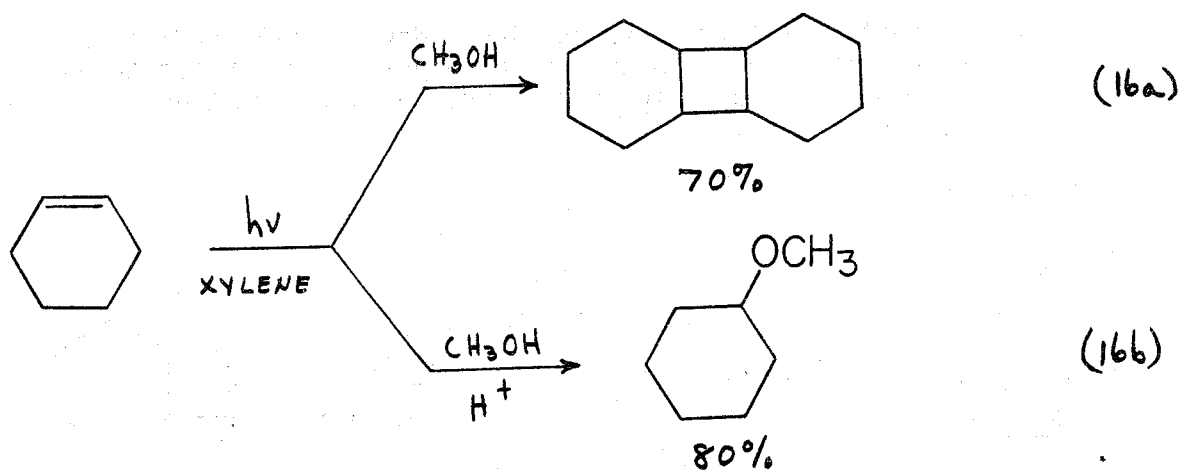
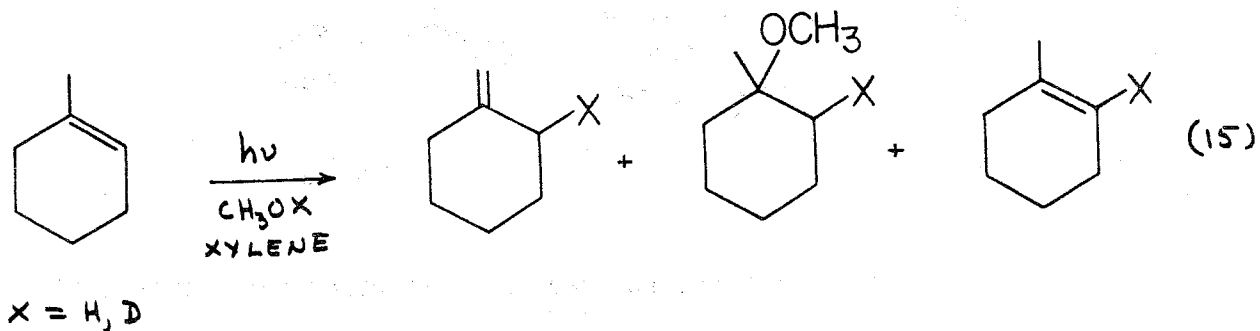


2. Effect of ring size

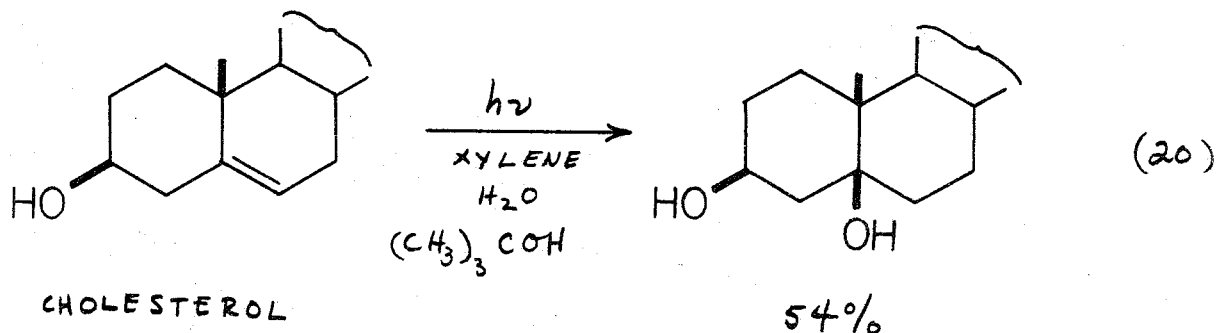


6.5 B. (continued)

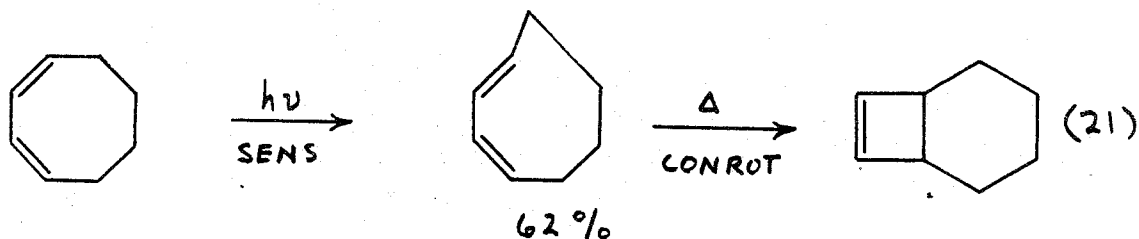
3. Examples



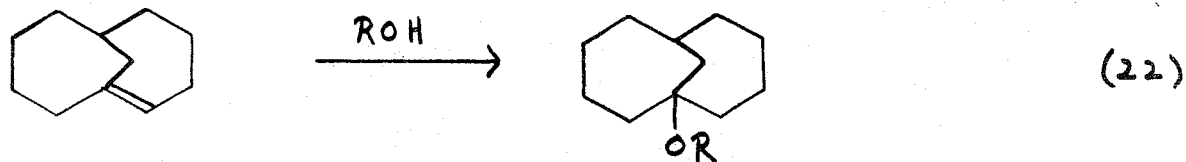
6.5 B. 3. (continued)



4. Rings smaller than 6 undergo radical like reaction: dimerization reduction, etc.
5. Synthetic utility: protonation under neutral conditions, specificity (endo versus exo or acyclic, more substituted in ring favored), ring size, endo to exo, formation of strained cyclic alkenes.
6. Cyclic polyenes



7.



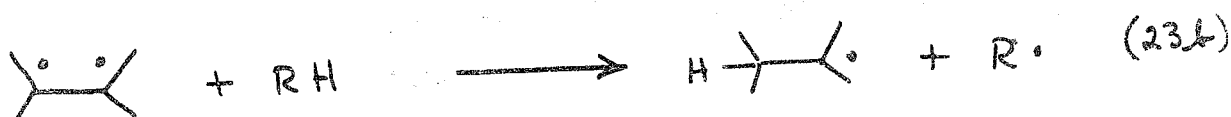
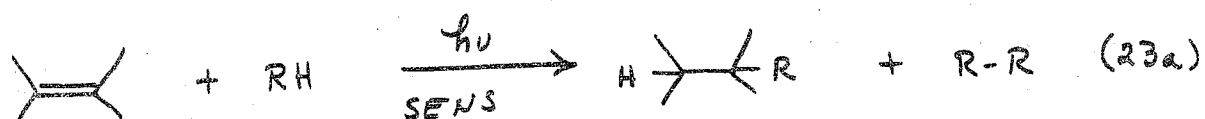
C. References to reactions

- (7) J. Amer. Chem. Soc., 89, 3950 (1967)
- (8) Prog. Reaction Kinetics, 2, 161 (1964)
- (9) J. Amer. Chem. Soc., 86, 3197 (1964)
- (14) through (19) J. Amer. Chem. Soc., 89, 5199 (1967)
- (20) J. Org. Chem., 34, 3774 (1969)
- (21) J. Amer. Chem. Soc., 89, 112 (1967)
- (22) J. Amer. Chem. Soc., 89, 5965, 5966 (1967)

6.6 HYDROGEN ABSTRACTION

A. Most common when other primary processes are inhibited and good hydrogen donor is present

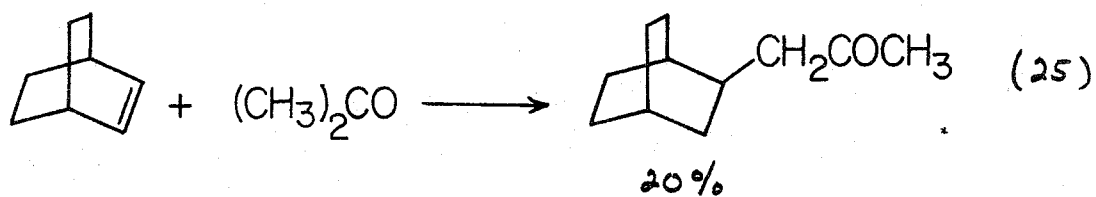
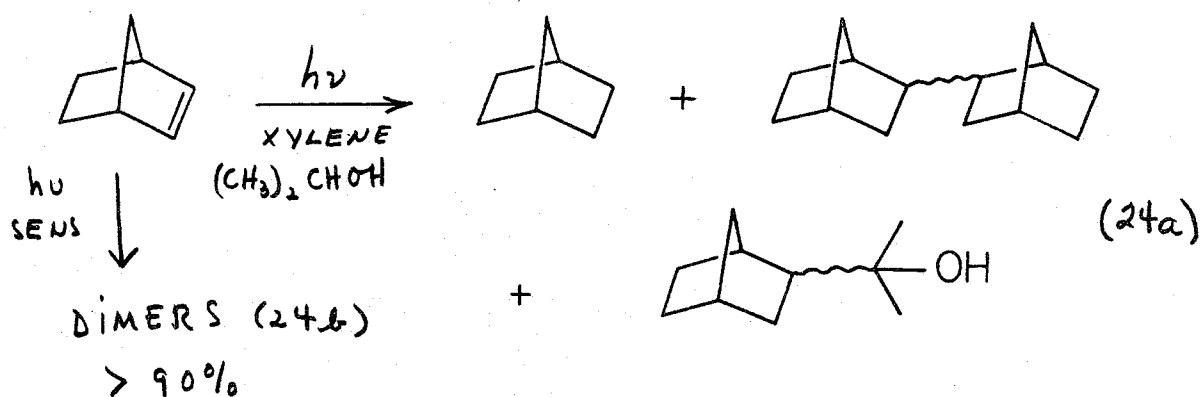
Rev.: Fortschrit. Chem. Forschung, 11, 216 (1969)



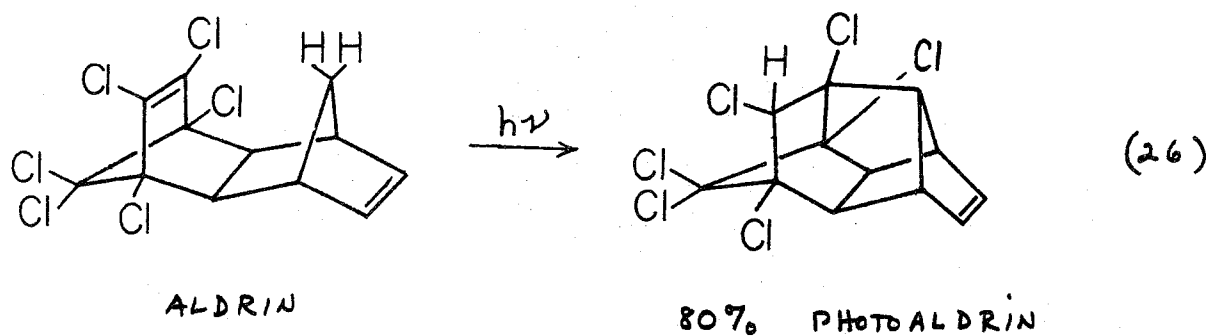
1. Cycloalkenes: 5, 4 and 3 rings
2. No ionic addends around
3. No good cycloaddends around
4. Good hydrogen donor available

6.6 (continued)

B. Examples



1. Photoecology: photoreactions of insecticides



6.6 B. (continued)

2. Presumably "radical energetics" will determine rate and stereoselectivity

3. "Best" radical produced by abstraction

4. $\text{Ph} \sim \text{H} \gg 3^\circ \text{H} > 2^\circ \text{H} > 1^\circ \text{H}$

5. Synthetic utility limited except in structurally favorable cases

C. References to reactions

(24) a. J. Amer. Chem. Soc., 91, 5783 (1969); Tetrahedron Letters; 4763 (1967);

b. Molec. Photochem., 2, 27 (1970).

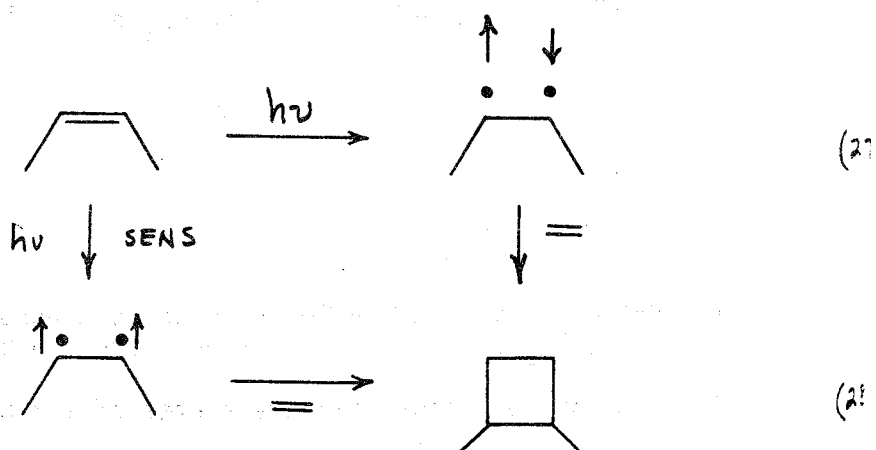
(25) Tetrahedron, 23, 3075 (1967)

(26) Science, 164, 318 (1969); J. Agr. Food Chem., 16, 536 (1968)

6.7 CYCLOADDITION AND CYCLOELIMINATION

A. Dimerization and "cross" additions

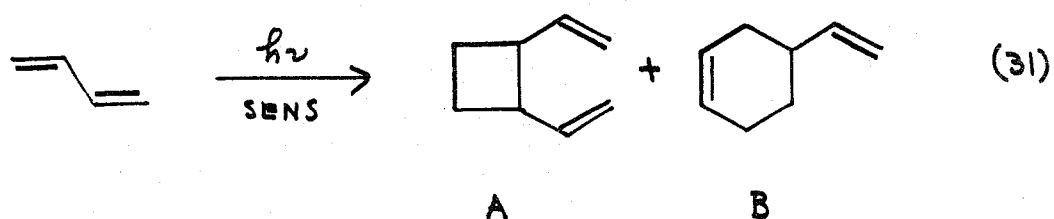
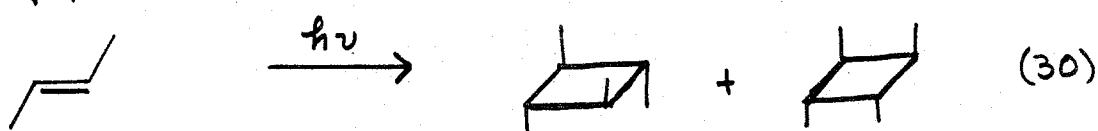
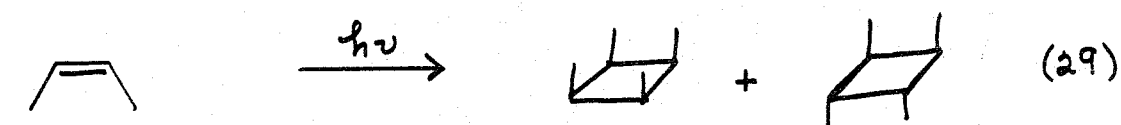
Rev.: Fortschrit. Chem. Forschung, 7, 445 (1967); Chem. Rev., 69, 845 (1969); Org. Photochem., 1, 283 (1968); Rev. Pure Appl. Chem., 16, 117 (1966)



6.7 A. (continued)

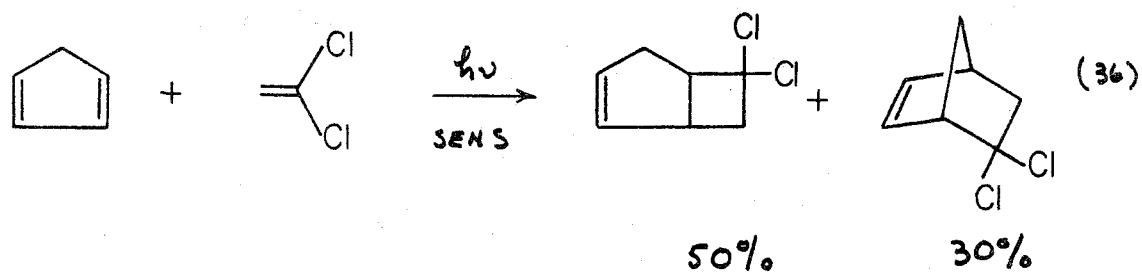
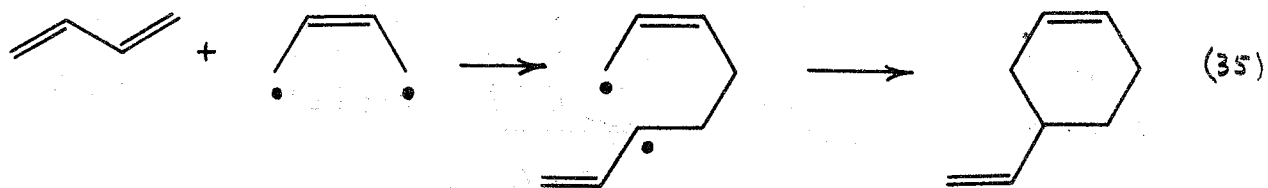
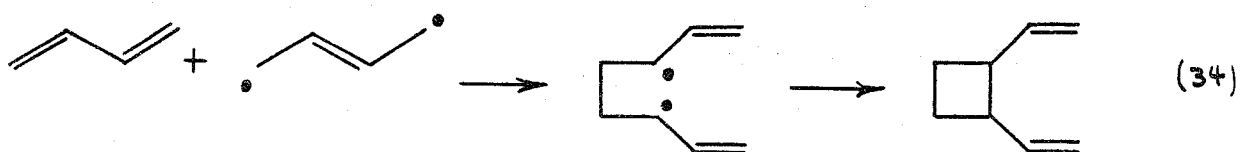
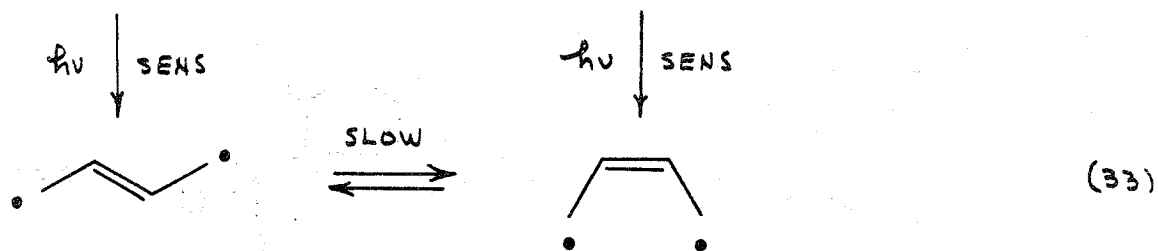
1. Intermolecular cycloadditions poor for S_1 ($\pi^n + \pi^m$)
2. Intermolecular cycloaddition satisfactory for cyclic alkenes in T_1 , but not for acyclic systems (biradical)
3. Intramolecular possible for S_1 ($\pi^n + \pi^m$) or T_1 (biradical)

B. Examples: intermolecular



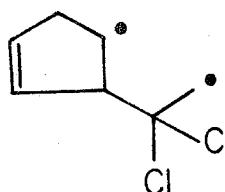
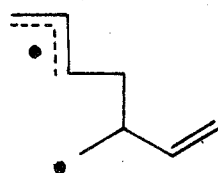
1. Ratio of cyclobutane to cyclohexene depends on $E_2(\text{SENS})$,
i.e., Ph_2CO : $A/B = 98:2$; fluorenone: $A/B = 50:50$
2. Similar to photostationary states of 1,3-pentadiene
3. Stereoisomeric triplets of dienes

6.7 B. (continued)



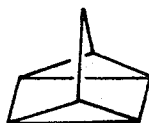
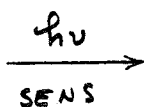
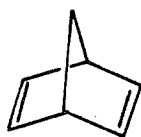
6.7 B. (continued)

4. "Cross additions" generally not synthetically useful
5. Dimerization and cross additions usually stereoselective



NOT FORMED

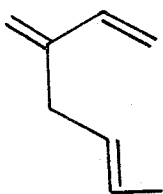
C. Examples: intramolecular



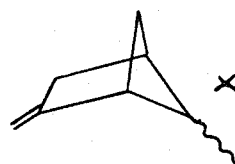
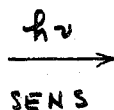
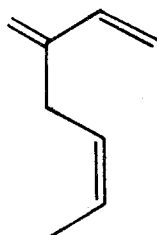
90%

P(2+2)

(37)



OR



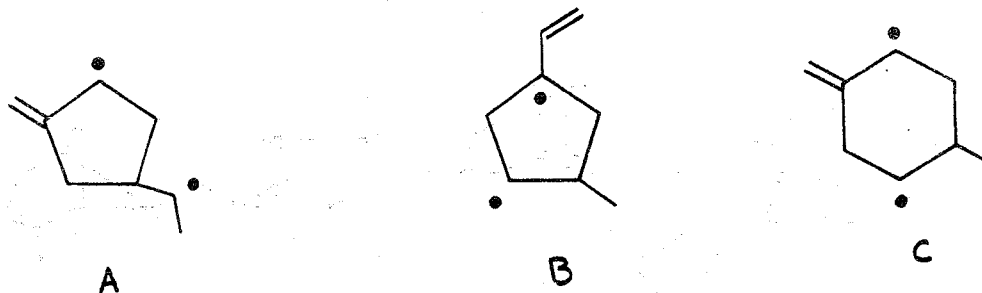
100%

X(2+2)

(38)

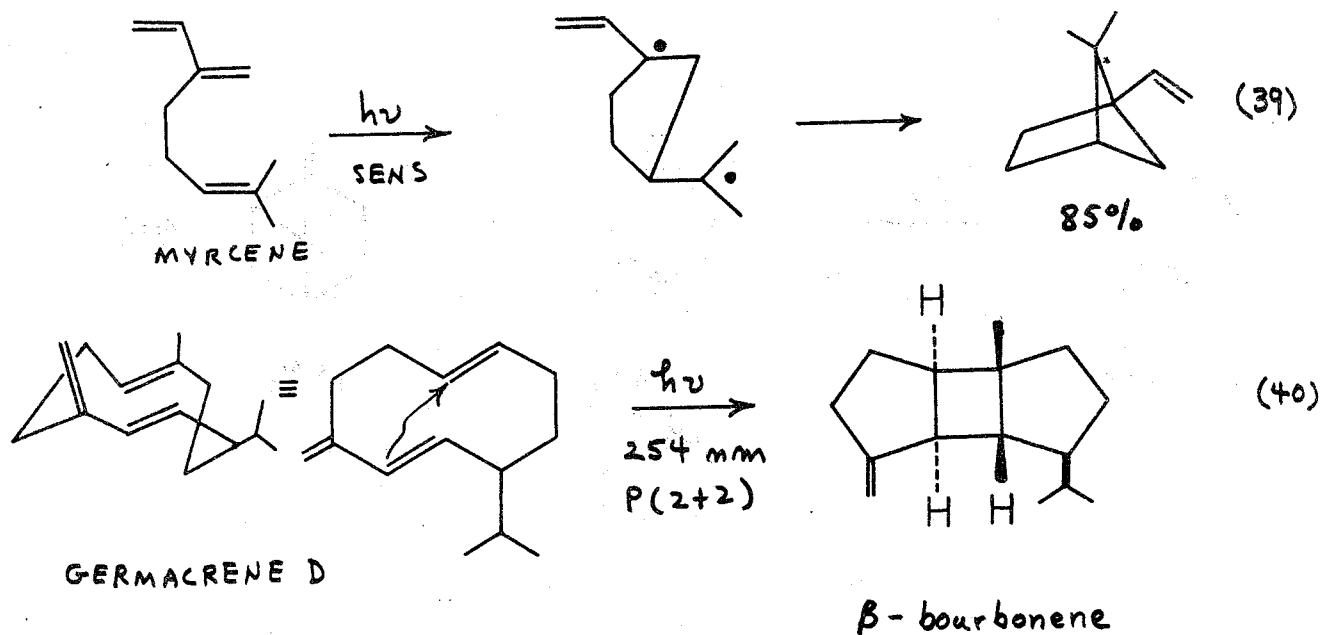
6.7 C. (continued)

1. Rule of "5": J. Amer. Chem. Soc., 89, 4936 (1967)



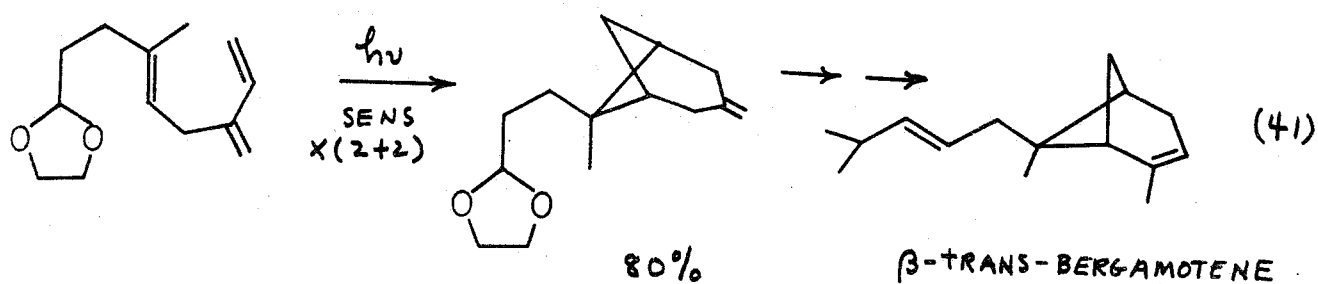
2. Synthetically useful

Rev.: J. Org. Chem., 37, 231 (1972)

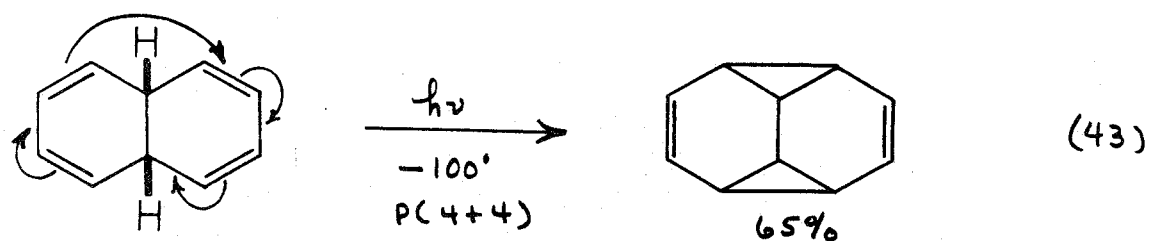
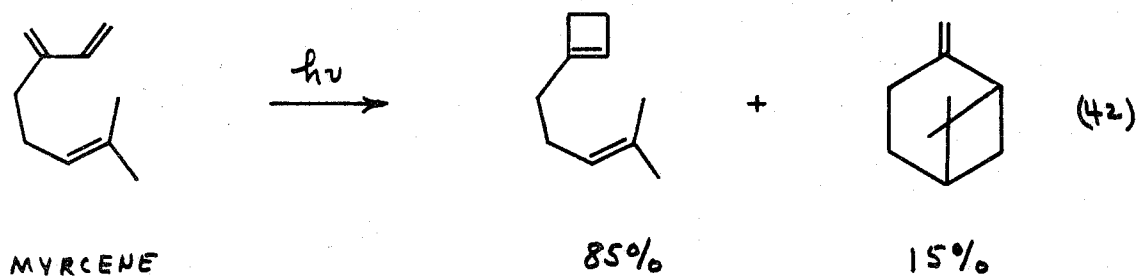


6.7 C. (continued)

3. Transannular interaction: λ_{\max} 259 nm, $\epsilon = 4500$

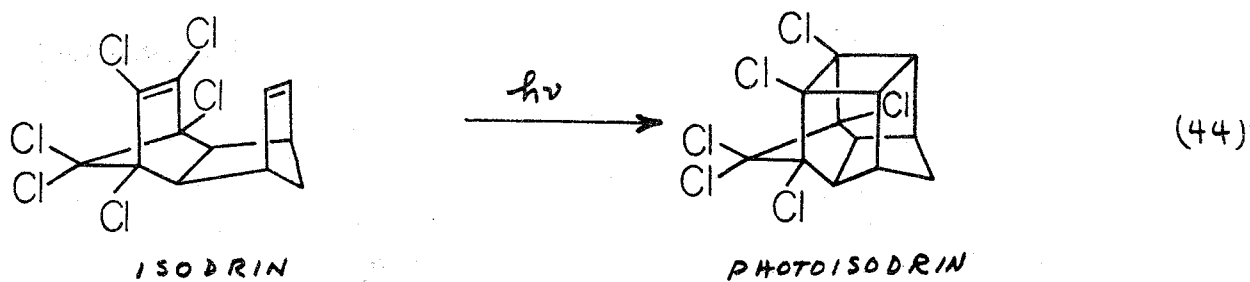


4. Direct excitation may be pericyclic

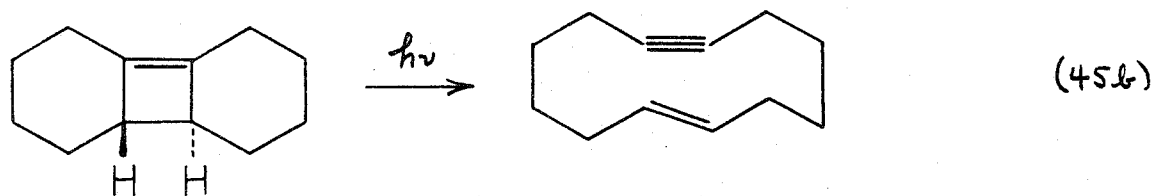
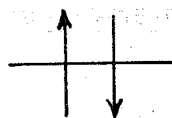
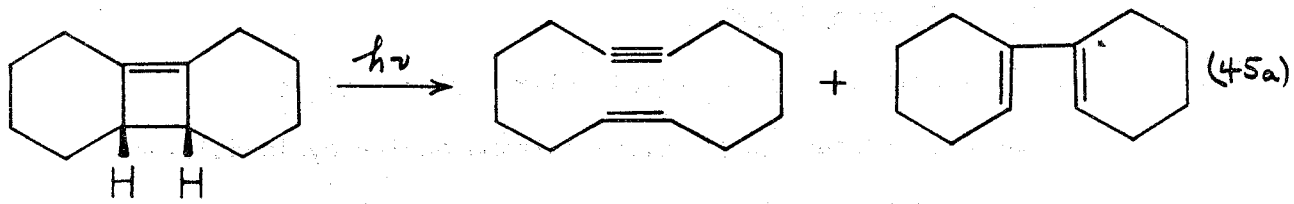


6.7 C. (continued)

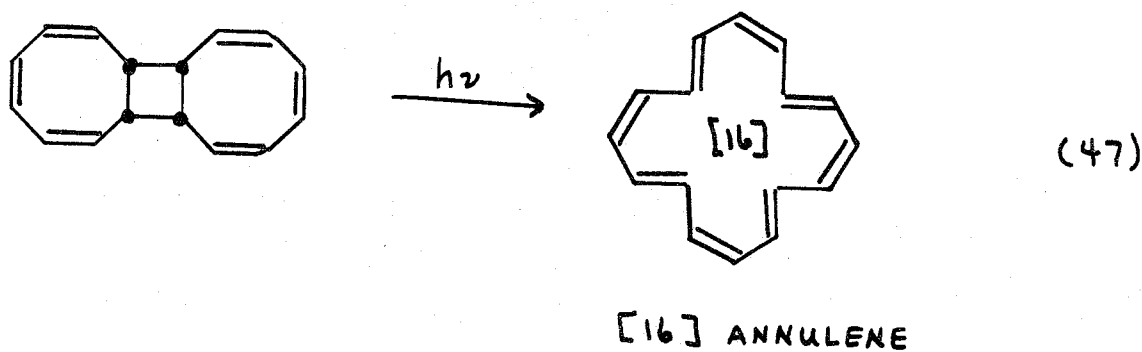
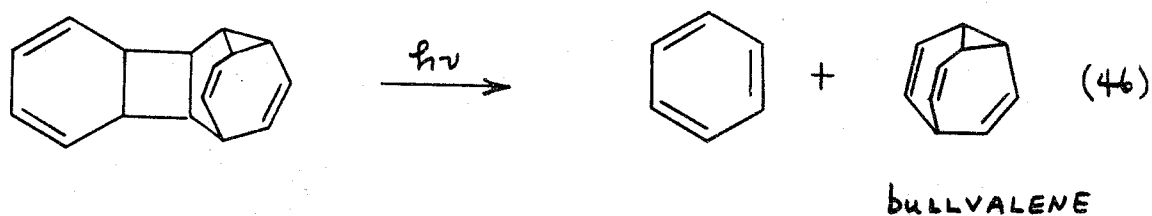
5. Photoecology



D. Cycloelimination reactions



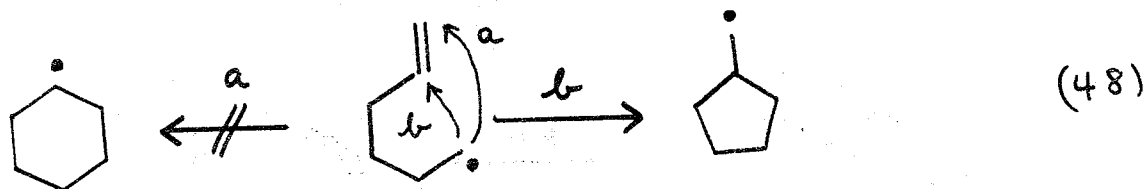
6.7 D. (continued)



E. Mechanistic considerations

1. S_1 inefficient at intermolecular cycloadditions
2. S_1 may undergo (pericyclic) intramolecular cycloadditions
3. T_1 involved in most intermolecular and intramolecular cycloadditions
4. T_1 reactions follow "best" biradical principle intermolecularly, good stereoselectivity, poor stereospecificity
5. T_1 reactions follow "rule of five" for intramolecular cycloadditions

6.7 E. (continued)



6. Considerable synthetic utility, especially intramolecular cases

7. Direct excitation: J. Amer. Chem. Soc., 93, 5593 (1971)

F. References to reactions

(29) and (30) J. Amer. Chem. Soc., 91, 520 (1969)

(31) J. Amer. Chem. Soc., 87, 3406 (1965)

(36) J. Org. Chem., 30, 1849 (1965)

(37) J. Amer. Chem. Soc., 83, 4647 (1961)

(38) J. Amer. Chem. Soc., 89, 4937 (1967)

(39) Tetrahedron Letters, 2159 (1966)

(40) Tetrahedron Letters, 2263 (1969)

(41) J. Amer. Chem. Soc., 93, 7016 (1971)

(42) Molec. Photochem., 1, 319 (1969)

(43) J. Amer. Chem. Soc., 90, 5286 (1968)

(44) J. Agr. Food Chem., 17, 404 (1969)

(45) J. Amer. Chem. Soc., 91, 5404 (1969)

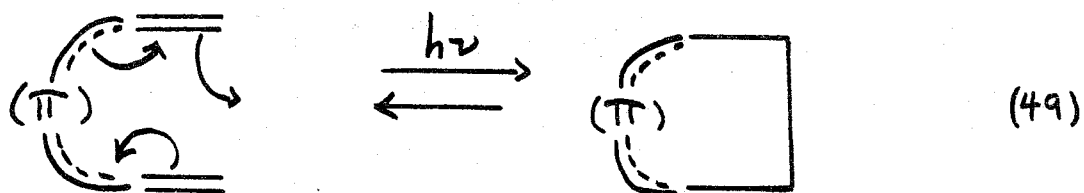
(46) Angew. Chem., inter. ed. Eng., 2, 481 (1963)

(47) J. Amer. Chem. Soc., 90, 4946 (1968)

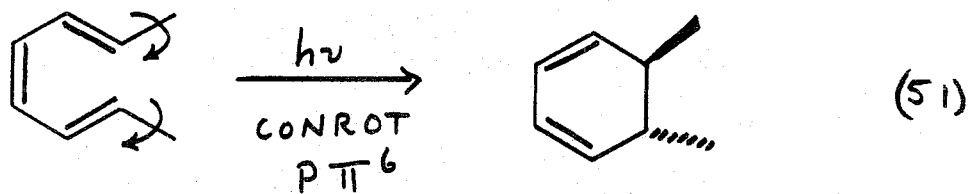
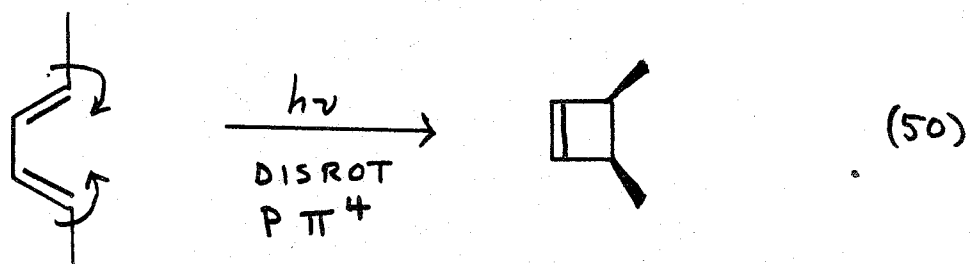
(48) J. Amer. Chem. Soc., 94, (1972); ibid., 94, 6059 (1972)

6.8 ELECTROCYCLIC REACTIONS

A. Generally S_1 , probably pericyclic

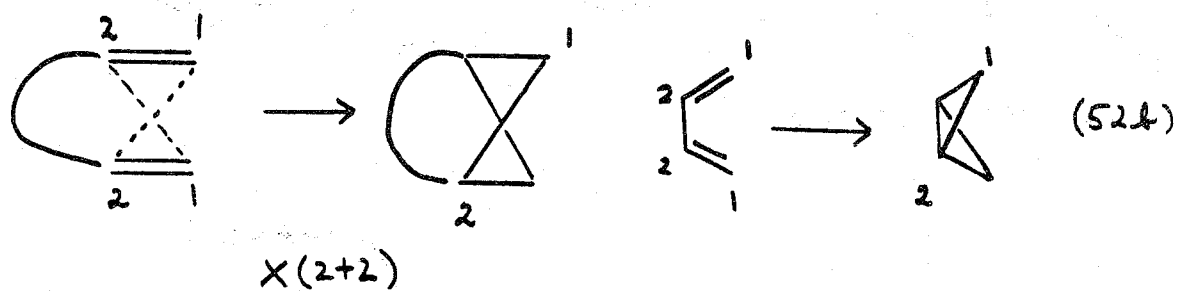
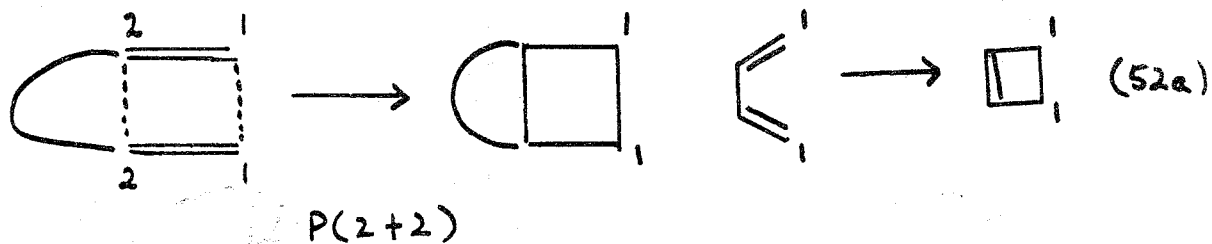


B. Selection rules generally obeyed (Chapter 5)



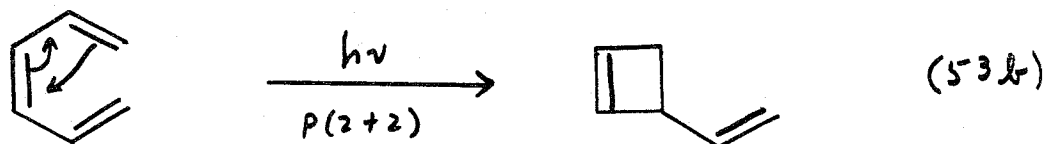
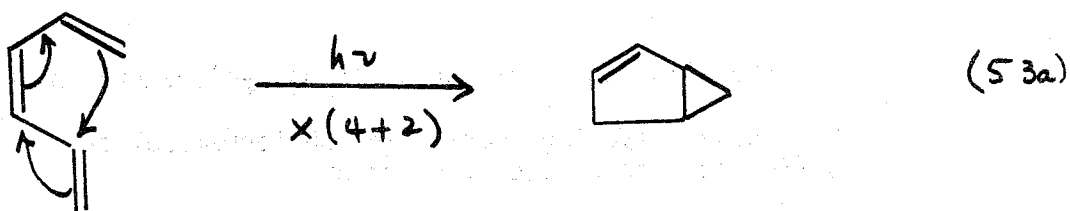
6.8 (continued)

C. Compare to intramolecular cycloadditions



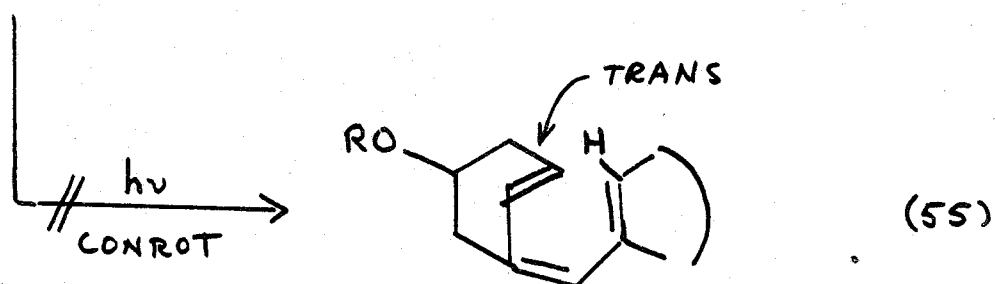
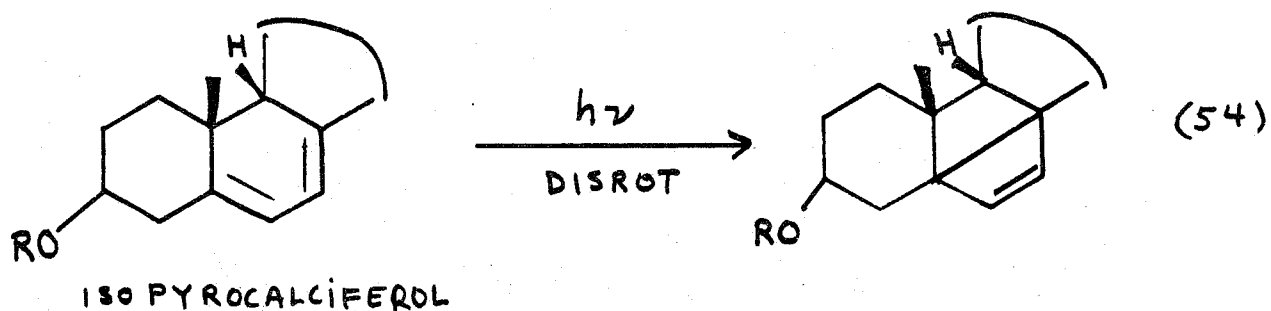
D. Examples

1. Conformational effects



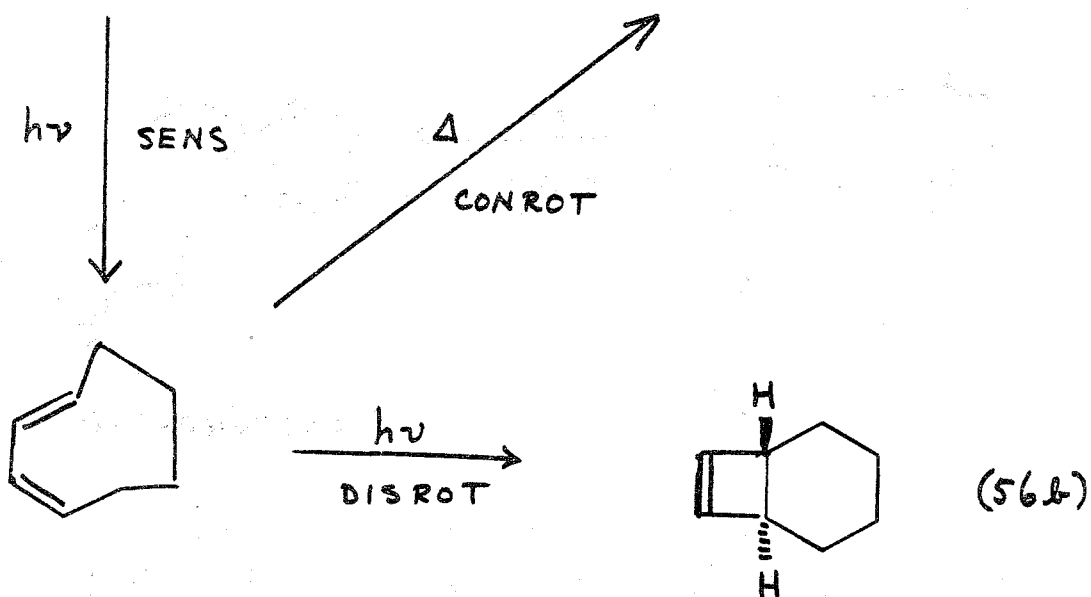
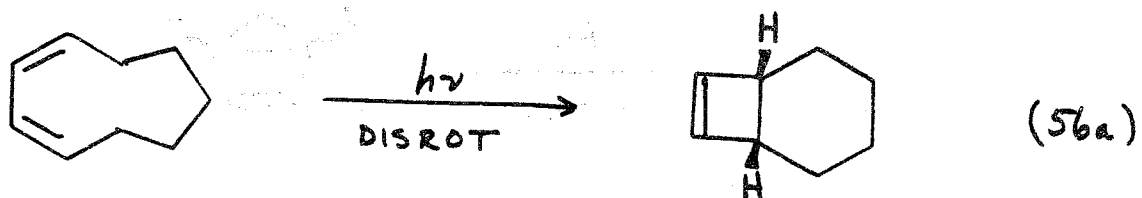
6.8 D. (continued)

2. Orbital symmetry factors

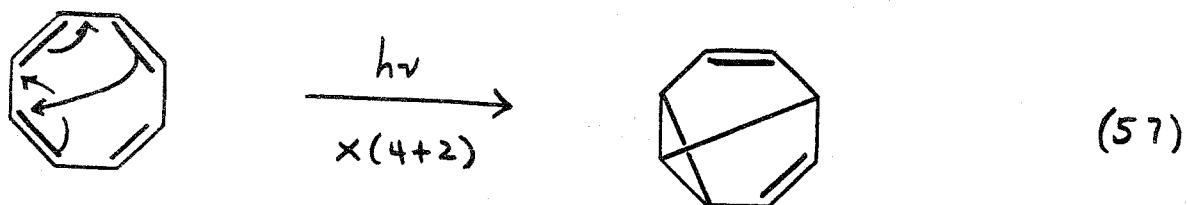


3. Reaction (55) would produce a trans-cyclohexene in ring A
4. Nice case comparing thermal and photochemical paths;
difference for S_1 and T_1 reactions

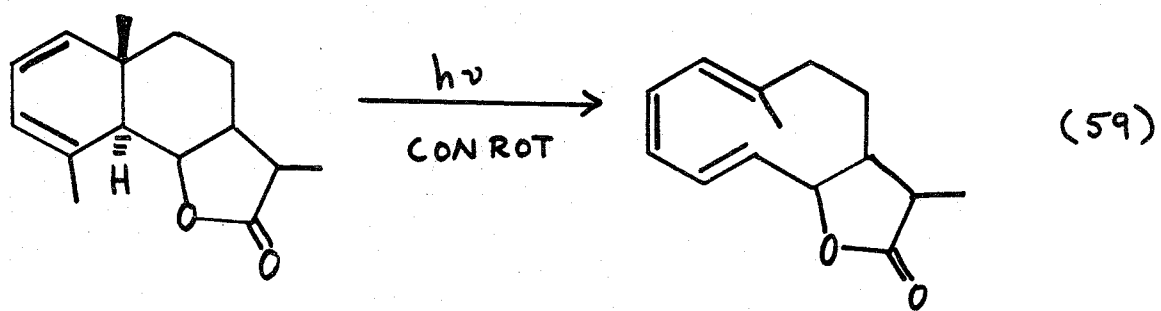
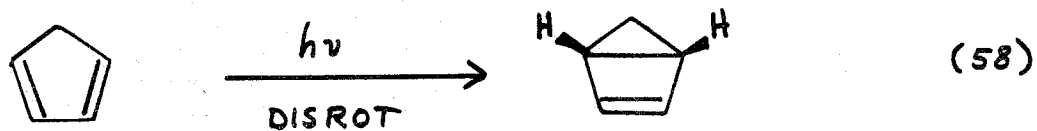
6.8 D. (continued)



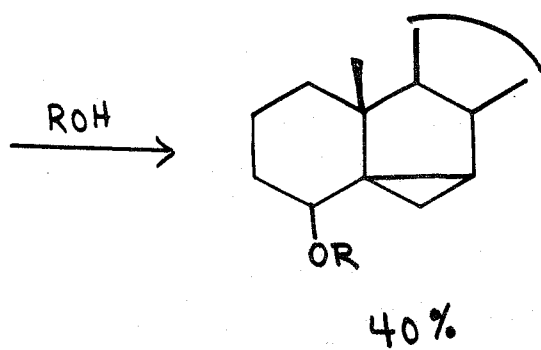
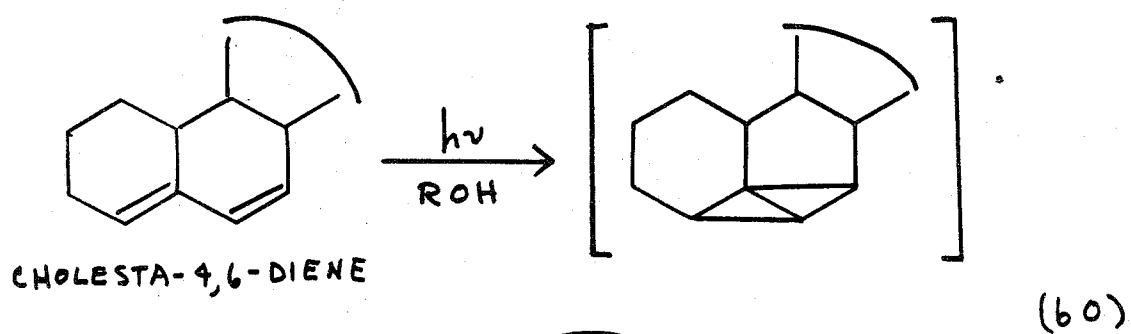
5. Synthetic applications



6.8 D. (continued)

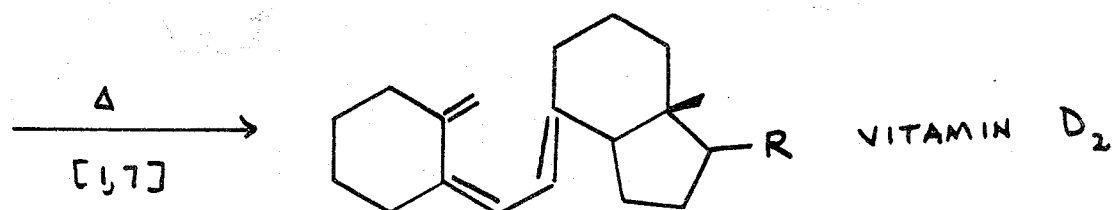
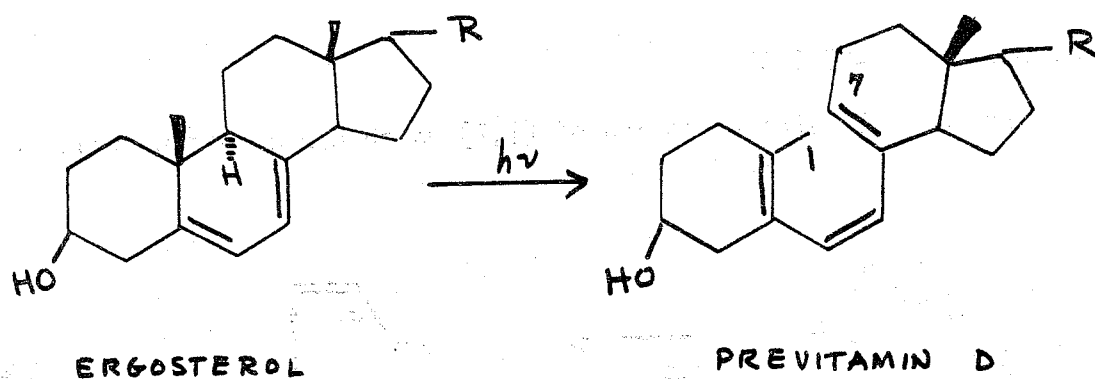


COSTUNOLIDE



40%

6.8 D. (continued)



E. Summary

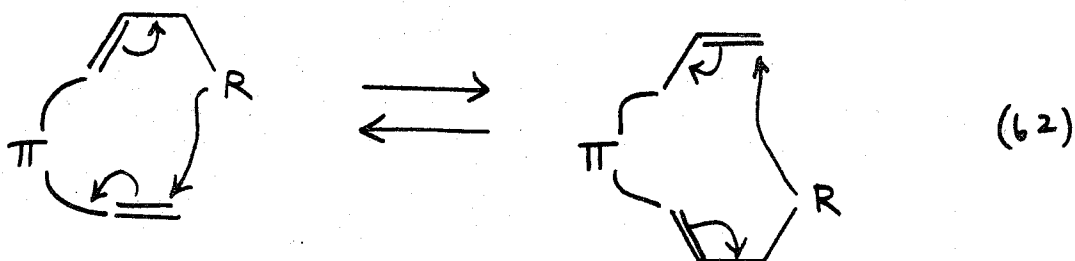
1. Pericyclic, S_1 reactions
2. Stereospecific (selection rules)
3. Synthetically useful, particularly for cyclobutenes

F. References to reactions

- (50) J. Amer. Chem. Soc., 90, 4498 (1968)
- (51) Tetrahedron Letters, 549 (1962)
- (52) J. Amer. Chem. Soc., 87, 3778 (1965)
- (53) J. Amer. Chem. Soc., 94, 4285 (1972); ibid., 88, 2850 (1966)
- (54) J. Amer. Chem. Soc., 81, 4060 (1959)
- (56) J. Amer. Chem. Soc., 88, 1073 (1966)
- (57) J. Amer. Chem. Soc., 88, 846 (1966)
- (58) J. Amer. Chem. Soc., 88, 846 (1966)
- (59) J. Amer. Chem. Soc., 85, 4033 (1966); ibid., 87, 5736 (1965)
- (60) Tetrahedron, 24, 4437 (1968)
- (61) Tetrahedron, 16, 146 (1961)

6.9 SIGMATROPIC REACTIONS

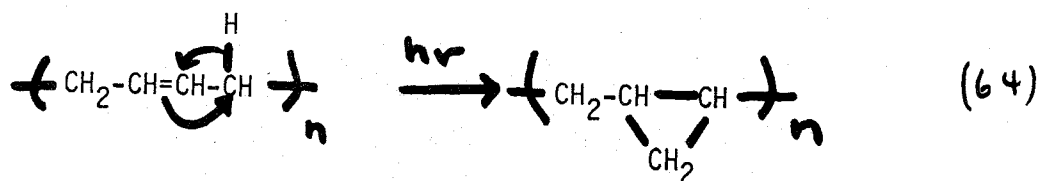
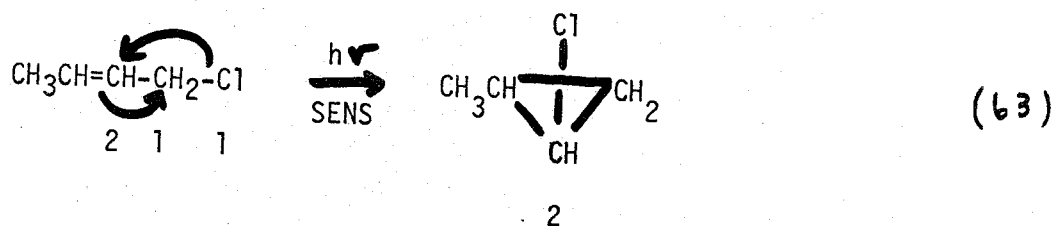
A. Generally S_1 with exception of [1,2] which can originate from T_1



B. Stereochemistry of interacting groups is crucial

C. Examples

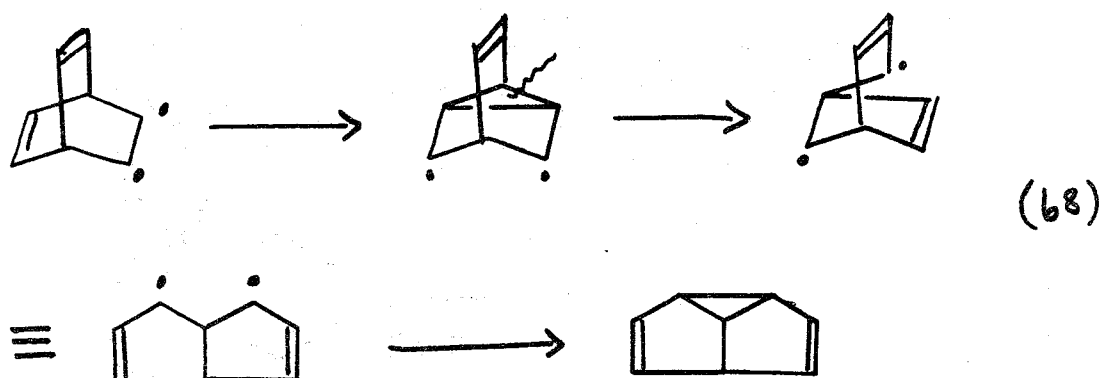
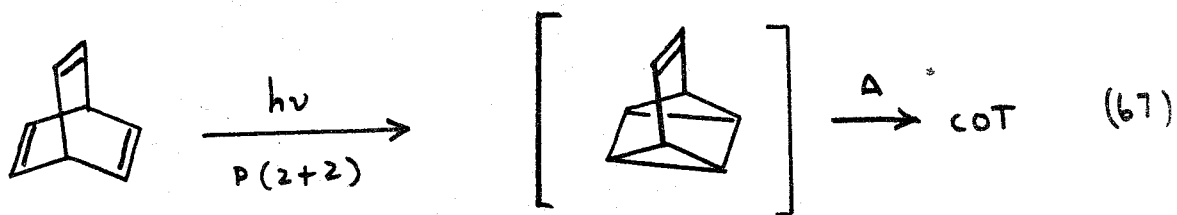
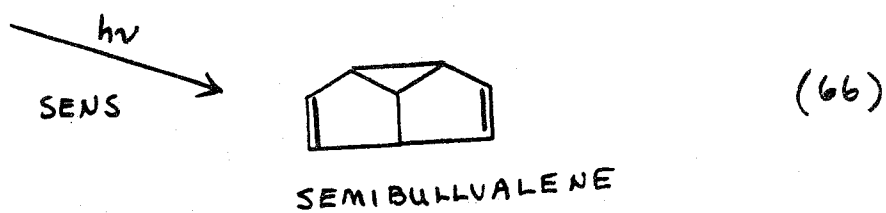
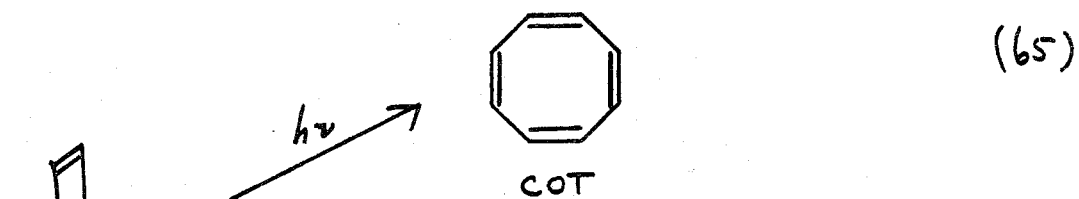
1. [1,2] shifts: 4 electrons; a-a or s-s according to the rules.
Can be sensitized



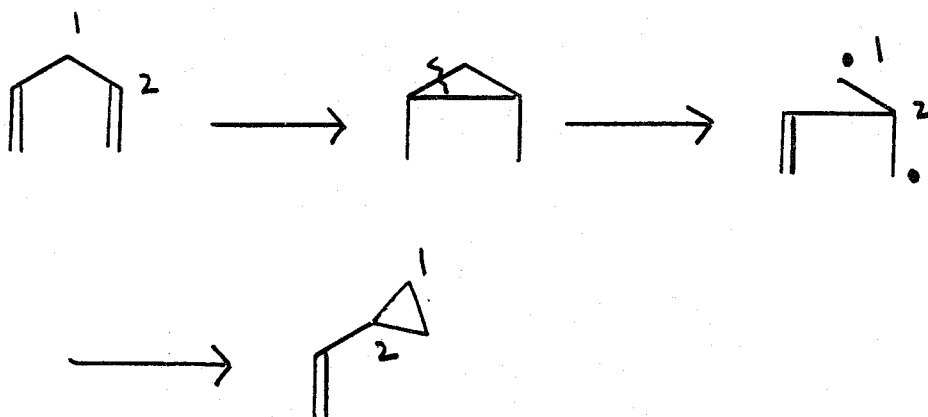
6.9 C. (continued)

2. Conformation problems. "Free rotor" effect. Recall eq. 18.

3. [1,2] Common in cyclic systems where geometry is favorable

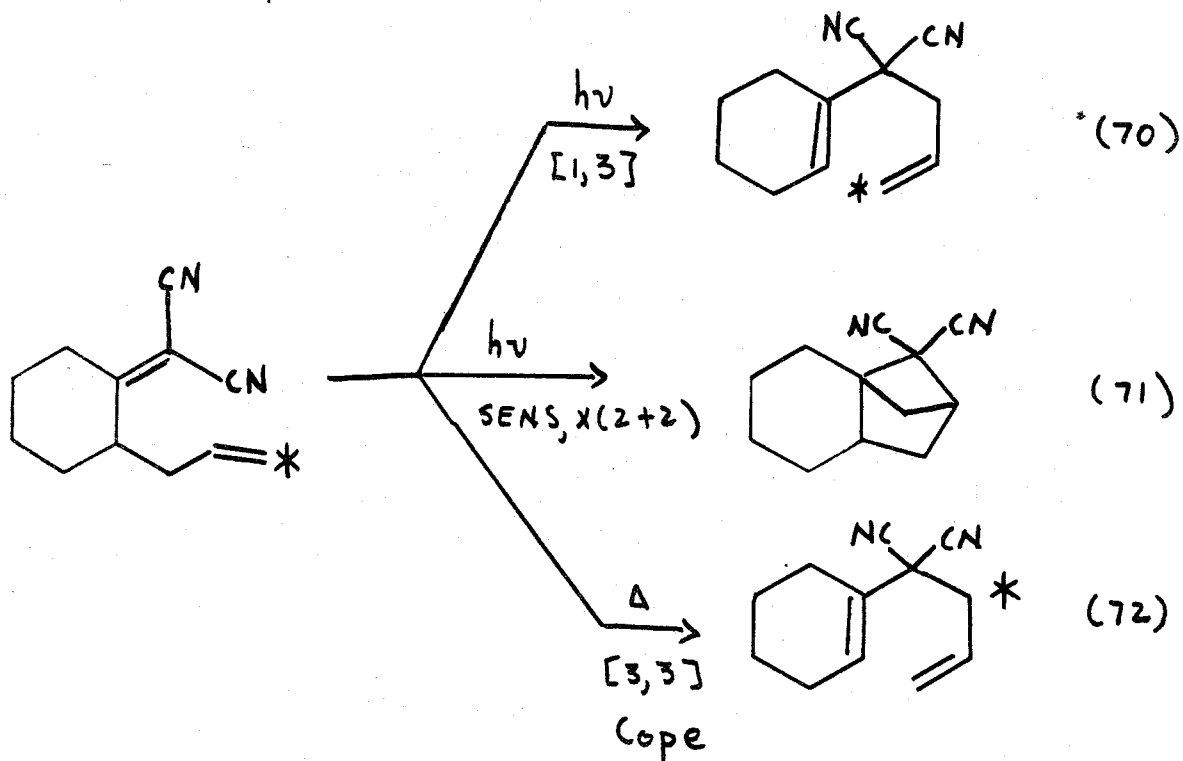


4. Also called "di-~~π~~-methane" rearrangement



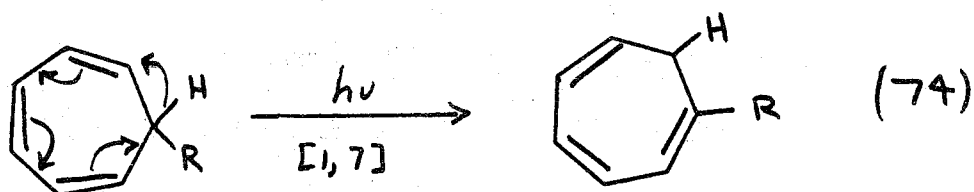
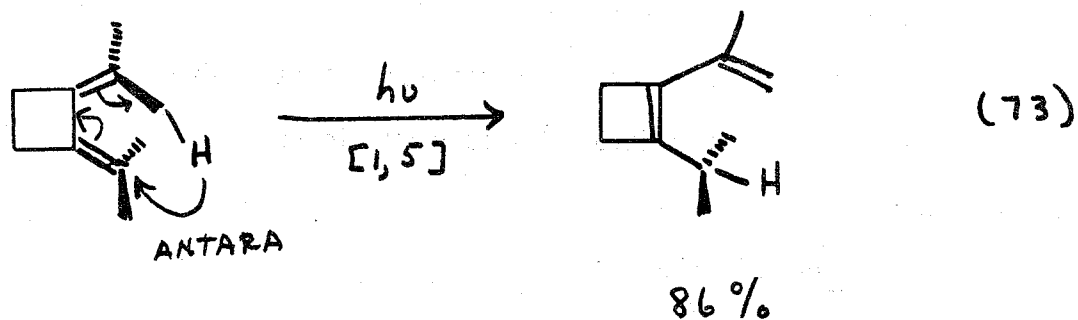
(69)

5. [1,3] Shifts: 4 electrons; a-a or s-s according to the rules.
Usually S_1

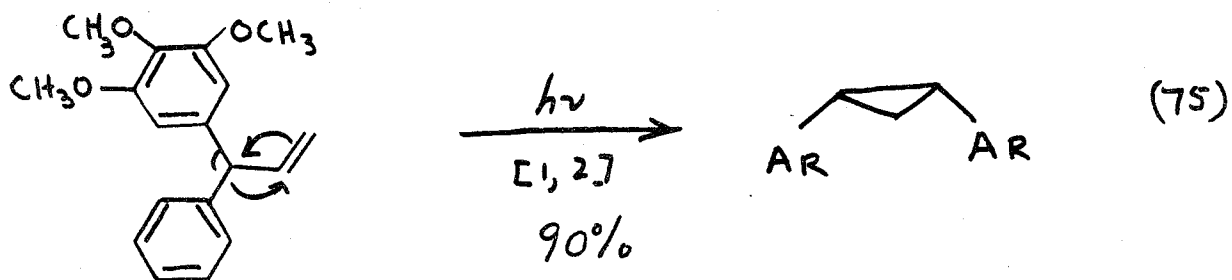


6. [1,4], [1,6], [1,n = even] not common

7. [1,5], [1,7], [1,n = odd]



8. Synthetic applications



6.9 (continued)

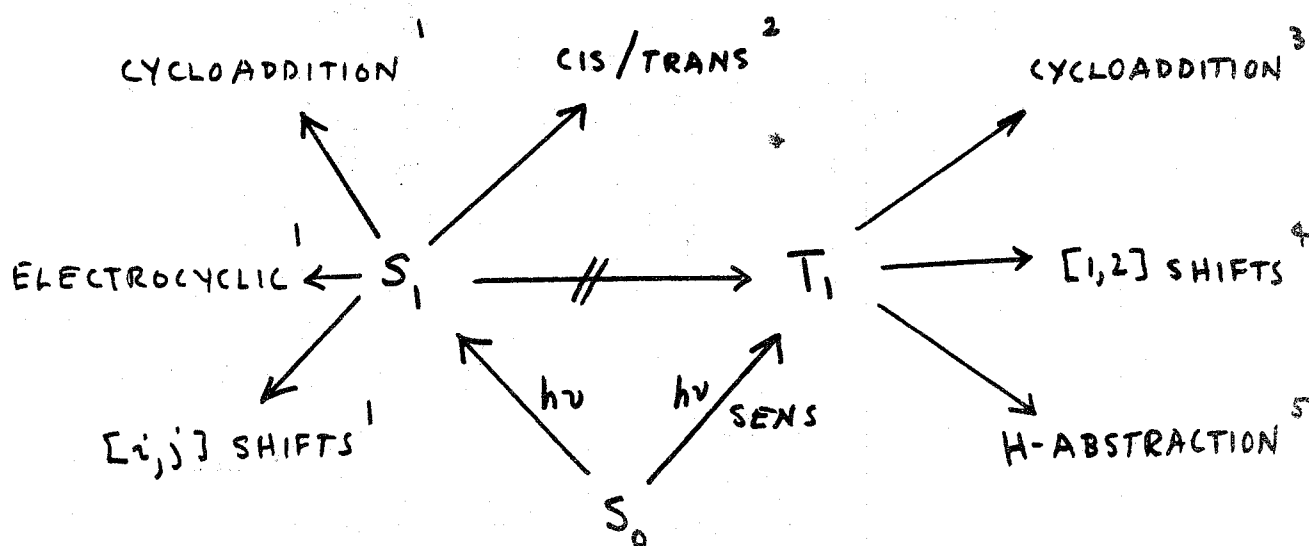
D. Summary

1. Except for cyclic systems which undergo [1,2] shifts, reactions appear to be S_1 , pericyclic
2. Good synthetic reactions, if geometry is favorable
3. Hardly any kinetic data, few quantum yields

E. References to reactions

- (63) Ann., 745, 176 (1971)
- (64) Macromolecules, 2, 550 (1969)
- (65) and (66) J. Amer. Chem. Soc., 91, 3317 (1969)
- (70)-(72) Rev: Quart. Rev., 22, 423 (1968)
- (73) J. Amer. Chem. Soc., 91, 4478 (1969)
- (74) Angew. Chem., 75, 921 (1963); Rec. trav. Chim., 88, 266 (1969)
- (75) Tetrahedron Letters, 4169 (1967)

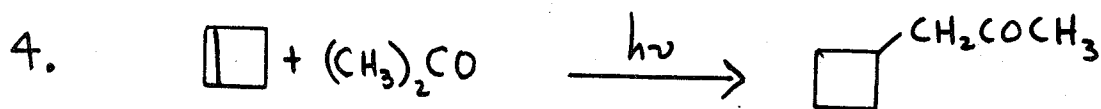
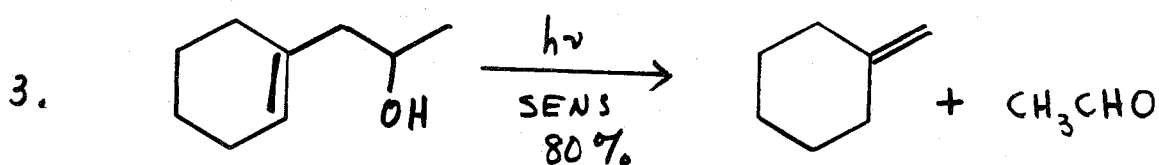
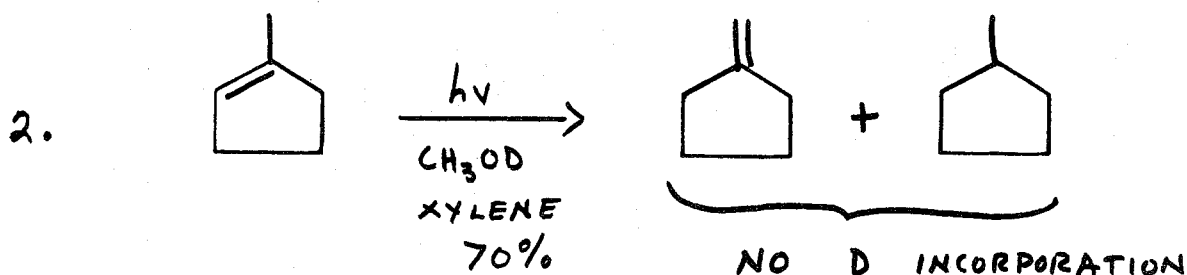
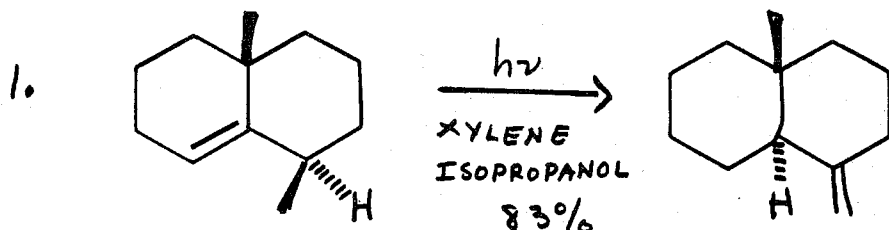
6.10 SUMMARY OF REACTIONS OF ALKENES AND CONJUGATED POLYENES



1. Appear to be pericyclic
2. Always a potential reaction except in rings of 5 carbons or less. Ionic or electrocyclic and cycloaddition ground state reactions of strained intermediates may occur.
3. Usually a biradical-like process. Intermolecular follows "best biradical" rule; intramolecular follows "rule of five."
4. Usually requires cyclic system due to otherwise rapid competitive decay of T_1 by twisting.
5. Usually "radical-like."

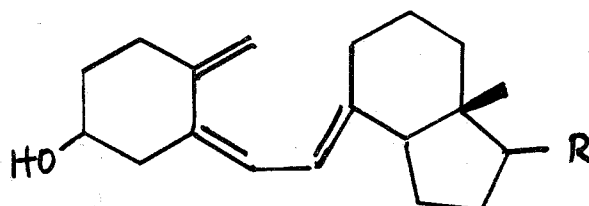
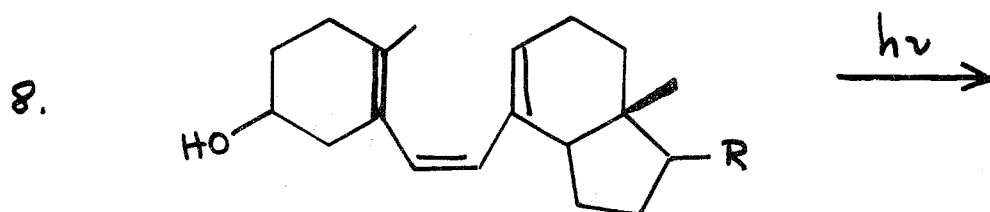
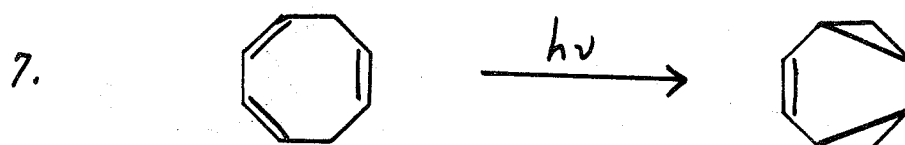
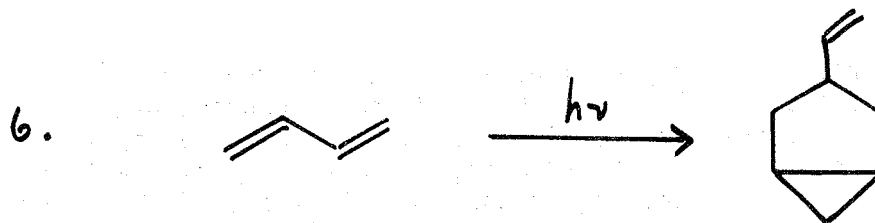
6.11 PROBLEMS

A. Classification problems. Try to classify each of the following reactions as occurring via a primary photochemical reaction discussed in this Chapter.

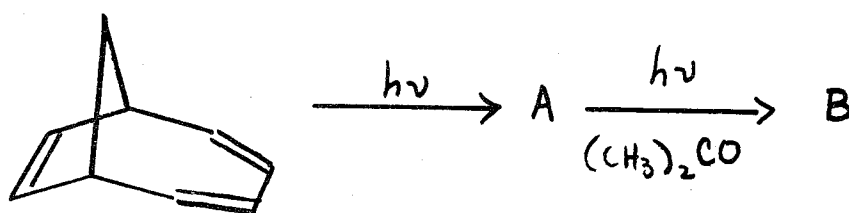


(continued)

6.11 A. (continued)

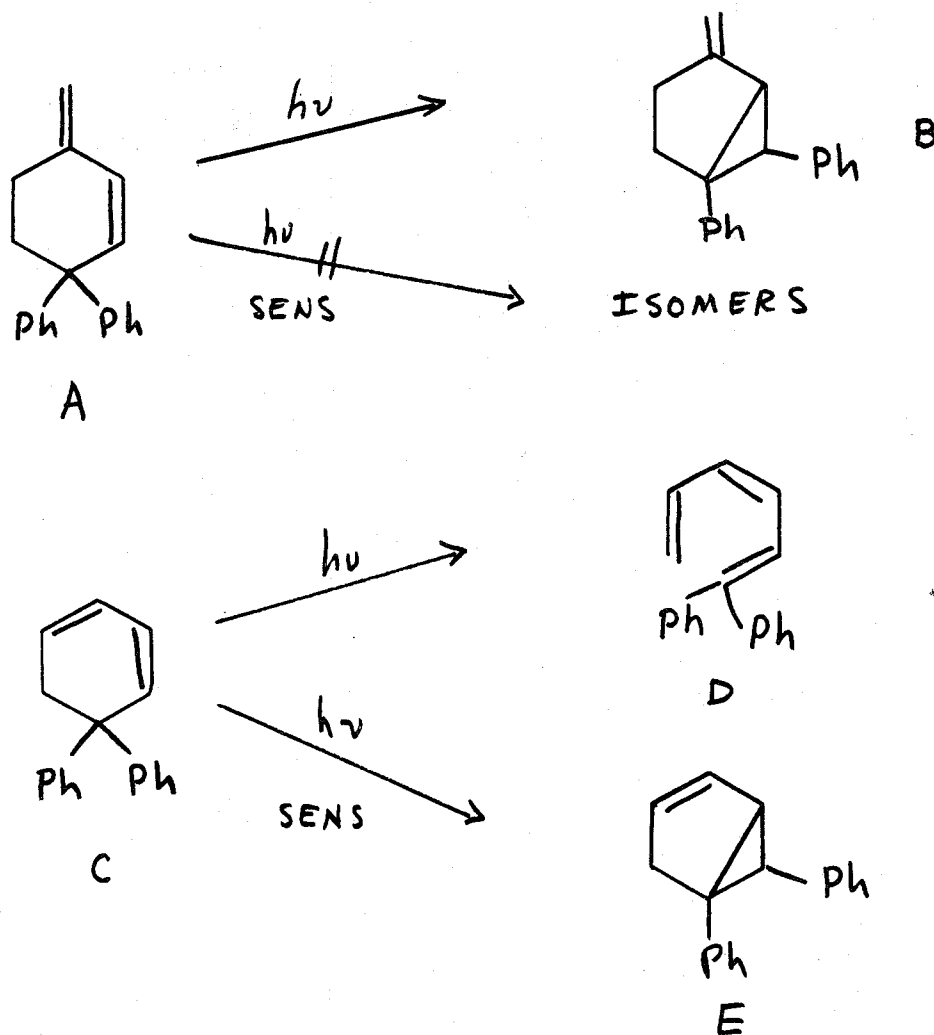


B. Suggest structures for the isomeric compounds A and B. A possesses 2 double bonds; B has none.



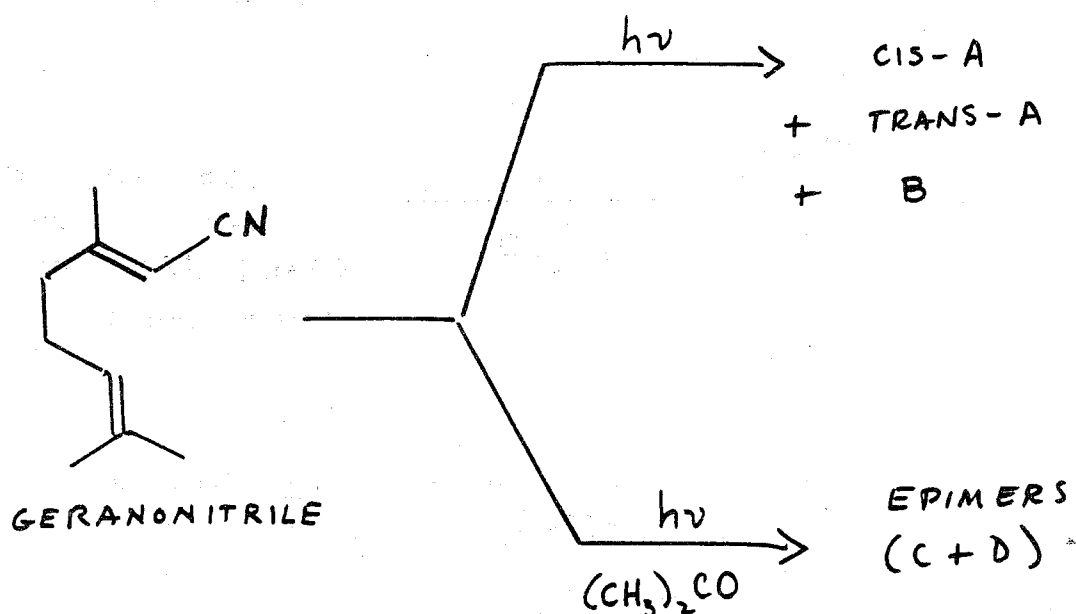
6.11 (continued)

- C. Direct irradiation of the diene A results in smooth conversion to the bicyclic system B. Although the diene A quenches benzophenone triplets, no B results from irradiation of A with benzophenone as photosensitizer. On the other hand, the diene C yields a triene (D) upon direct excitation and the bicyclic system E when benzophenone is employed as sensitizer. Rationalize these results.

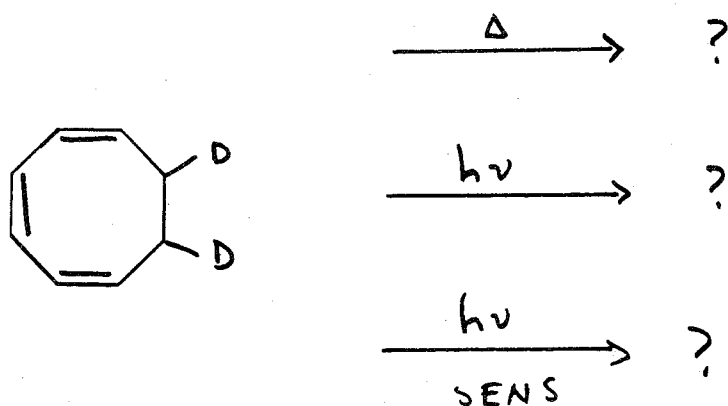


6.11 (continued)

- D. Direct irradiation of geranonitrile results in a mixture of isomeric products, two of which are cis-trans isomers. Suggest structures for these products based on analogy with the 1,5-dienes discussed above. Sensitized excitation of geranonitrile results in formation of an (epimeric) pair of isomers in the ratio of 80 to 20. Suggest structures for the epimers.

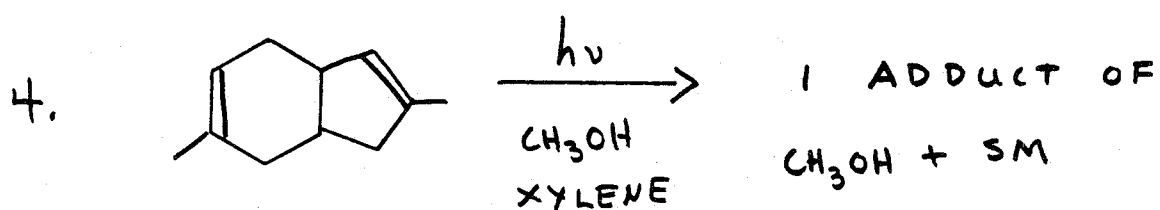
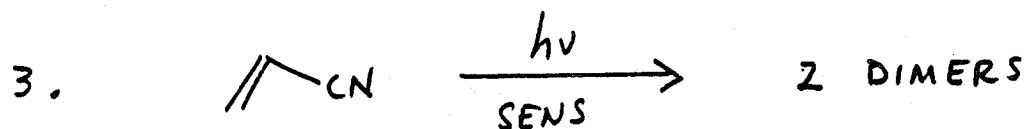
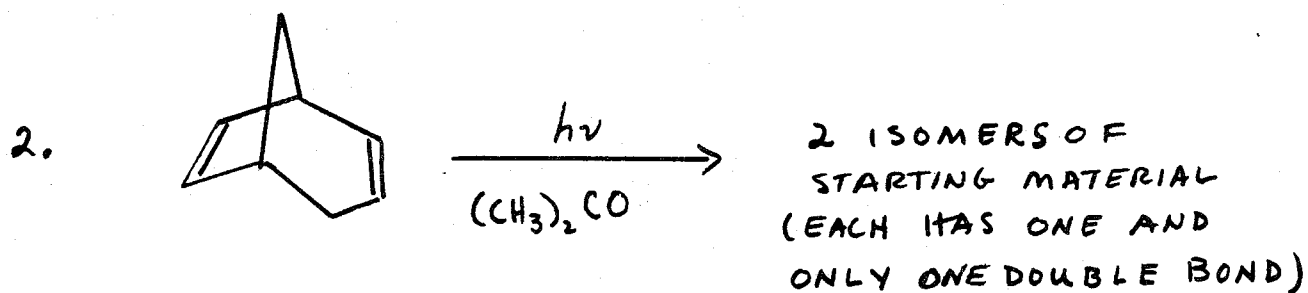
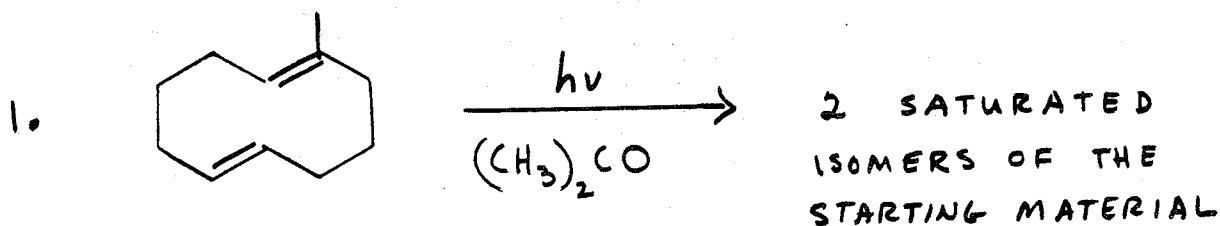


- E. (1) Consider the orbital symmetry rules for sigmatropic shifts and predict how extended heating or irradiation (or both) will scramble the deuterium label in A. Assume that sigmatropic rearrangement is the only reaction which occurs. (2) What are the other unimolecular primary photochemical processes expected from irradiation of A? (3) What are the expected products of triplet sensitized excitation of A?



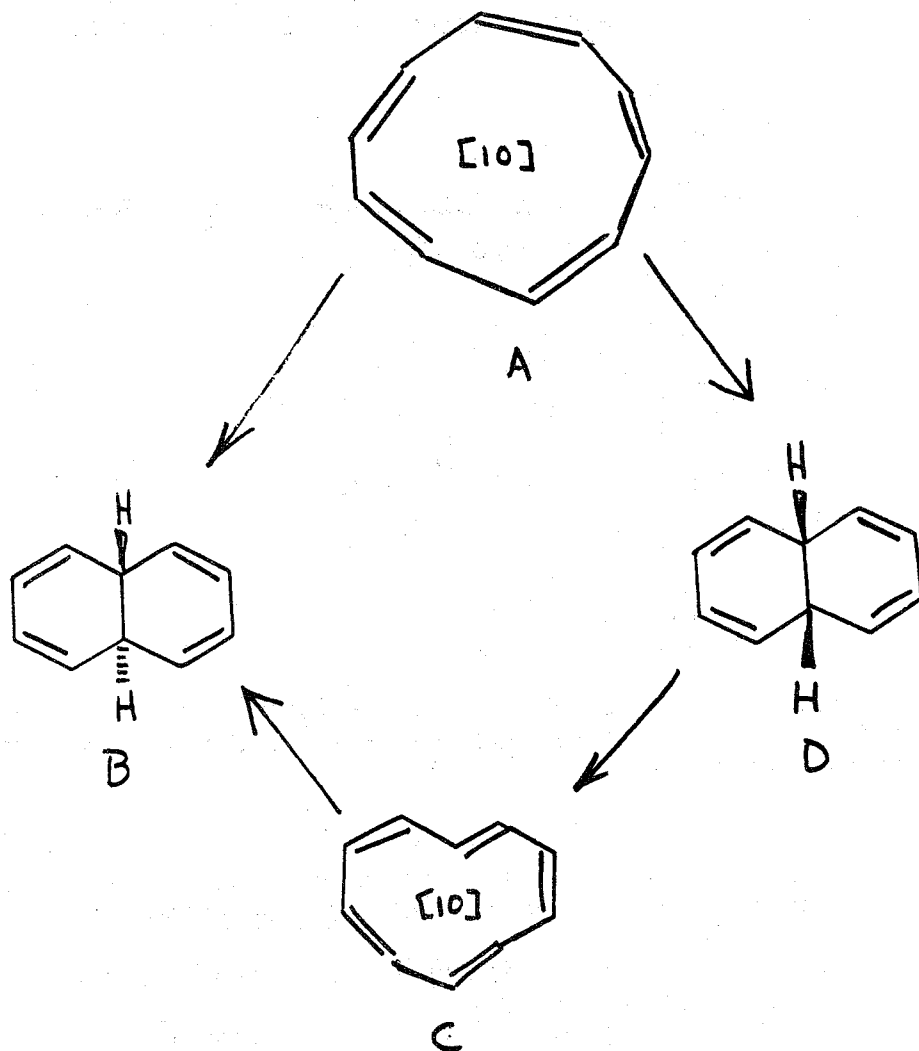
6.11 (continued)

F. Predict the major product(s) expected from the following reactions.



6.11 (continued)

- G. Indicate the nature of each of the following interconversions in terms of (a) the number of electrons participating in the reaction; (b) the rotational process (conrot or disrot) and (c) whether or not the process is allowed or forbidden photochemically.

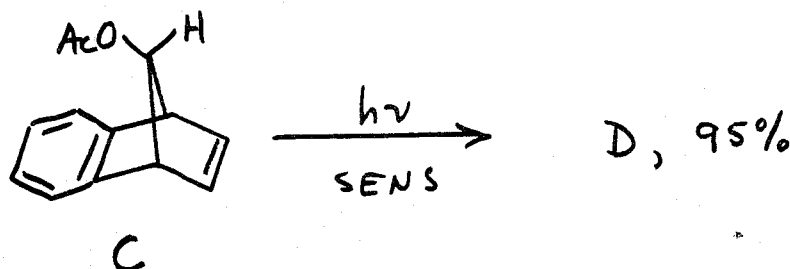
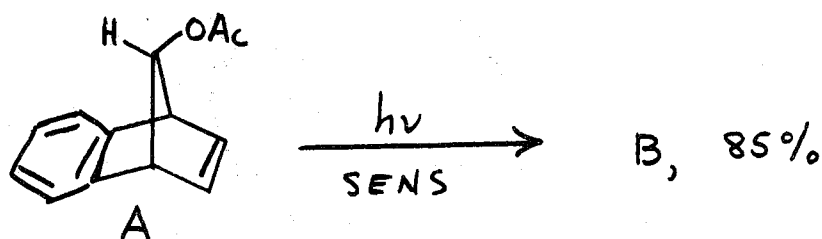


- H. Predict which chromophore will possess the bulk of electronic excitation in S_1 and T_1 for

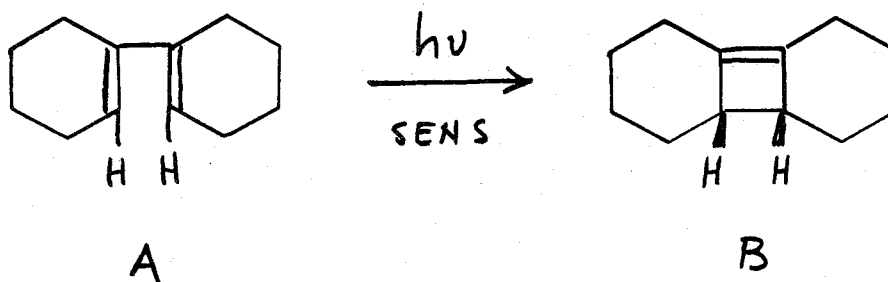
1. $\text{PhCO}-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}=\text{CH}_2$
2. $\text{Ph}-\text{CH}_2-\text{CH}=\text{CH}_2$
3. $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}-\text{CH}=\text{CH}_2$

6.11 (continued)

- I. The xylene sensitized addition of alcohols to cyclic alkenes is generally believed to involve triplet energy transfer from the sensitizer to the alkene. (1) How would you establish that S_1 of the sensitizer is definitely not involved? (2) Sensitized cyclic alkene dimerization accompanies sensitized addition of solvent. How would you establish whether the dimer and adduct are derived from the same reactive state?
- J. Sensitized excitation of A yields an isomer B, while sensitized excitation of C yields an isomer D. Suggest structures of B and C.

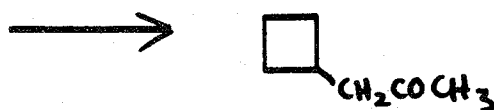
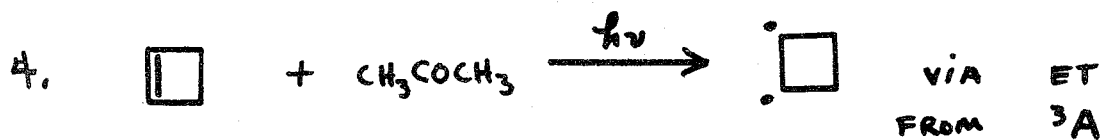
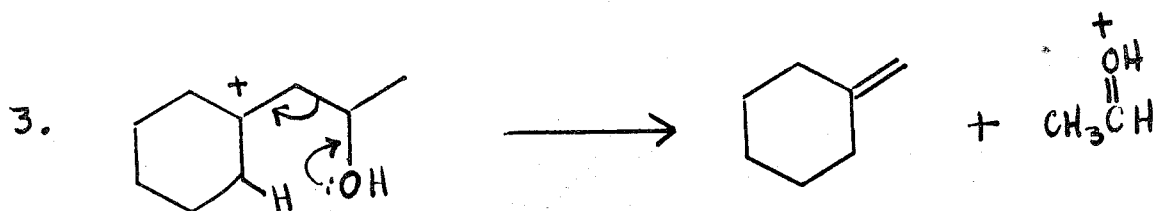
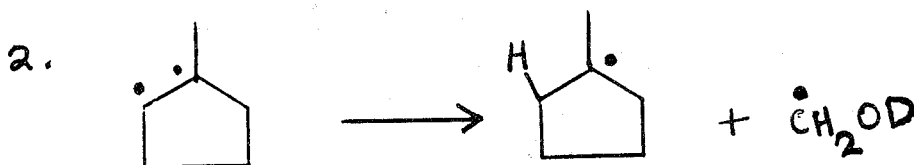
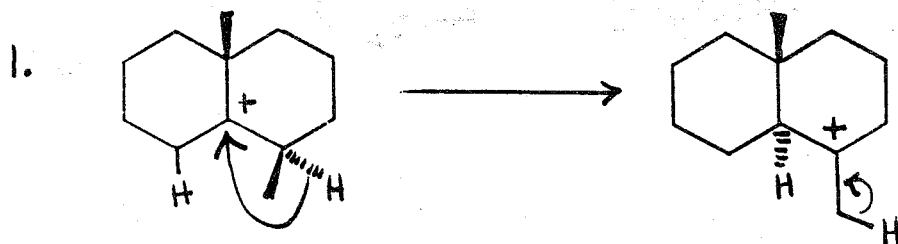


- K. Suggest a rationale for the observation that the norbornadiene triplet ring closes to quadricyclane but the benzonorbornadiene triplet undergoes a [1,2] shift.
- L. Oxygen quenches the fluorescence quantum yield of $\text{PhCH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{CHCH}_3$ but enhances the quantum yield of cis-trans-isomerization. Explain.
- M. It has been found that triphenylene photosensitizes the isomerization of 1,1'-bicyclohexenyl A to the cyclobutene B. Does this reaction necessarily constitute an exception to the rule that triplet sensitizers do not effect electrocyclic reactions?

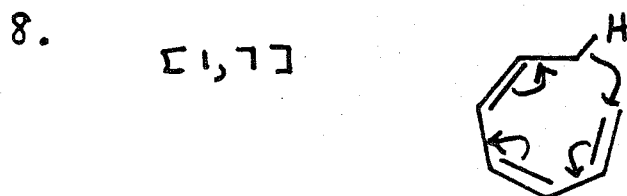
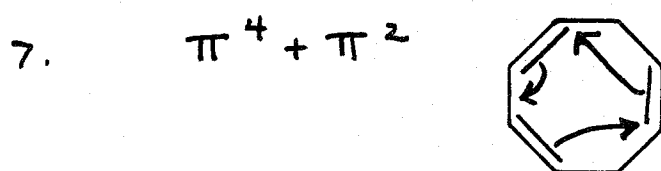
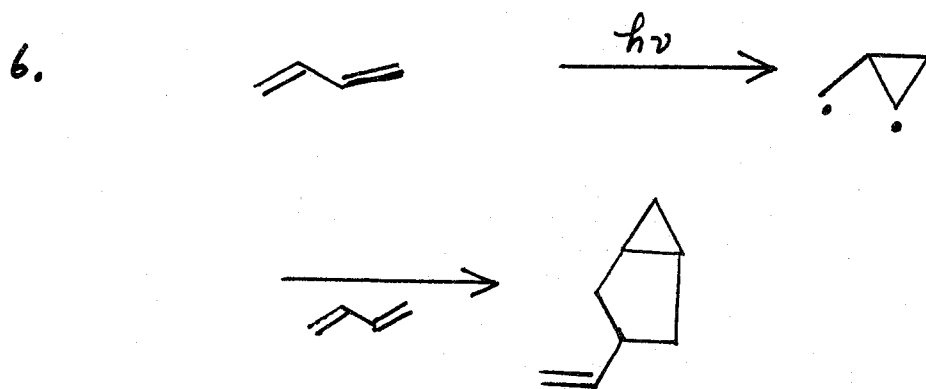
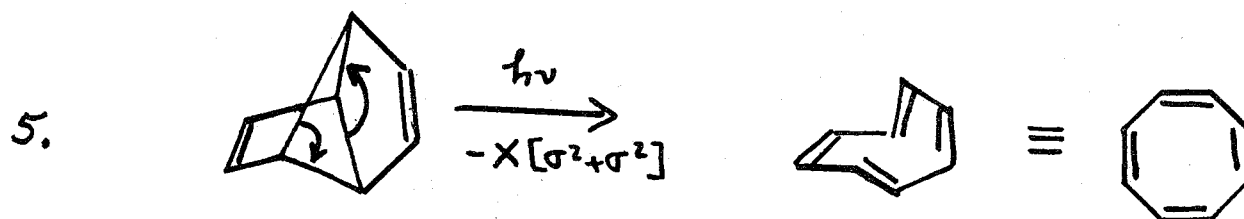


6.12 ANSWERS TO PROBLEMS

A. Classification problems

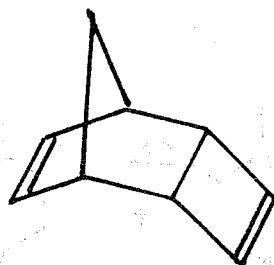


6.12 A. (continued)

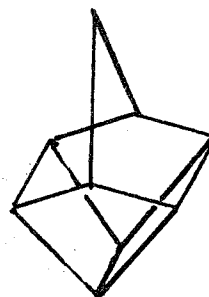


6.12 (continued)

B.

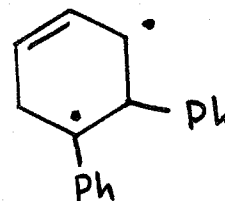
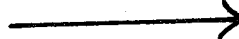
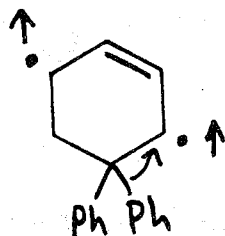
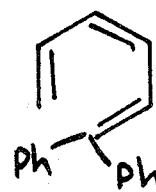
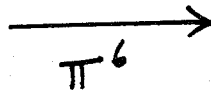
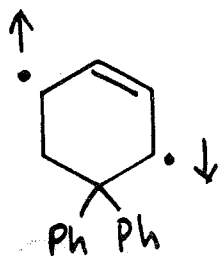
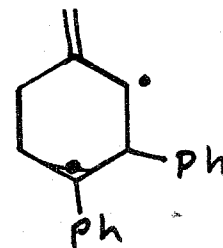
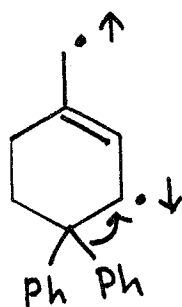


A π^4

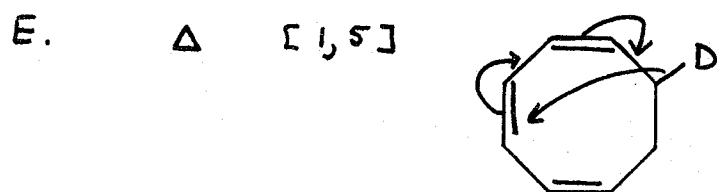
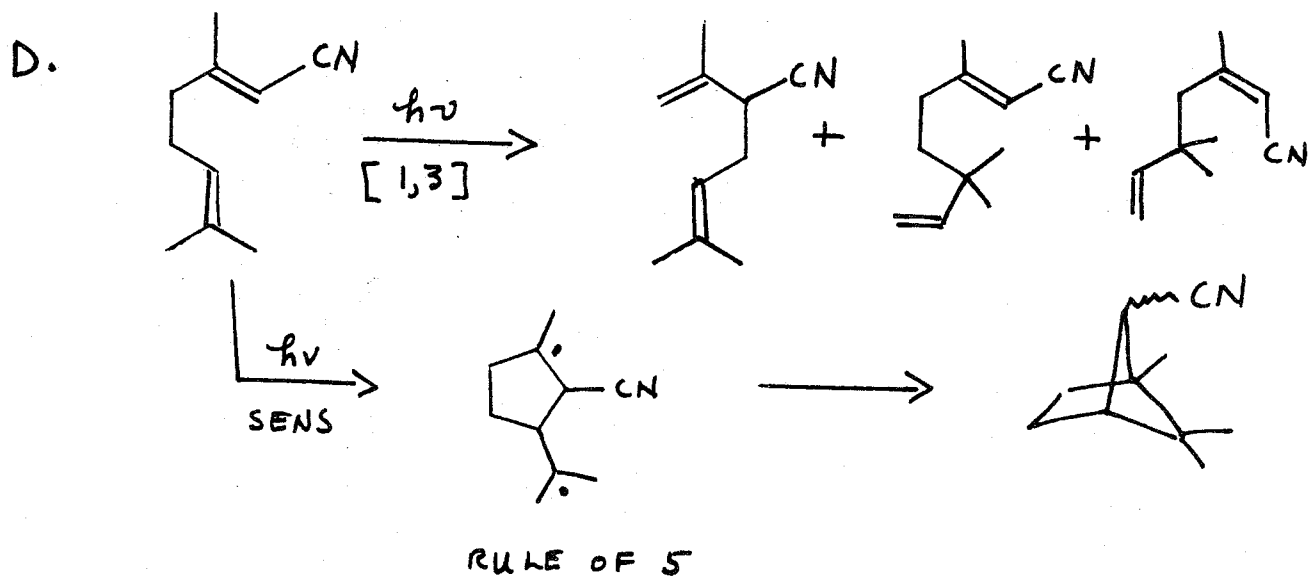


B $\pi^2 + \pi^2$

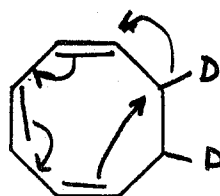
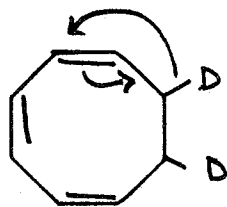
C.



6.12 (continued)



$h\nu$ [1,3] or [1,7]

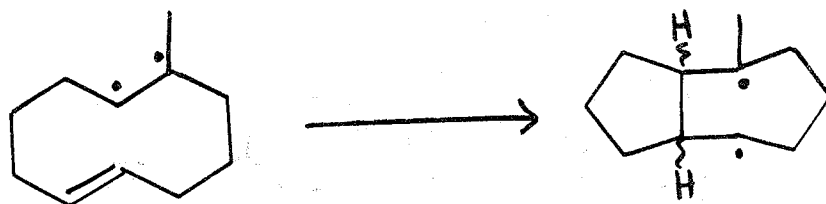


SENS CIS-TRANS OR DIMERS

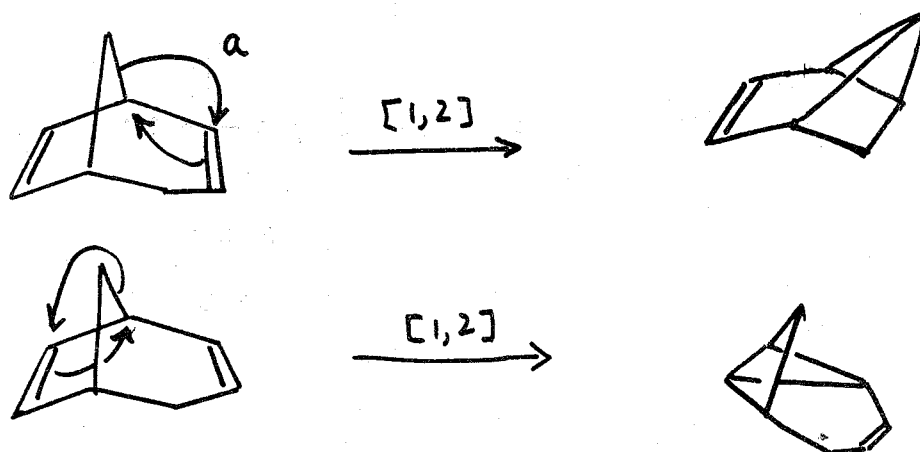
6.12 (continued)

F.

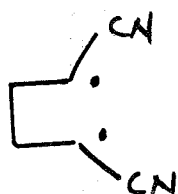
1.



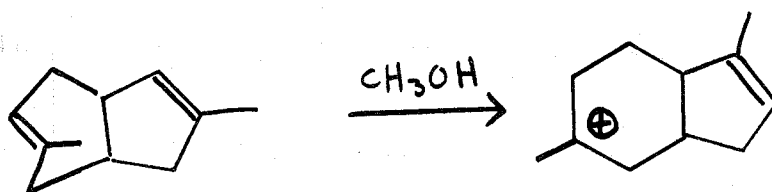
2.



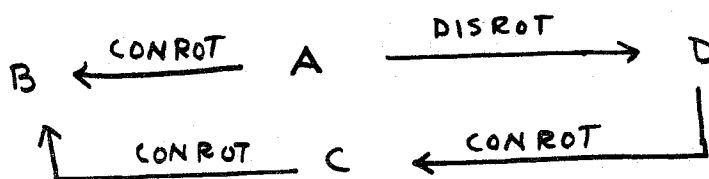
3.



4.

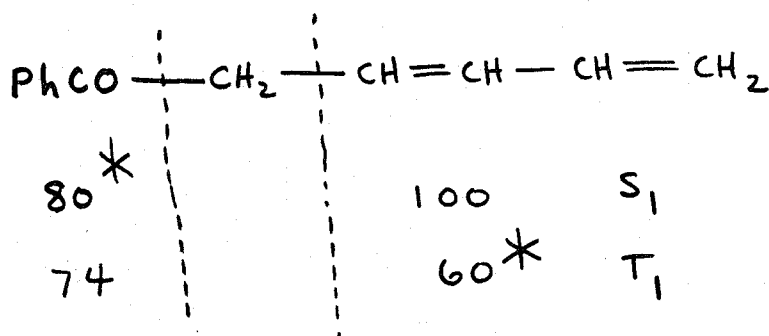


G.

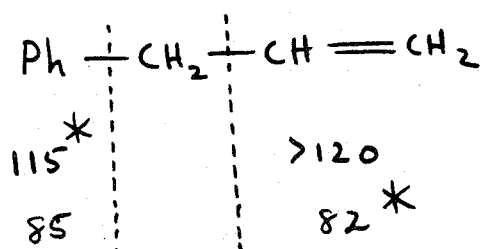


6.12 (continued)

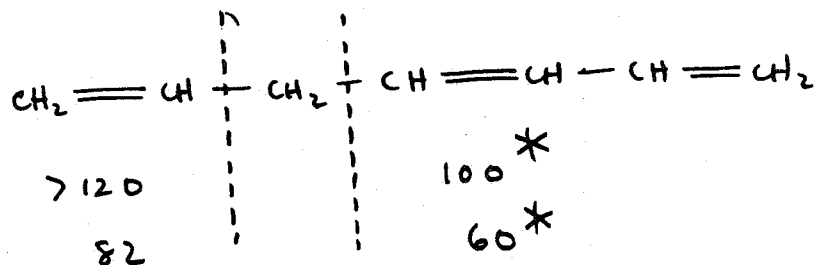
H. 1.



2.



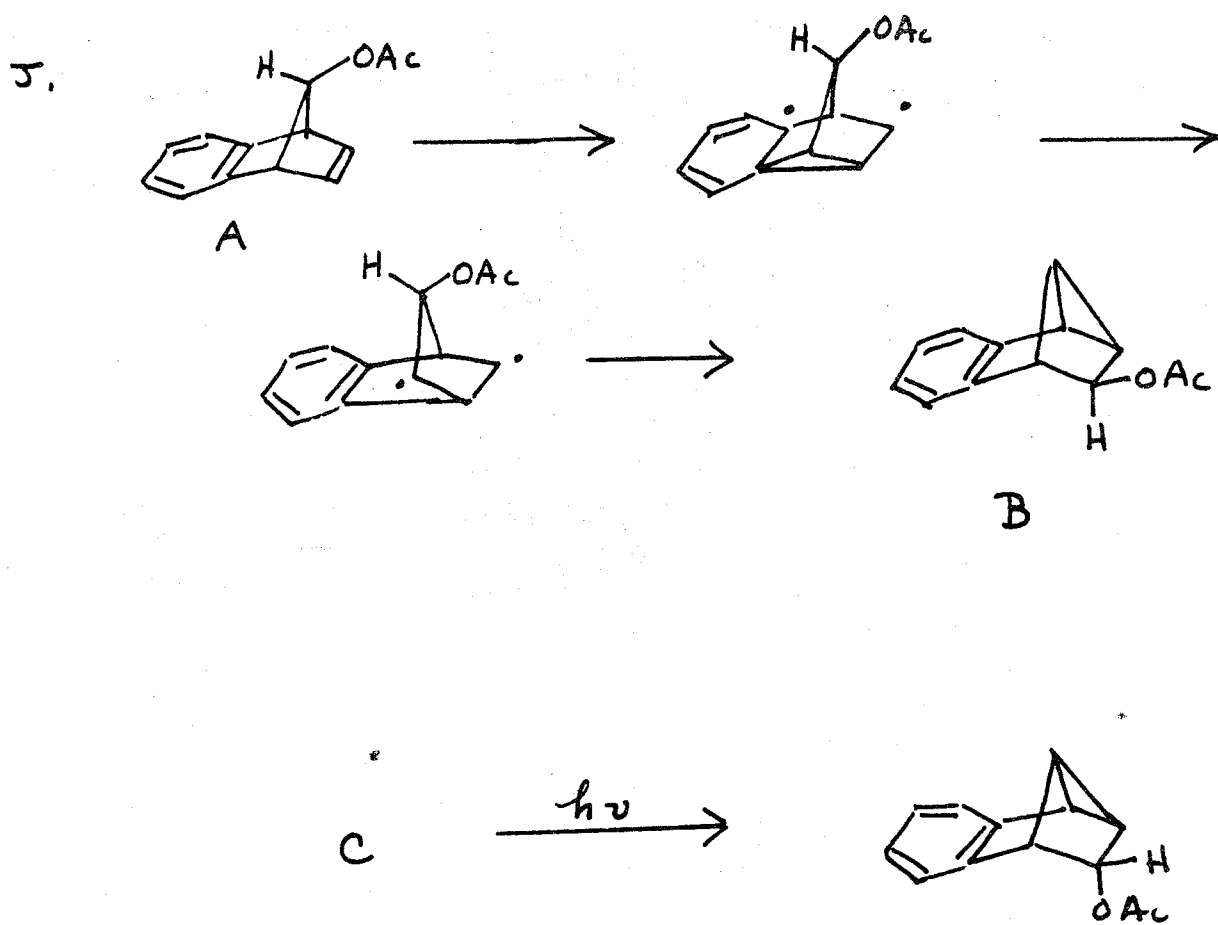
3.



I. FLUORESCENCE QUENCHING

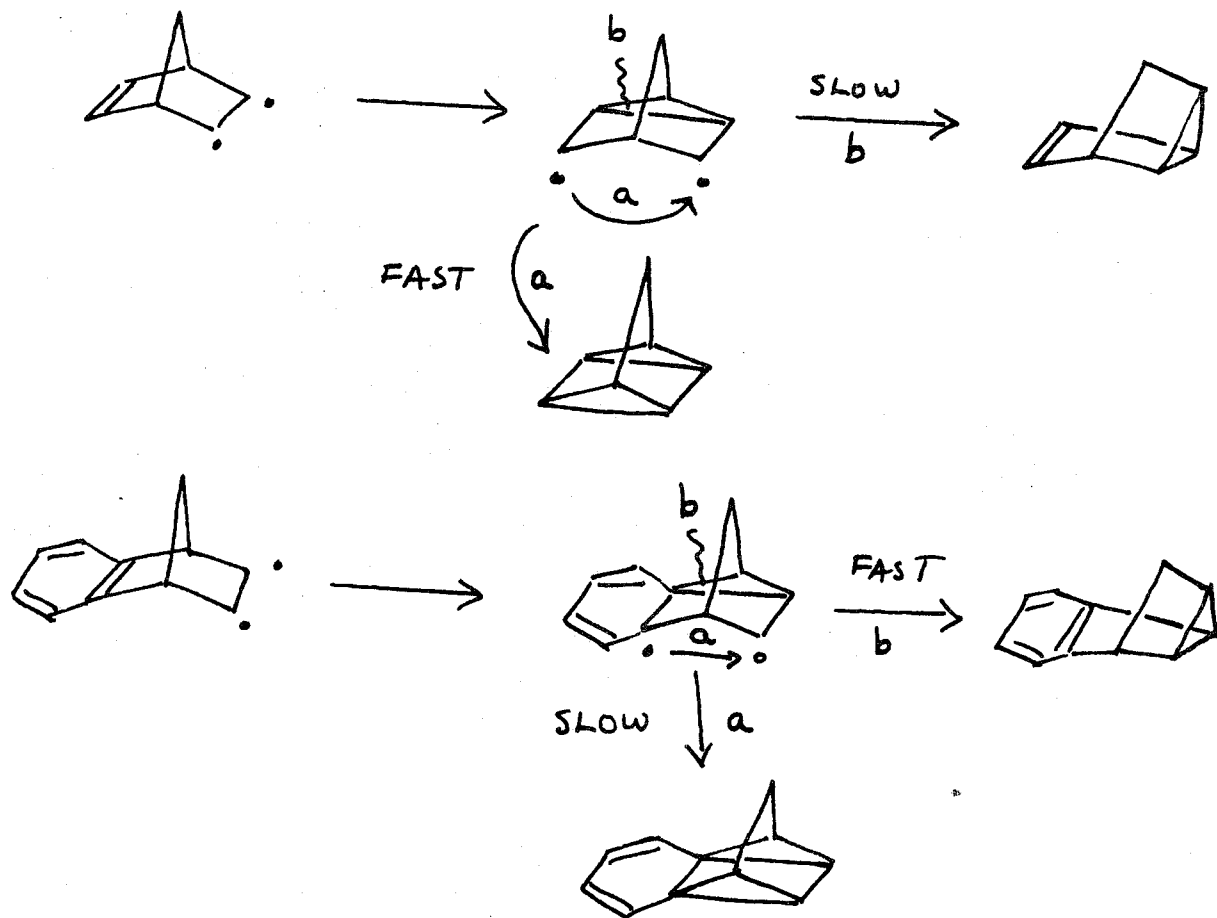
VARIATION OF CONCENTRATION
OF ALKENE AND SOLVENT

6.12 (continued)

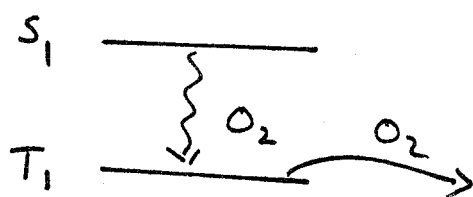


6.12 (continued)

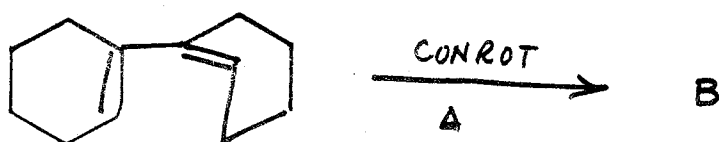
K.



L.



M.



CHAPTER 7

PHOTOCHEMISTRY OF AROMATIC HYDROCARBONS

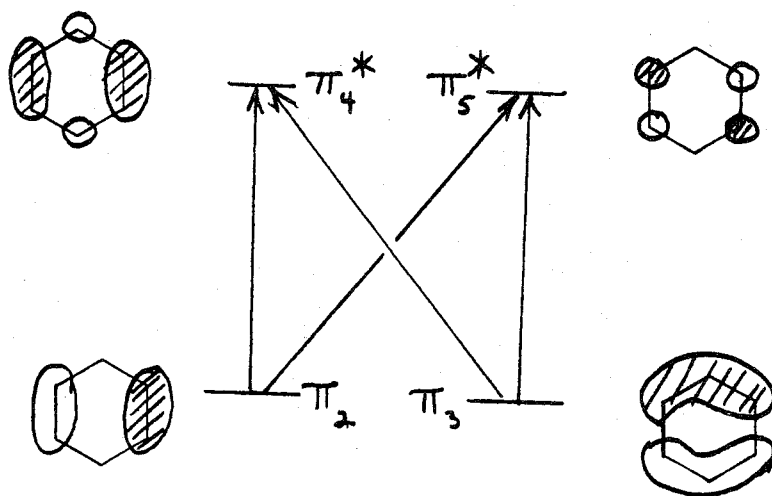
7.1 GENERAL CONSIDERATIONS

Rev.: J. Birks, "Photophysics of Aromatic Hydrocarbons," John Wiley & Sons, New York, New York, 1970.

- A. Model for the electronically excited states of aromatic hydrocarbons
- B. Energetics and dynamics of the electronically excited states of aromatic hydrocarbons
- C. Primary photochemical processes of aromatic hydrocarbons

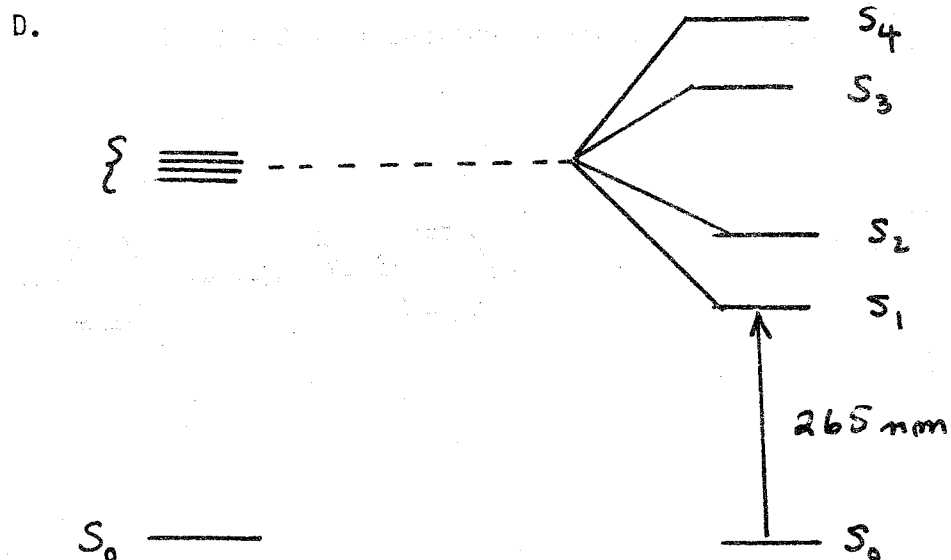
7.2 MODEL FOR ELECTRONICALLY EXCITED STATES

- A. $\pi \rightarrow \pi^*$ "degenerate"
- B. Orbital description of a problem

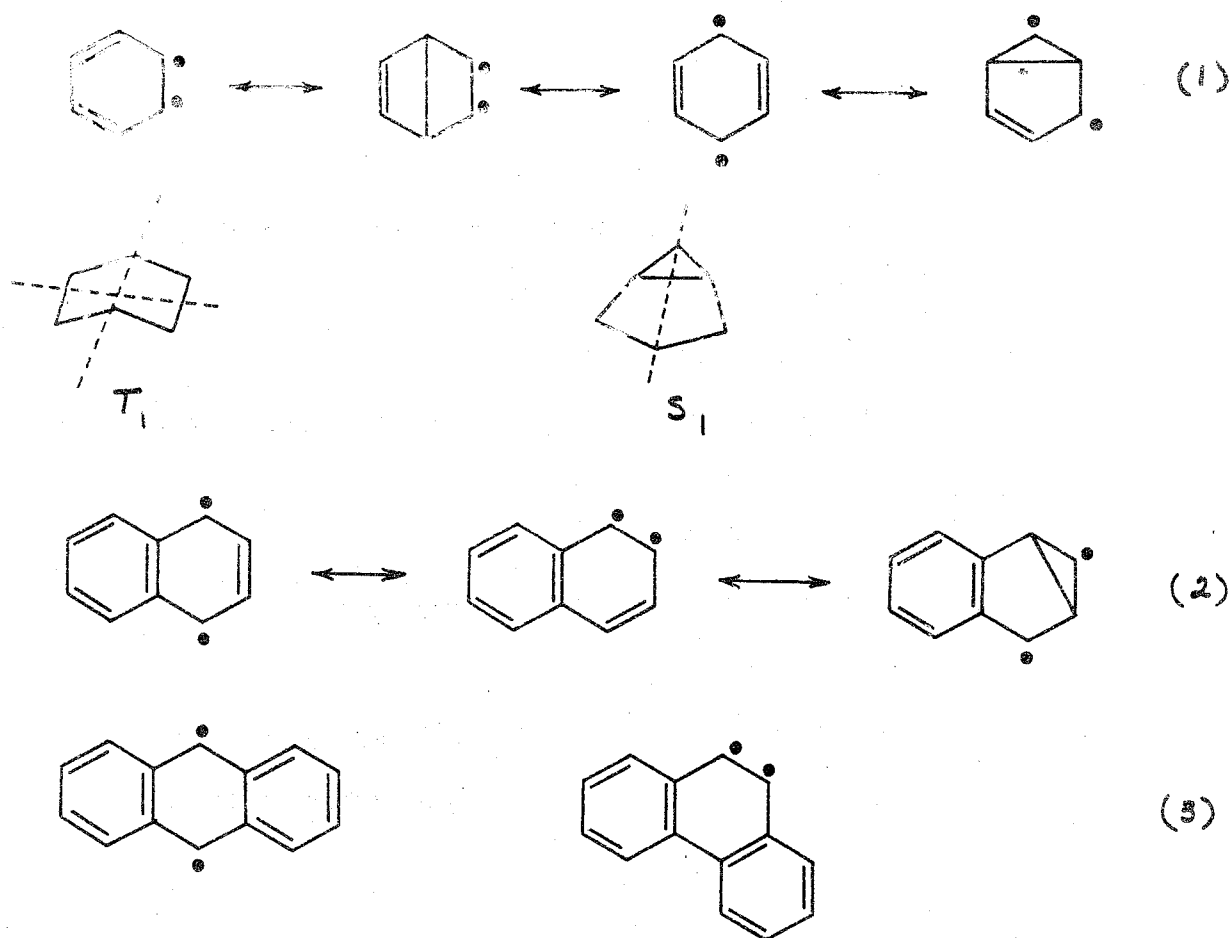


- C. $\pi_2 \rightarrow \pi_4^*$, $\pi_2 \rightarrow \pi_5^*$, $\pi_3 \rightarrow \pi_4^*$
 $\pi_3 \rightarrow \pi_5^*$

7.2 (continued)

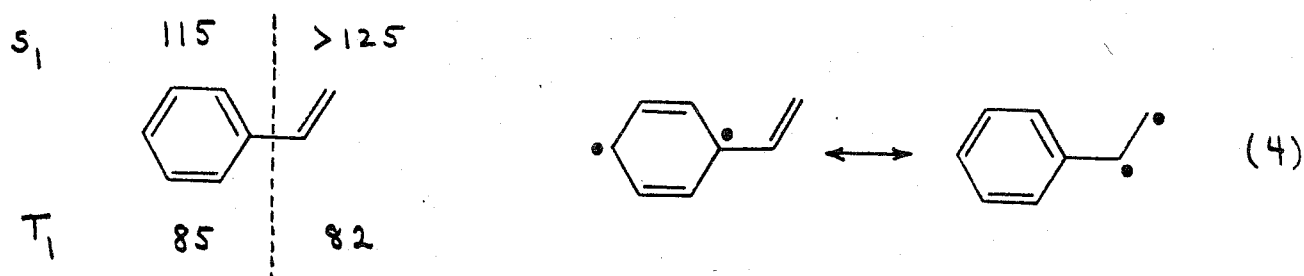


E. Valence bond description: Molec. Phys., 6 545 (1963); ibid., 16, 45 (1969); Chem. Commun., 593 (1966).



7.2 (continued)

G. Conjugation of aromatic nucleus to a C=C bond



H. Summary

1. S_1 may have tendency to form cyclopropanes
2. T_1 may have tendency to form cyclobutanes and 1,4 bonds
3. "Resonance" between shapes of similar energy makes definite predictions difficult

7.3 ENERGISTICS AND DYNAMICS

A. Energetics (Table 7-1 on p. 161)

1. Fluorescence and phosphorescence common at 77°K
2. Fluorescence common at 20°C
3. Large S_1 - T_1 energy gaps
4. Highest available E_1 and E_3 usable for energy transfer (benzenes)

B. Dynamics (Table 7-1 on p. 161)

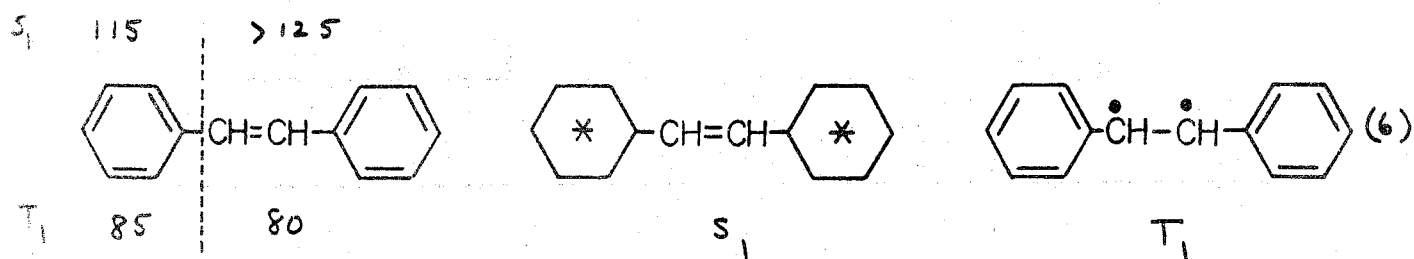
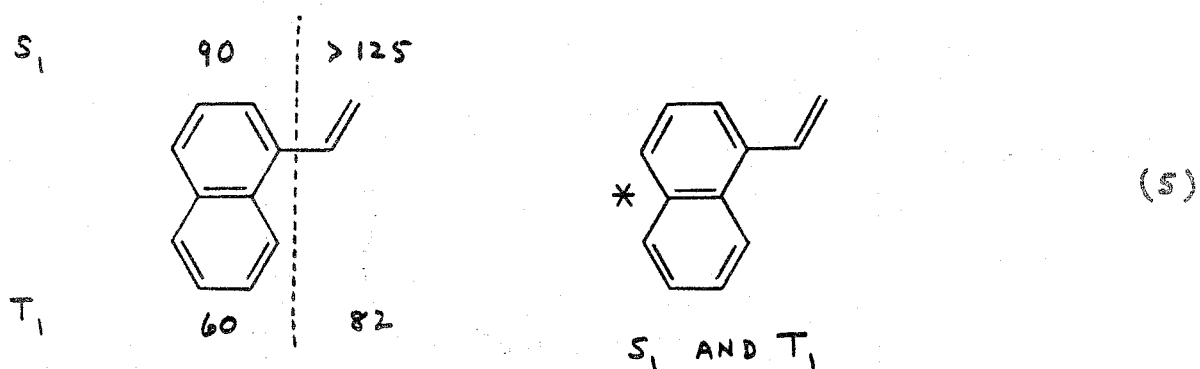
1. k_F varies 10^6 - 10^8 sec^{-1}
2. k_{ST} varies 10^6 - 10^7 sec^{-1} , ϕ_{ST} variable
3. $S_1 \rightarrow S_0$ negligible, $\phi_F + \phi_{ST} \sim 1$
4. $k_p \sim 1$ to 0.01 sec^{-1} ; at 20° $k_q[Q] \gg k_p$
5. k_T 10^4 - 10^7 probably quenching or reaction limited

Table 7-1

Energetics and Dynamics of Aromatic Hydrocarbons

| <u>Molecule</u> | E_1 | E_3 | k_F | k_{ST} | k_T | ϕ_{ST} |
|-----------------------|-------|-------|--------|----------|--------|-------------|
| Benzene | 115 | 85 | 10^6 | 10^7 | 10^7 | 0.4 |
| Naphthalene | 90 | 61 | 10^6 | 10^7 | 10^4 | 0.7 |
| Anthracene | 76 | 42 | 10^8 | 10^7 | 10^4 | 0.7 |
| Styrene | 100 | 62 | | | | |
| <u>trans-Stilbene</u> | 90 | 51 | | | | |
| <u>cis-Stilbene</u> | 90 | 56 | | | | |

C. Energy diagram (Figures 7-1 on p. 162 and 7-2 on p. 163)



7.3 C. (continued)

Figure 7-1

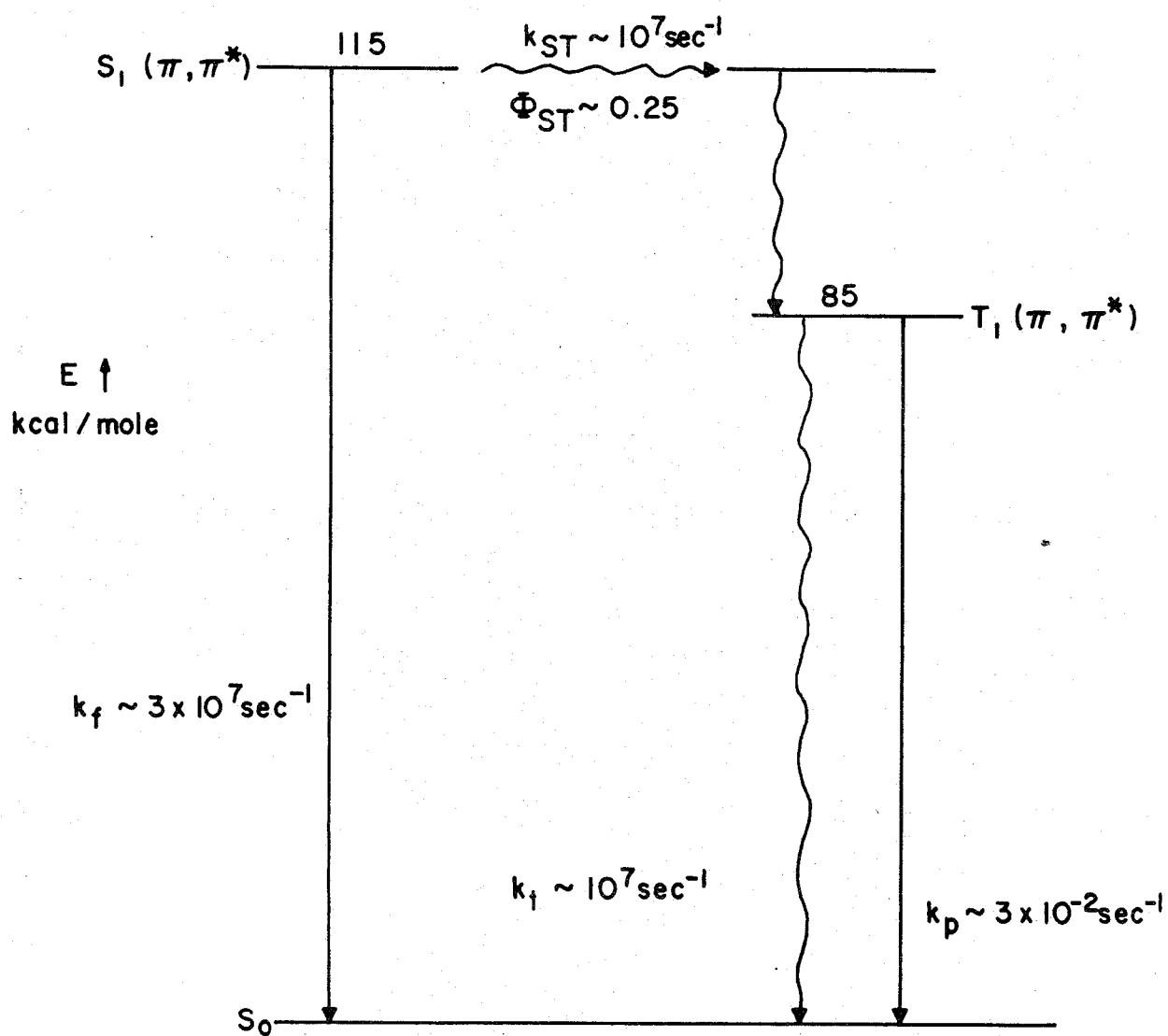
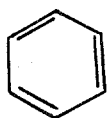
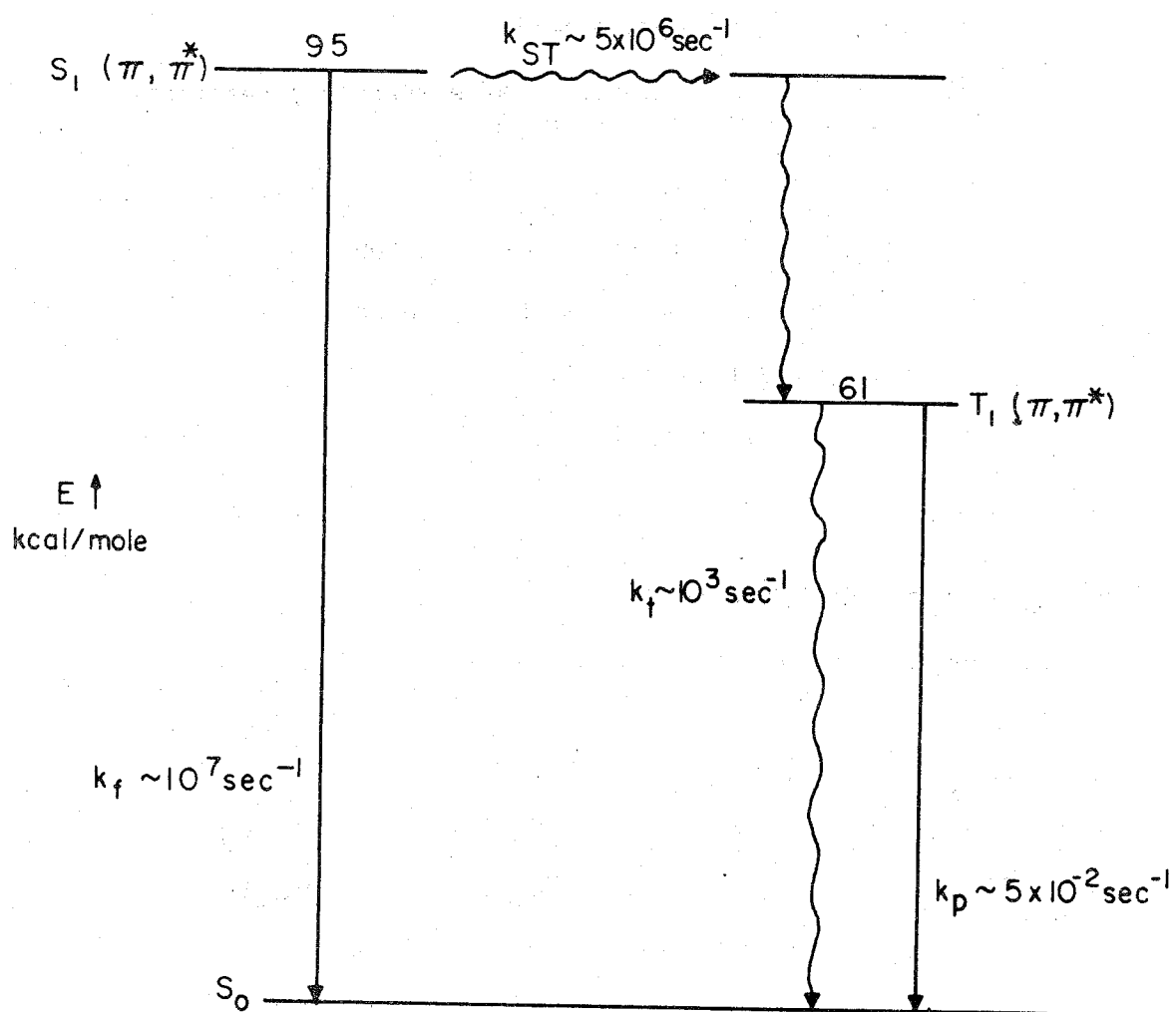
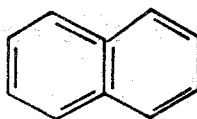


Figure 7-2



7.4 PRIMARY PHOTOCHEMICAL PROCESSES

A. Classification similar to that for alkenes and polyenes.

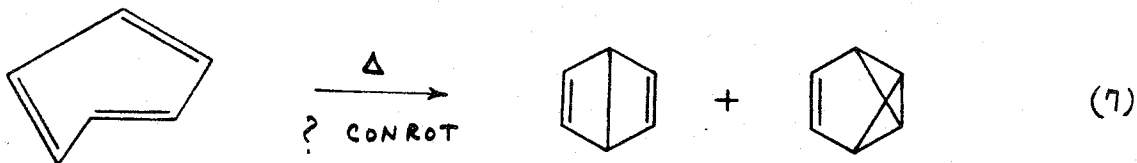
1. cis-trans Isomerization
2. Hydrogen abstraction
3. Cycloadditions and cycloeliminations
4. Electrocyclic closures and openings
5. Sigmatropic rearrangements
6. Miscellaneous: Ionic (charge transfer) reactions, fragmentation of weak bonds

B. Writing mechanisms

1. S_1 likely to be pericyclic; 1,3 bonding
2. T_1 biradical-like; 1,2 and 1,4 bonding
3. Energy transfer from T_1
4. Excimer formation

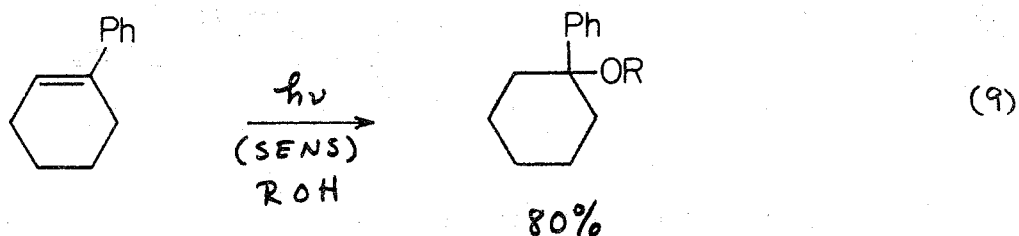
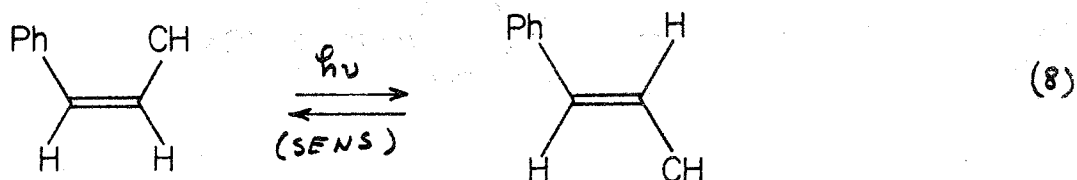
7.5 cis-trans ISOMERIZATION

A. Possibility of ring isomerization



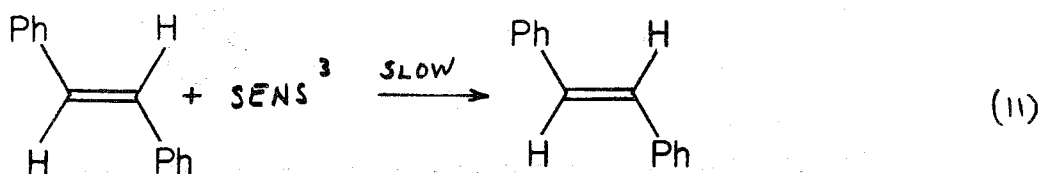
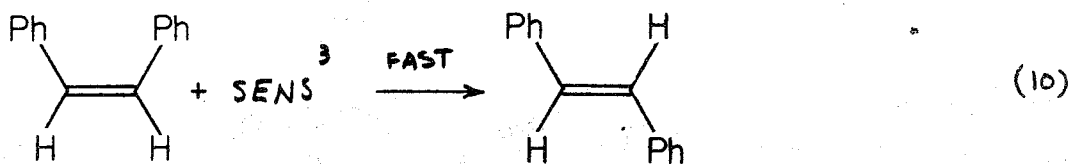
7.5 (continued)

B. Conjugated C=C groups "normal"



C. Special effects

1. Nonvertical energy transfer
2. Quenching of twisted C=C faster than expected from theory



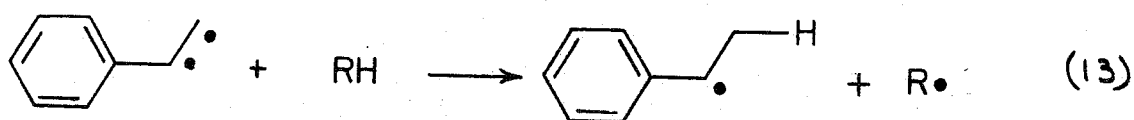
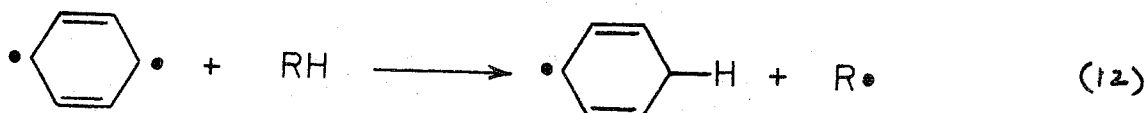
3. Chemical spectroscopy (Review 6.5 A)

D. References to reactions

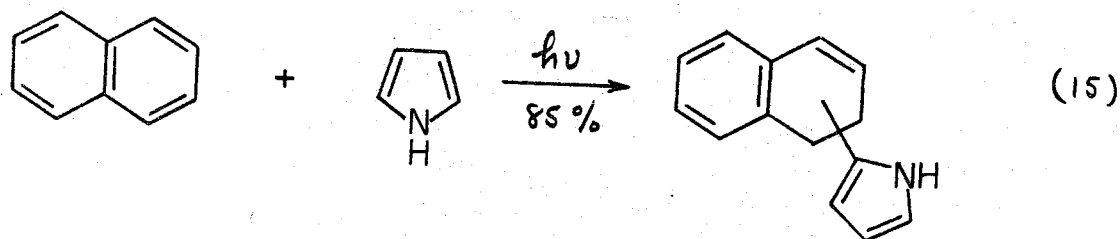
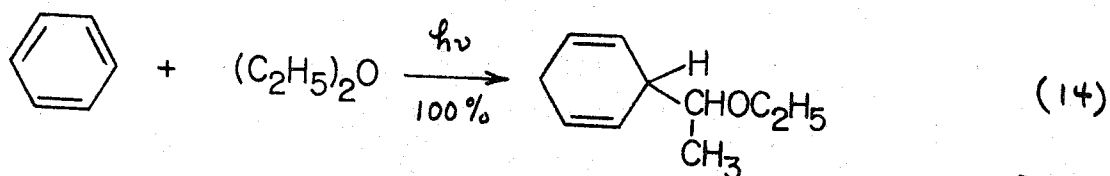
- (7) Tetrahedron Letters, 6465 (1965).
- (8) J. Amer. Chem. Soc., 86, 3197 (1964)
- (9) J. Amer. Chem. Soc., 91, 5783 (1969)
- (10) and (11) J. Amer. Chem. Soc., 88, 4769 (1966).

7.6 HYDROGEN ABSTRACTION

A. Appears to be a T_1 reaction



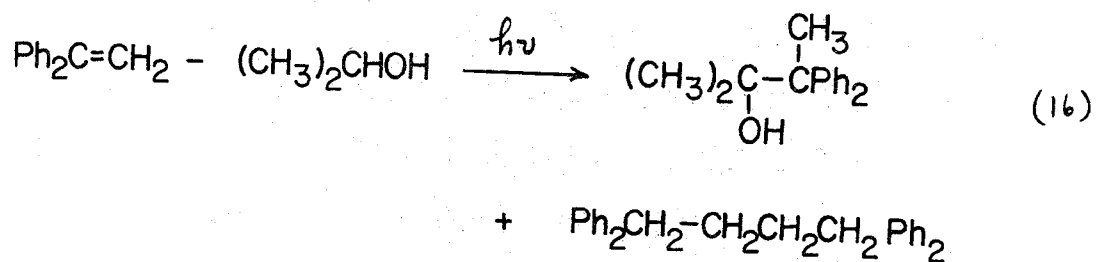
B. Additions to the aromatic nucleus



C. Mechanisms involving ionic intermediates may also occur

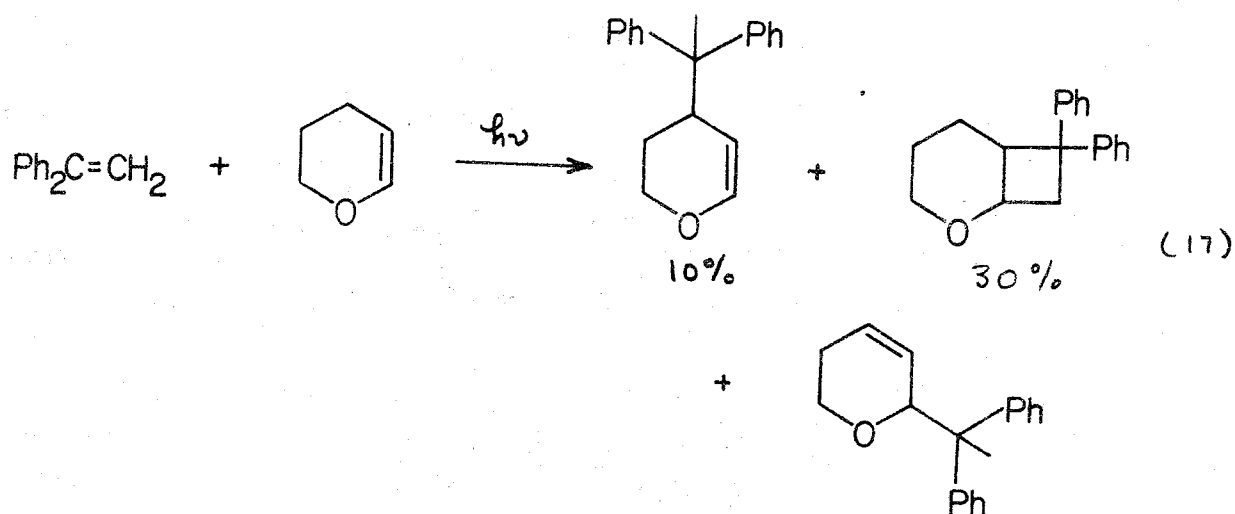
D. Conjugated C=C groups

1. Can be triplet sensitized and inhibited by triplet quenchers



7.6 D. (continued)

2. Abstraction may be competitive with other primary processes.



E. Mechanistic considerations

1. Appears to be T_1 reaction (sensitization and quenching)
2. Expect radical stability rule to determine stereoselectivity
3. Good hydrogen donor
4. Ionic mechanisms may lead to the same products

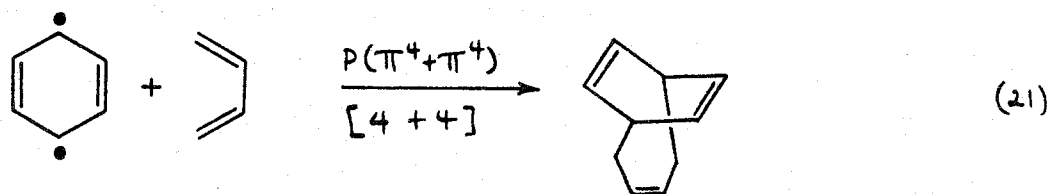
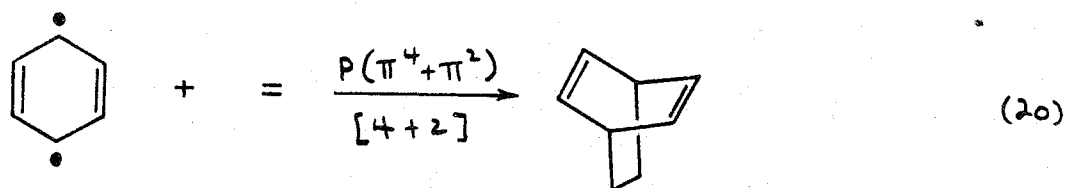
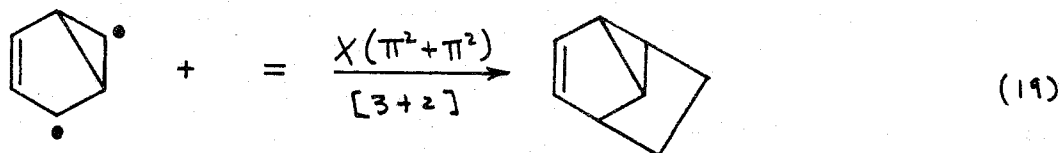
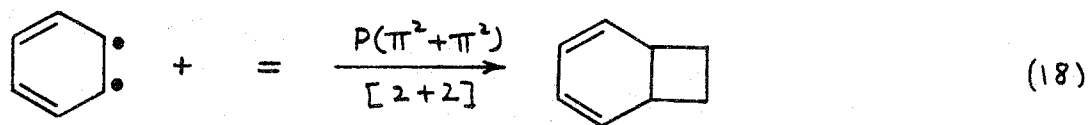
F. References to reactions

- (14) Chem. Commun., 915 (1971)
- (15) J. Chem. Soc., Perkin II, 370 (1972)
- (16) J. Amer. Chem. Soc., 92, 4746 (1970)
- (17) Can. J. Chem., 47, 4295 (1969)

7.7 CYCLOADDITION AND CYCLOELIMINATION

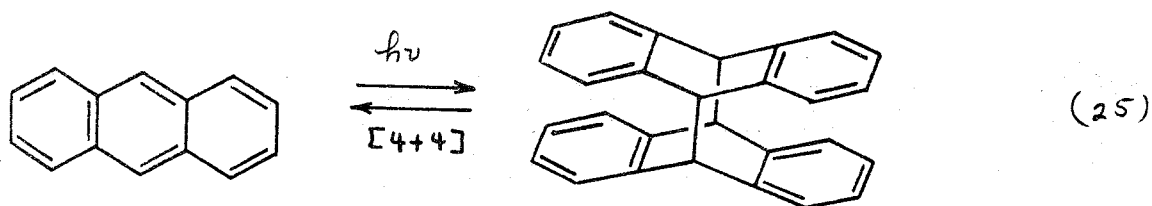
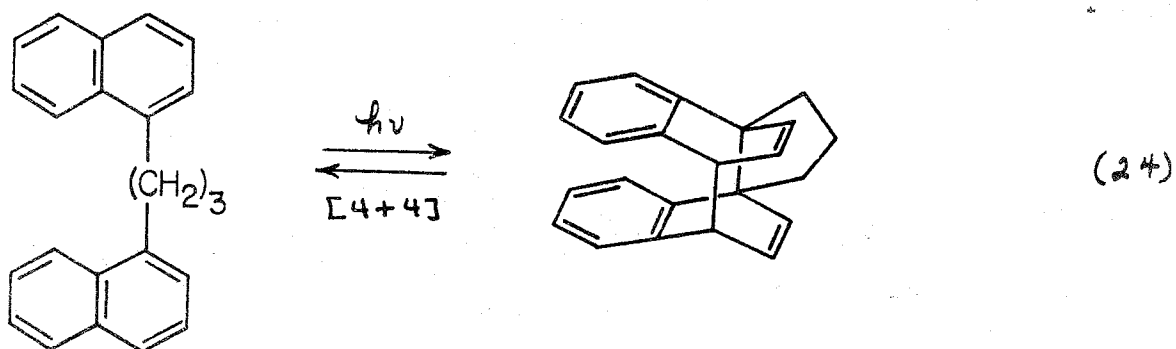
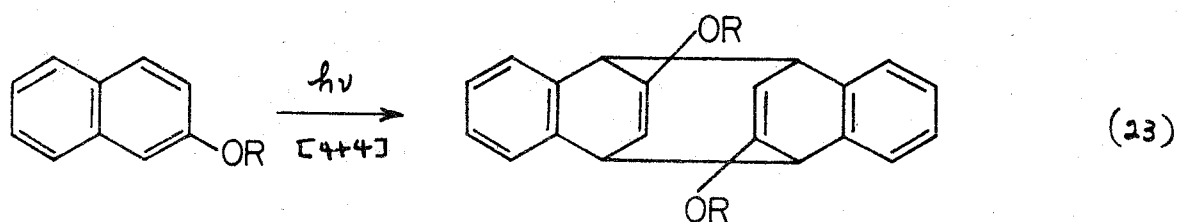
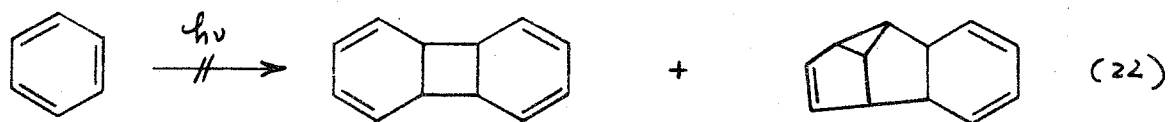
A. Dimerization and cross additions

Rev.: Pure Appl., 16, 47 (1968)



7.7 (continued)

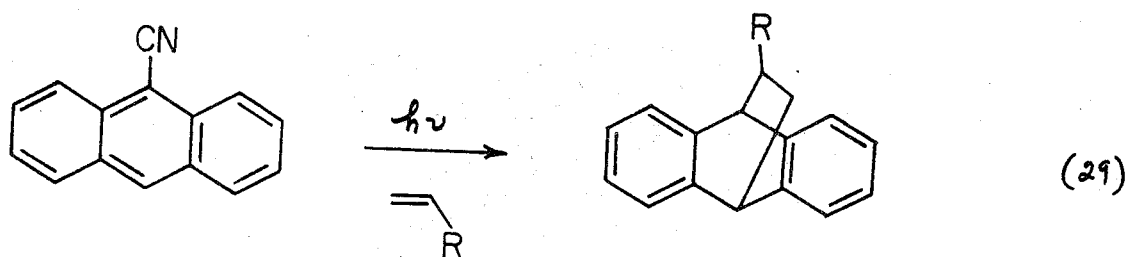
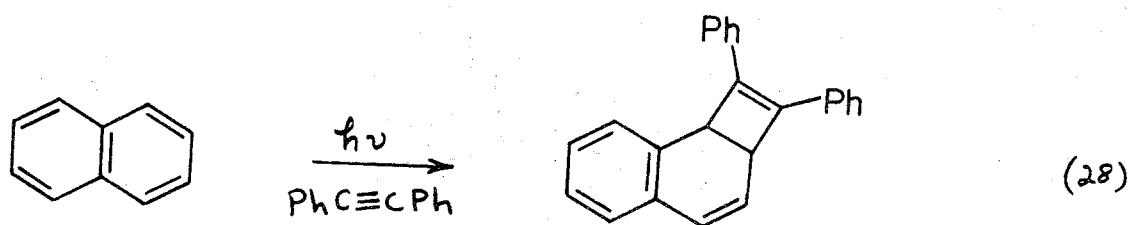
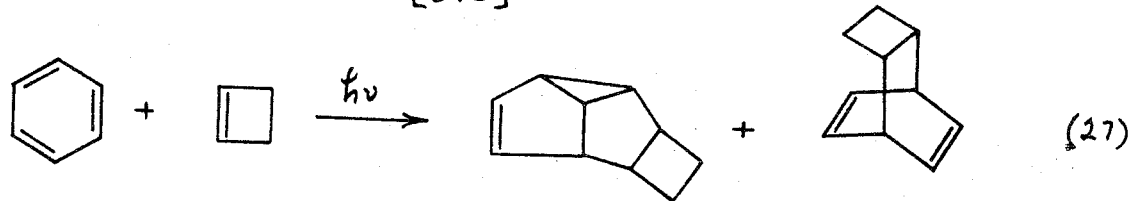
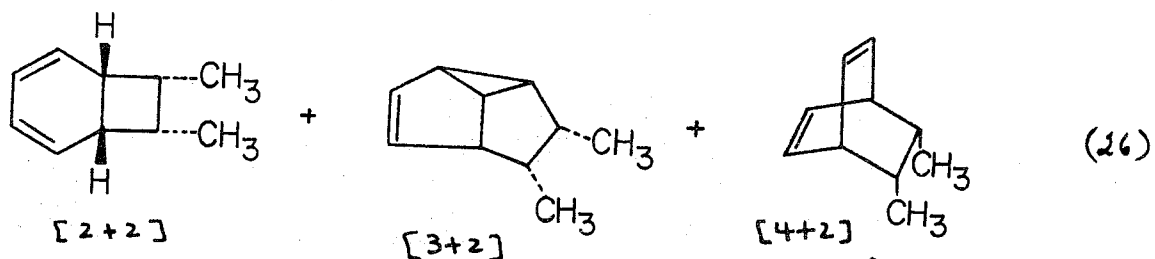
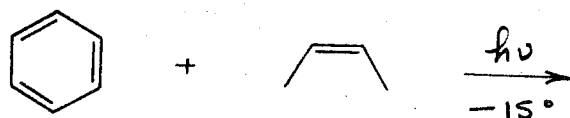
B. Dimerizations: commonly (4 + 4). Reversible. Cycloeliminations



7.7 (continued)

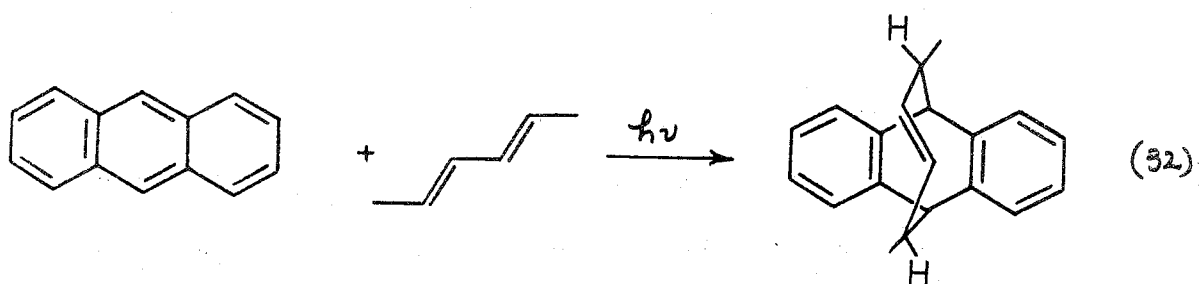
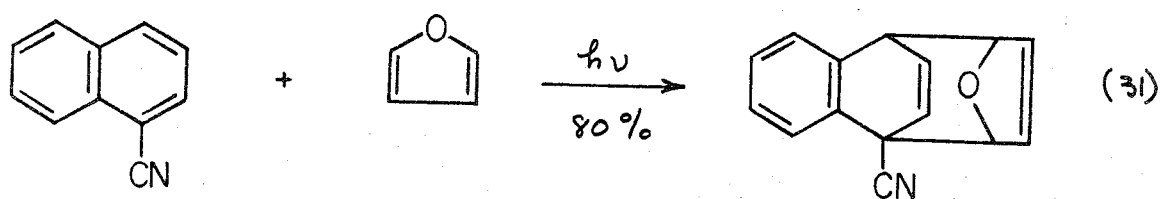
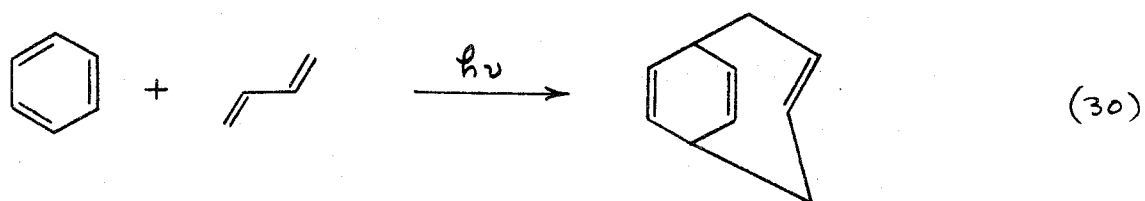
C. Cross additions

1. Ethylenes: [2+2], [3+2], [4+2] all are known



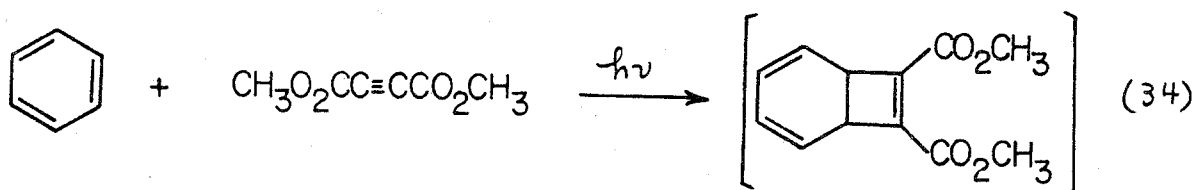
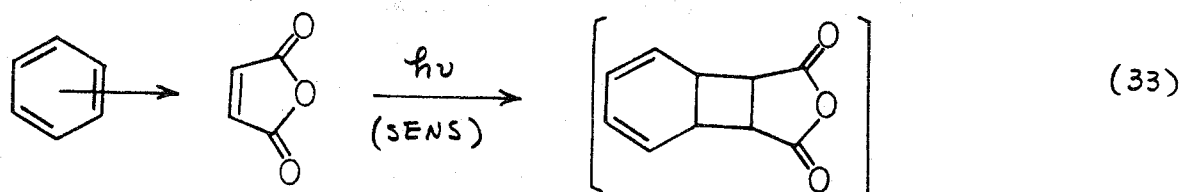
7.7 C. (continued)

2. Polyenes: [4+4] common, others known

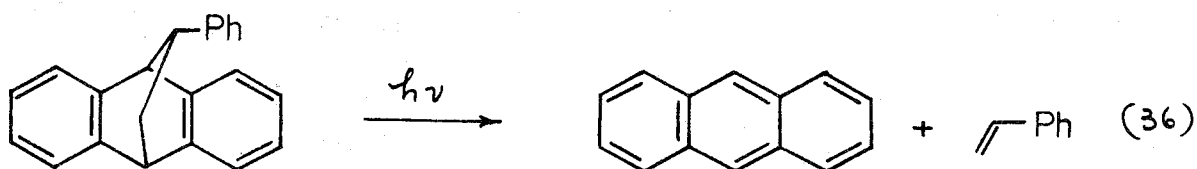
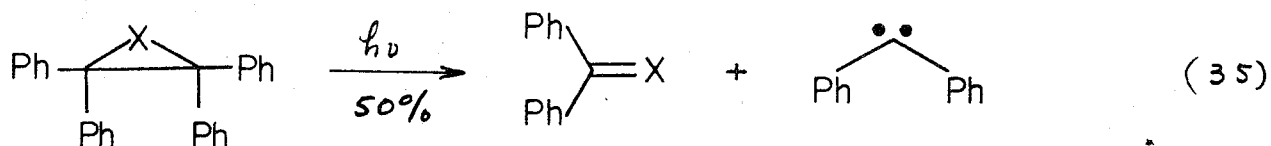


7.7. (continued)

D. Exciplexes, charge transfer complexes



E. Cycloelimination reactions



F. Mechanistic considerations

1. Both S_1 and T_1 may participate. S_1 may be more common.
2. Difficult to predict selectivity but reaction may be of synthetic utility.

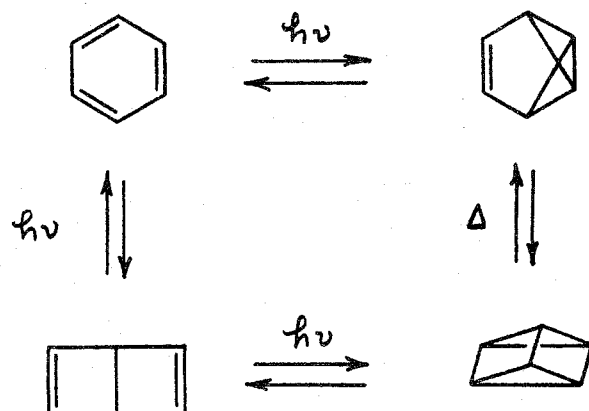
7.7 (continued)

G. References to reactions

- (23) Chem. Commun., 978 (1969)
- (24) J. Amer. Chem. Soc., 92, 703 (1970)
- (25) Bull. Soc. Chim. France, 1356 (1960)
- (26) J. Amer. Chem. Soc., 93, 2073 (1971)
- (27) ibid., 94, 8117 (1972)
- (28) Aust. J. Chem., 22, 1257 (1969)
- (29) J. Amer. Chem. Soc., 94, 1406 (1972)
- (30) Tetrahedron Letters, 4357 (1967)
- (31) Chemistry Letters (Japan), 39 (1972)
- (32) J. Amer. Chem. Soc., 94, 1405 (1972)
- (33) J. Chem. Soc., C, 390 (1967)
- (34) J. Chem. Soc., 695 (1963)
- (35) Chem. Ind., 1562 (1966); Rev.: Angew. Chem. intern. ed. Eng.
10, 537 (1971)
- (36) Tetrahedron, 25, 1661 (1969)

7.8 ELECTROCYCLIC REACTIONS

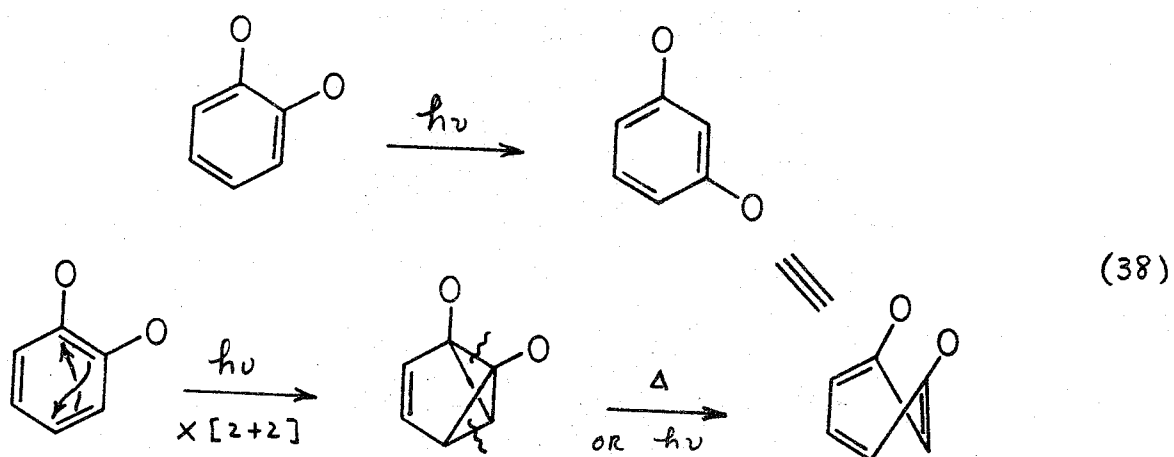
A. Valence isomers of benzene



(37)

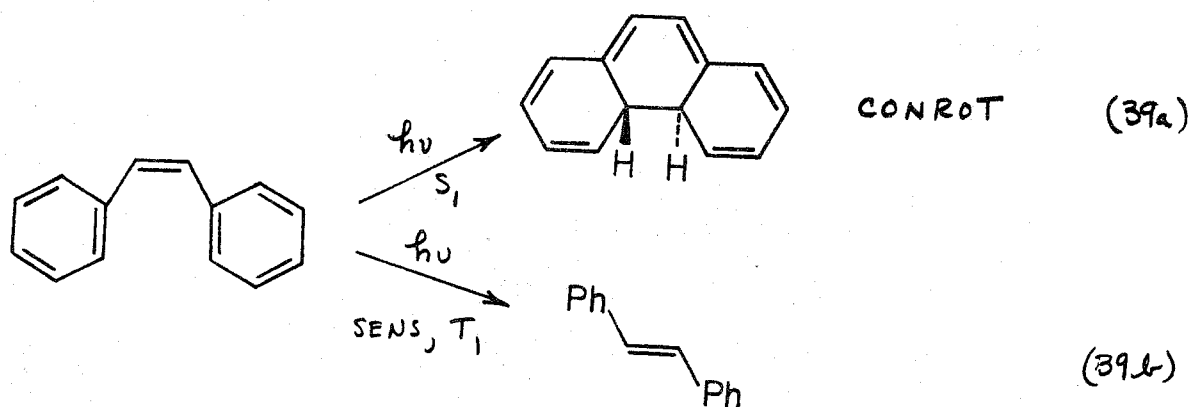
7.8 (continued)

B. Transposition of ring carbon atoms



C. Few examples with other aromatic hydrocarbons

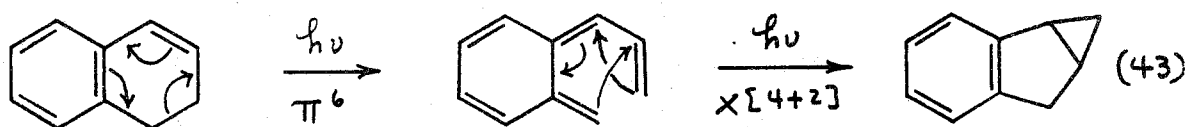
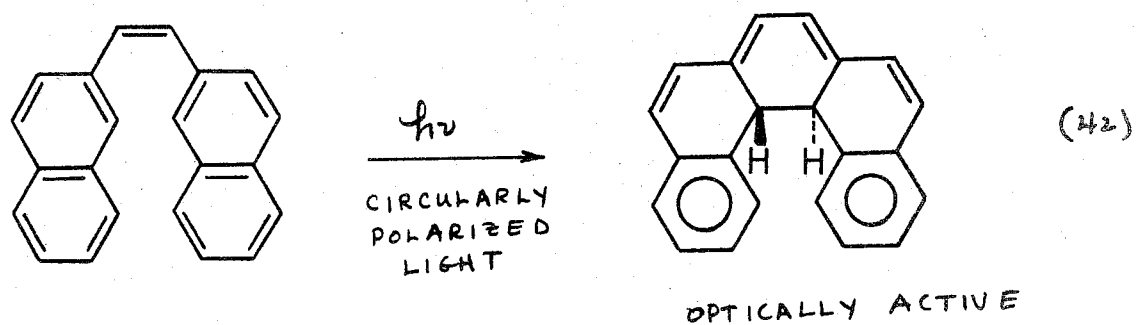
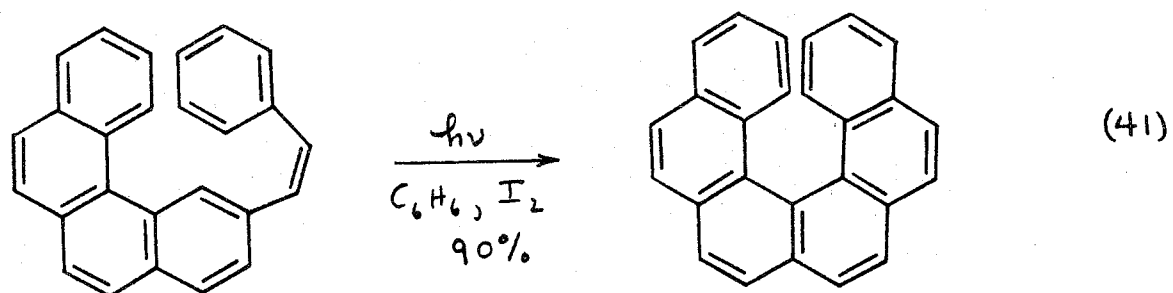
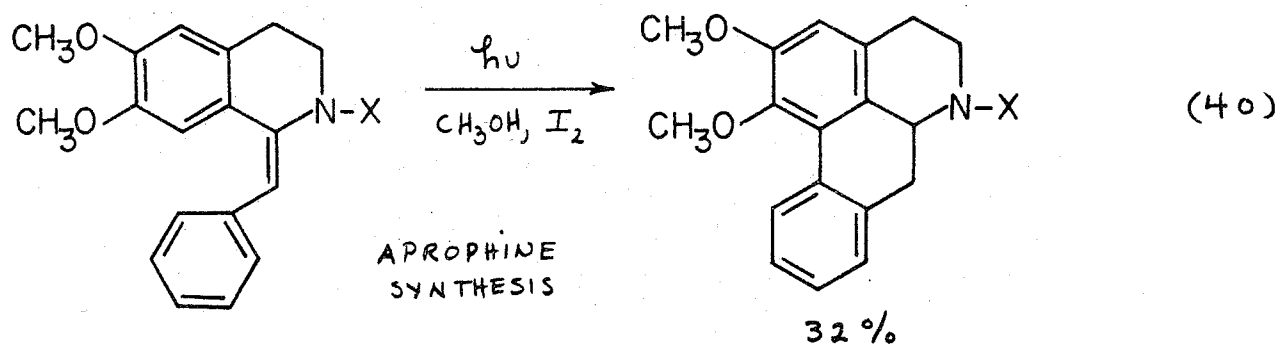
D. Conjugated systems



(39b)

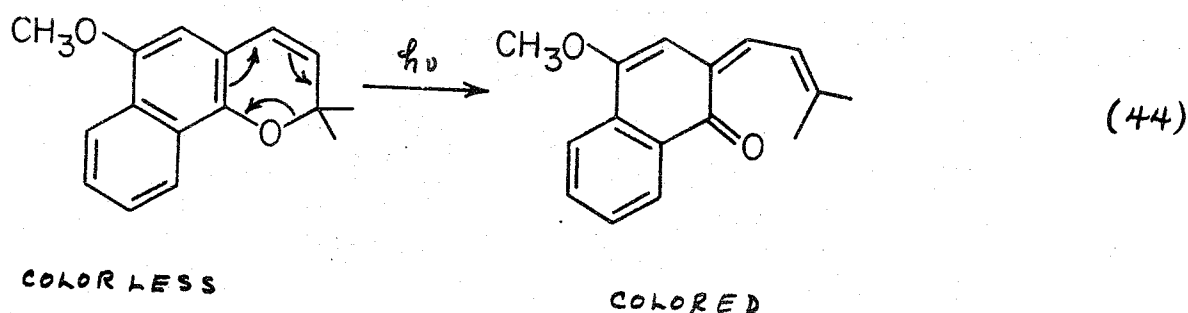
7.8 (continued)

E. Electrocyclic ring openings



7.8 E. (continued)

1. Photochromism
2. 2-H-chromenes and ring openings: memory storage in plants



F. Mechanistic considerations

1. Pericyclic, S_N reactions
2. Synthetically useful for stilbene cyclizations

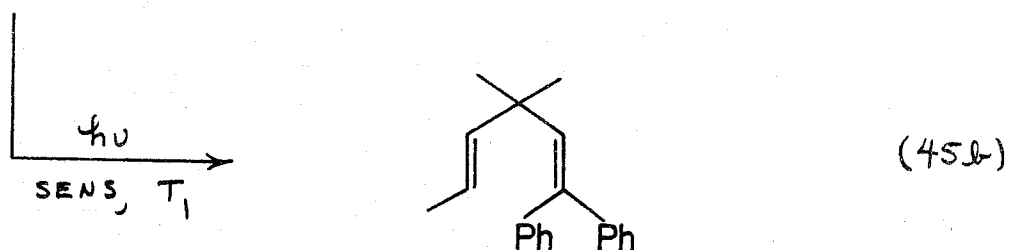
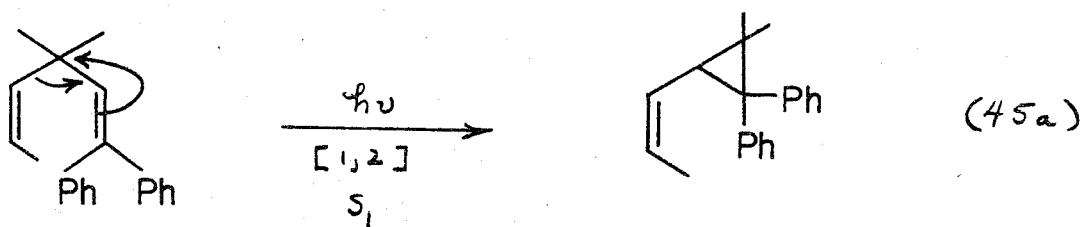
G. References to reactions

- (37) J. Amer. Chem. Soc., 90, 5868 (1968); Rev.: Chem. Rev., 72, 245 (1972); Russ. Chem. Rev., 37, 666 (1968)
- (38) J. Amer. Chem. Soc., 87, 675 (1965)
- (39) a. Rev.: Org. Photochem., 1, 247 (1967); Quart. Rev., 23, 482 (1969)
- b. J. Amer. Chem. Soc., 94, 3449 (1972) and references therein
- (40) J. Org. Chem., 35, 175 (1970)
- (41) Tetrahedron Letters, 3679 (1969)
- (42) Chem. Phys. Letters, 492 (1972); J. Amer. Chem. Soc., 94, 5914 (1972)
- (43) Tetrahedron Letters, 737 (1971)
- (44) J. Chem. Phys., 50 239 (1969)

7.9 SIGMATROPIC REARRANGEMENTS

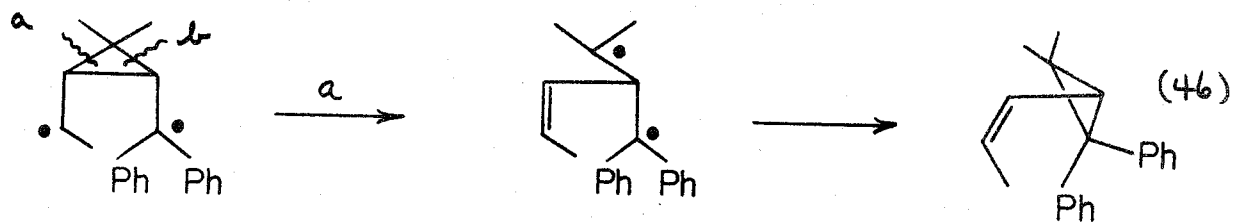
A. Comparable to sigmatropic reactions of alkenes and polyenes
(Section 6.9)

B. Acyclic [1,2]



1. Rearrangement via S_1 , cis-trans via T_1

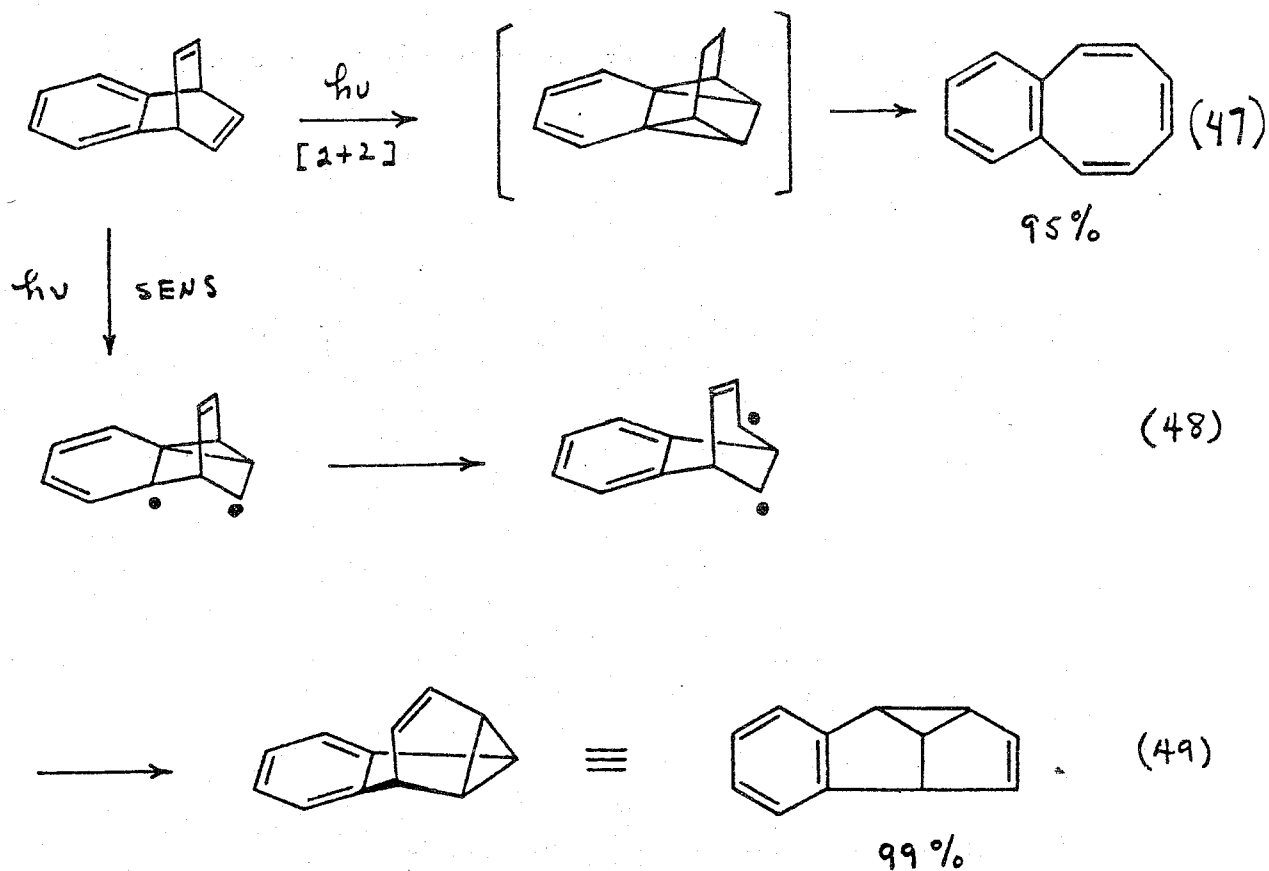
2. Di- π -methane rearrangement



7.9 (continued)

C. Cyclic [1,2]

1. S_1 undergoes cycloaddition, T_1 undergoes [1,2] shift

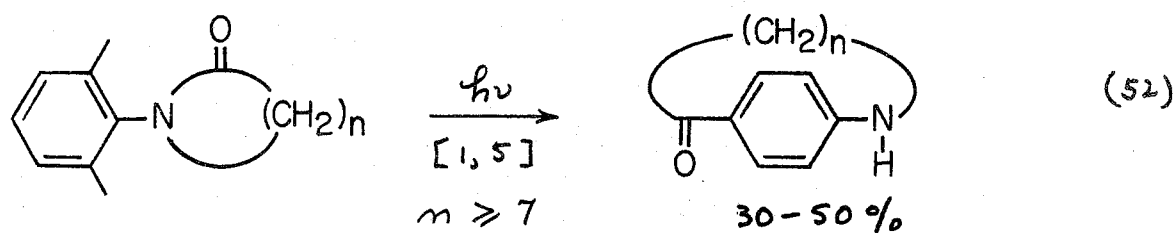
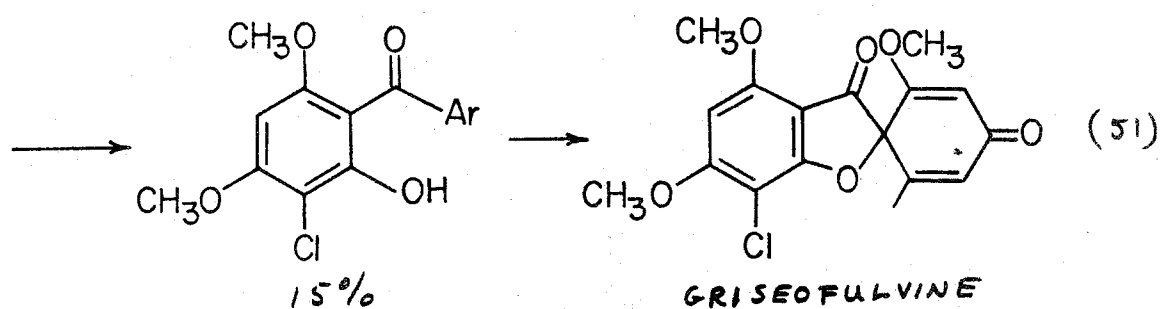
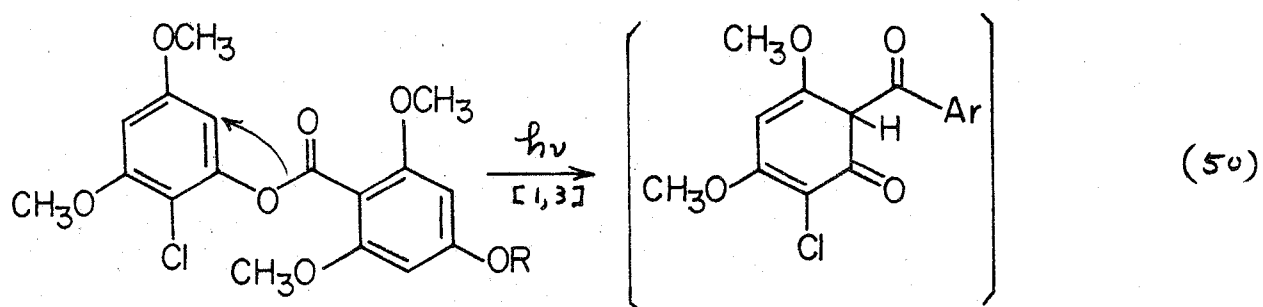


2. Di- π -methane mechanism allows rationalization of stereoselectivity

7.9 (continued)

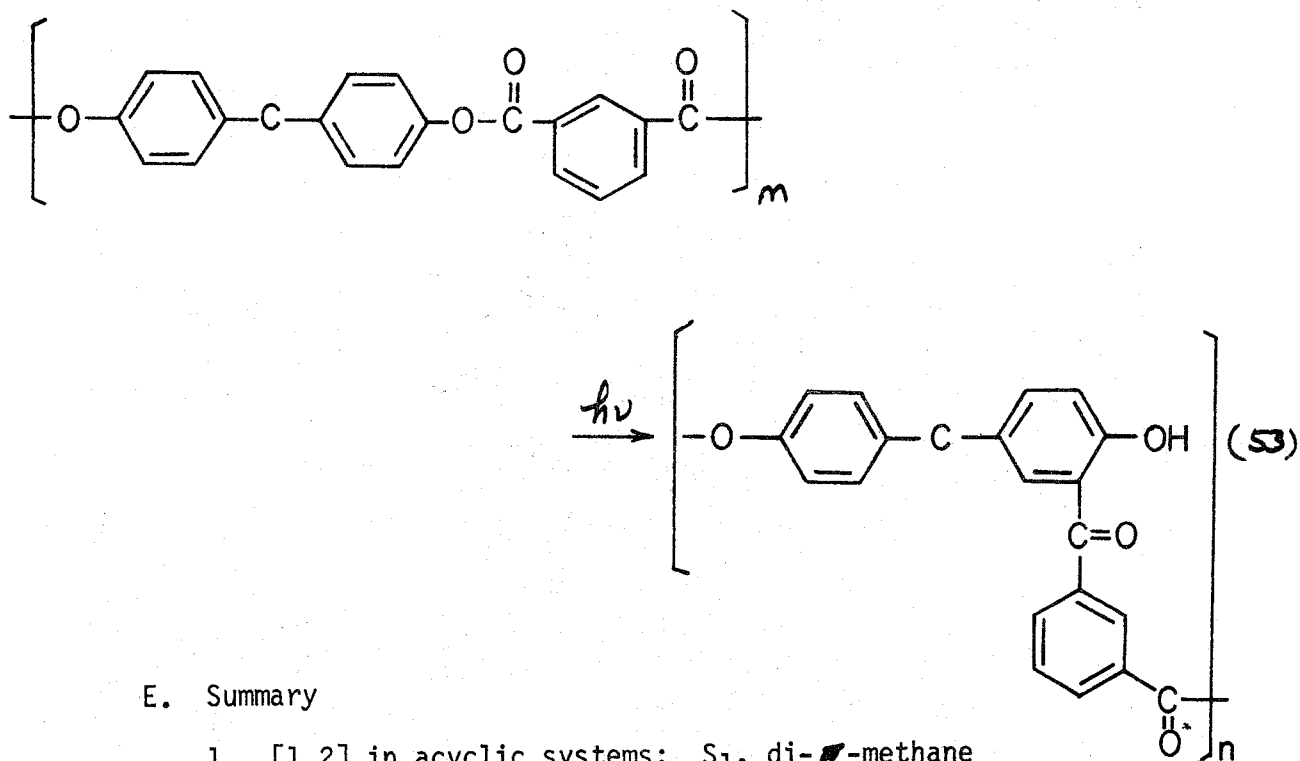
D. [i,j] shifts uncommon unless substituents are present:
 Rev: Chem. Rev., 67, 599 (1967)

1. Synthesis



7.9 D. (continued)

2. Photoyellowing of polymers



E. Summary

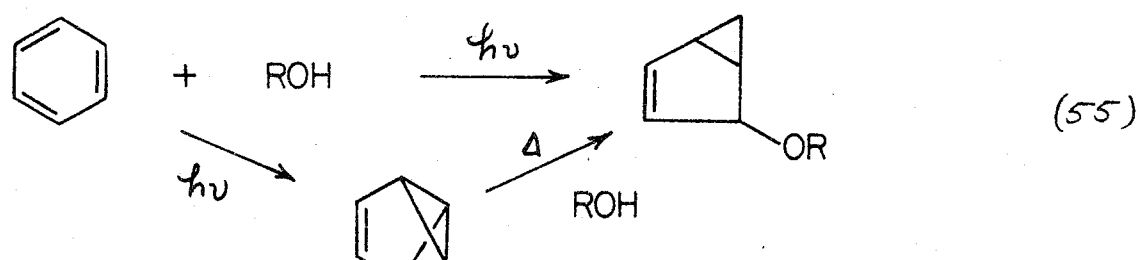
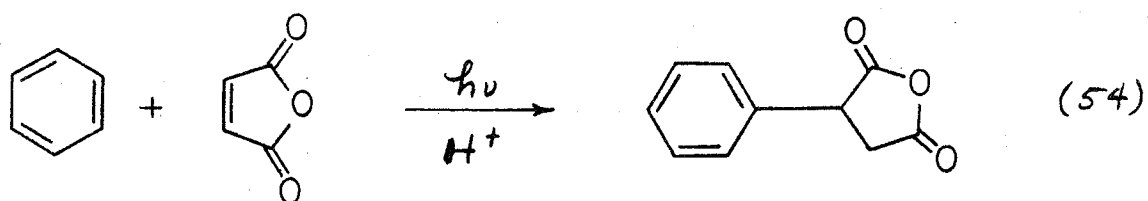
1. [1,2] in acyclic systems: S_1 , di-~~π~~-methane
2. [1,2] in cyclic systems: T_1 di-~~π~~=methane
3. [i,j] shifts from S_1
4. Shifts involving conjugated C=C bonds "normal."

F. References to reactions

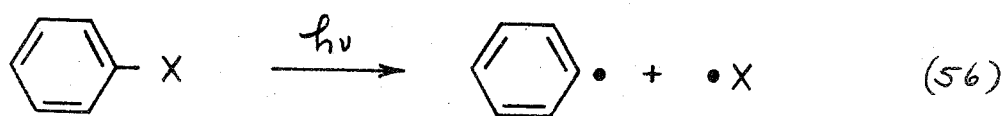
- (45) J. Amer. Chem. Soc., 92, 6267 (1970)
- (47) and (49) J. Amer. Chem. Soc., 90, 4465 (1968)
- (50) and (51) Tetrahedron, 19, 1 (1963)
- (52) Tetrahedron letters, 2281 (1969)
- (53) J. Polymer Sci., 3A, 487 (1965)

7.10 MISCELLANEOUS REACTIONS

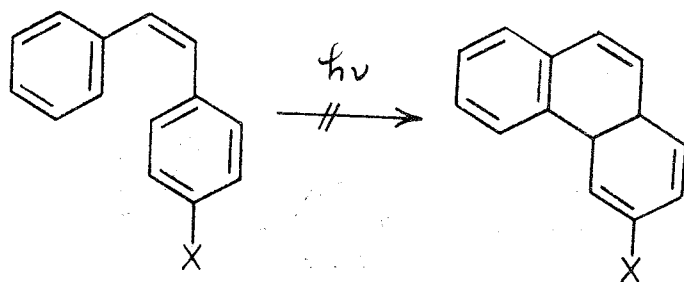
A. Ionic and polar additions



B. Fragmentations of side groups

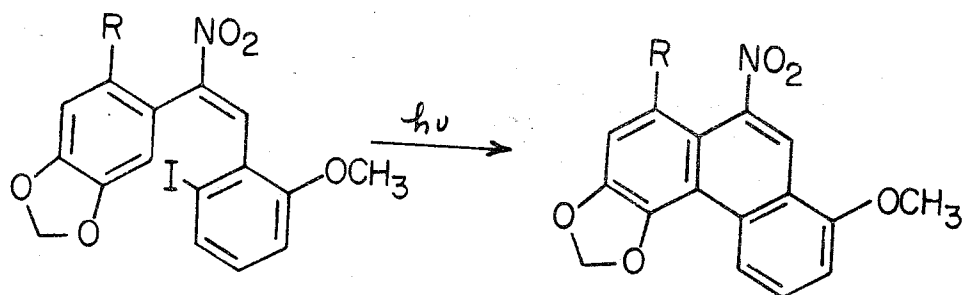


7. 10 B. (continued)



(57)

$X = \text{Br}, \text{I}, \text{COCH}_3$



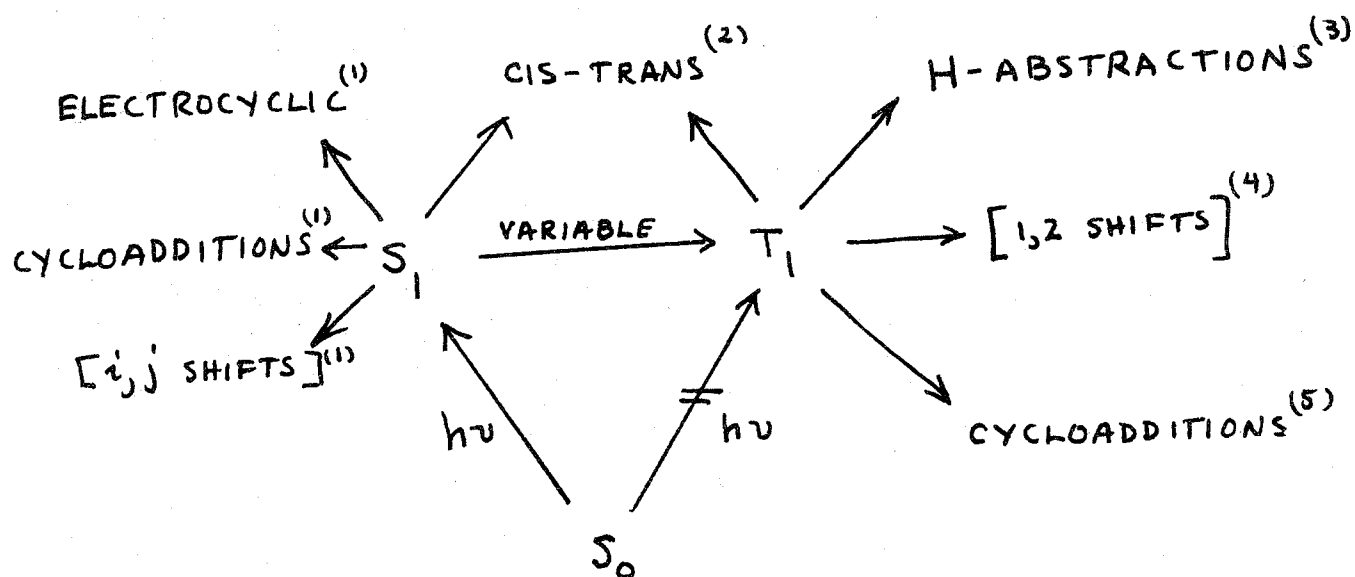
(58)

50% ARISTOLOCHIC ACID
TUMOR INHIBITOR

C. References to reactions

- (54) Chem. Commun., 561 (1970)
- (55) J. Amer. Chem. Soc., 94, 8638 (1972)
- (56) Rev.: Angew. Chem., intern. ed. Eng., 7, 36 (1967)
- (57) J. Amer. Chem. Soc., 85, 828 (1963)
- (58) J. Org. Chem., 30, 3792 (1965)

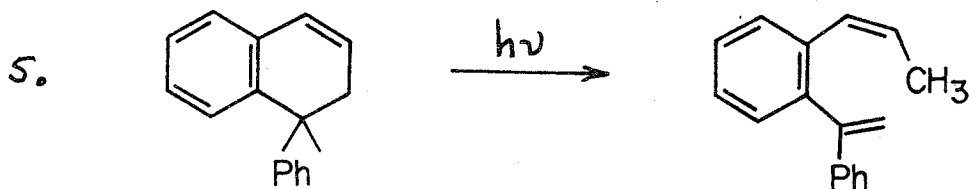
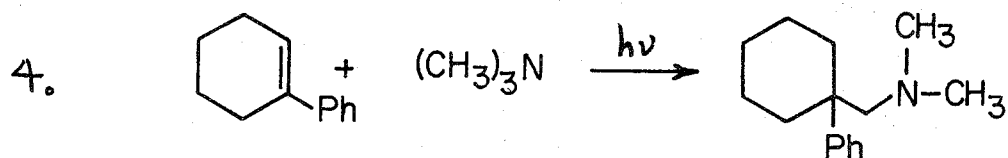
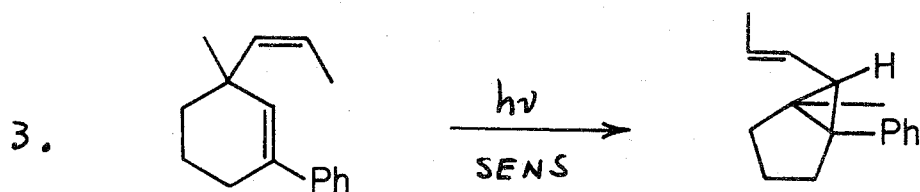
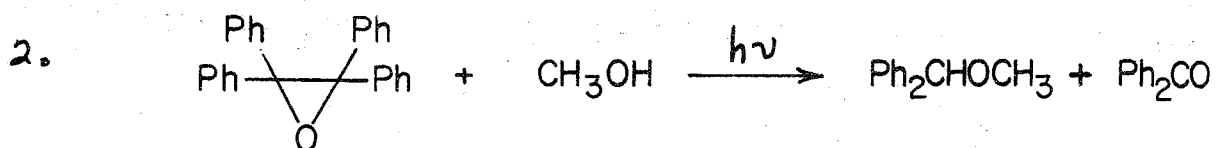
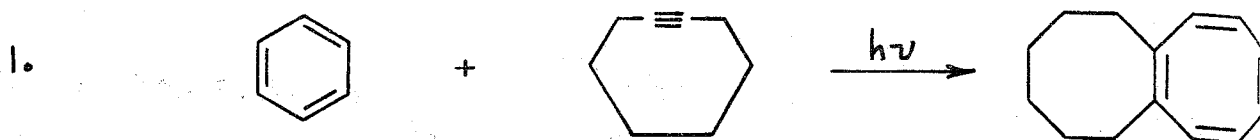
7.11 SUMMARY OF REACTIONS OF AROMATIC HYDROCARBONS



1. Appear to be pericyclic
2. Strained trans intermediates may be produced and react further
3. Radicallike
4. Di- π -methane reaction
5. Biradical probable

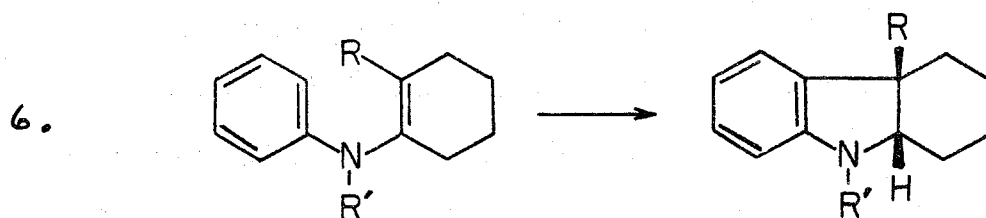
7.12 PROBLEMS

A. Classify the following reactions in terms of the primary photochemical processes discussed in this chapter.

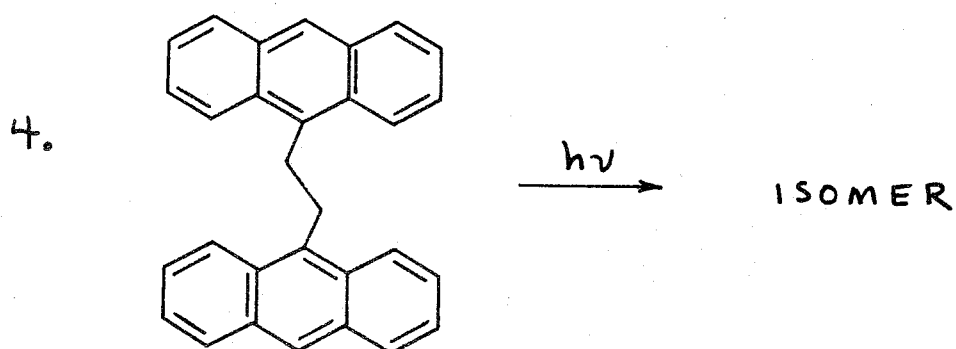
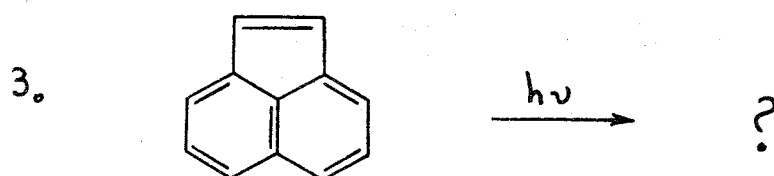
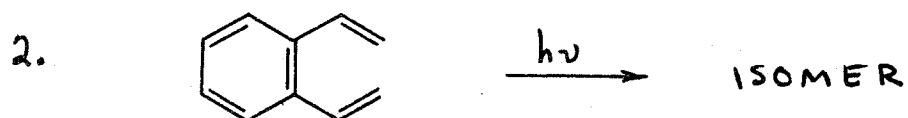
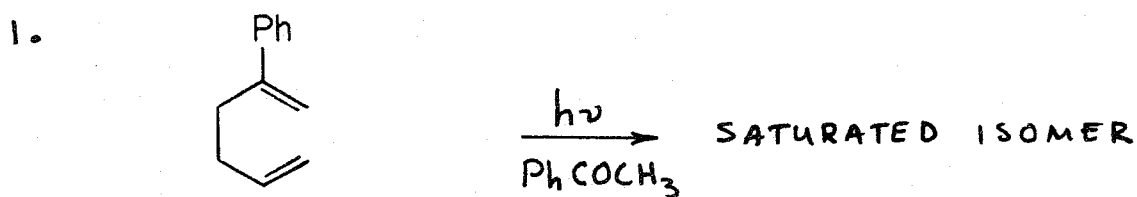


(continued)

7.12 (continued)

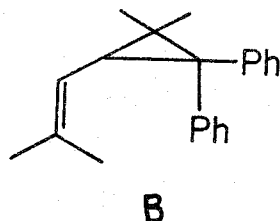
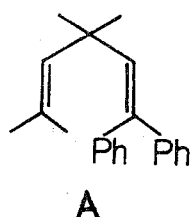


B. Predict the major product of the following photoreactions.

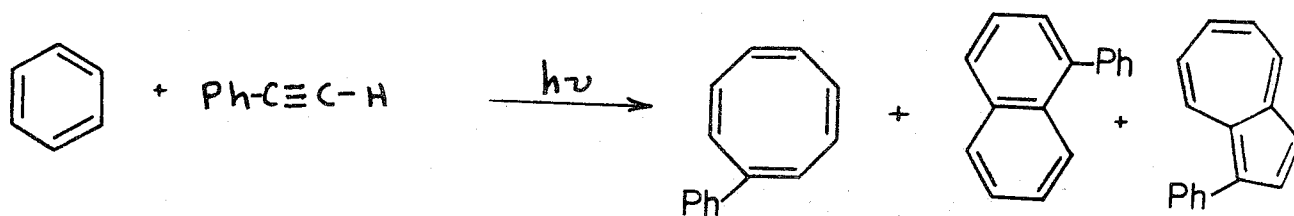


7.12 (continued)

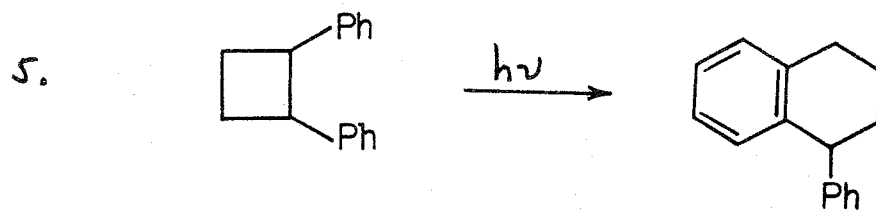
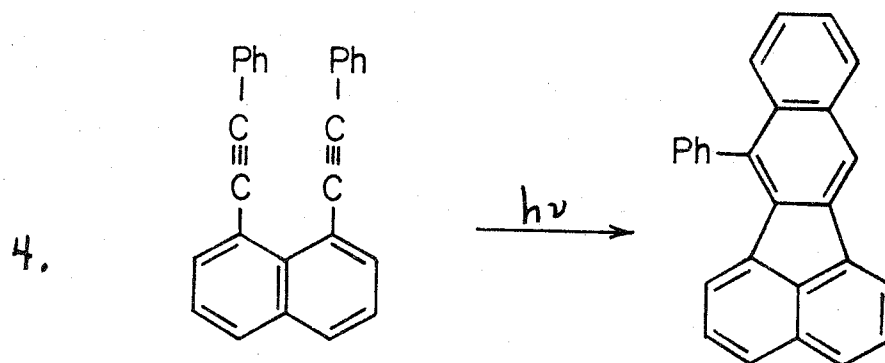
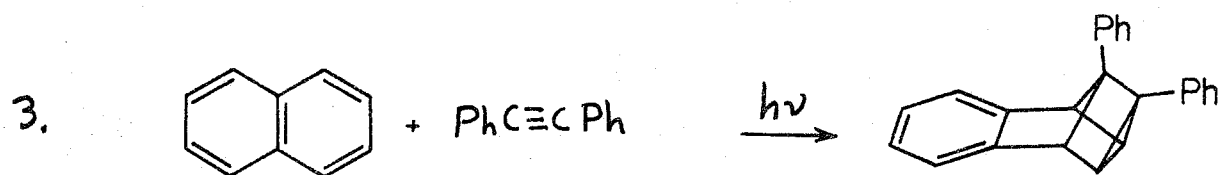
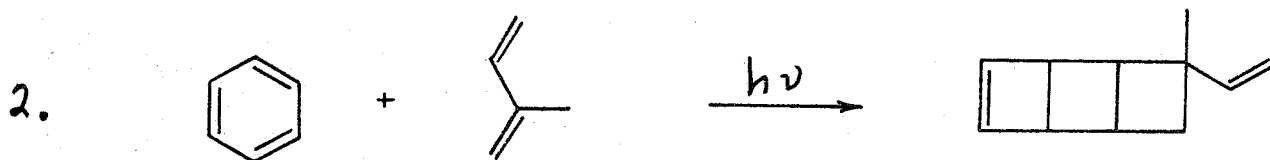
- C. Rationalize the observation that while many substituted stilbenes undergo oxidative photocyclization to phenanthrenes para bromo-substituted stilbenes only undergo cis-trans isomerization.
- D. The rearrangement of A to B is known to be a S_1 reaction because triplet sensitizers are strongly quenched by A, but do not cause reaction. The fluorescence yield of A = 3×10^{-4} ; the quantum yield reaction is 0.008. Compound A shows an ϵ_{max} of 1.6×10^4 at 250 nm for its $S_0 \rightarrow S_1$ absorption (half width = 6000 cm^{-1}). Calculate k_r for reaction of A.



- E. Propose mechanisms for the following transformations.

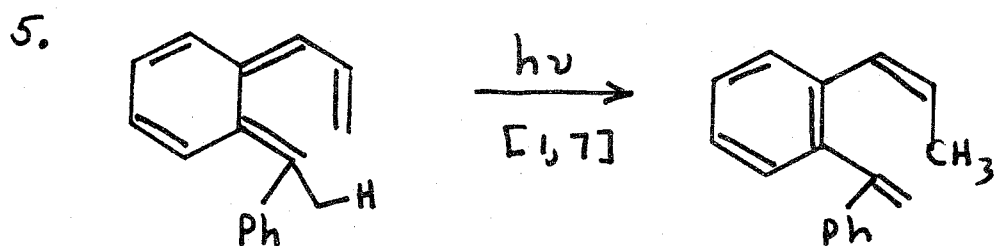
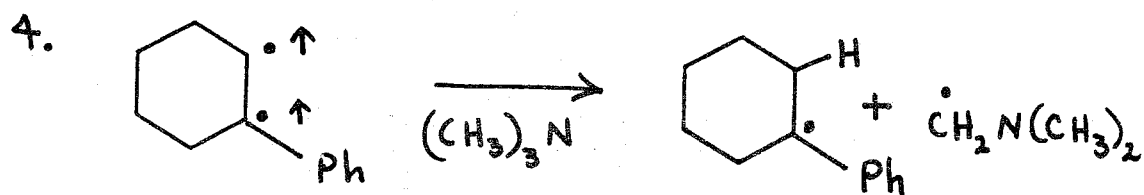
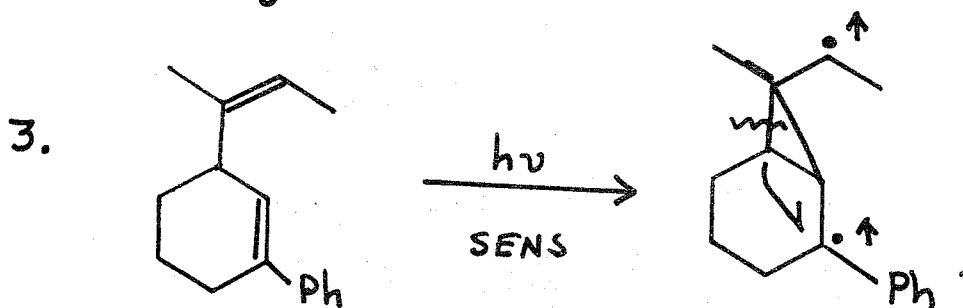
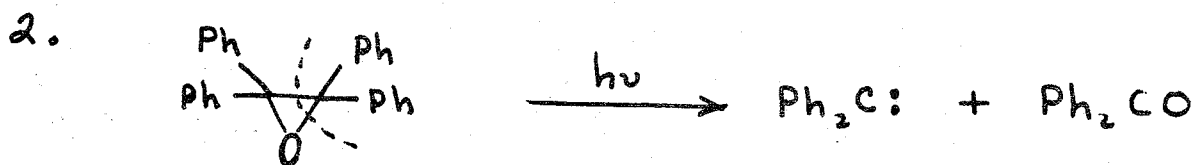
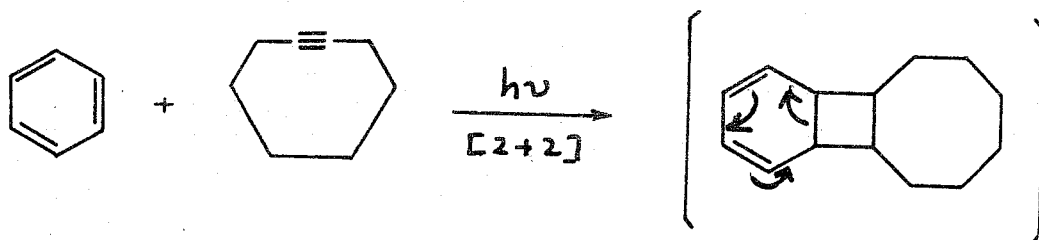


7.12 E. (continued)

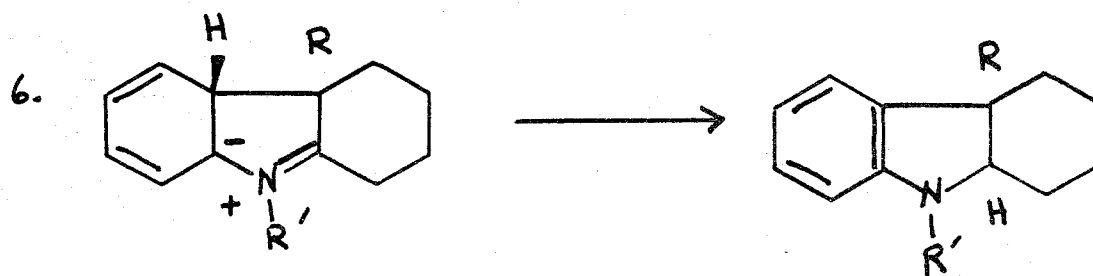


7.13 ANSWERS TO THE PROBLEMS

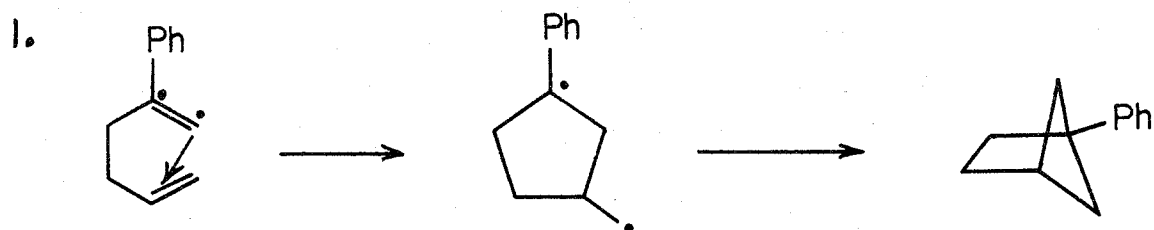
A. 1.



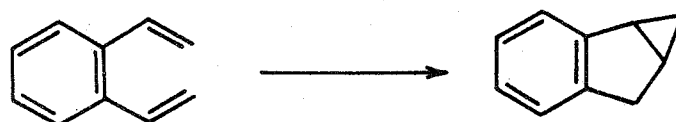
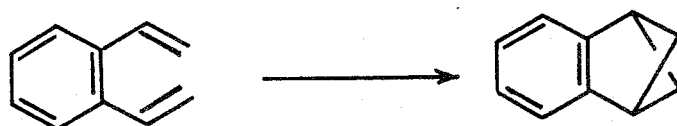
7.13 A. (continued)



B.

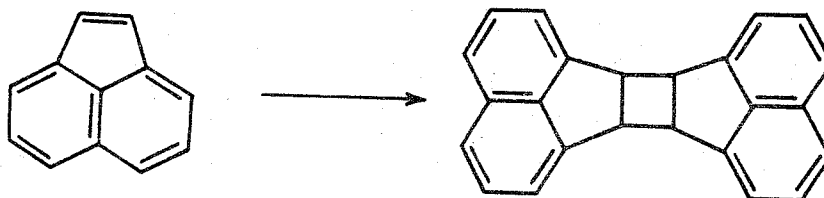


2.

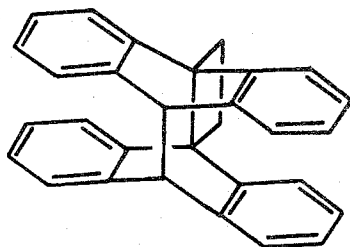


7.13 B. (continued)

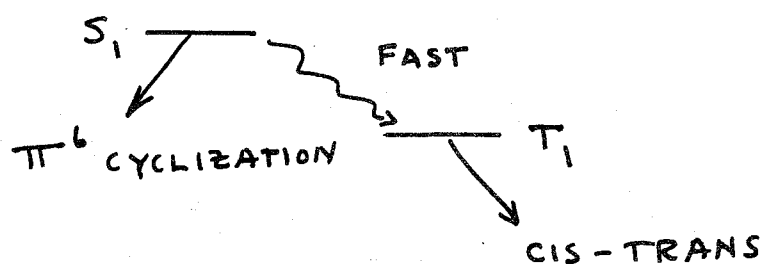
3.



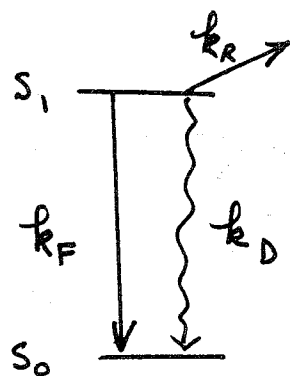
4.



C.



D.



$$\phi_F = k_F / (k_F + k_D + k_R) = 3 \times 10^{-4}$$

$$\phi_R = k_R / (k_F + k_D + k_R) = 8 \times 10^{-3}$$

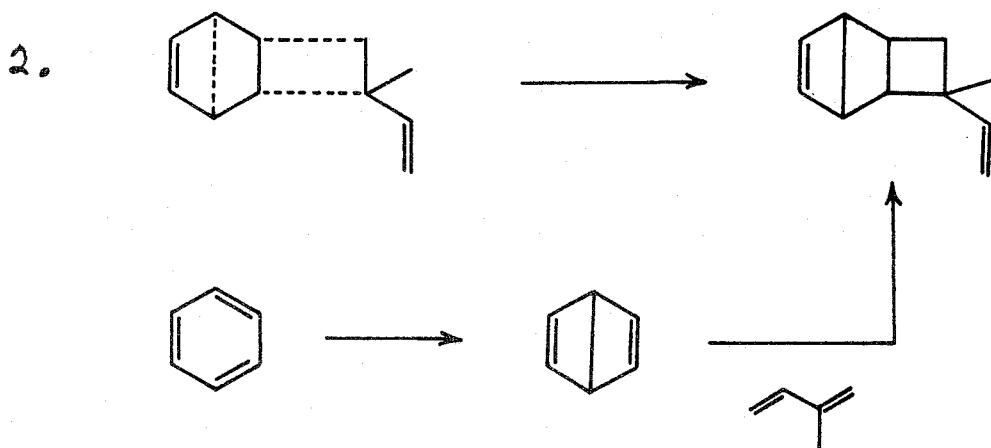
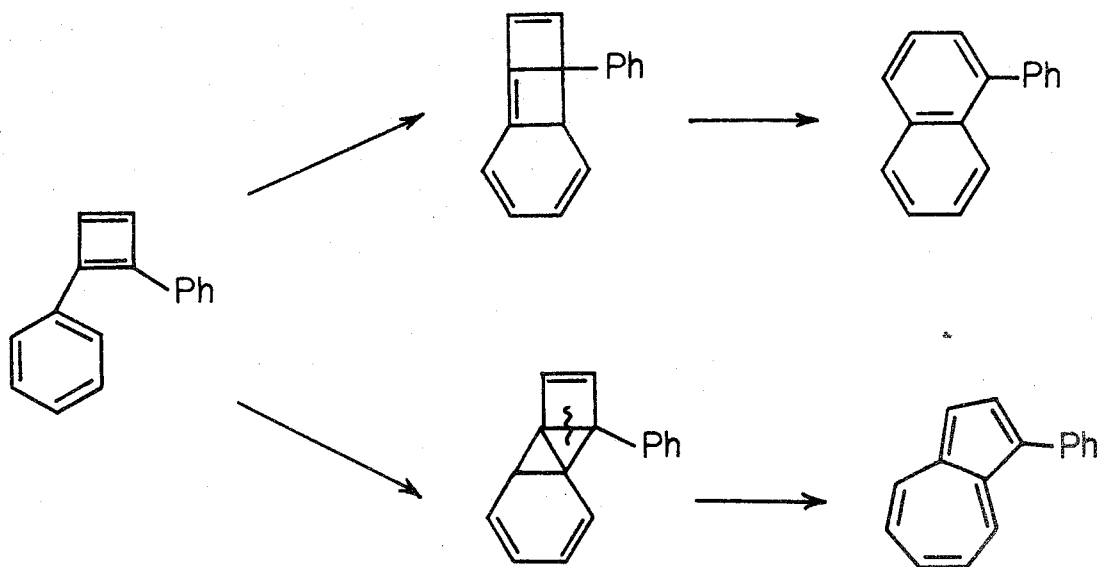
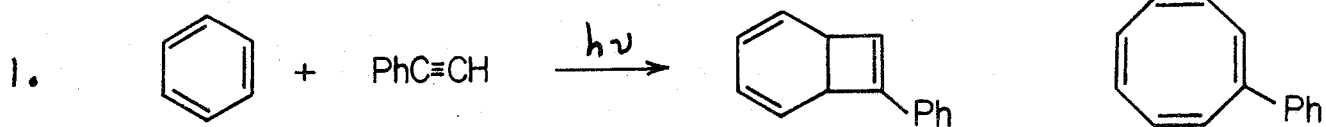
$$k_F \sim 5 \times 10^8 \text{ SEC}^{-1}$$

$$(k_F + k_D + k_R) = 5 \times 10^8 / 3 \times 10^{-4} \\ = 1.7 \times 10^{12} \text{ SEC}^{-1}$$

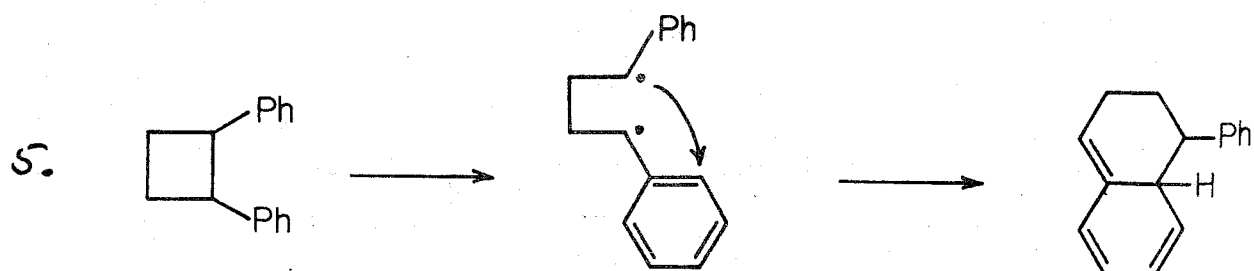
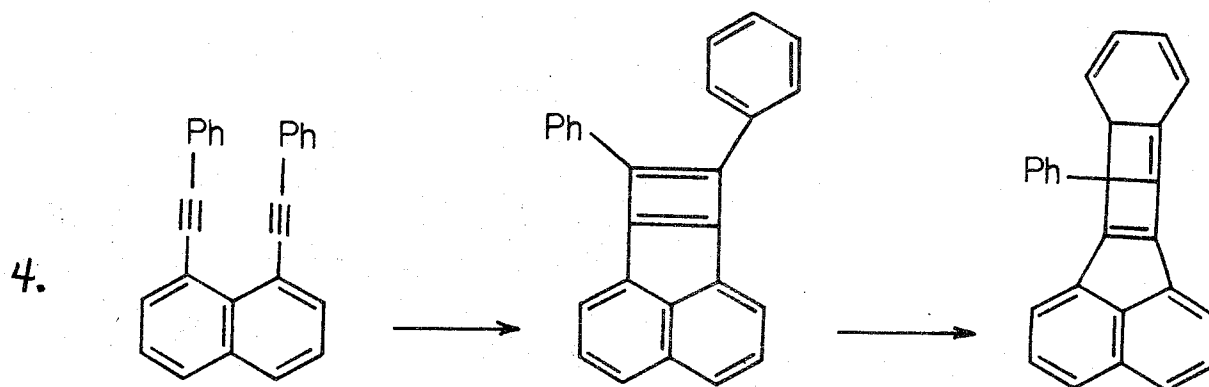
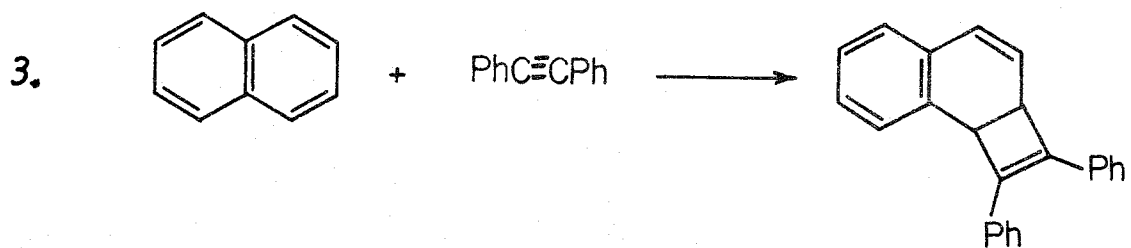
7.13 D (continued)

$$k_R = 8 \times 10^{-3} (k_F + k_D + k_R) = 1.2 \times 10^{10} \text{ sec}^{-1}$$

E.



7.13 E. (continued)



CHAPTER 8
PHOTOCHEMISTRY OF CARBONYL COMPOUNDS

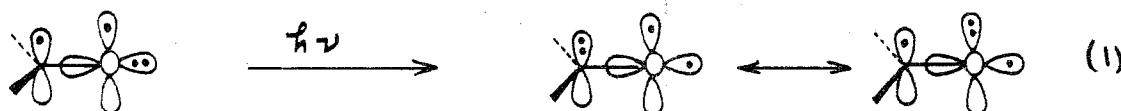
8.1 GENERAL CONSIDERATIONS

Revs: "The Chemistry of the Carbonyl Group," ed. S. Patai, Wiley-Interscience, New York, New York, 1966, p. 823.

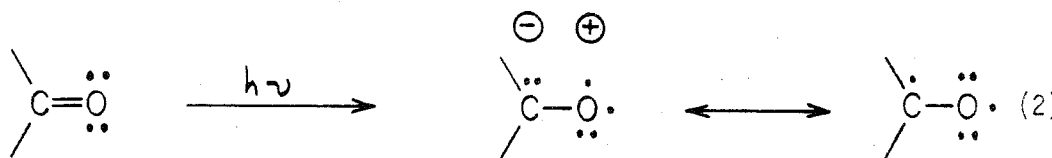
- A. Model for the electronically excited states of carbonyl compounds
- B. Energetics and dynamics of the electronically excited states of carbonyl compounds
- C. Primary photochemical processes of carbonyl compounds

8.2 MODEL FOR ELECTRONICALLY EXCITED STATES

- A. $n \rightarrow \pi^*$ excitation
- B. Orbital description



- C. Valence bond description



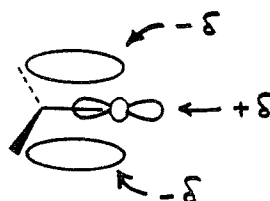
- D. Structure



1. pyramidal
2. long C-O bond (1.35 Å)
3. decreased dipole moment (1.5 D)

- E. Both S_1 and T_1 are structurally similar
- F. Expected reactivity: amphoteric

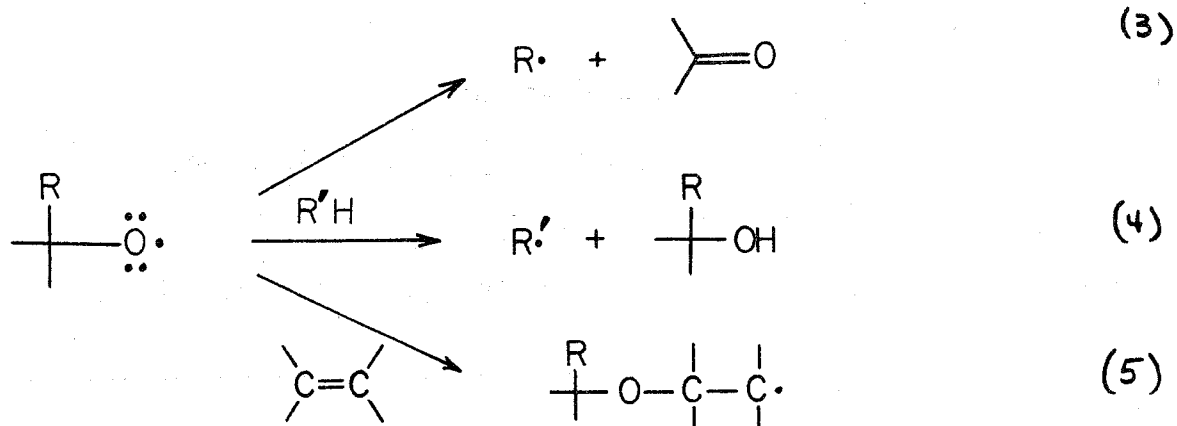
1. Nucleophilic π system
2. Electrophilic n orbital



8.2 (continued)

G. Ground state model

1. Alkoxy radical: for n-orbital reactions. Rev: Pure Appl. Chem., 15, 69 (1967).



2. Nucleophilic additions (in reverse) for π^* orbital reactions

H. Summary

1. S_1 and T_1 comparable in reactivity
2. Effect of spin may show up in pericyclic reactions
3. Both electrophilic and nucleophilic reactions are possible
4. Electrophilic tendency in plane of carbonyl near the "edge"
5. Nucleophilic tendency above and below faces of carbonyl

8.3 ENERGETICS AND DYNAMICS

A. Energetics (Table 8-1)

1. Fluorescence weak for alkanones ($\phi_F \approx 0.01$); negligible for most aryl ketones
2. Low E_1 , high E_3 , small S_1-T_1 gap

B. Dynamics (Table 8-1)

1. Alkanones versus aryl ketones
2. ϕ_{ST} generally high unless reaction from S_1 occurs
3. τ_T usually impurity quenching limited; O_2
4. Phosphorescence observed in highly purified solutions

Table 8-1

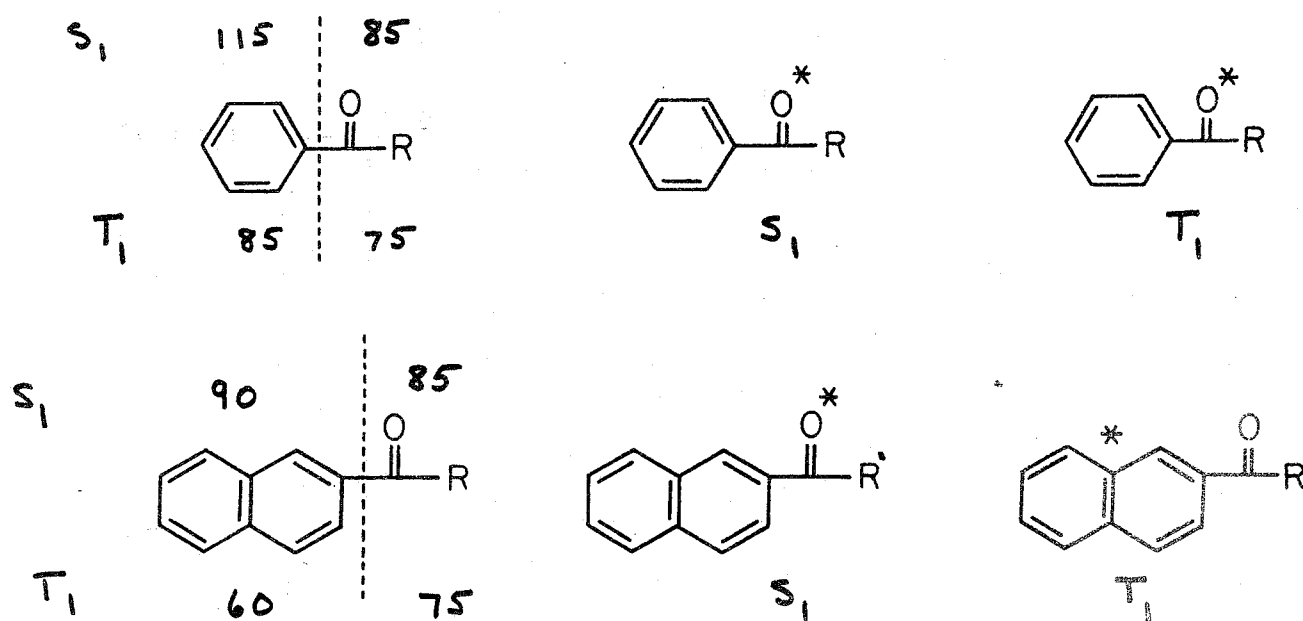
Energetics and Dynamics of Carbonyl Compounds

| <u>Molecule</u> | E_1 | E_3 | k_S | k_{ST} | k_T | ϕ_{ST} |
|----------------------|-------|-------|-----------|-----------|--------|-------------|
| Acetone | 84 | 78 | 10^9 | 10^9 | 10^6 | 1.0 |
| 2-Pentanone | 84 | 78 | 10^9 | 10^9 | 10^7 | 0.9 |
| 2-Hexanone | 84 | 78 | 10^9 | 10^9 | 10^8 | 0.5 |
| Cyclobutanone | 84 | 78 | 10^{11} | 10^9 | - | 0.00 |
| Cyclopentanone | 84 | 78 | 10^9 | 10^9 | 10^8 | 1.0 |
| Cyclohexanone | 84 | 78 | 10^9 | 10^9 | 10^7 | 1.0 |
| Acetophenone | 80 | 74 | 10^{10} | 10^{10} | 10^5 | 1.0 |
| Benzophenone | 76 | 69 | 10^{11} | 10^{11} | 10^5 | 1.0 |
| 2-Acetophenone | 77 | 59 | 10^{10} | 10^{10} | 10^3 | 0.84 |
| 4-Phenylbenzophenone | 75 | 62 | 10^{10} | 10^{10} | 10^3 | 1.0 |
| Fluorenone | 65 | 53 | 10^9 | 10^9 | 10^4 | 0.93 |
| 2-Acetylnaphthalene | 75 | 58 | 10^9 | 10^9 | 10^4 | 0.9 |

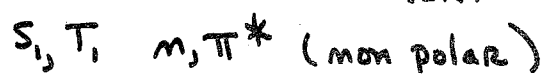
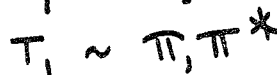
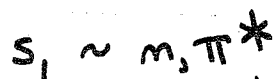
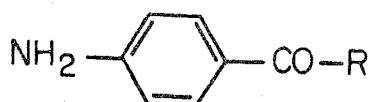
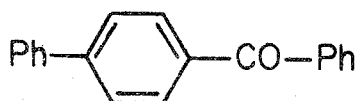
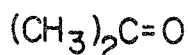
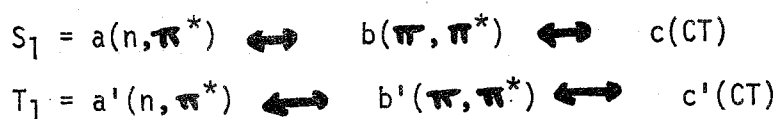
8.3 (continued)

C. Energy diagrams

1. S_1 and T_1 n, π^* for alkanones (Figure 8-1 on p. 198)
2. S_1 and T_1 n, π^* for certain aryl ketones (Figure 8-2 on p. 199)
3. S_1 and T_1 may be π, π^* or "charge transfer" for certain aryl ketones (Figure 8-3 on p. 200)
4. Commonly employed "triplet sensitizers:" short τ_S , high ϕ_{ST} , τ_T , high E_3 , convenient absorption spectrum
5. Energy sink concept



6. Mixing of states



SOLVENT

Figure 8-1

S_1 and T_1 (n, π^*) for Alkanones

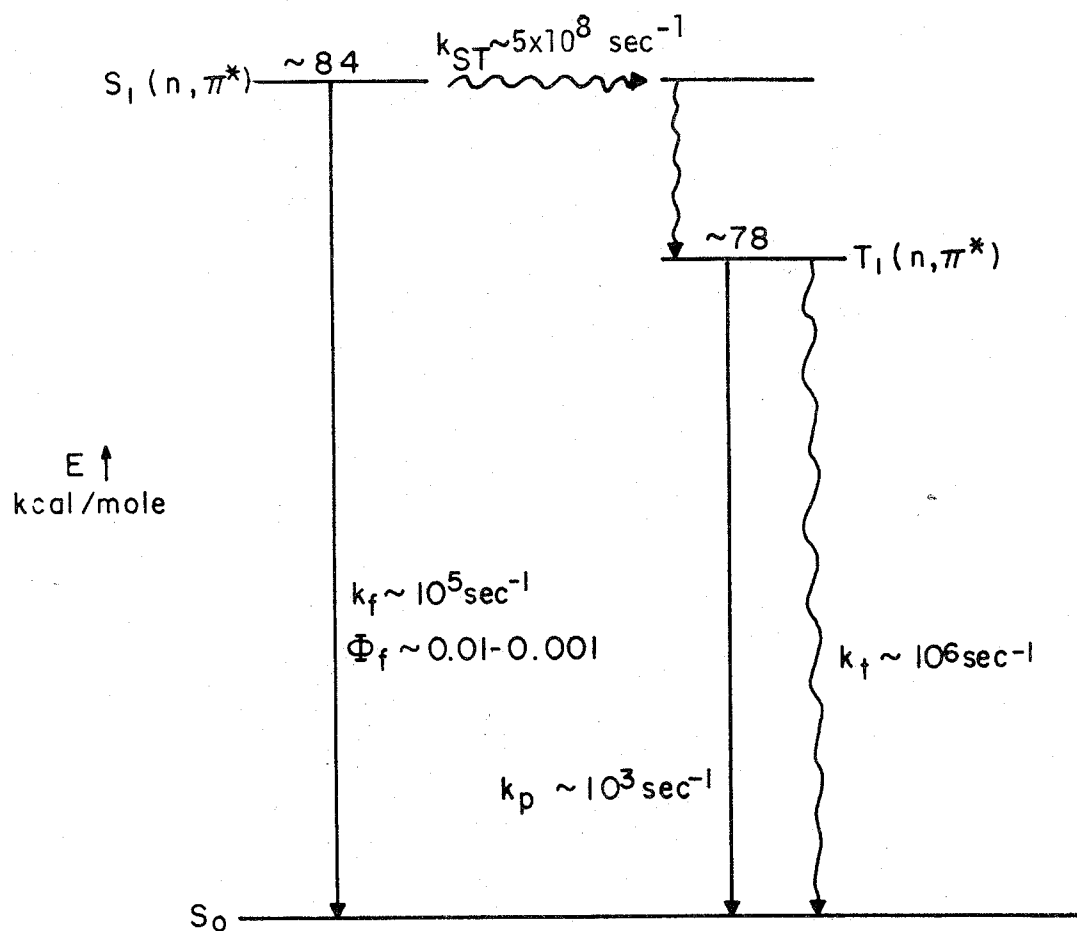
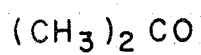


Figure 8-2

S_1 and T_1 (n, π^*) for Certain Aryl Ketones

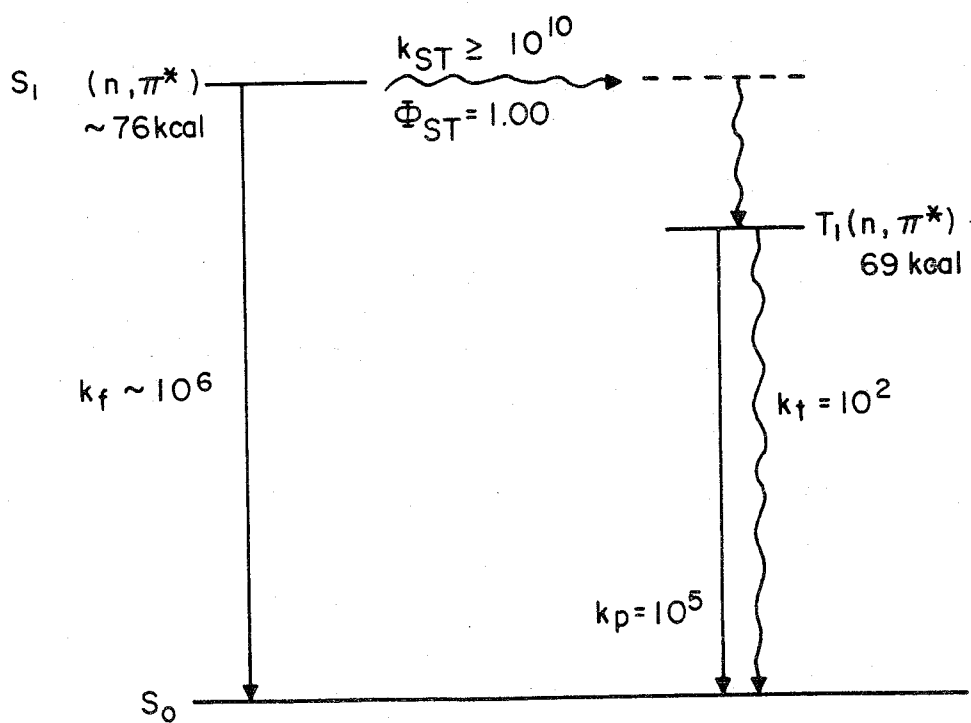
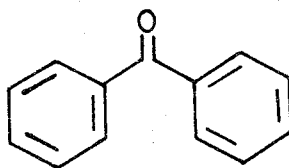
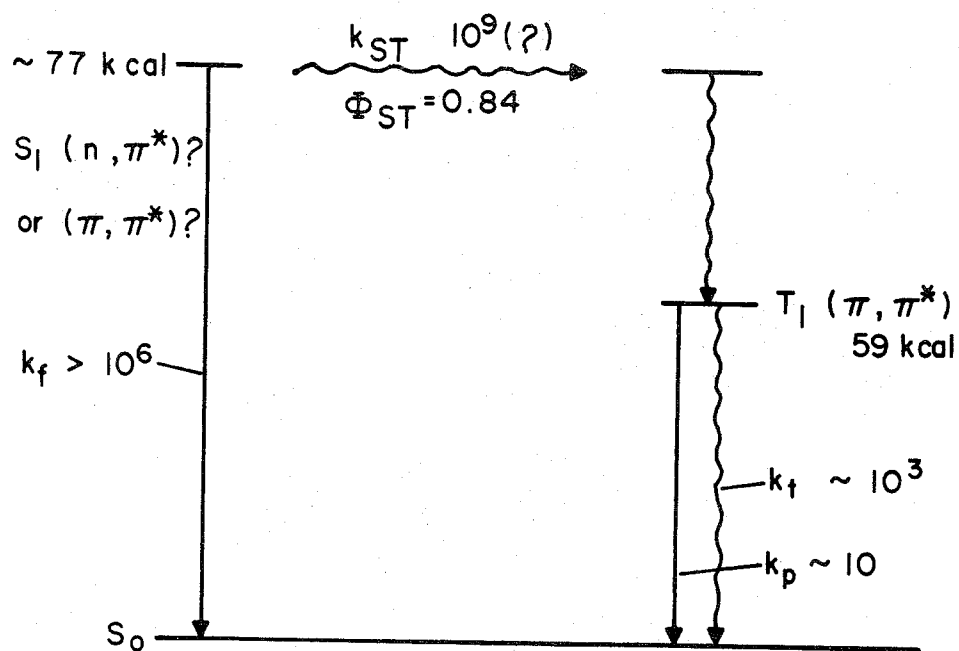
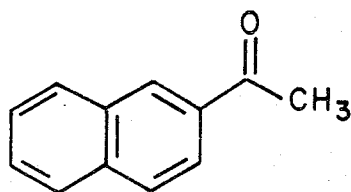


Figure 8-3

S₁ and T₁ (π, π^*) or "Charge Transfer" for
Certain Aryl Ketones



8.4 PRIMARY PHOTOCHEMICAL PROCESSES

A. α -Cleavage

1. Expected for n, π^* states from alkoxy model
2. Much different rate expected for π, π^*
3. Expect structural effects related to radical stabilities

B. Hydrogen abstraction

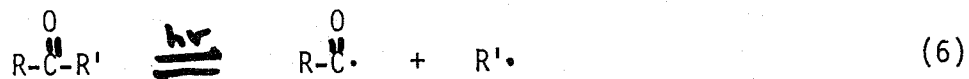
1. Expected for n, π^* states from alkoxy model
2. Abstraction by oxygen atom at the "edge"
3. Expect very different behavior for π, π^* states

C. Cycloaddition reactions

1. Expected for n, π^* states from alkoxy model; biradical or CT in nature
2. Stereoelectronics suggested by n, π^* model; electrophilic at the edge, nucleophilic at the faces
3. Different stereospecificity for $S_1(n, \pi^*)$ and $T_1(n, \pi^*)$
4. Expect different rates for π, π^*
5. Expect energy transfer to compete

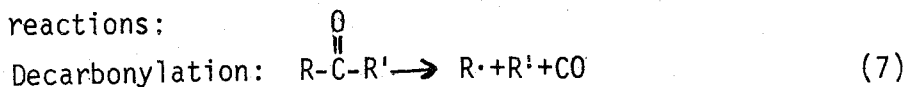
8.5 α -CLEAVAGE REACTIONS

A.



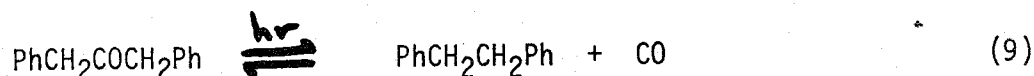
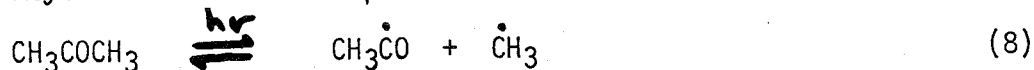
1. Goes best when $\text{R}'\cdot$ is stabilized or when $\text{CO}-\text{R}'$ is weakened due to structural effect
2. Generally reversible (fast radical recombination)
3. Intramolecular stabilization can compete with recombination: cyclic ketones
4. Usually T_1 , cyclic ketones, stable $\text{R}\cdot$

5. Net reactions:

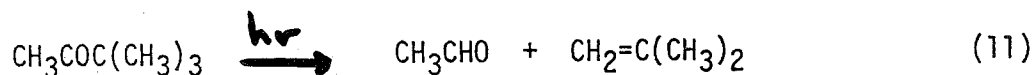


Disproportionation and biradical trapping

B. Acyclic ketones: examples



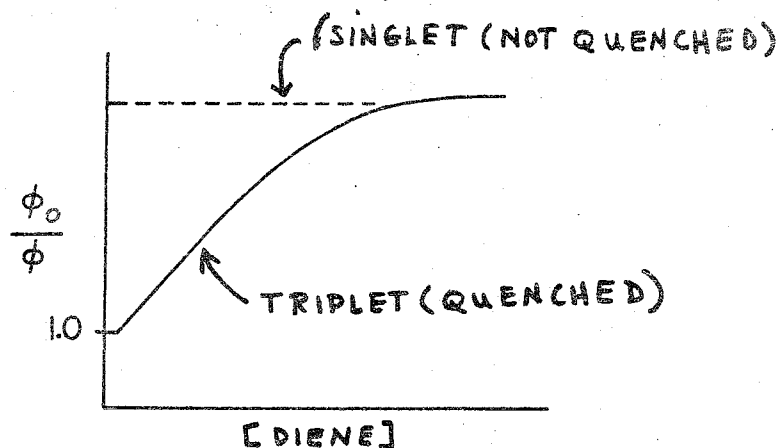
(10)



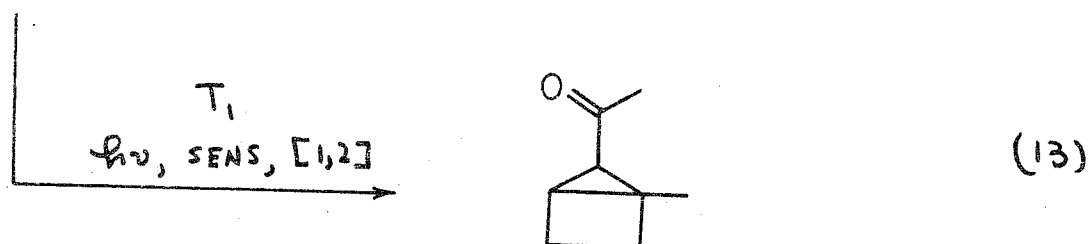
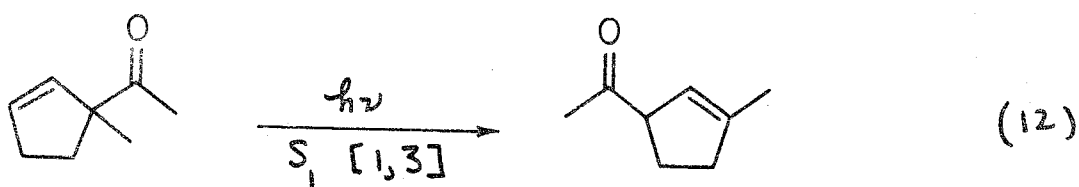
1. Quenching studies: Usually T_1 , unless substitution makes cleavage fast enough to compete with k_{ST}

8.5 B. (continued)

2. Diene quenching to separate S_1 and T_1 reactions: Stern-Volmer quenching

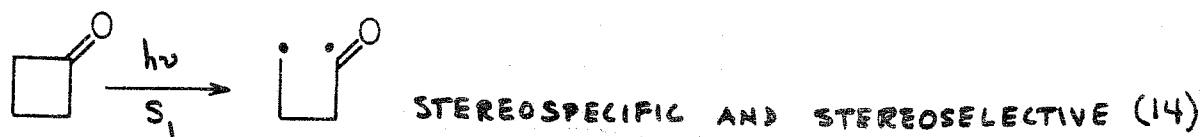


3. Differing reactivity of S_1 and T_1 : β,γ -unsaturated enones

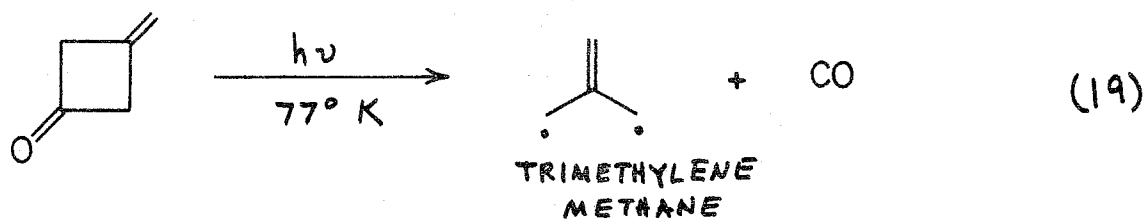
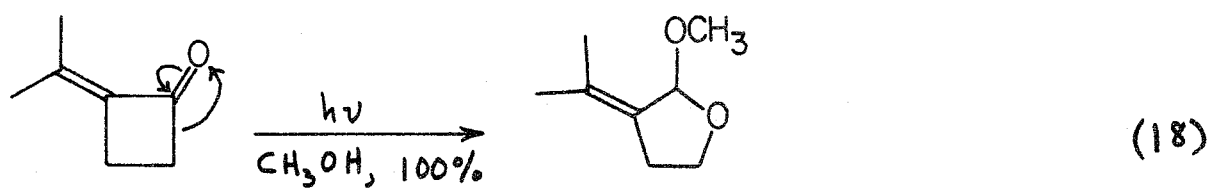


8.5 (continued)

C. Examples: Cyclic ketones

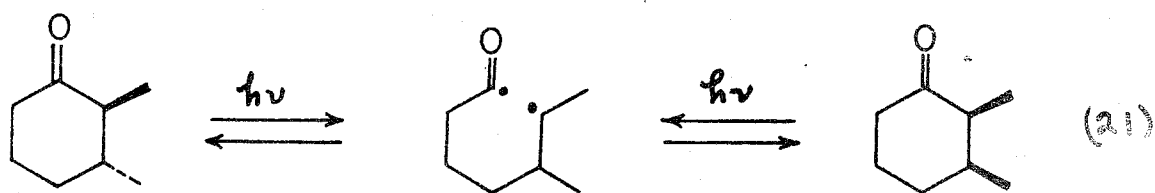
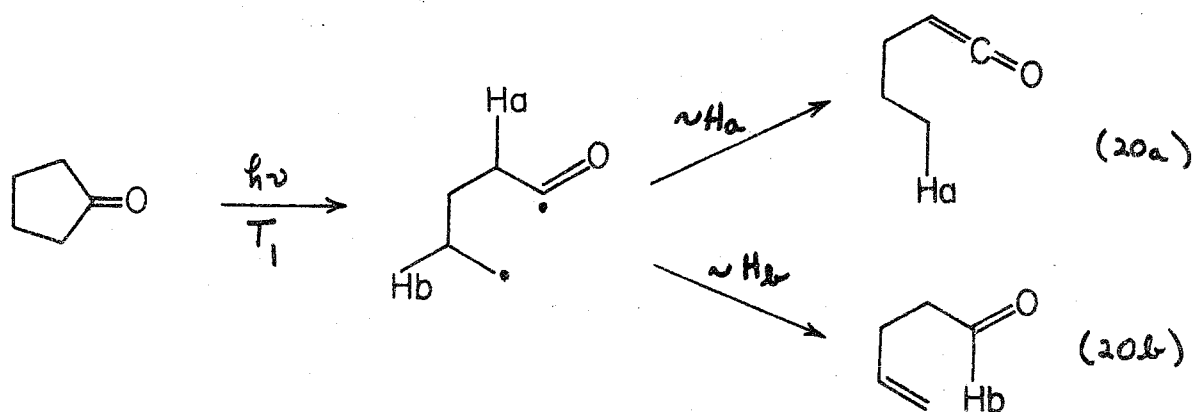


1. Synthetic applications



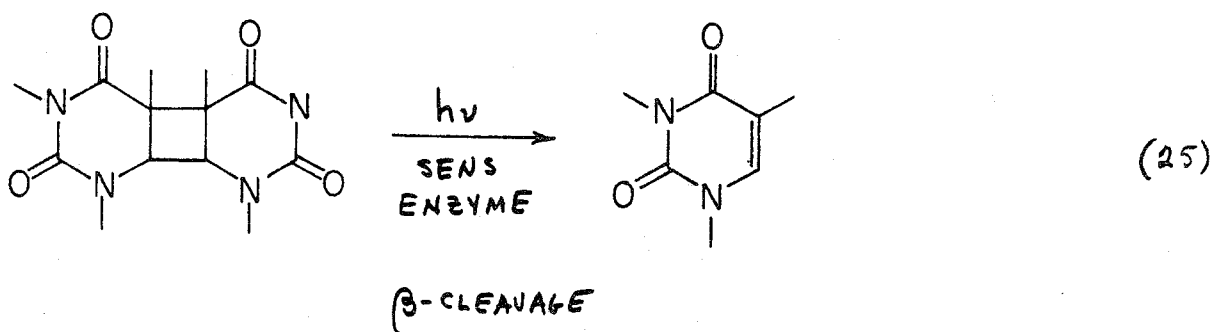
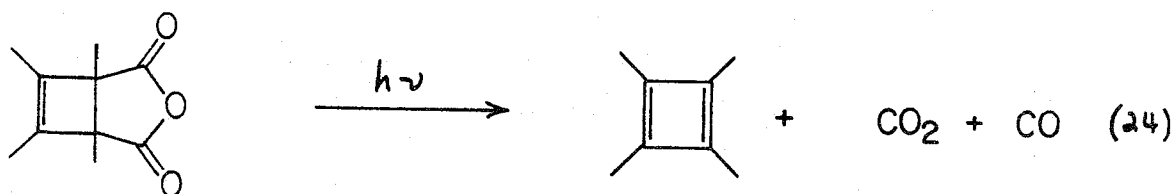
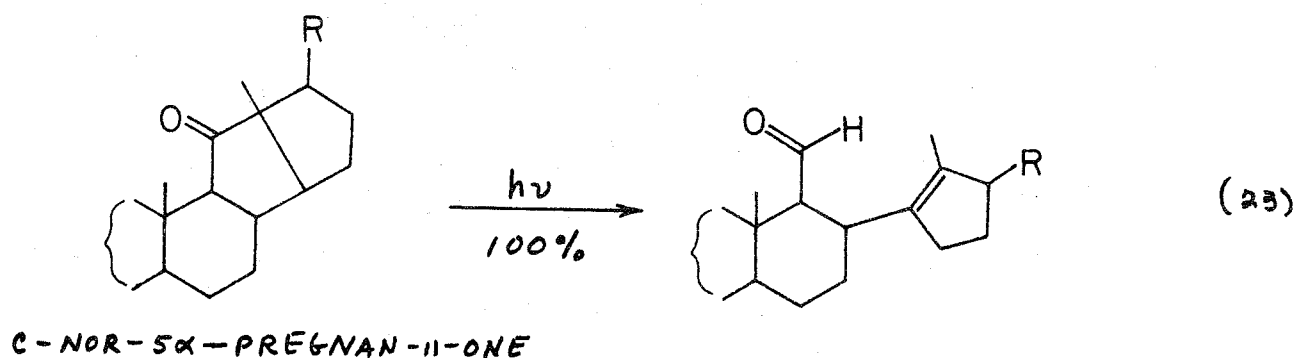
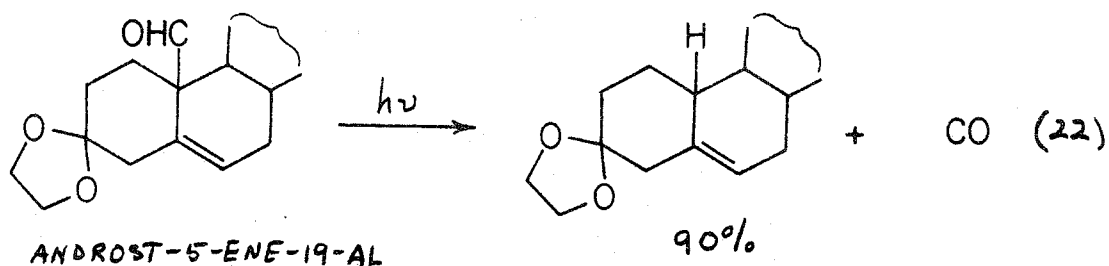
8.5 C. (continued)

2. Medium ring ketones



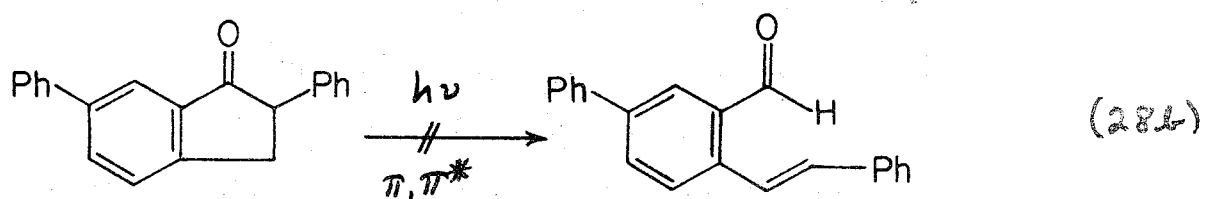
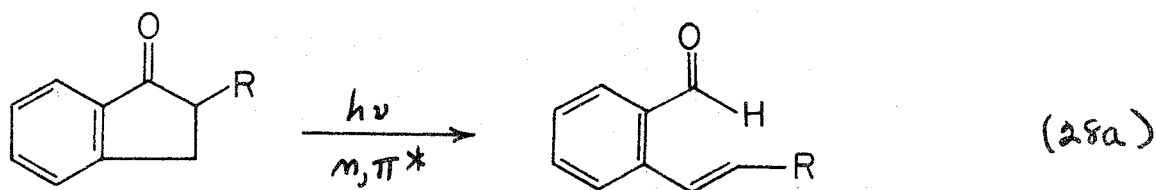
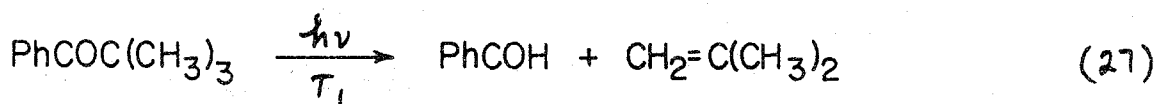
8.5 C. (continued)

3. Biradical explains relative rates, stereoselectivity, lack of stereospecificity, product structures



8.5 C. (continued)

4. Aryl ketones: diaryl ketones unreactive, aryl alkyl depend on R group, structure, state



D. Summary

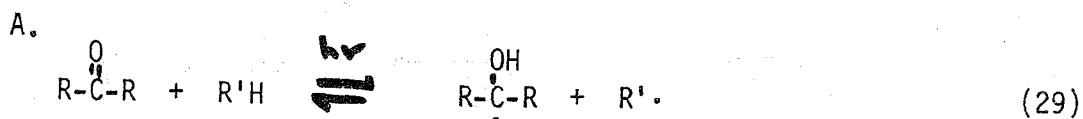
1. T_1 except for special structural effects
2. Biradical model explains all
3. Goes best when strain is relieved or stabilized radical pair is generated
4. Products determined by available decomposition paths of biradical
5. $3n, \pi^* \gg 1n, \pi^* \gg \pi, \pi^*$

8.5 (continued)

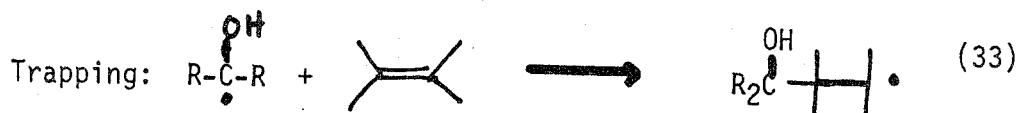
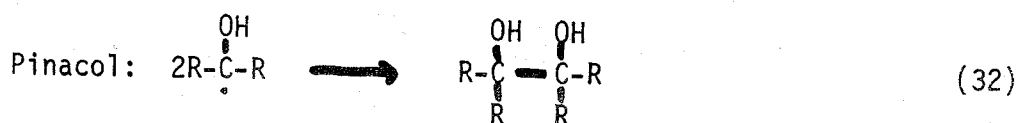
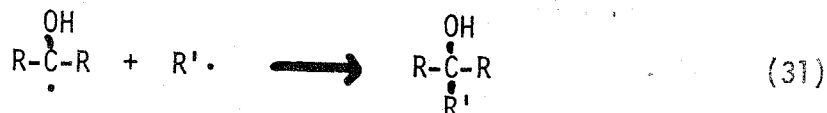
E. References to reactions

- (8) J. Chem. Phys., 73, 1011 (1969)
- (9) J. Amer. Chem. Soc., 92, 6074, 6076 (1970)
- (10) Tetrahedron Letters, 1863 (1963)
- (11) J. Amer. Chem. Soc., 92, 6974 (1970); ibid, 90, 504 (1968)
- (12) and (13) Chem. Commun., 1103 (1969)
- (14) through (17) Accounts Chem. Research, 5, 92, (1972)
- (18) J. Amer. Chem. Soc., 92, 4349 (1970)
- (19) J. Amer. Chem. Soc., 84, 715 (1967)
- (20) J. Amer. Chem. Soc., 93, 7213 (1971)
- (21) Chem. Commun., 1081 (1969)
- (22) Helv. Chim. Acta, 49, 292 (1966)
- (23) Helv. Chim. Acta, 44, 1255 (1964)
- (24) Angew. Chem., Int. Ed. Eng., 7, 536 (1968)
- (25) J. Amer. Chem. Soc., 88, 813 (1966)
- (27) Tetrahedron Letters, 1373 (1970); Ann., 732, 165 (1970)
- (28) J. Amer. Chem. Soc., 94, 6866 (1972)

8.6 HYDROGEN ABSTRACTION

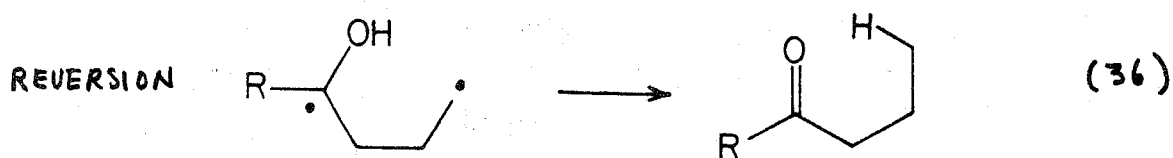
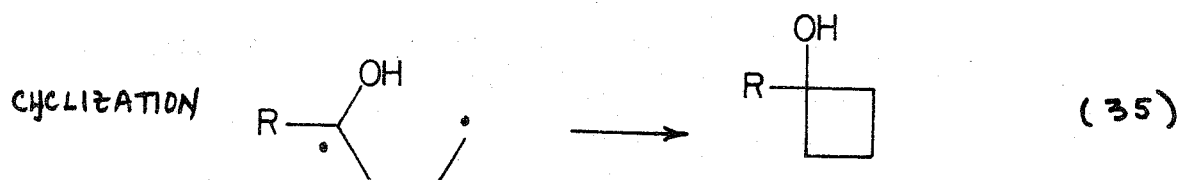
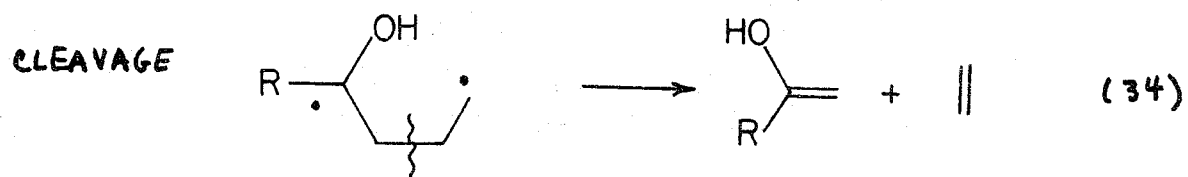


1. General reaction of n, π^* states
2. Goes best when $\text{R}'\text{-H}$ is electron rich: edge attack by n -orbital
3. Potentially reversible
4. Intramolecular case: cyclic six favored, then depends on structure, type of R-H bond
5. Net reactions: intermolecular

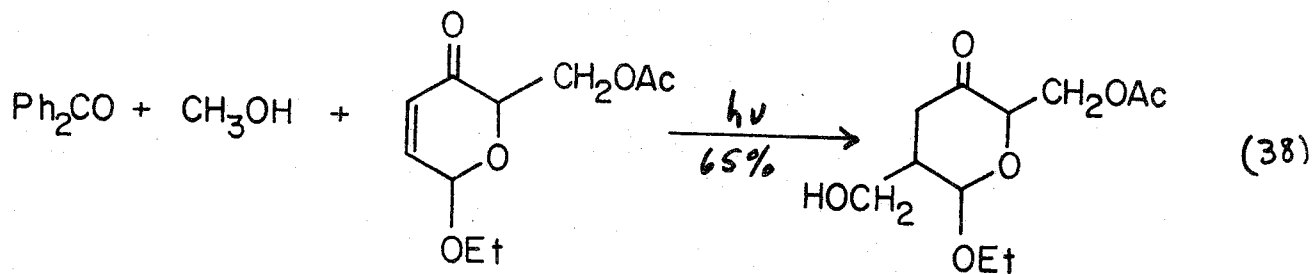
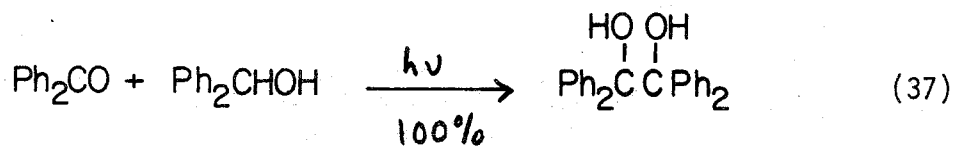


8.6 A. (continued)

6. Net reactions: intramolecular (Type II)



B. Examples: Intermolecular



8.6 B. (continued)

2. Dependence of rate and efficiency on ketone structure

$$\phi_r = \left[\frac{k_r[R'H]}{k_r[R'H] + k_d} \right] \phi_{ST} \quad (39)$$

3. $k_d(n, \pi^*) > k_d(\pi, \pi^*), k_d(CT)$

4. $k_r(n, \pi^*) \gg k_d(\pi, \pi^*), k_d(CT)$

5. Model for n, π^* states

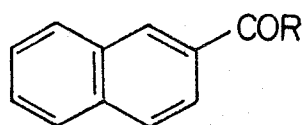
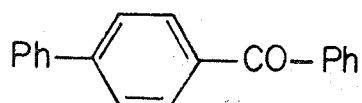
$\text{Ph}_2\text{CO}, \text{PhCOCH}_3, \text{CH}_3\text{COCH}_3 : k_r \text{ comparable}$

6. Hydrogen donors

| Type | $k_r(n, \pi^*)$ in $\text{M}^{-1} \text{sec}^{-1}$ |
|---|--|
| $-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{CH}_2-$ | $\sim 10^4-10^5$ |
| $\text{Ar}-\text{CH}_3$ | $\sim 10^5$ |
| $-\text{CH}_2-\text{CH}-(\text{CH}_2)_2-$ | $\sim 10^6$ |
| $\text{R}_2\text{CHOR}'$ | $\sim 10^6-10^7$ |
| $n\text{Bu}_3\text{SnH}$ | $\sim 10^8$ |

7. $k_d \sim 10^5$; ϕ_r variable, can approach 1.0

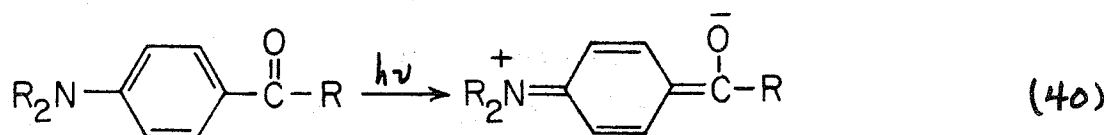
8. Model for π, π^* states



8.6 B. (continued)

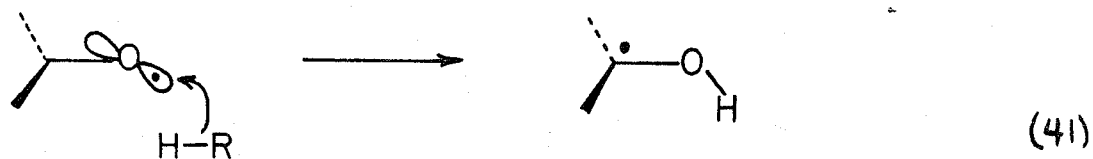
9. $k_r \sim 10^3-10^4$; $k_d \sim 10^4-10^5$; ϕ usually low

10. Model for C-T states



11. $k_r \sim 10^3$; $k_d \sim 10^5$; ϕ low

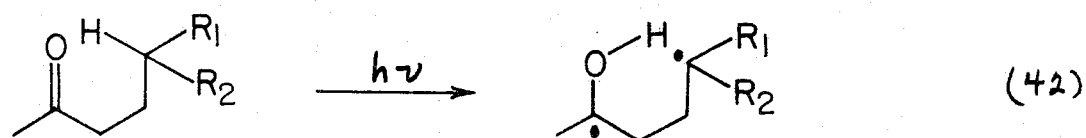
12. Mechanism: n-orbital attack



C. Examples: intramolecular

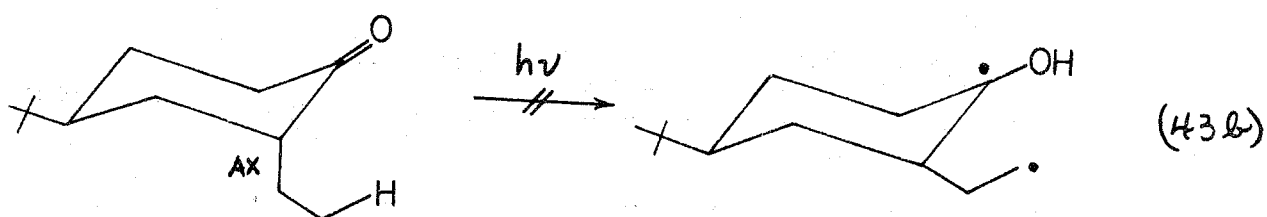
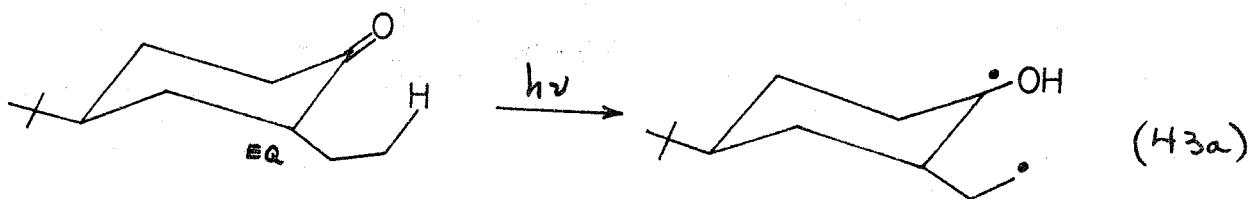
Rev.: Accounts Chem. Research, 4, 168 (1971)

1. Biradical intermediate



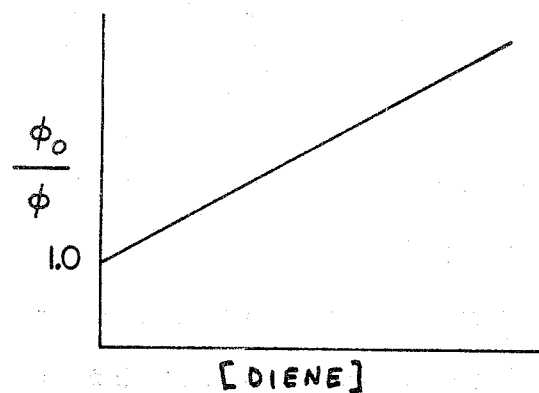
8.6 C. (continued)

2. General if γ -H is available and sterically accessible to n-orbital

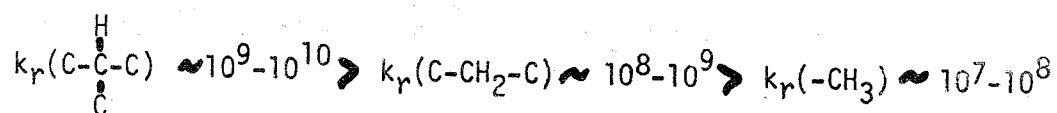


3. Alkanones: S_1 and $T_1(n, \pi^*)$ reactive

4. Aryl alkyl ketones: T_1 only reactive, $k_{ST} \gg k_r$

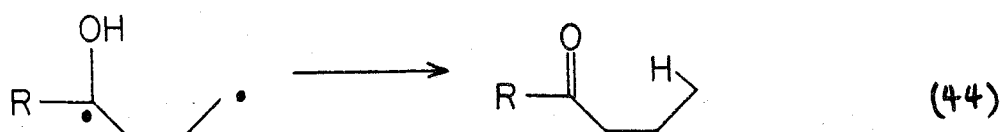


5. Dependence on "hydrogen donor"

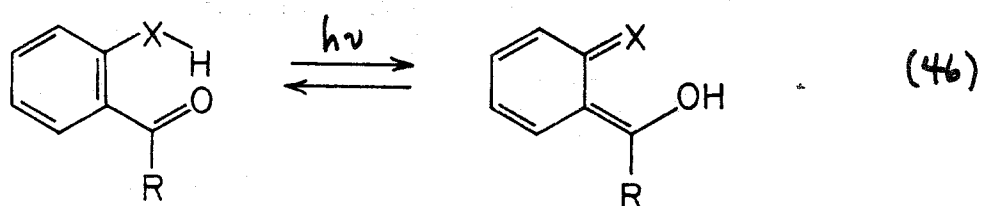
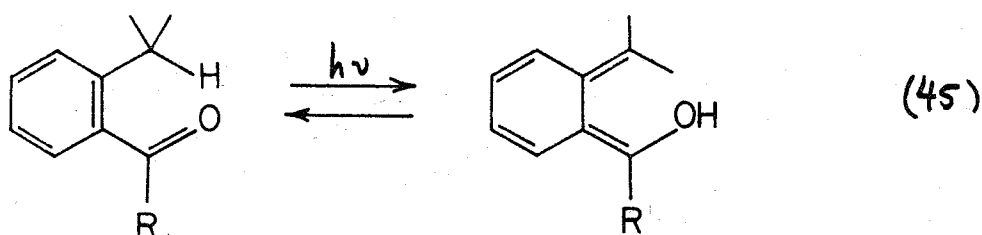


8.6 C. (continued)

6. Reversibility reduces efficiency: solvent dependent



7. 2-alkyl, 2-amino and 2-hydroxy aryl ketones



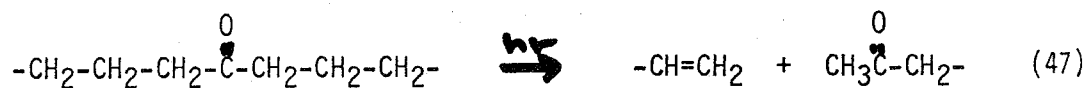
8. Intermolecular hydrogen abstraction inhibited

9. Enol may be trapped

10. Photostabilizers: "cooling off" mechanism

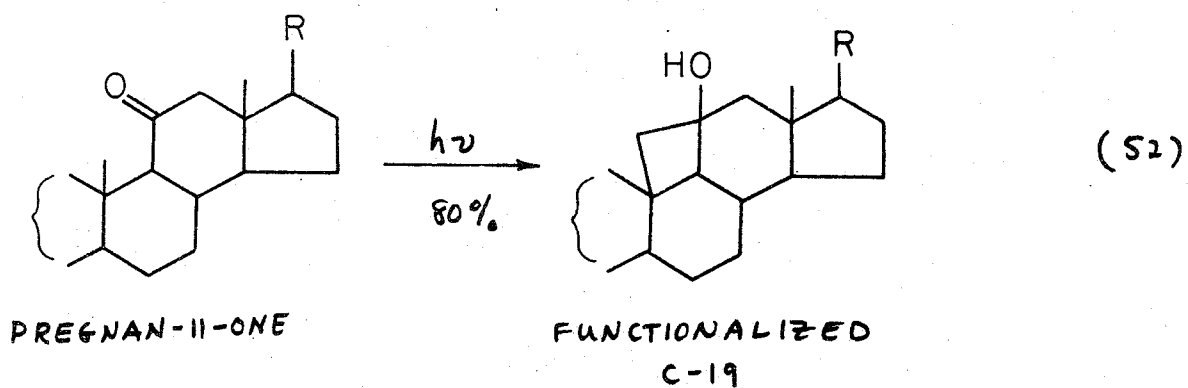
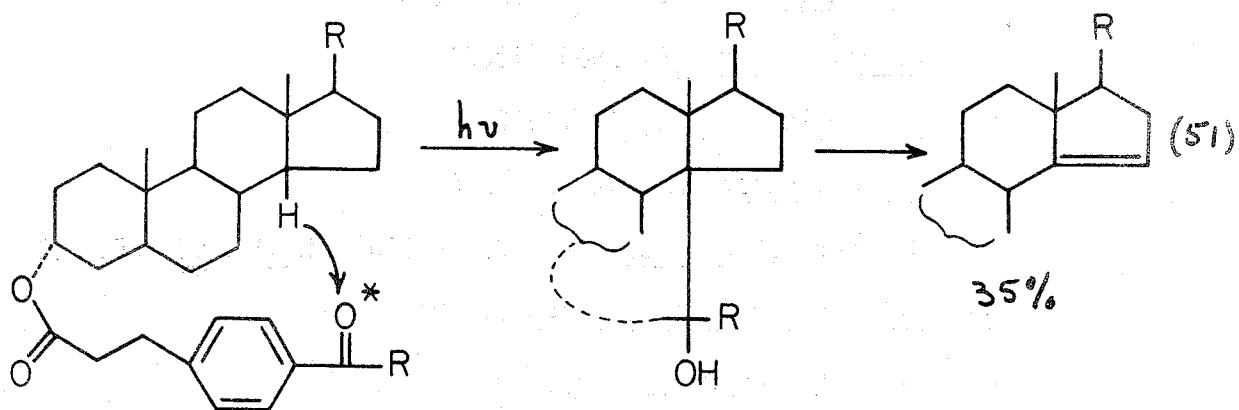
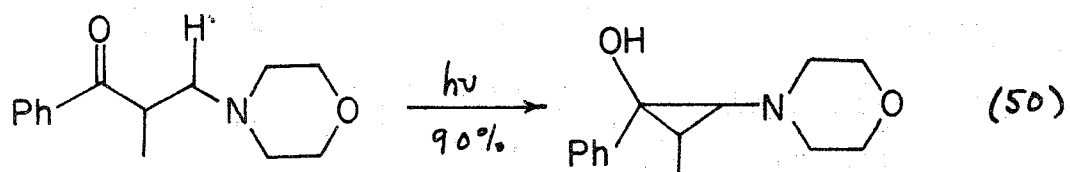
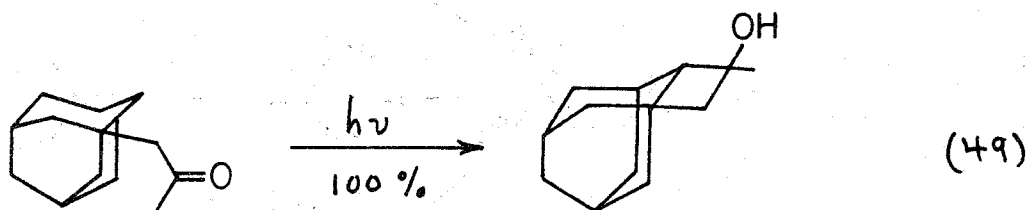
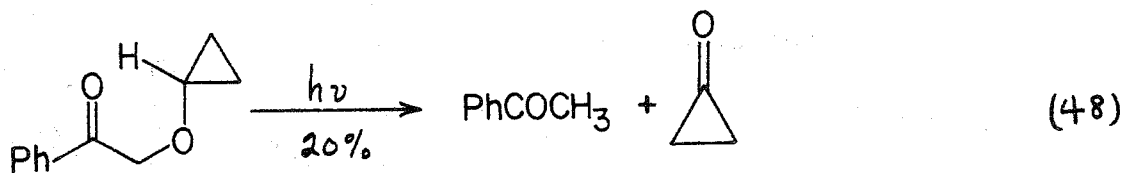
11. Substituent effects: $n, \pi^* > \pi, \pi^* \gg \text{CT}$

12. Polymer degradation



8.6 (continued)

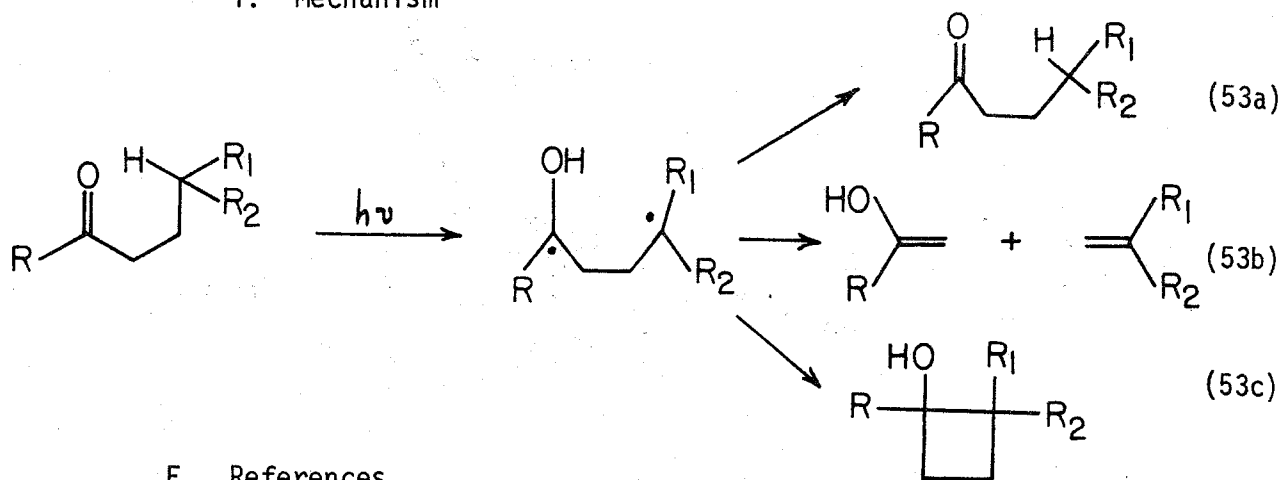
D. Synthetic applications



8.6 (continued)

E. Summary

1. Mechanism



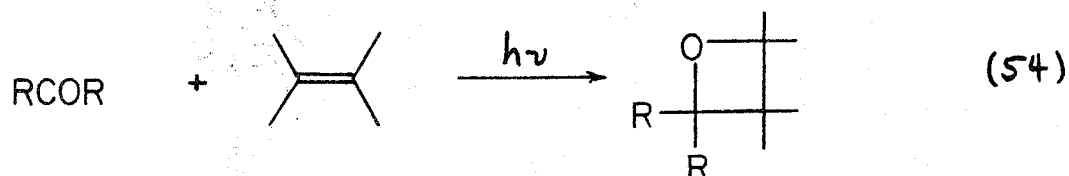
F. References

- (37) J. Amer. Chem. Soc., 83, 2789 (1961)
- (38) Chem. Commun., 1286 (1961)
- (43) J. Amer. Chem. Soc., 90, 2185 (1968)
- (45) J. Amer. Chem. Soc., 83, 2213 (1961)
- (46) J. Phys. Chem. 70, 2634 (1966)
- (47) Macromolecules, 5, 63 (1972)
- (48) Molec. Photochem., 2, 259 (1970)
- (49) J. Amer. Chem. Soc., 92, 4752 (1970); ibid., 93, 5521 (1971)
- (50) Tetrahedron Letters, 2445 (1970)
- (51) J. Amer. Chem. Soc., 92, 732 (1970)
- (52) Helv. Chim. Acta, 46, 1599 (1963)

8.7 CYCLOADDITION: OXETANE FORMATION

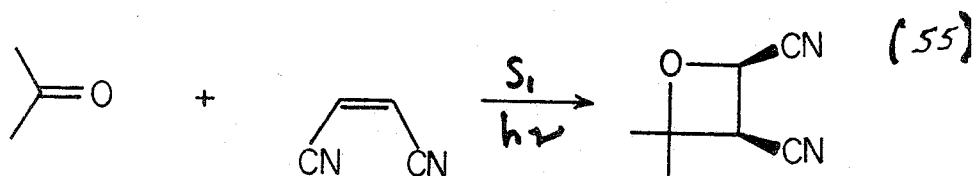
A. Good synthetic reaction for oxetanes

Rev: Adv. Photochem., 6, 301 (1968)



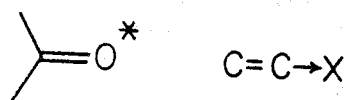
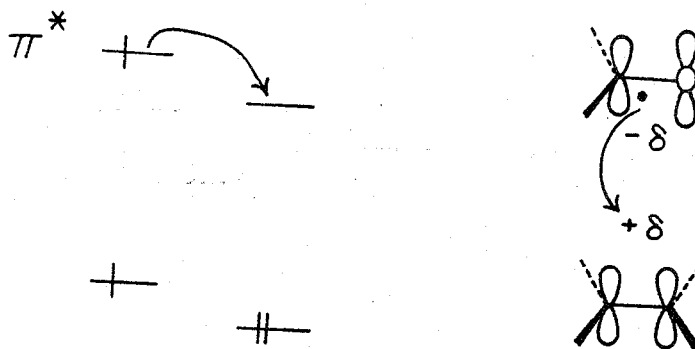
1. May be concerted (S_1) or multistep (T_1)
2. Goes with electron poor (π^* attack) and electron-rich (n attack) ethylenes
3. Stereoselectivity and stereochemistry
4. Competing energy transfer to ethylene

B. Examples: electron poor ethylenes



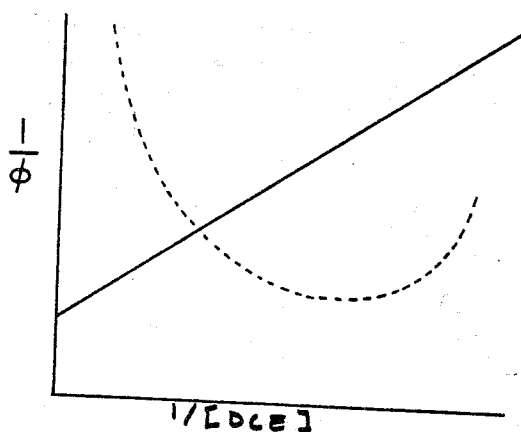
8.7 B. (continued)

1. Charge transfer interaction (π^* attack)



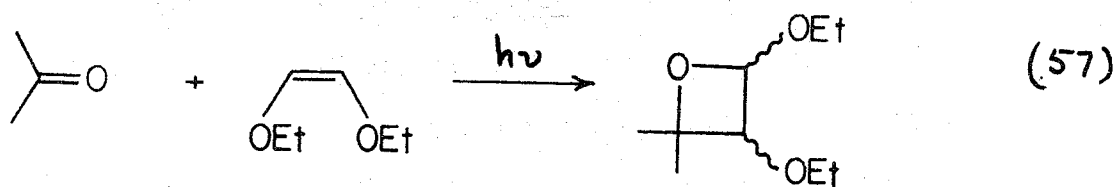
2. S_1 of ethylene too high for ET

3. Kinetics: J. Amer. Chem. Soc., 92, 1318 (1970)



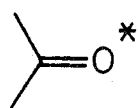
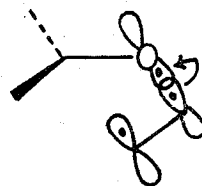
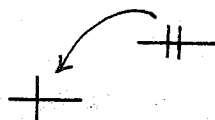
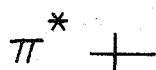
8.7 (continued)

C. Examples: electron-rich ethylenes

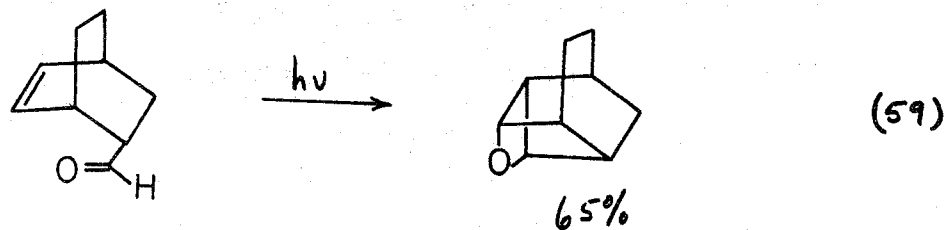
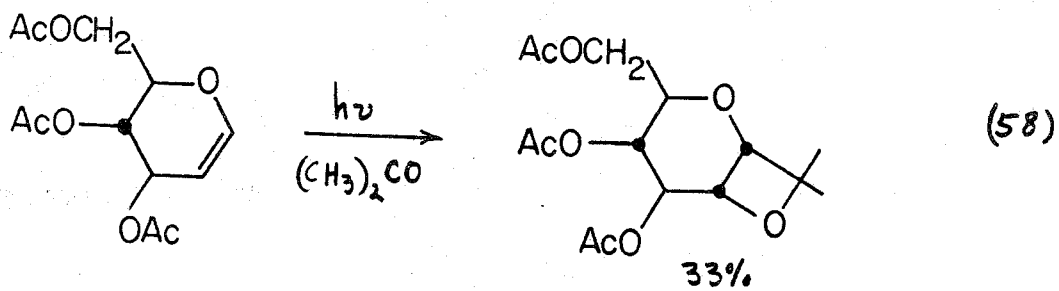


1. Both S_1 and T_1 are active

2. Charge transfer interaction (n orbital attack)



D. Synthetic applications



8.7 (continued)

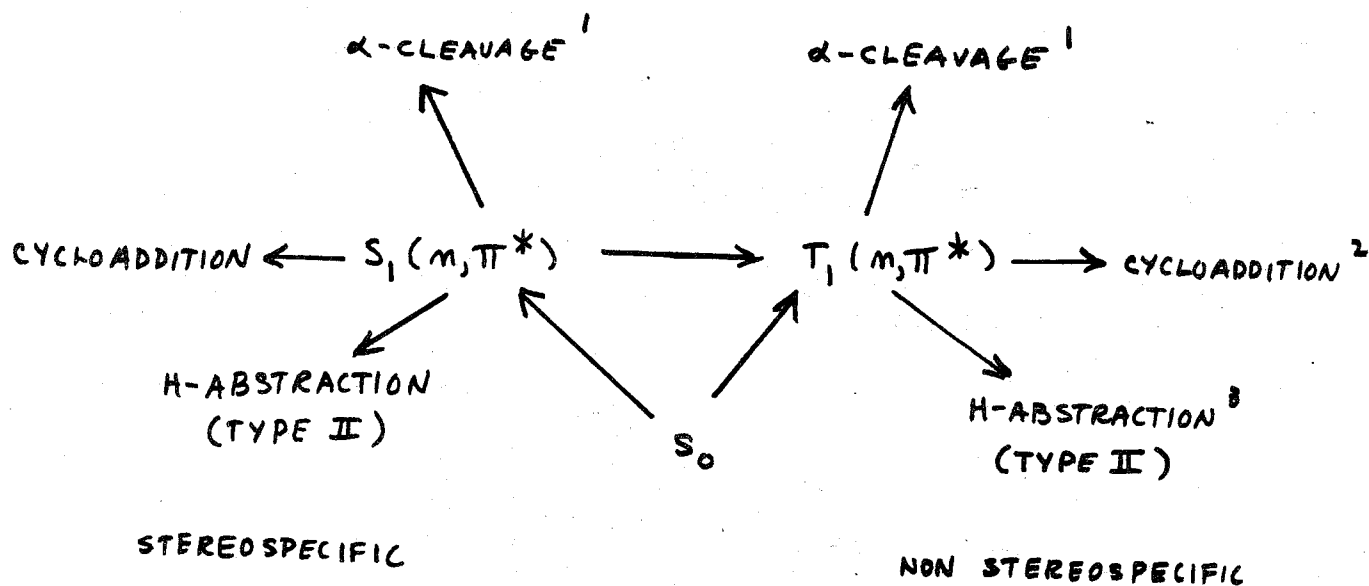
E. References to reactions

- (55) and (56) J. Amer. Chem. Soc., 92, 1318 (1970)
- (57) J. Amer. Chem. Soc., 92, 320 (1970)
- (58) J. Org. Chem., 37, 572 (1972)
- (59) J. Org. Chem., 34, 2301 (1969); Tetrahedron Letters, 79 (1969)

F. Mechanism

1. S_1 and T_1 reactive for alkanones; only T_1 for aryl ketones;
 S_1 concerted for π^* attack; S_1 and T_1 biradical for n attack
2. ET always a possibility (reactions of ethylenes observed)
3. n, π^* required for best results

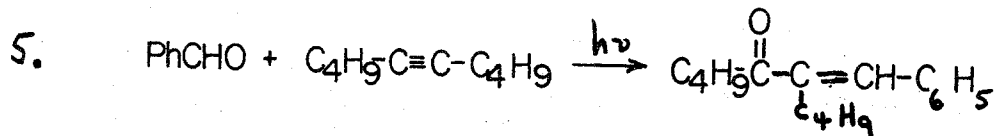
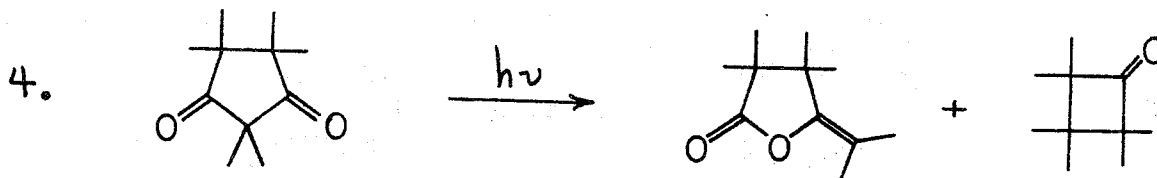
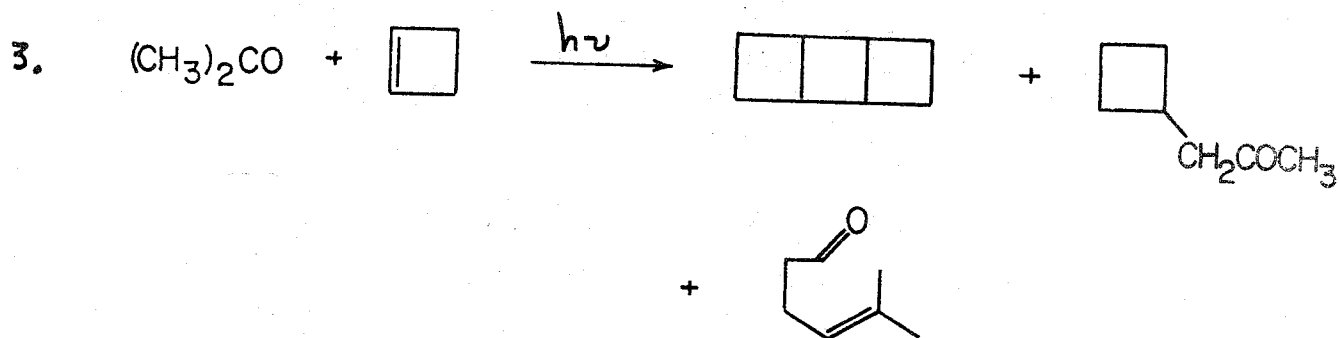
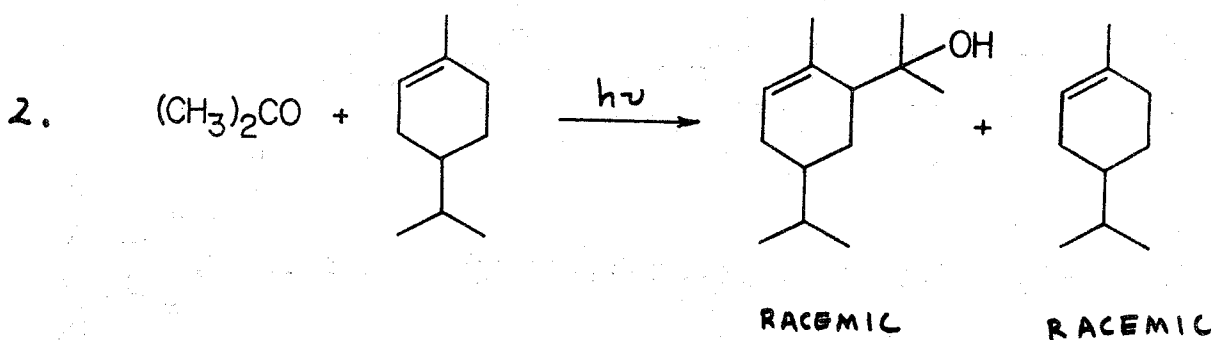
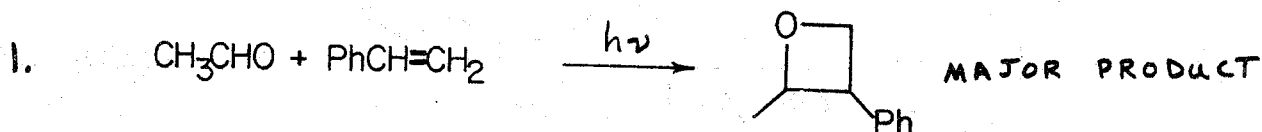
8.8 SUMMARY



1. Cleavage generally faster for T_1 than S_1
2. Generally involve biradical intermediates
3. May be Type II or intermolecular

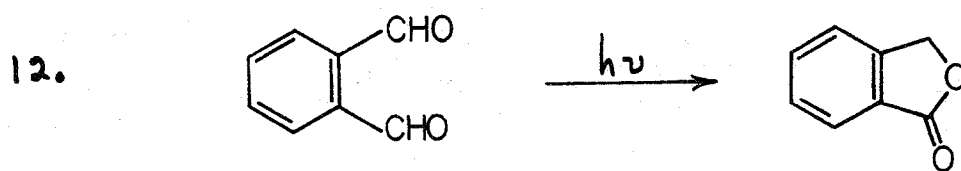
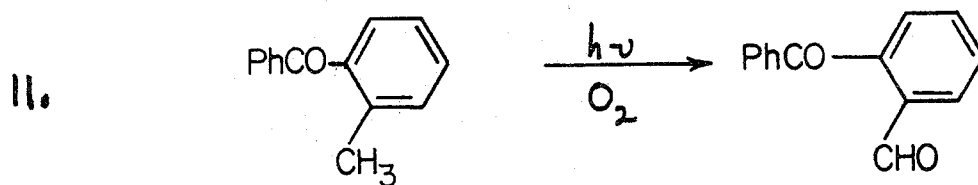
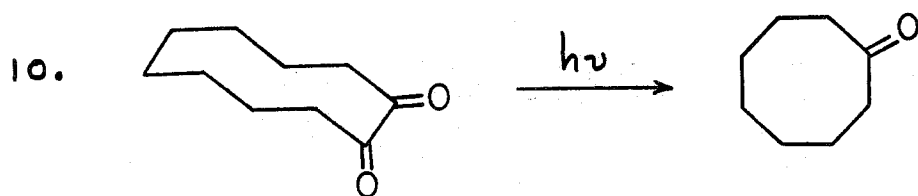
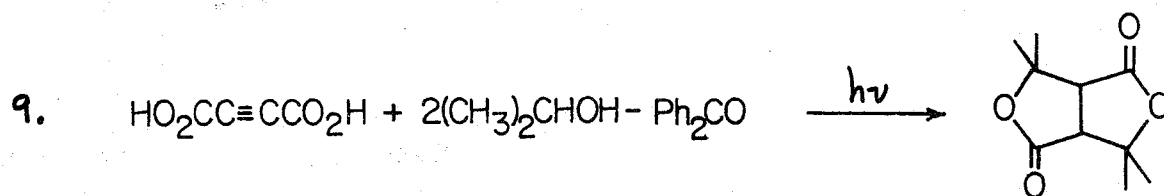
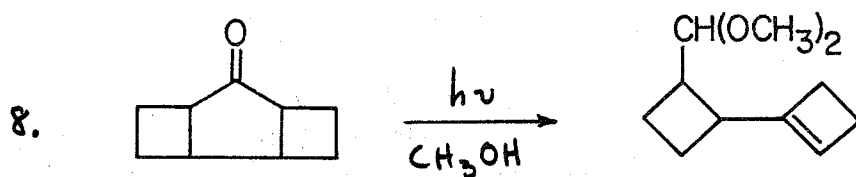
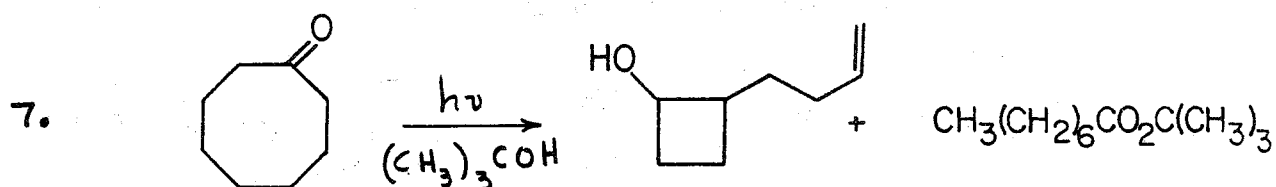
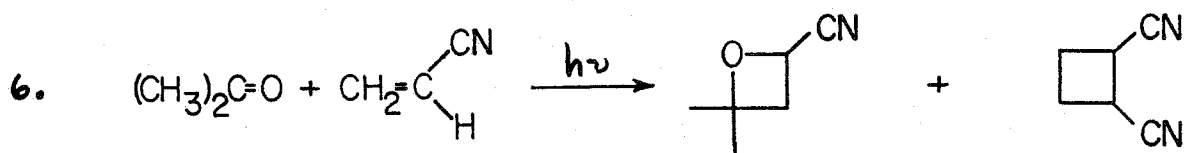
8.9 PROBLEMS

A. Rationalize the formation of the following products in terms of the primary photochemical processes discussed in this chapter. The ketones absorb the incident radiation in cases where there are more than one reactant.



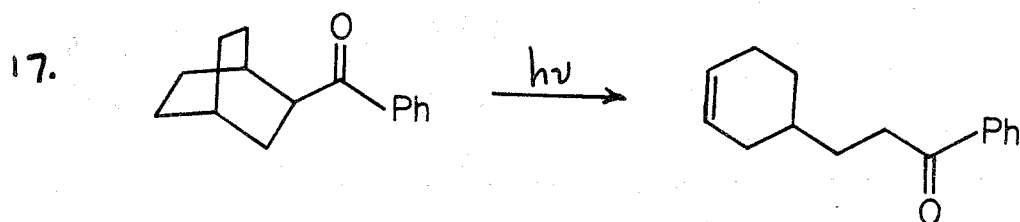
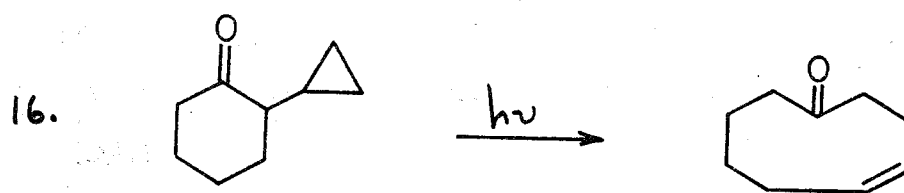
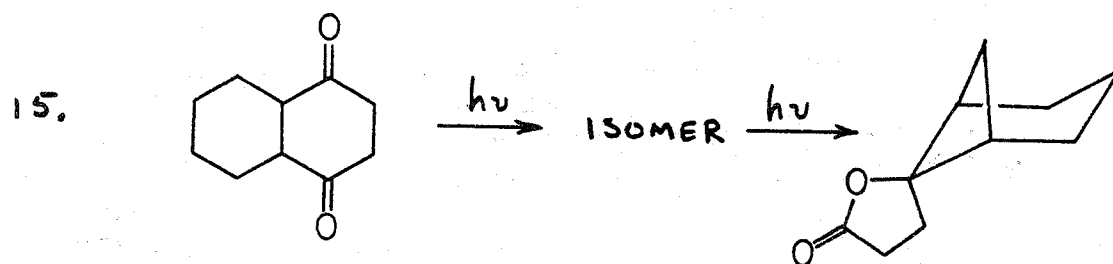
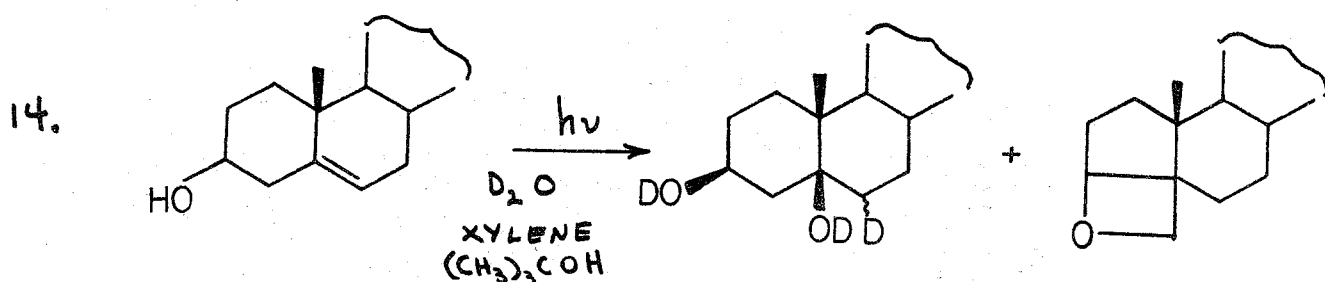
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8.9 A. (continued)

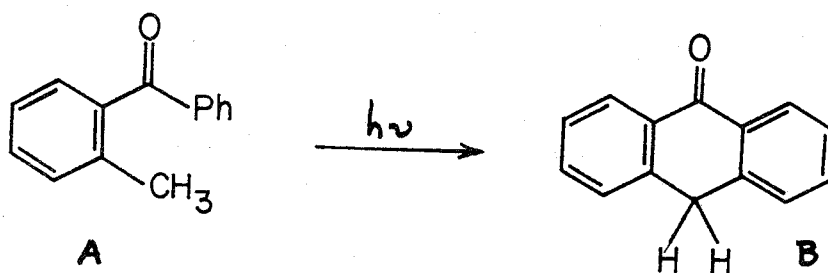


(continued)

8.9 A. (continued)

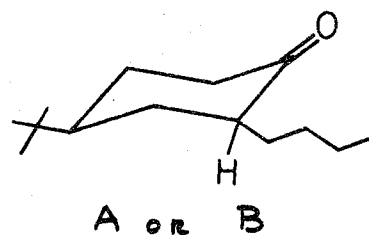
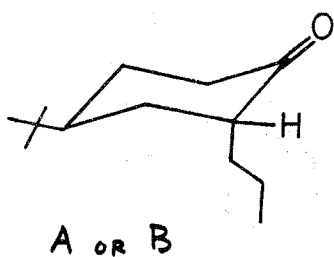


B. Prolonged irradiation of 2-methylbenzophenone A with a broad band (200-500 nm) lamp, yields a small amount of the anthrone B. The reaction requires the presence of an oxidizing agent. Suggest a path for the conversion of A to B.



8.9 (continued)

- E. Two epimers are formed upon alkylation of 4-tert-butyl cyclohexanone. The relative fluorescence of epimer A to the fluorescence of epimer B is 4:1. Assign structures to A and B based on this information.

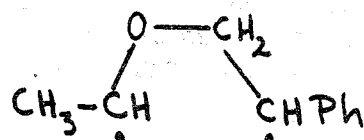


$$\frac{\phi_F^A}{\phi_F^B} = 4$$

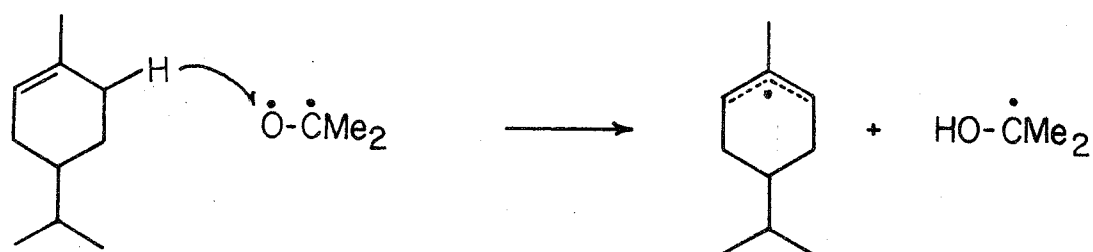
8.10 ANSWERS TO THE PROBLEMS

A.

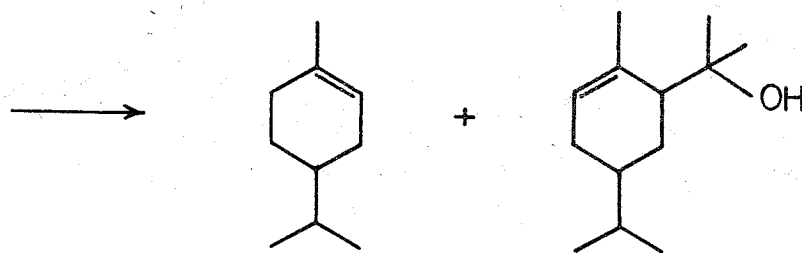
1.



2.



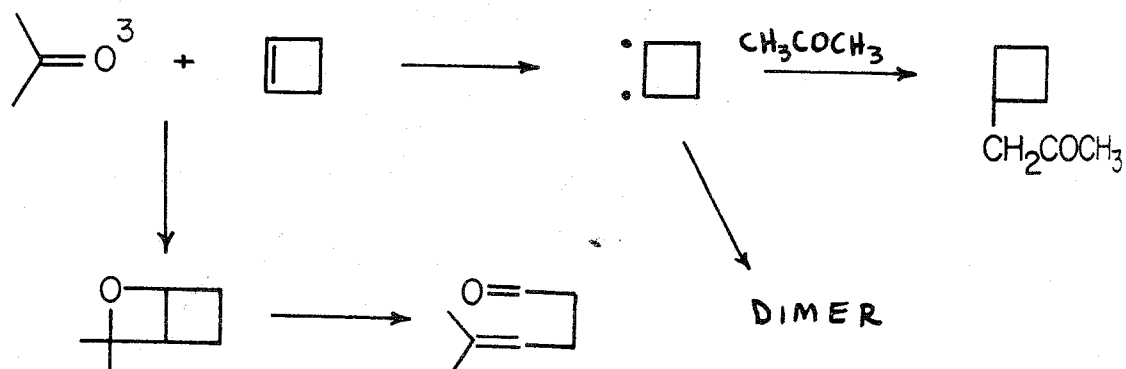
SYMMETRICAL



RACEMIC

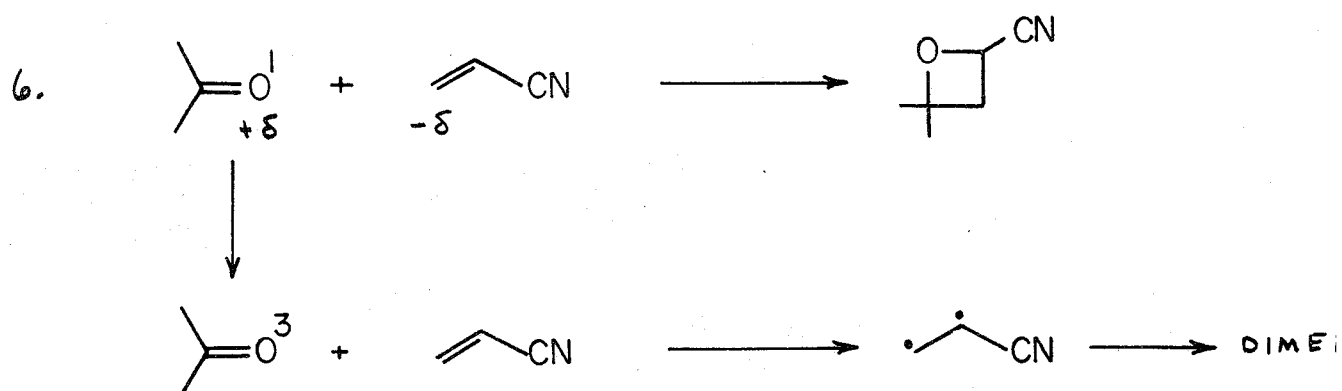
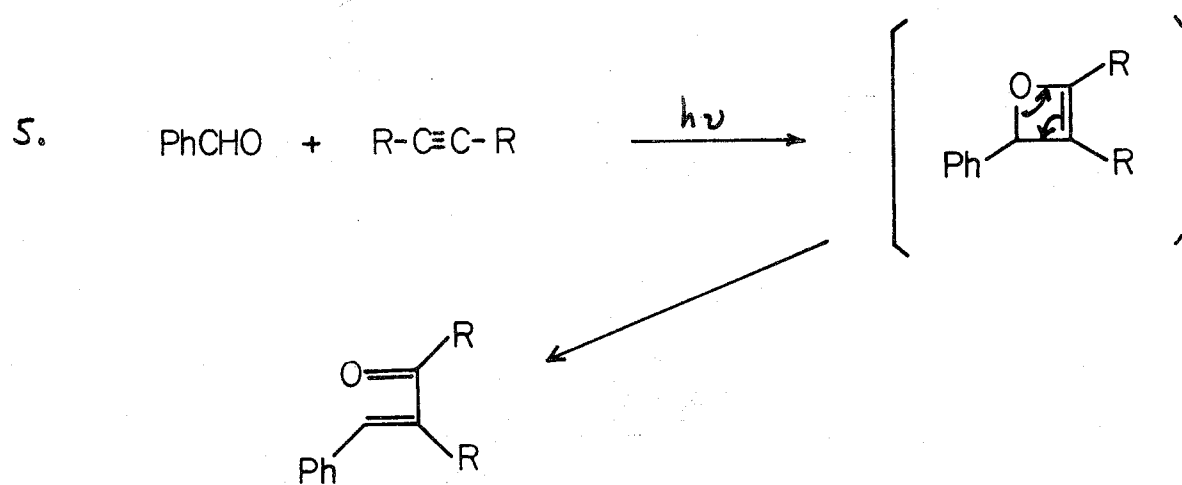
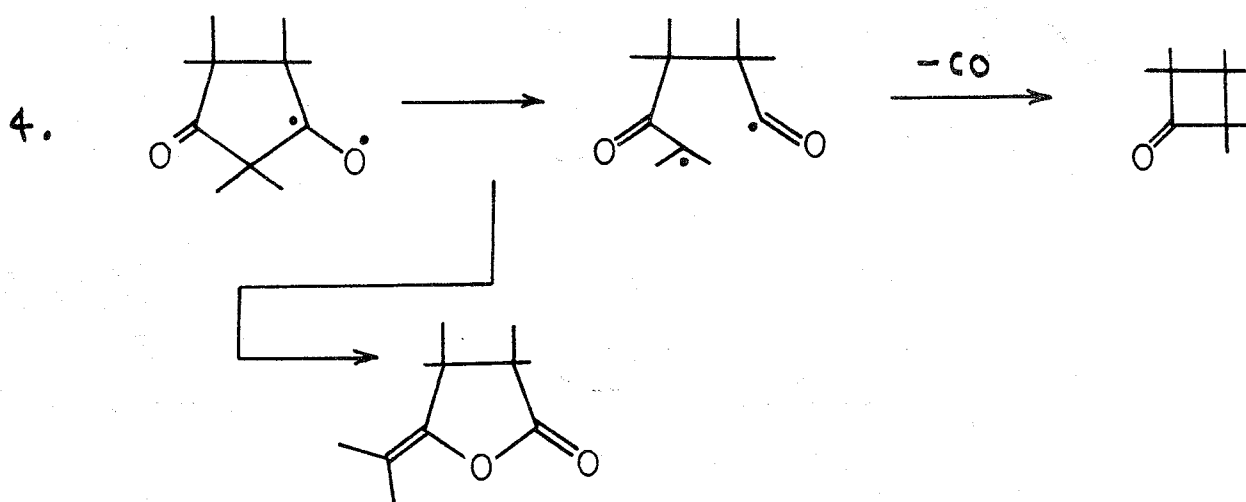
RACEMIC

3

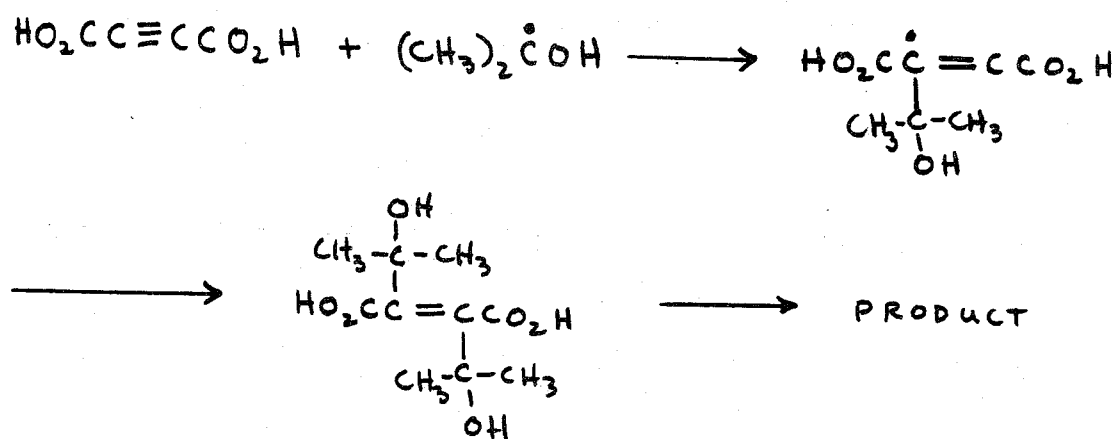
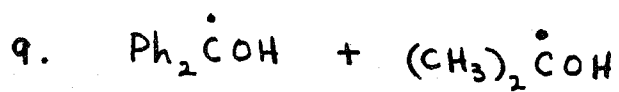
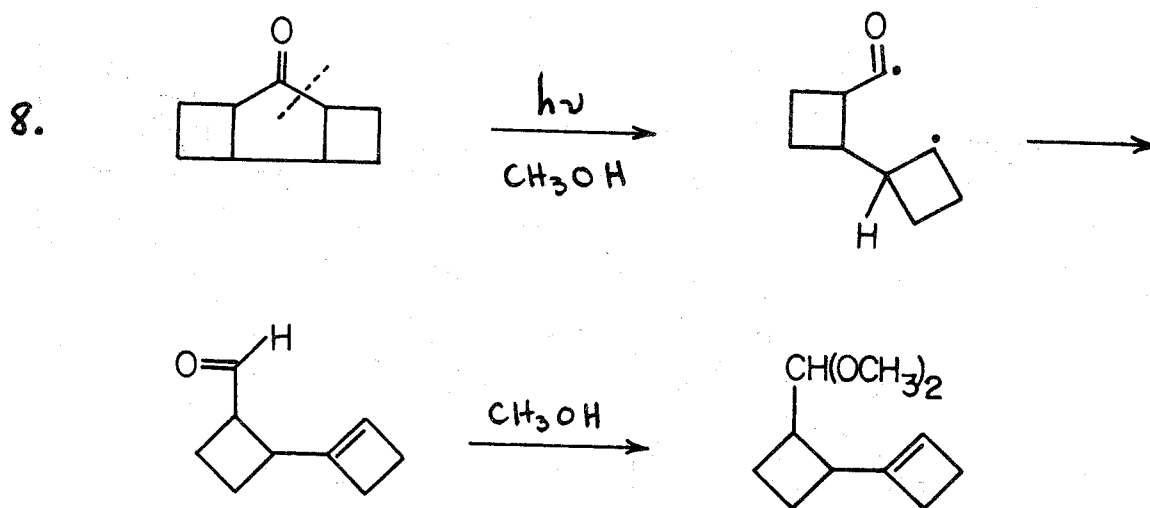
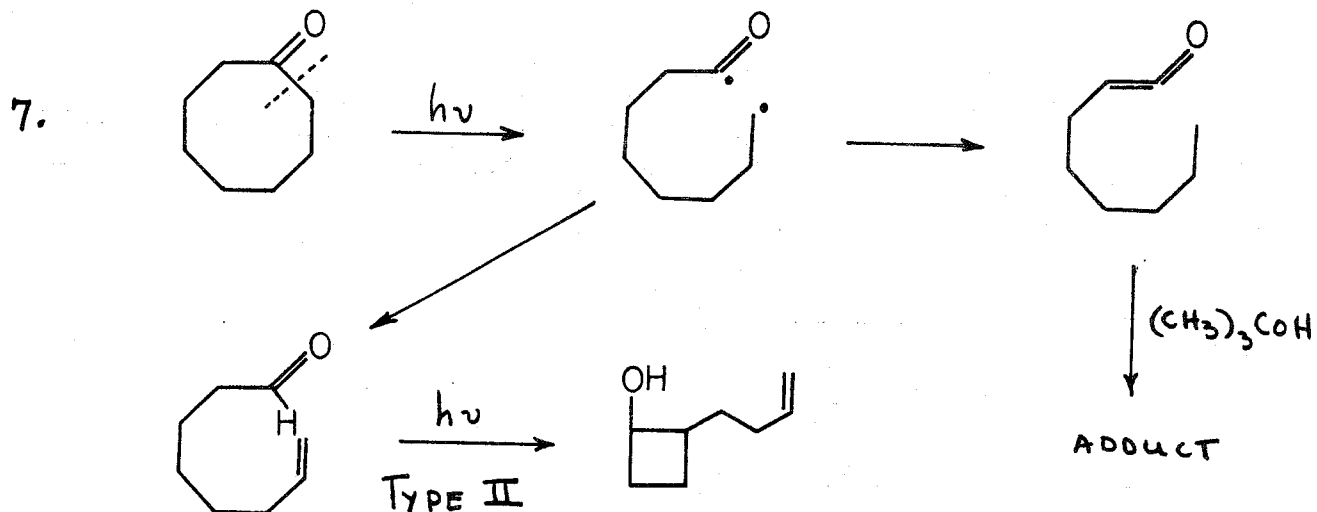


DIMER

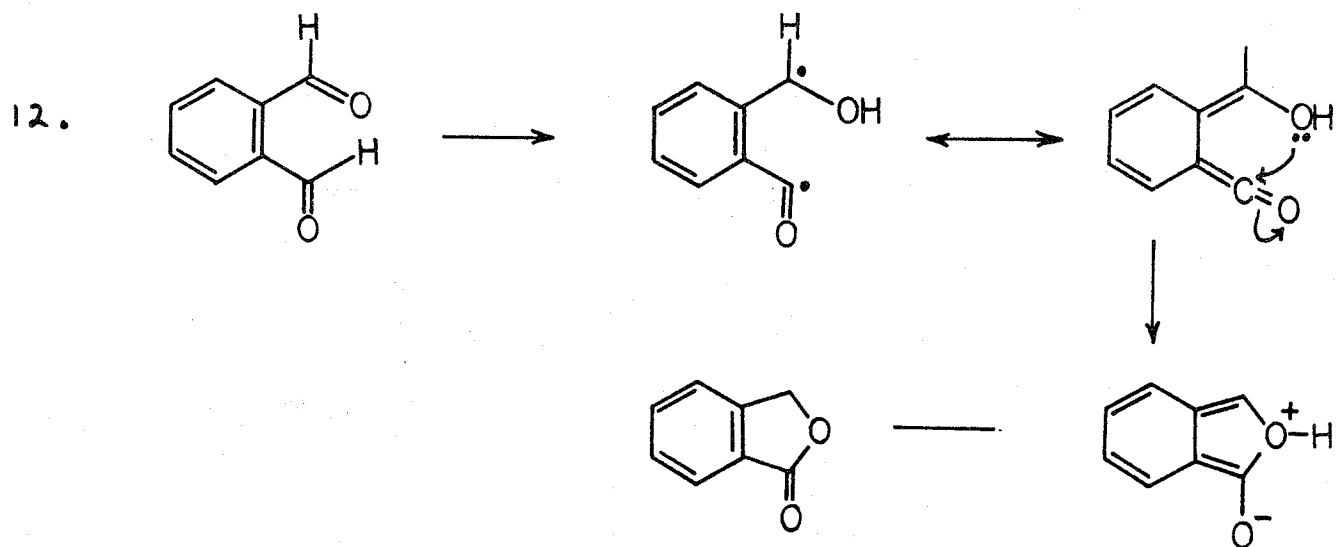
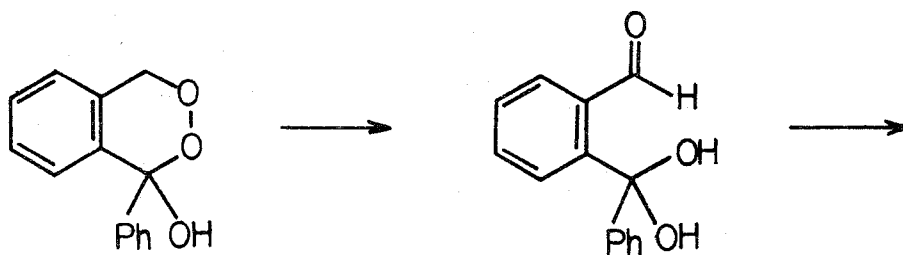
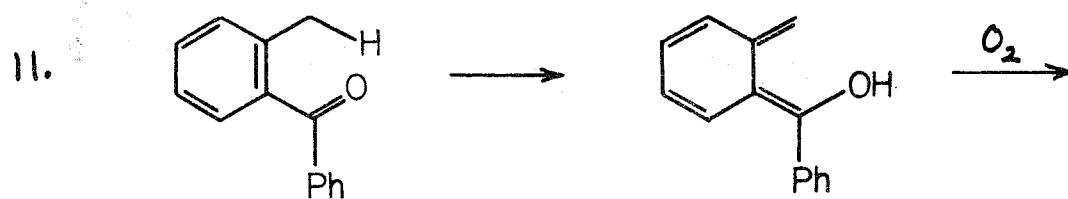
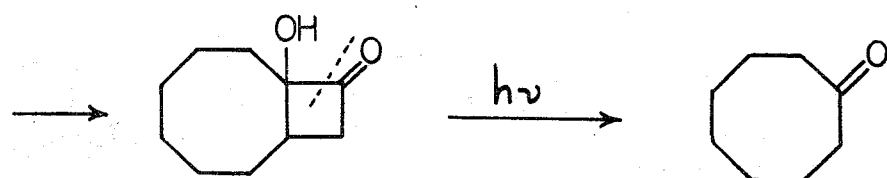
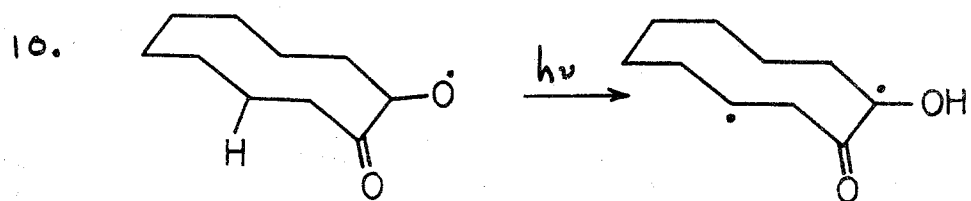
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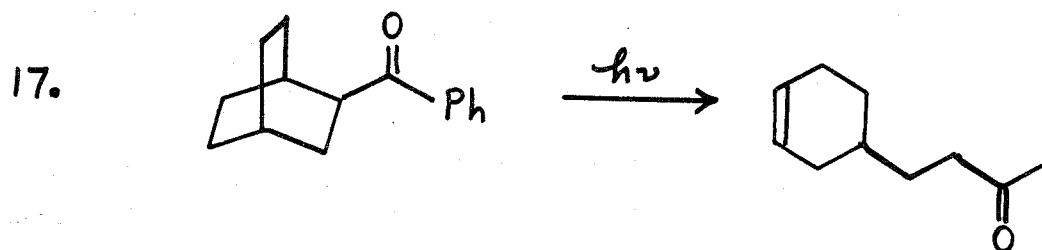
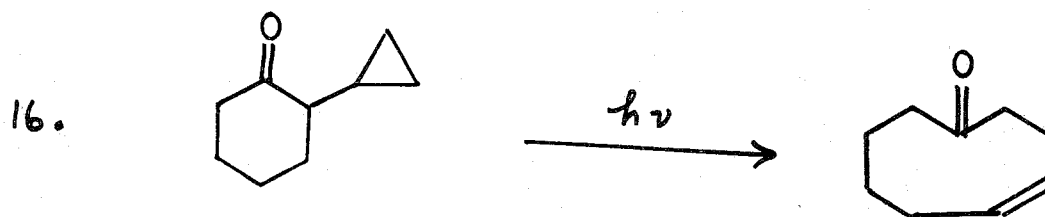
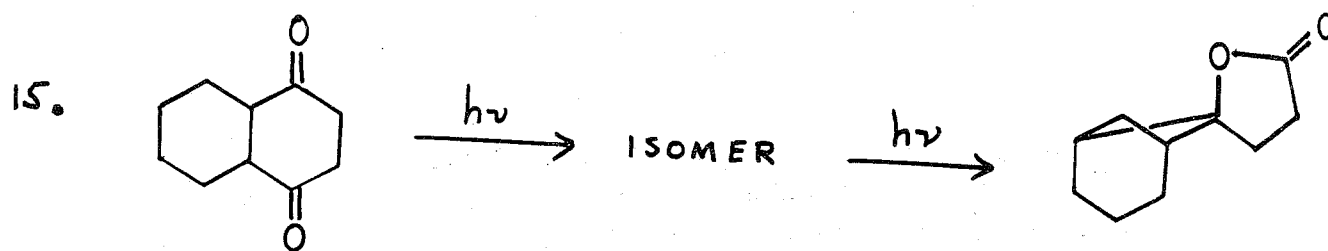
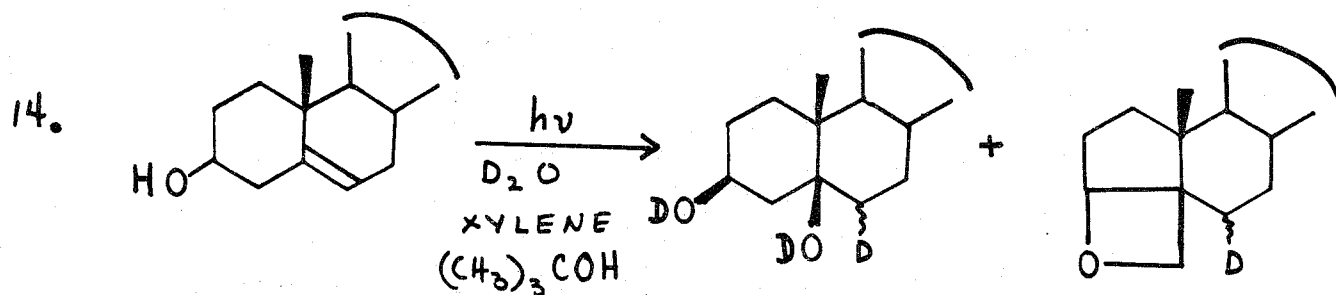
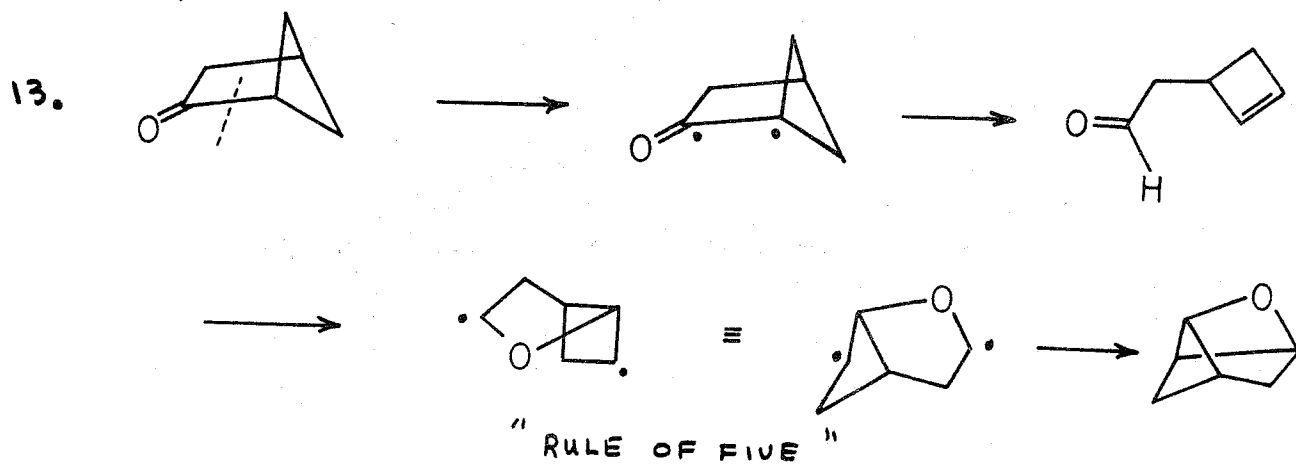
8.10 A. (continued)



8.10 A. (continued)

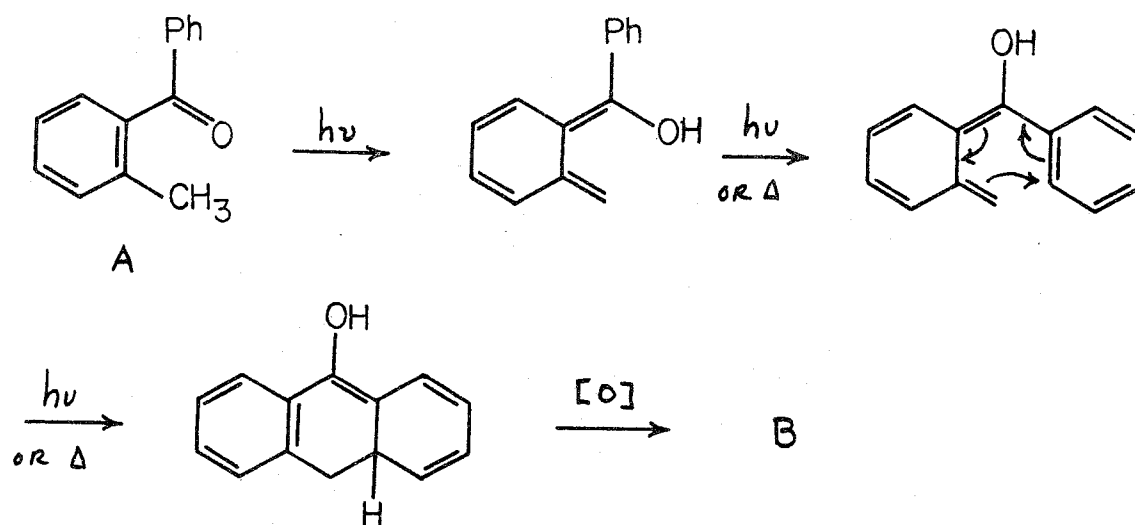


8.10 (continued)



8.10 (continued)

B.



C.

PLOT $\{\phi^0/\phi - 1\}$ VERSUS $[Q]$

FOR $(CH_3)_2C=CHCH_3$ $k_q\tau = 16 M^{-1}$

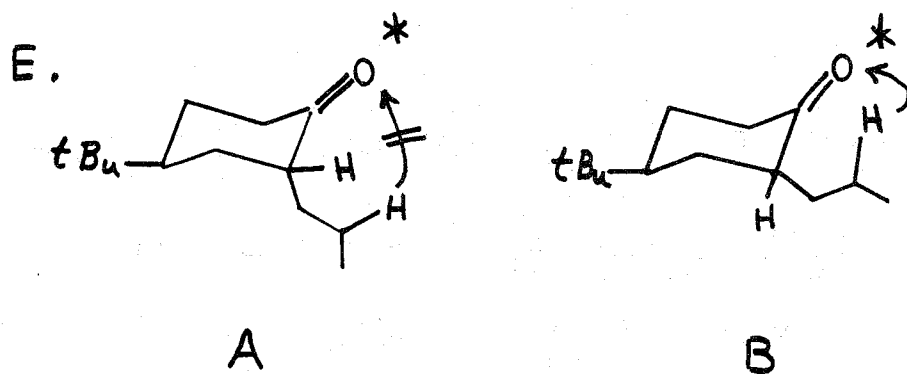
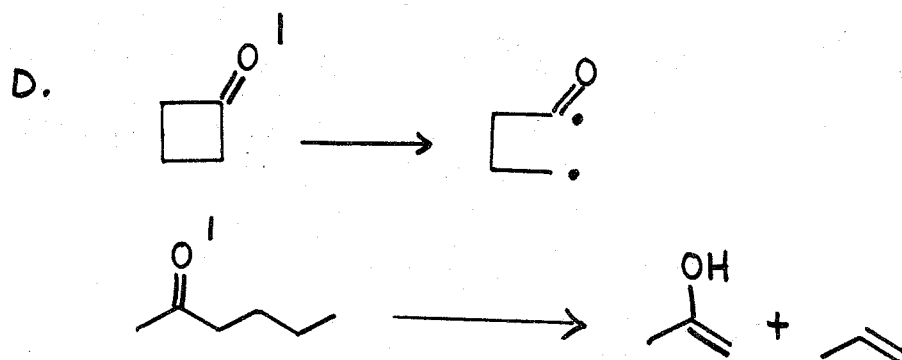
FOR $CHCl=CHCl$ $k_q\tau = 40 M^{-1}$

ASSUME $k_q = 5 \times 10^9 M^{-1} sec^{-1}$

k_q FOR $(CH_3)_2C=CHCH_3 = 1.1 \times 10^8 M^{-1} sec^{-1}$

k_q FOR $CHCl=CHCl = 2.9 \times 10^8 M^{-1} sec^{-1}$

8.10 (continued)



MORE FLUORESCENCE

CHAPTER 9
PHOTOCHEMISTRY OF CONJUGATED ENONES AND RELATED COMPOUNDS

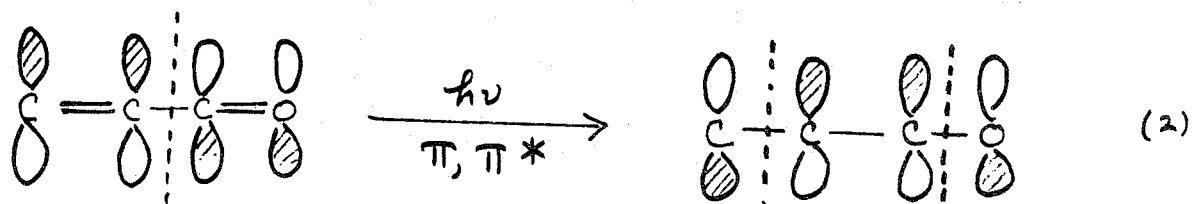
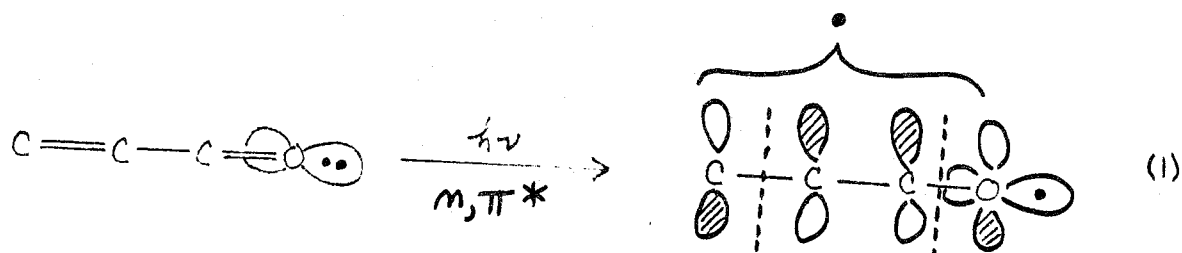
9.1 GENERAL CONSIDERATIONS

Rev: Org. Photochem., 1, 1 (1968); Adv. Photochem., 3, 81 (1966)

- A. Models for the electronically excited states of conjugated enones and related compounds
- B. Energetics and dynamics of the electronically excited states of conjugated enones and related compounds
- C. Primary photochemical processes of conjugated enones and related compounds

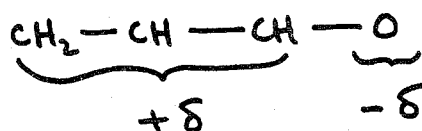
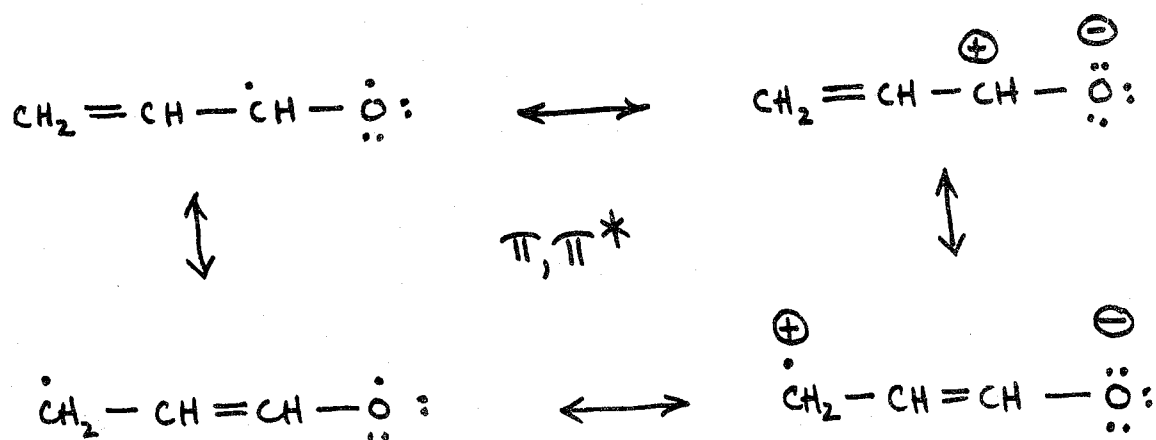
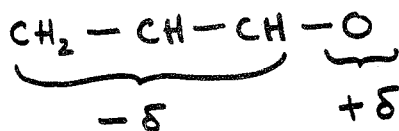
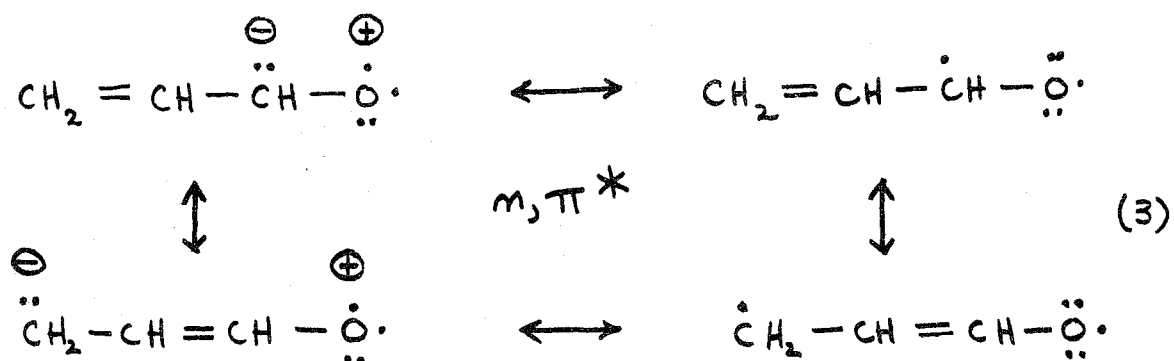
9.2 MODEL FOR ELECTRONICALLY EXCITED STATES

- A. n, π^* and π, π^* of enones
- B. Orbital description



9.2 (continued)

C. Valence bond description

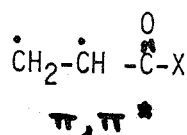


9.2 (continued)

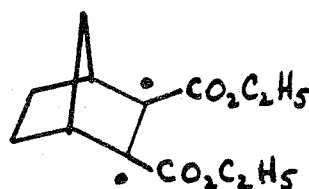
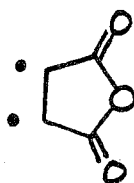
D. Conjugated acids and derivatives

1. n, π^* moves to higher energies

2.

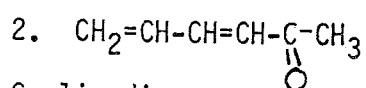
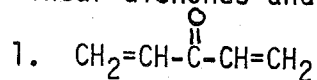


$\text{X} = \text{OR}, \text{NR}_2, \text{etc.}$

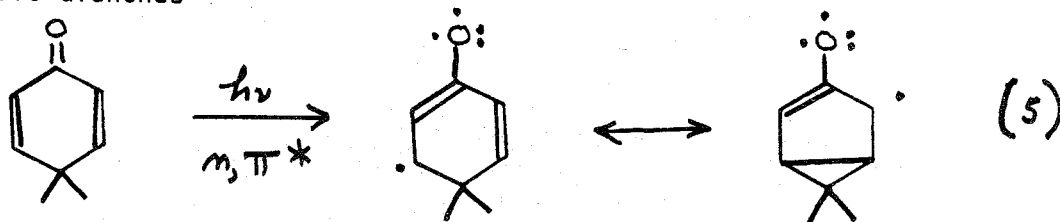


(4)

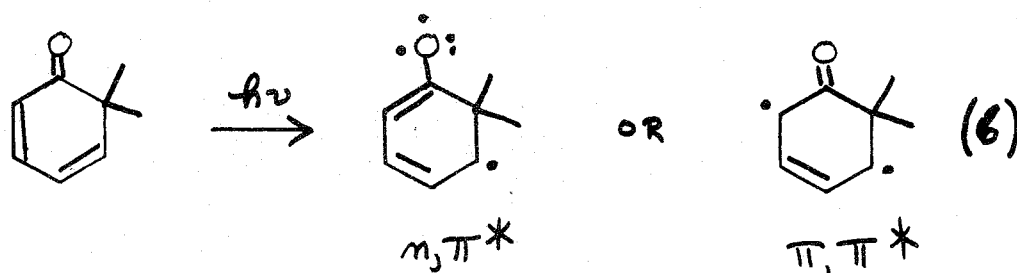
E. Linear dienones and enediones



F. Cyclic dienones



(5)



(6)

G. Summary

1. Both n, π^* and π, π^* reactivity anticipated

2. Configuration of S_1 and T_1 will determine reactivity

9.3 ENERGETICS AND DYNAMICS

A. Energetics (see Table 9-1 on p. 238)

1. Acyclic enones do not emit
2. For enones: $^1(n, \pi^*) \gg ^3(\pi, \pi^*) \sim ^3(n, \pi^*)$

B. Dynamics

1. $k_F \sim 10^7 \text{ sec}^{-1}$
2. $\phi_{ST} \sim 1.0$, therefore, $k_S \sim 10^9 \text{ sec}^{-1}$
3. $k_T \sim 10^7 \text{ sec}^{-1}$

C. Energy diagram of an enone

Figure 9-1

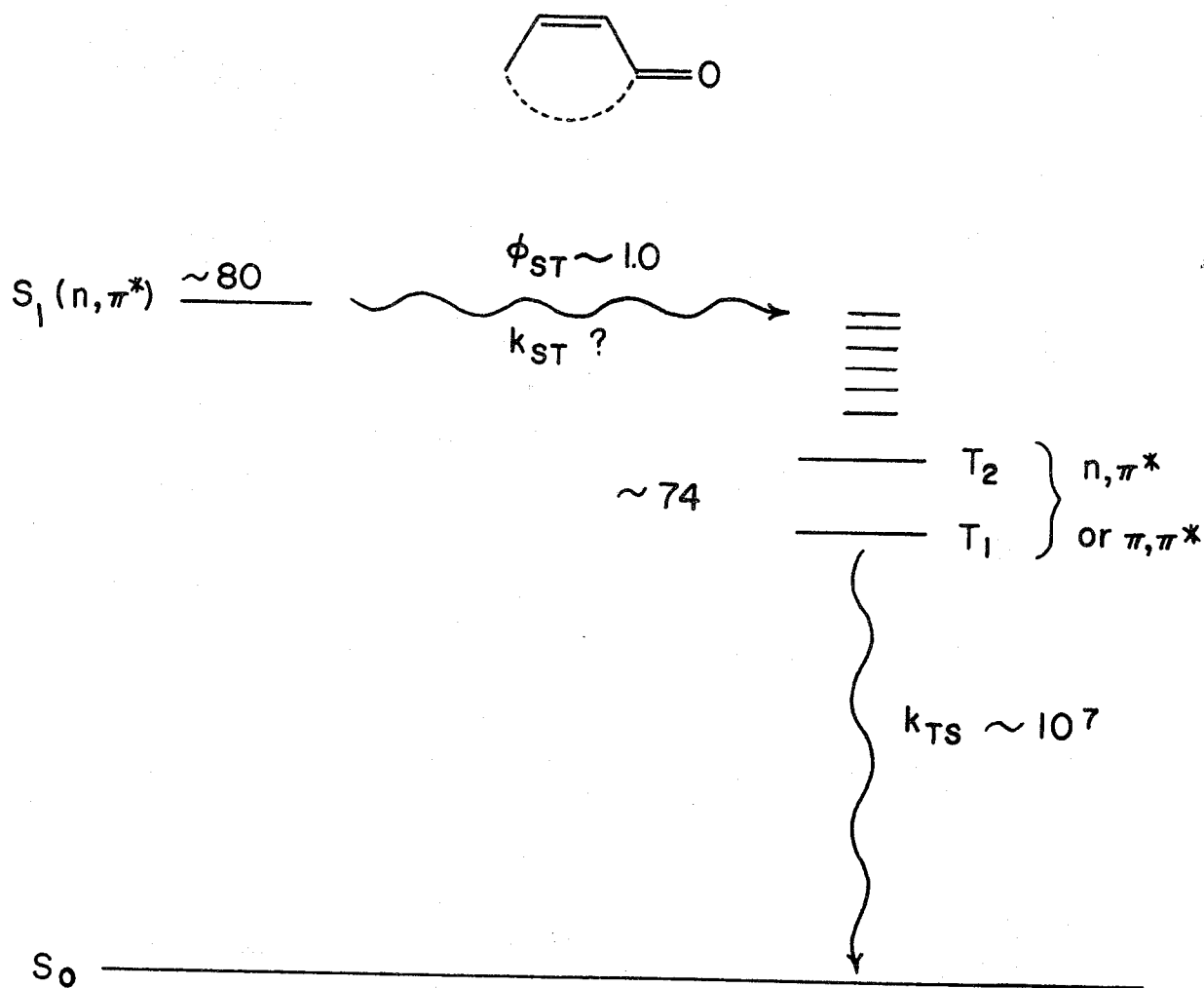
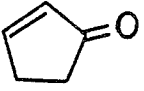
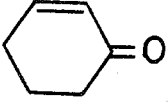
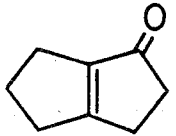
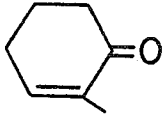
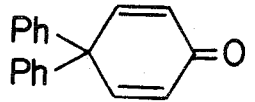
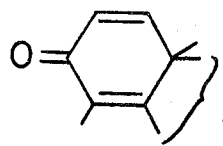



Table 9-1

| <u>Molecule</u> | E_1 | E_3 |
|--|-----------|--|
| $\text{CH}_2=\text{CH}-\text{CHO}$ | 74 | 70 |
|  | 83 | 74 |
|  | 80 | 75 (n, π^*) 74 (π, π^*) |
|  | 81 | 75 |
|  | ~ 76 | 76 (n, π^*) 68 (π, π^*) |
|  | ~ 78 | 69 (n, π^*) |
|  SANTONIN | — | 70 (π, π^*) |
| $\text{CH}_3(\text{CH}=\text{CH})_3\text{CHO}$ | — | 44 (π, π^*) |
| $\text{CH}_3(\text{CH}=\text{CH})_4\text{CHO}$ | — | 36 (π, π^*) |
| $\text{CH}_3(\text{CH}=\text{CH})_5\text{CHO}$ | — | 32 (π, π^*) |
|  | 56 | 50 (n, π^*) |

9.4 PRIMARY PHOTOCHEMICAL PROCESSES

A. cis-trans-Isomerization

1. Review section 6.5
2. Similar to alkene-polyene photochemistry

B. Hydrogen abstraction

1. Review sections 6.6 and 8.6
2. May be initiated by n, π^* and/or π, π^*

C. Cycloadditions and cycloeliminations

1. Review sections 6.7 and 8.7
2. May be initiated by n, π^* and/or π, π^*

D. Electrocyclic openings and closures

1. Review section 6.8
2. Expected to be π, π^* reaction

E. Sigmatropic rearrangement

1. Review section 6.9
2. Usually π, π^* rearrangements

F. α -Cleavage reactions

1. Review section 8.5
2. Expected to be n, π^* reaction
3. Compare to electrocyclic ring openings

G. Miscellaneous

1. Fragmentations of weak bonds
2. Additions and rearrangements

H. Summary

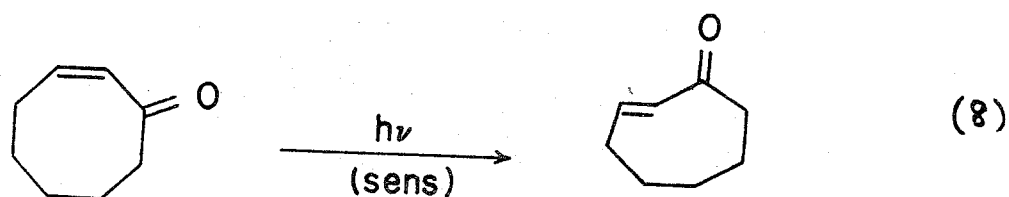
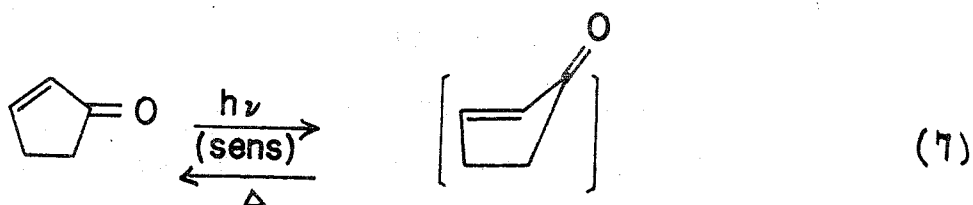
1. Reactions determined by S_1 and T_1 configurations
2. Chemistry of n, π^* and π, π^* good starting point

9.5 cis-trans-ISOMERIZATION

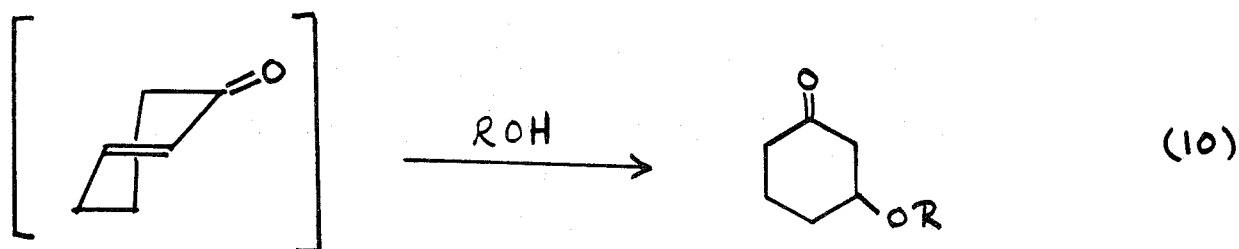
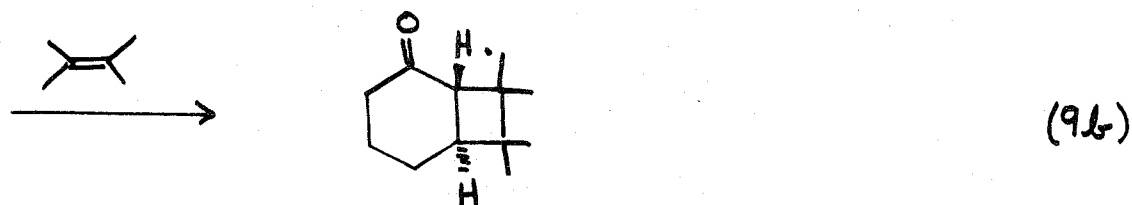
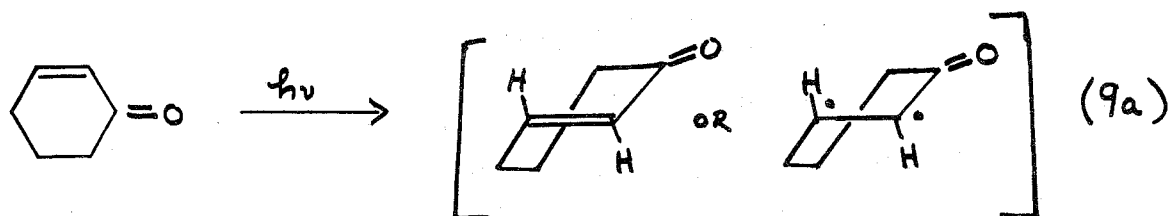
A. Acyclic systems: comparable to alkenes and conjugated polyenes.
Direct or sensitized

B. Cyclic systems

1. Generation of strained trans-cycloalkenones

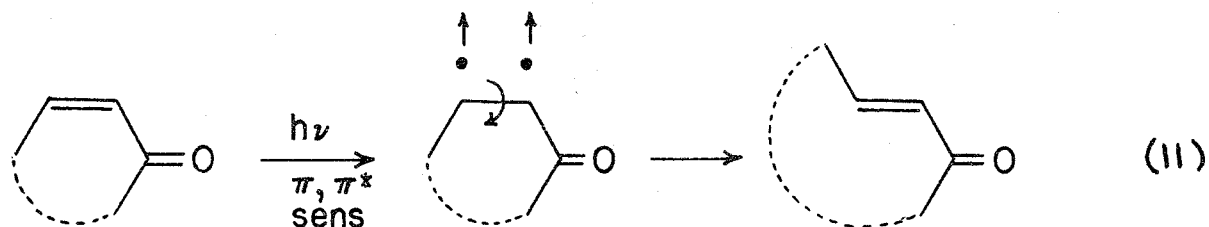


2. Possible intermediates in cycloaddition, solvent addition:
compare cyclic alkenes



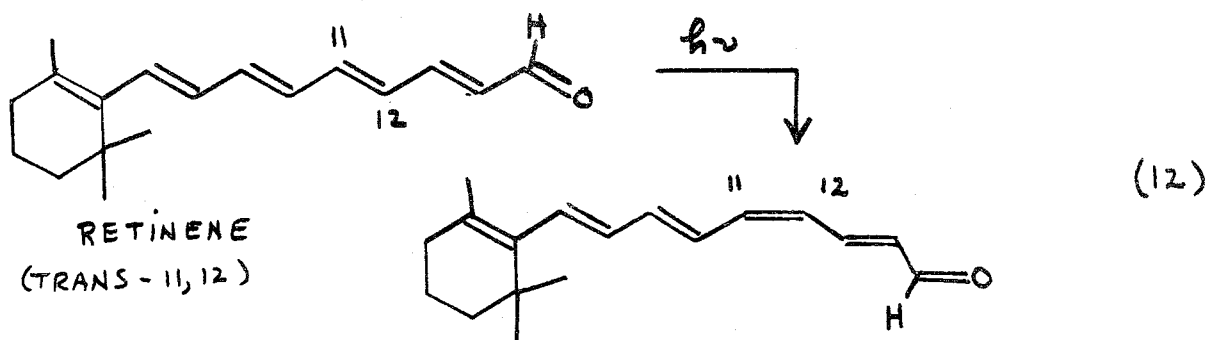
9.5 (continued)

C. Mechanism



D. Photobiology: The mechanism of vision

Rev: Sci. American, 216, 36 (1967)



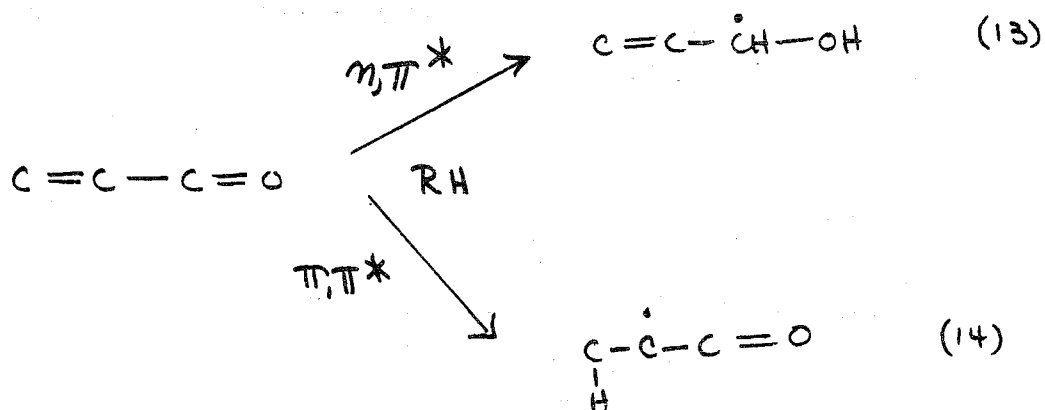
E. References

- (8) Tetrahedron Letters, 2025 (1968)
- (9) J. Amer. Chem. Soc., 86, 485 (1964); J. Org. Chem., 34, 811 (1969)
- (10) Israel J. Chem., 7, 49 (1969)

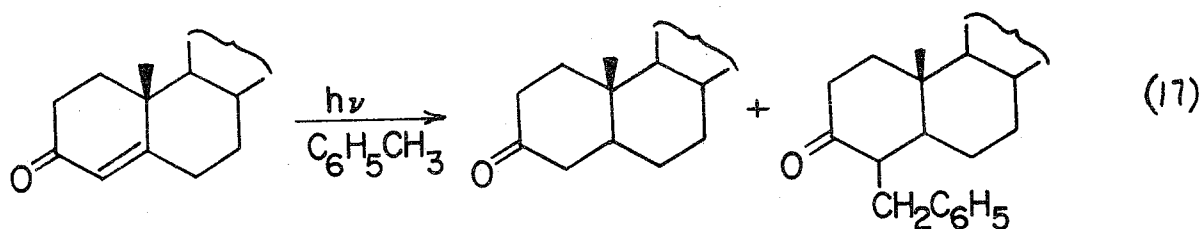
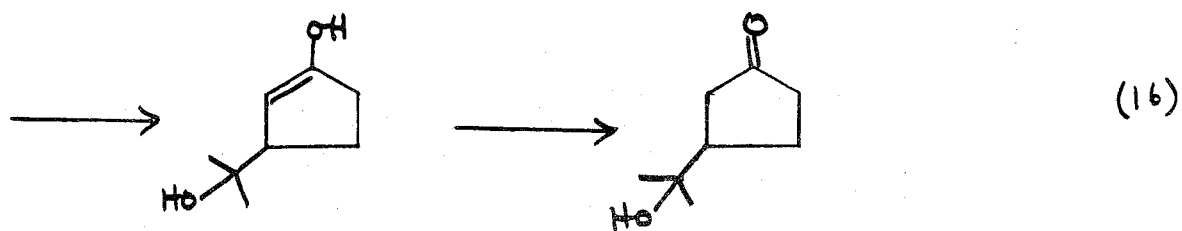
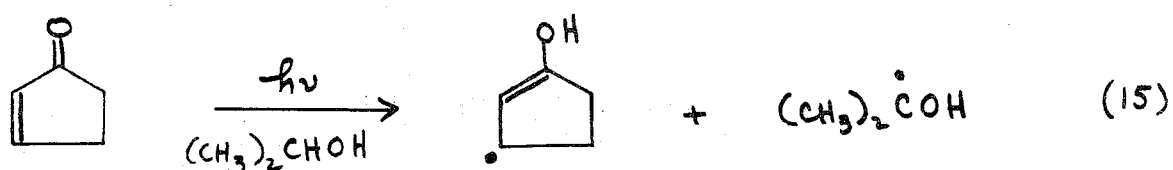
9.6 HYDROGEN ABSTRACTION

A. Intermolecular: usually not important unless other processes inhibited and good hydrogen donor is present

1. May be initiated by n, π^* (oxygen abstraction) or by π, π^* (carbon abstraction)
2. Products determined by behavior of ketyl radicals produced in the first step



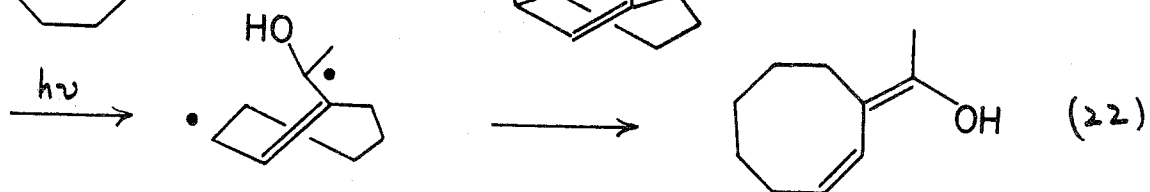
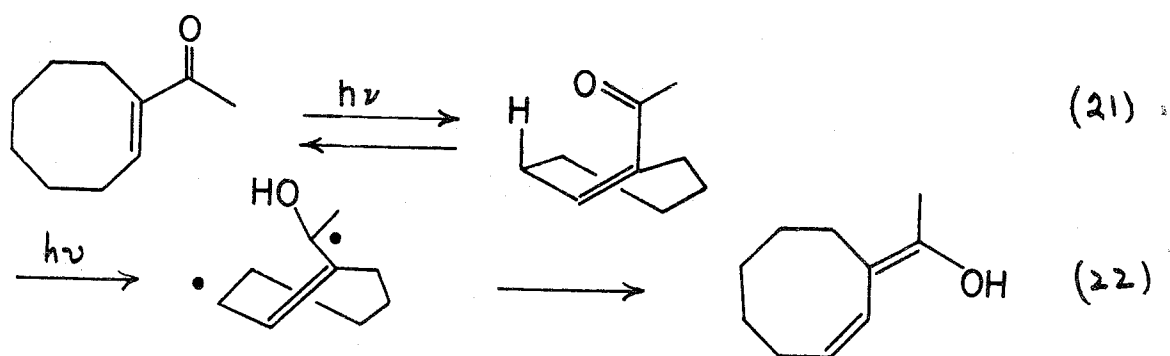
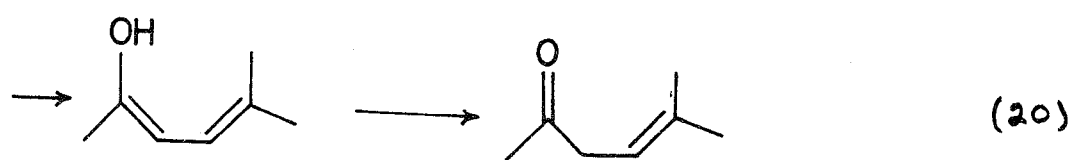
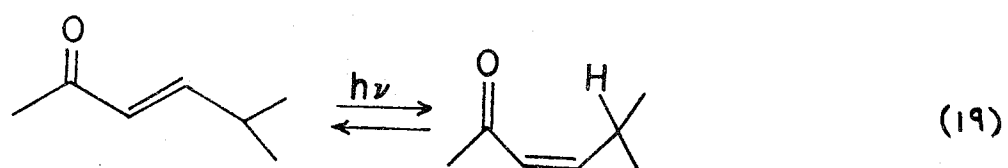
3. Ketone may be regenerated via enol



9.6 (continued)

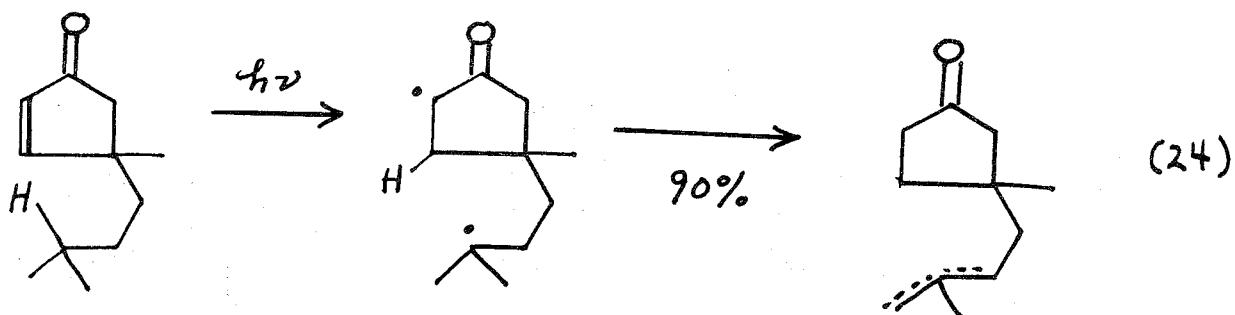
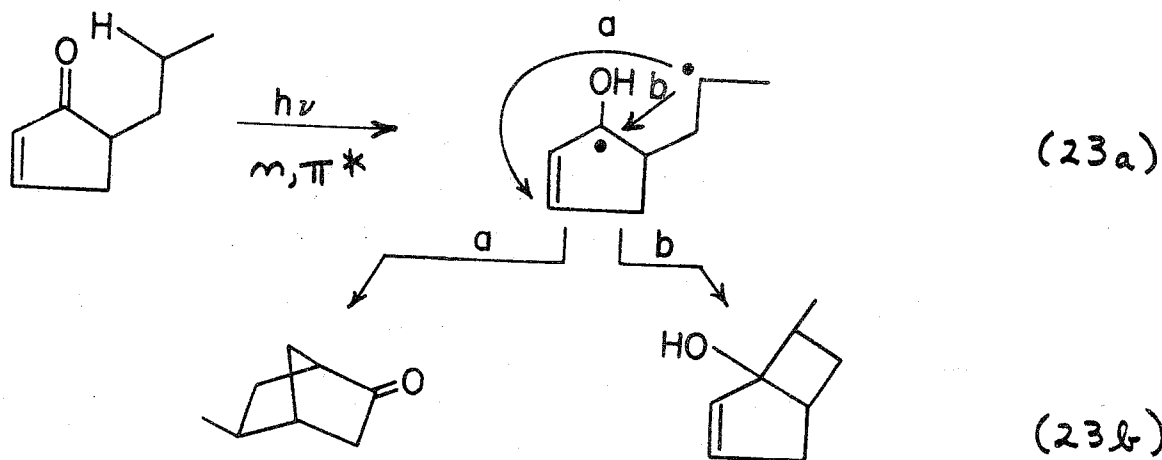
B. Intramolecular

1. Deconjugation: [1,3] shifts



9.6 B. (continued)

2. Type II analogues



C. References

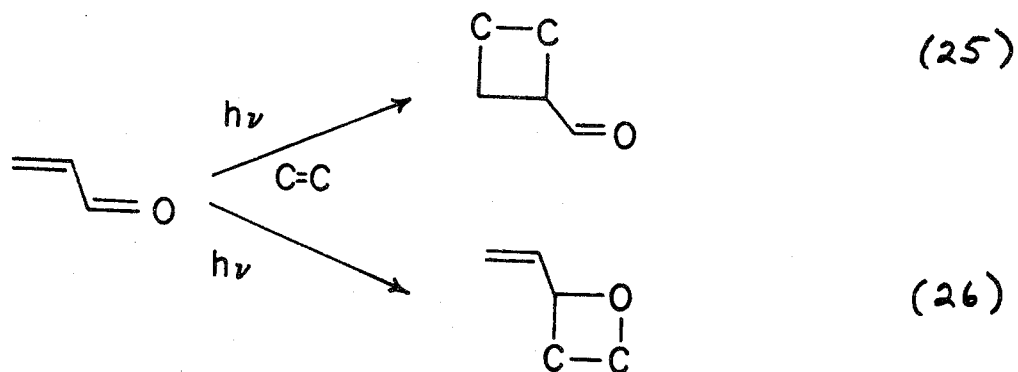
- (15) and (16) Can. J. Chem., **46**, 2535 (1968)
- (17) and (18) Chimia, **23**, 182 (1969)
- (19) and (20) Tetrahedron Letters, 1203 (1964)
- (21) and (22) J. Amer. Chem. Soc., **92**, 6699 (1970)
- (23) Chem. Commun., 343 (1971)
- (24) J. Amer. Chem. Soc., **94**, 7797 (1972)

9.7 CYCLOADDITIONS AND CYCLOELIMINATIONS

A. Dimerizations and "cross" additions

Rev: Accounts Chem. Research, 1, 65 (1968)

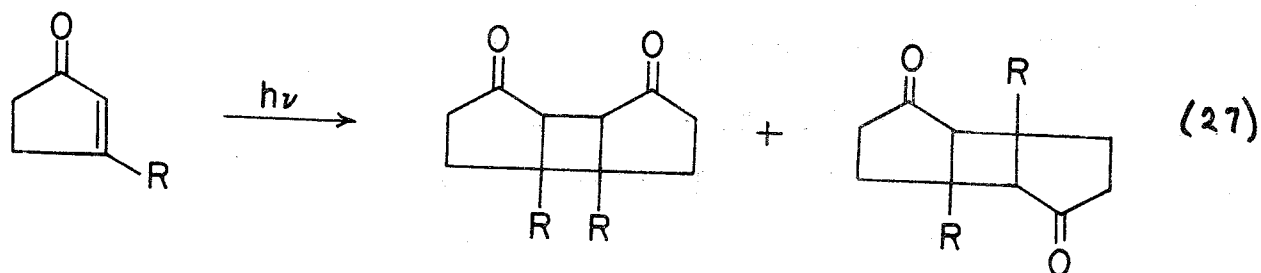
1. Addition to C=C more common than addition to C=O



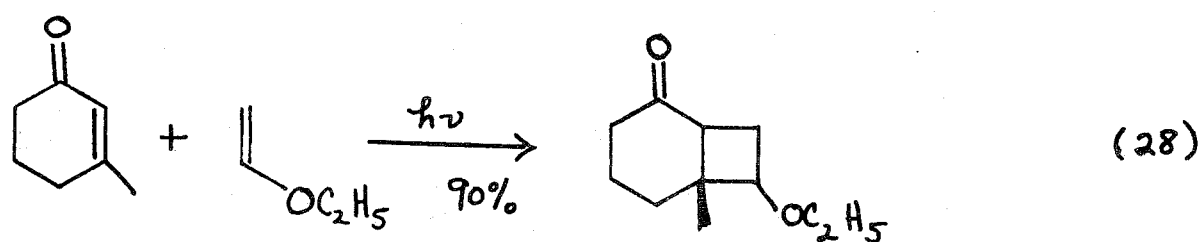
2. π, π^* may be lower than n, π^* or just more reactive

9.6 (continued)

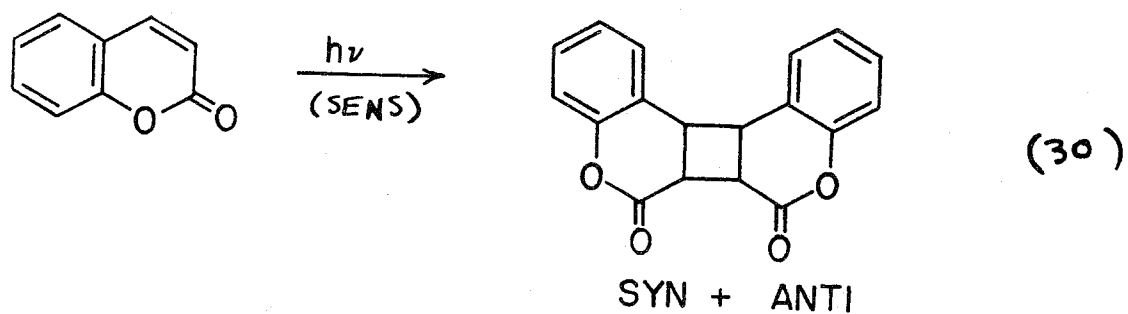
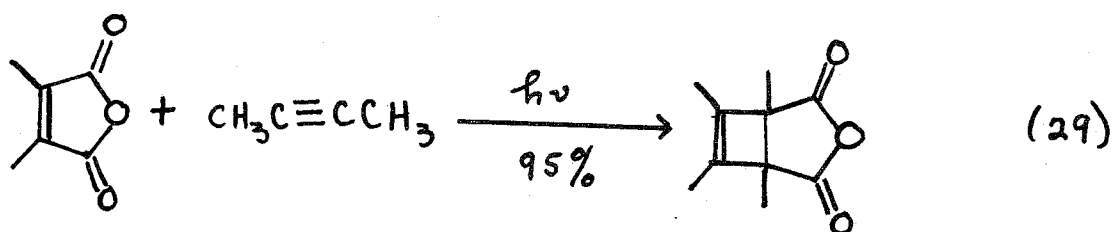
B. Intermolecular



1. Triplet reactions
2. Solvent dependence of product ratios
3. Not very stereoselective



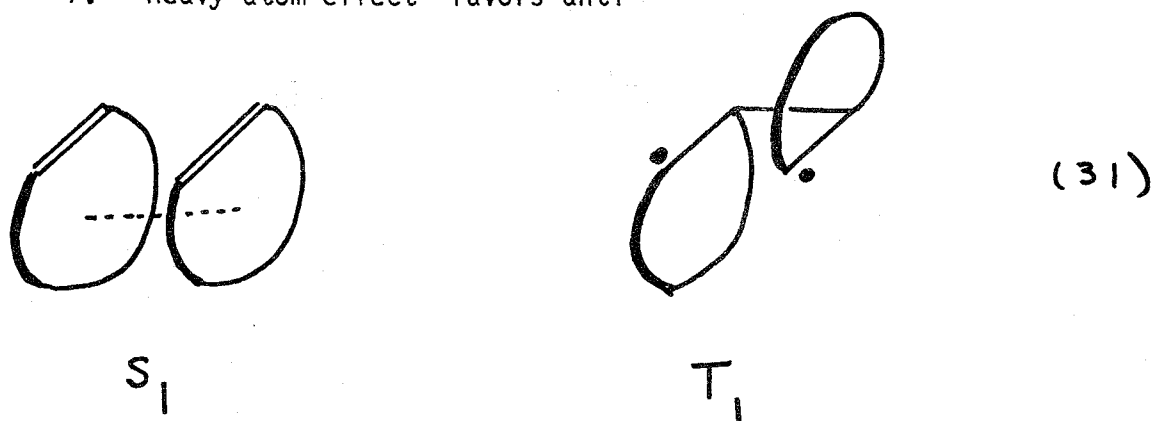
4. $\text{CH}_2=\text{C}(\text{OCH}_3)_2 \gg \text{CH}_2=\text{C}(\text{CH}_3)_2 \gg \text{CH}_2=\text{CHCN}$
5. Stereoselectivity suggests charge transfer



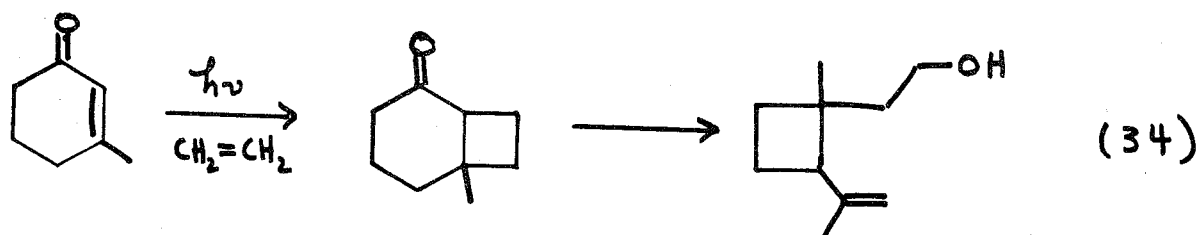
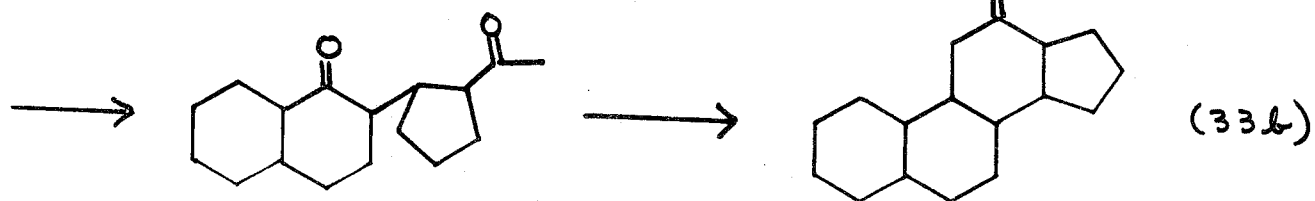
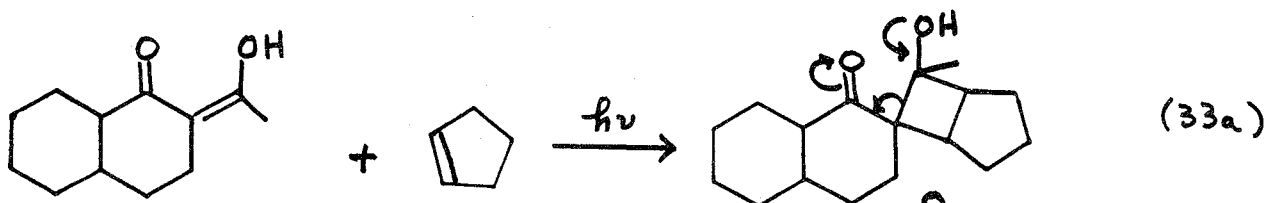
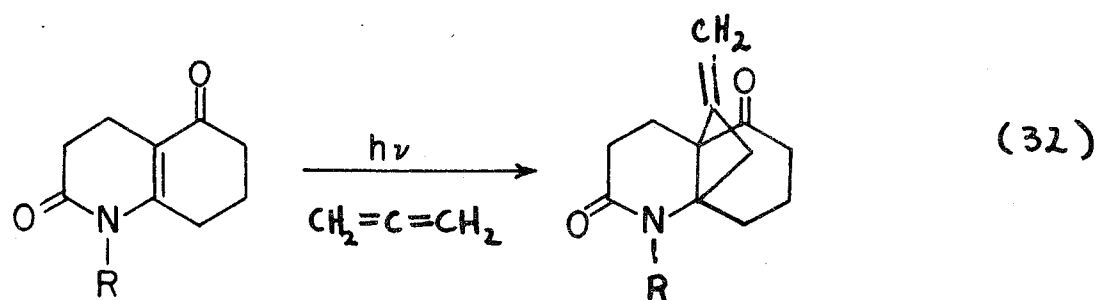
9.6 B. (continued)

6. S_1 favors syn(exciplex); T_1 favors anti (biradical)

7. "Heavy atom effect" favors anti



C. Synthetic applications



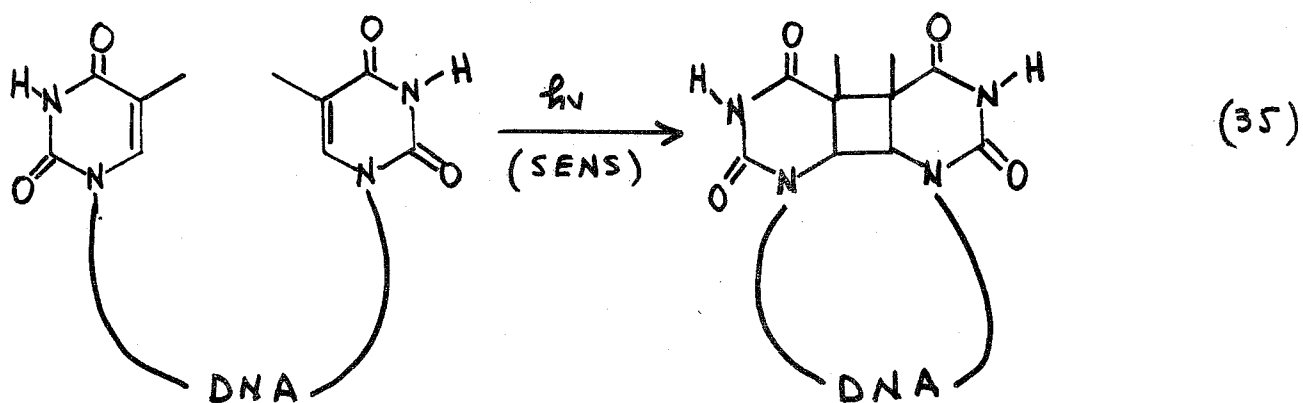
COTTON BOLL WEEVIL
SEX ATTRACTANT

9.7 (continued)

D. Photobiology: Photodynamic action

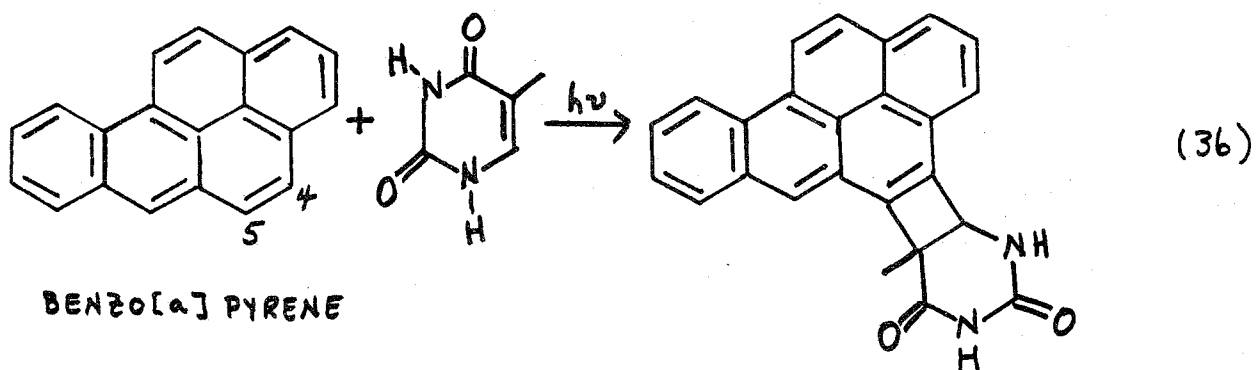
Rev: Prog. Org. Biol. and Medicinal Chem., 3, North Holland, Amsterdam (1970); "Introduction to Photobiology," Ed., C.P. Swanson, Prentice-Hall, Engelwood Cliffs, New Jersey, 1969

1. Dimerization of pyrimidine bases



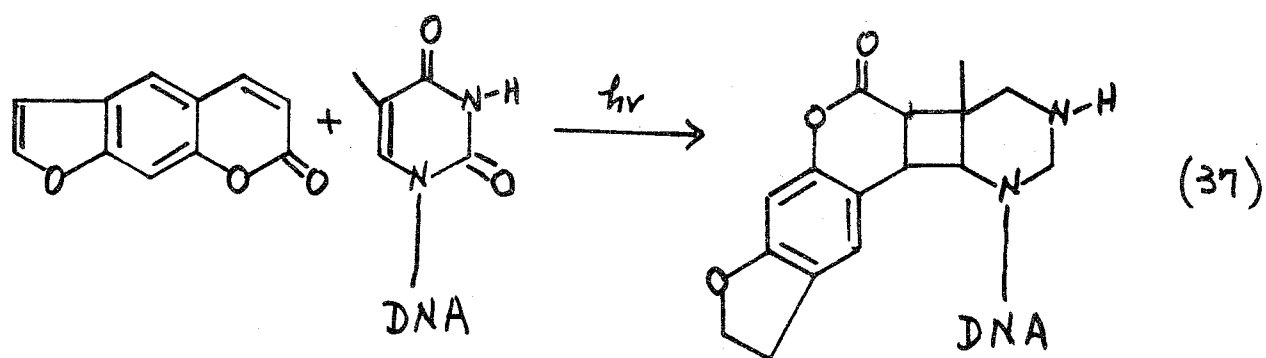
2. Carcinogenic effects

Rev: H.F. Blum, "Carcinogenesis by Ultraviolet Light," Princeton University Press, 1959



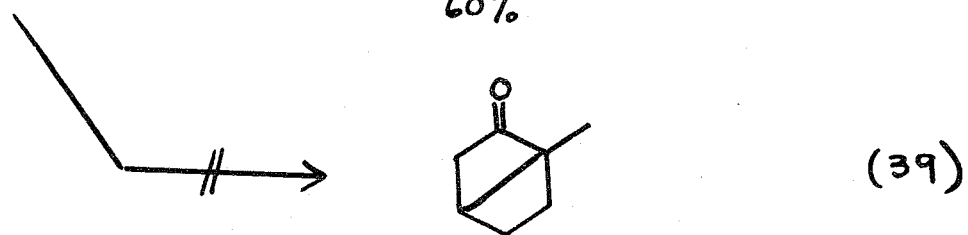
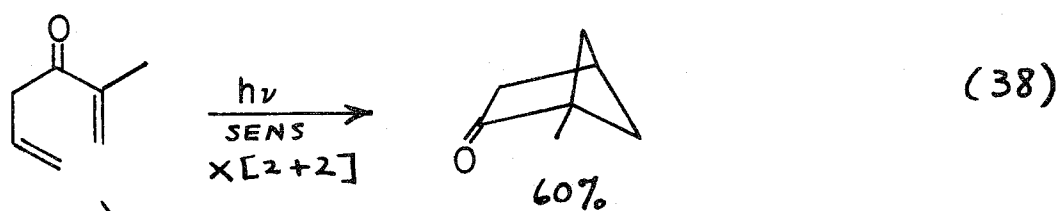
9.7 D. (continued)

3. Photosensitization by drugs: furocoumarins



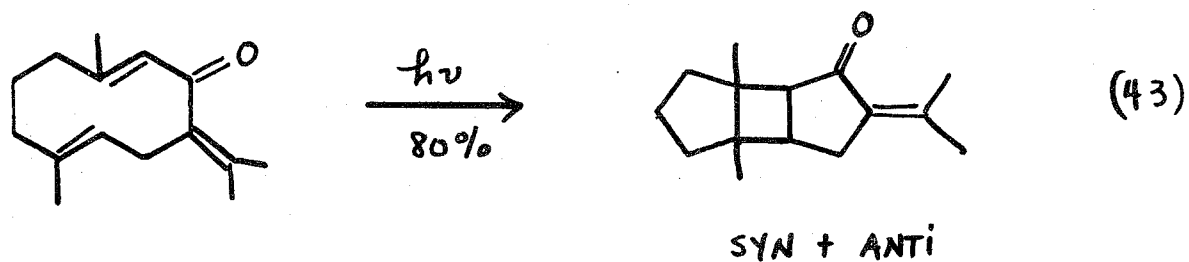
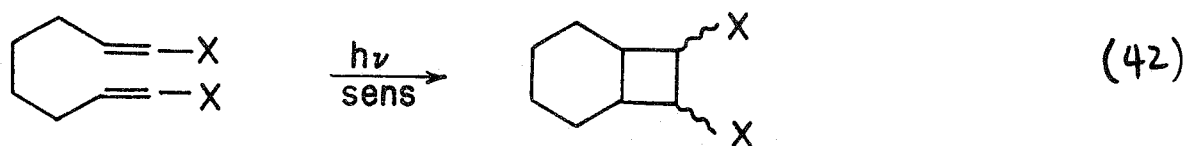
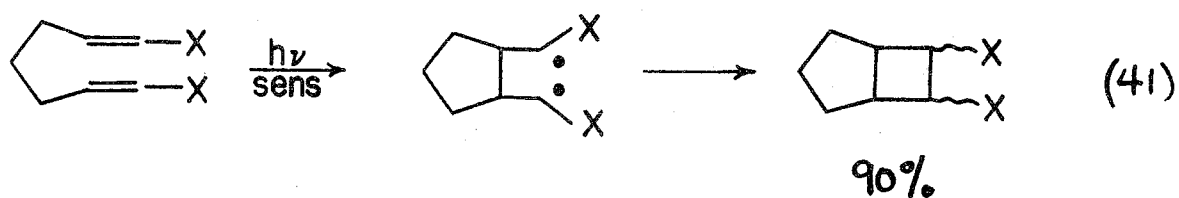
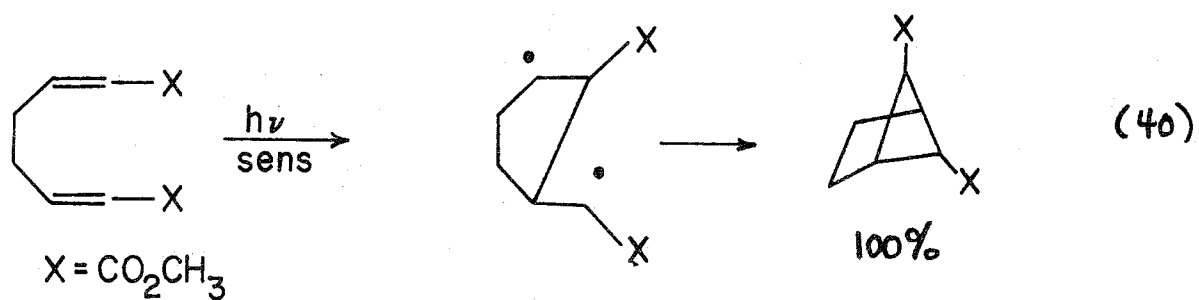
E. Intramolecular

1. Usually T_1
2. "Rule of 5" again



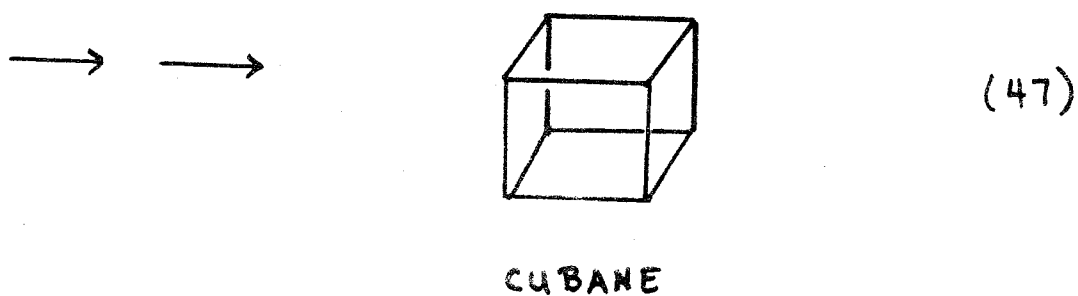
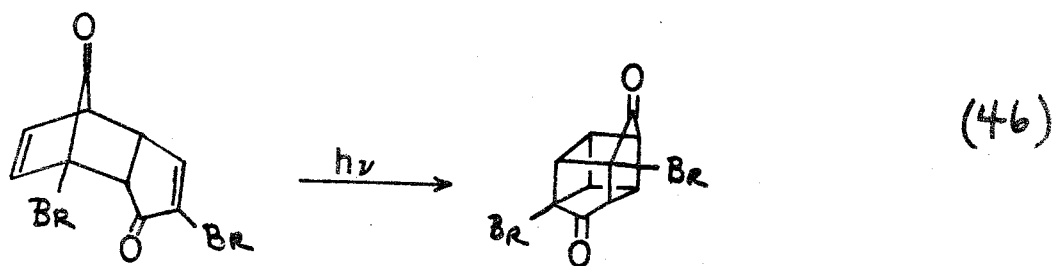
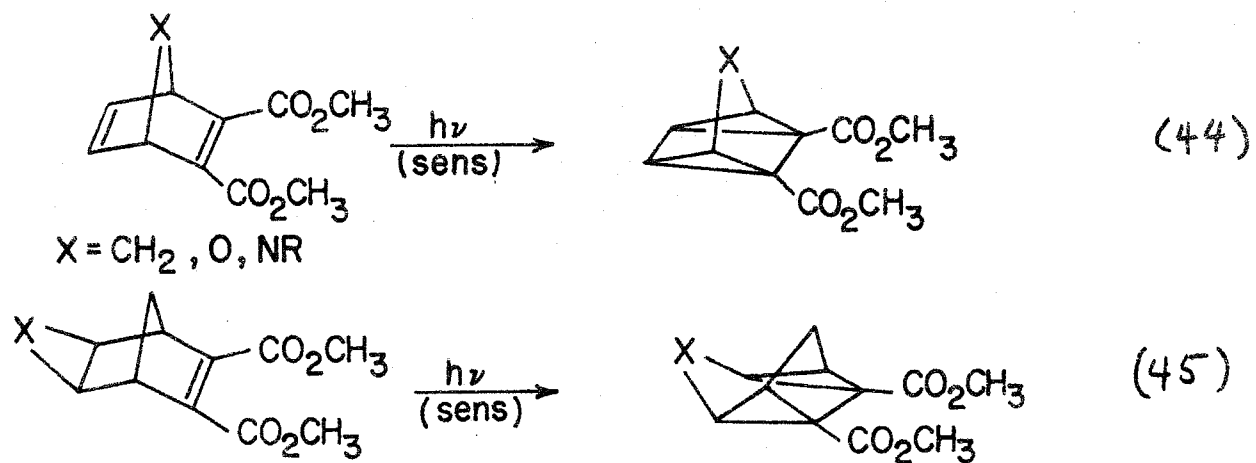
9.7 E. (continued)

3. Synthetic applications



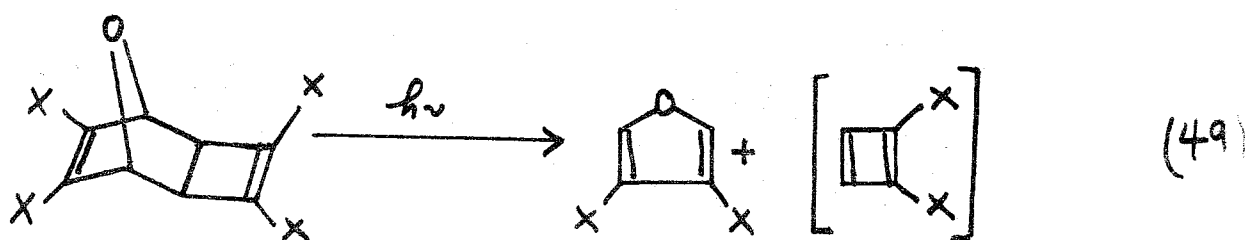
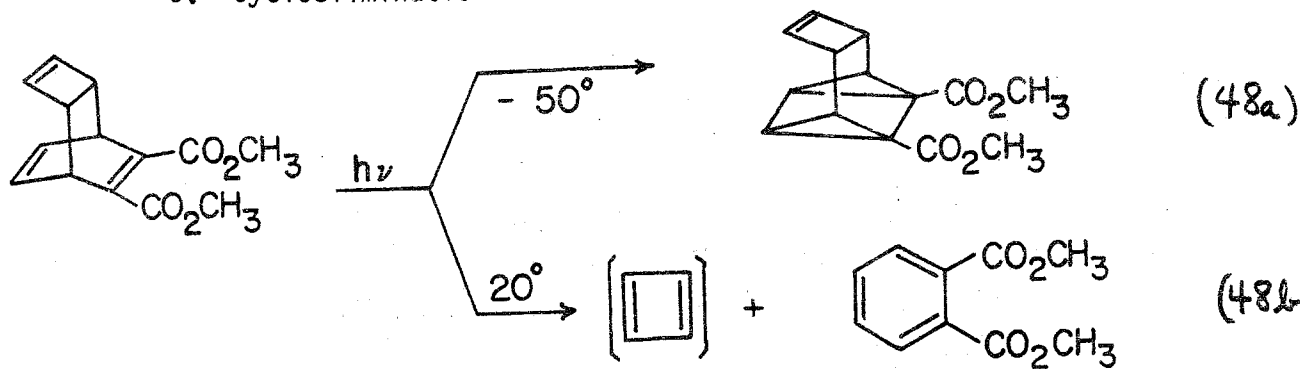
9.7 E. (continued)

4. Constrained systems



9.7 E. (continued)

5. Cycloelimination



F. Summary

1. Good synthetic reaction
2. T_1 usually involved; selectivity variable
3. Especially good in intramolecular cases
4. Rule of 5

9.7 (continued)

G. References

- (27) J. Amer. Chem. Soc., 88, 5038 (1966)
- (28) Chem. Ber., 97, 2942 (1964)
- (30) J. Amer. Chem. Soc., 86, 3103 (1964); ibid, 88, 5415 (1966)
- (31) J. Org. Chem., 36, 102 (1971)
- (32) Can. J. Chem., 47, 433 (1969)
- (33) Tetrahedron, 24, 1821 (1968)
- (34) Chem. Eng. News, Jan 26, 1970, p. 40
- (35) Adv. Photochem., 6, 193 (1968)
- (36) Tetrahedron Letters, 589 (1972)
- (37) Z. Naturforsch. B, 26, 561 (1971)
- (38) and (39) J. Org. Chem., 37, 1148 (1972)
- (40) and (41) Chem. Commun., 1217 (1971)
- (42) J. Amer. Chem. Soc., 94, 5490 (1972)
- (43) Tetrahedron Letters, 4005 (1969)
- (44) For examples see Helv. Chim. Acta, 54, 2579 (1971)
- (45) For examples see Angew. Chem., (Int. ed. Eng), 6, 247 (1967)
- (46) and (47) J. Amer. Chem. Soc., 86, 962, 3158 (1964)
- (48) J. Amer. Chem. Soc., 91, 5401 (1969)
- (49) Chimia, 25, 2481 (1971)

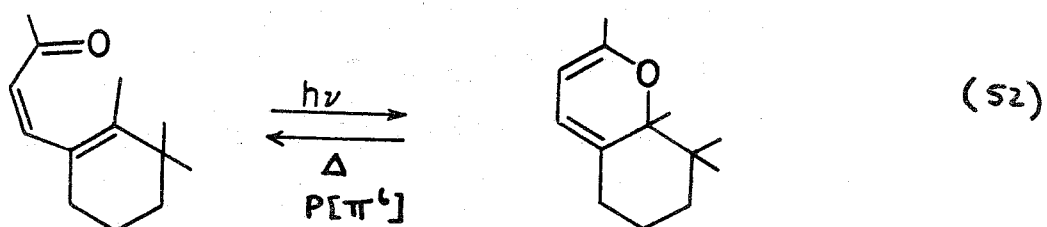
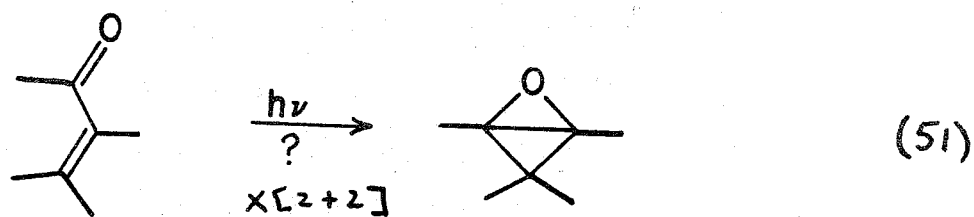
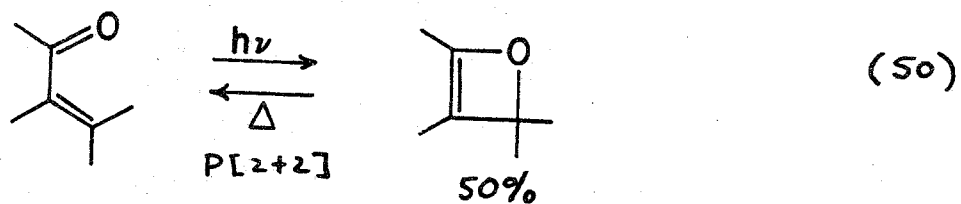
9.8 ELECTROCYCLIC REACTIONS

A. Generally pericyclic S_1 reactions

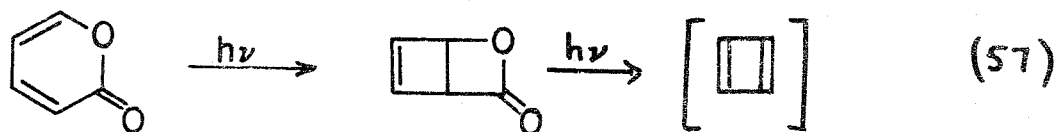
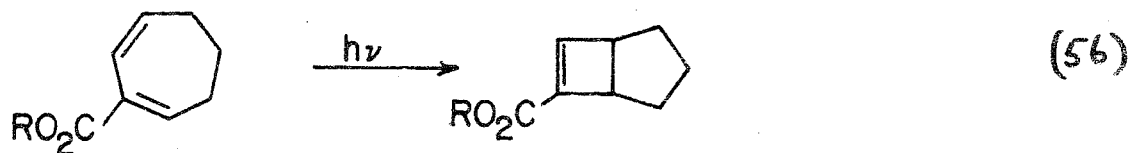
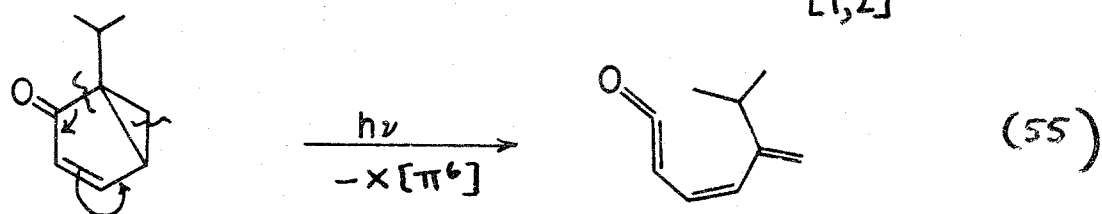
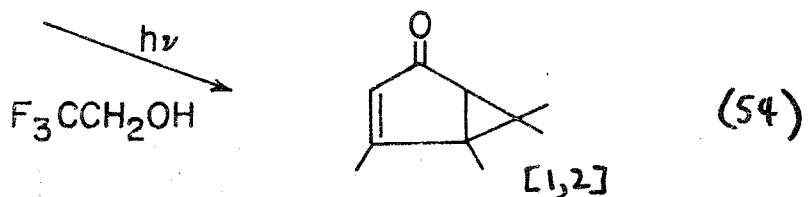
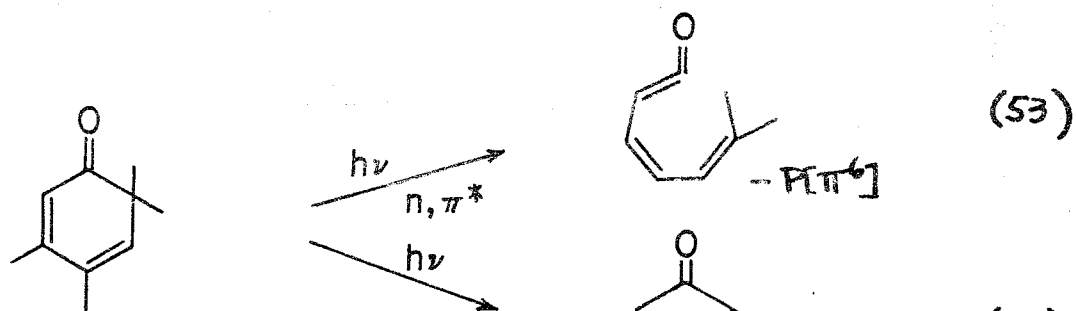
Rev: Section 5 and 6.8

B. Conrotatory and disrotatory no longer measurable: no stereochemical label on O

C. Examples



9.8 C. (continued)



D. References

- (50) J. Amer. Chem. Soc., 91, 7204 (1969)
- (52) J. Amer. Chem. Soc., 88, 619 (1966)
- (53) and (54) J. Amer. Chem. Soc., 90, 5296 (1968)
- (55) J. Amer. Chem. Soc., 90, 5933 (1968)
- (56) J. Org. Chem., 27, 2786 (1962)
- (57) J. Amer. Chem. Soc., 86, 950 (1964)

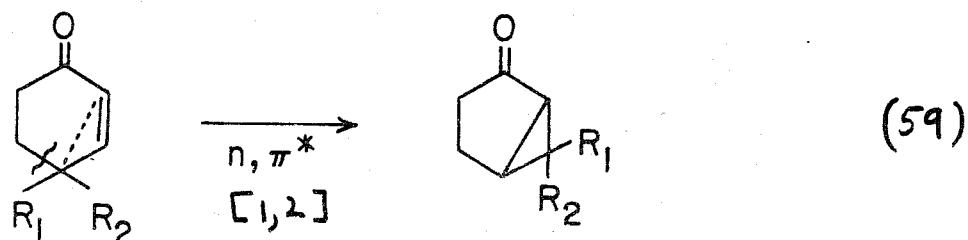
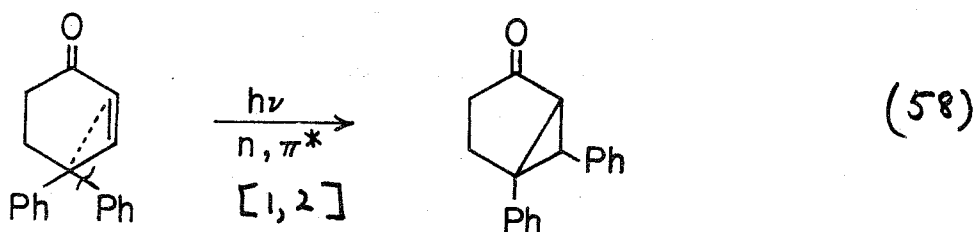
9.9 SIGMATROPIC REACTIONS

A. Many variations

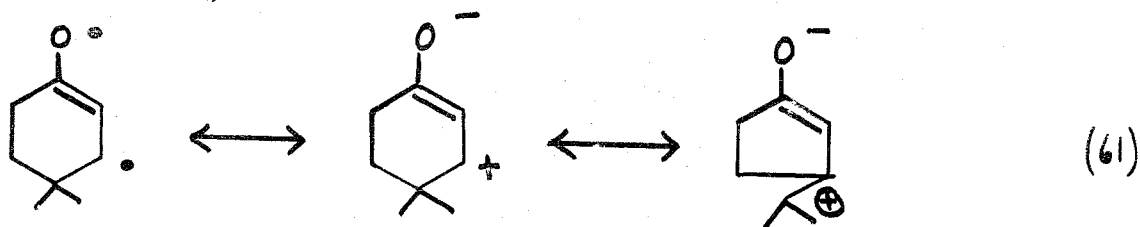
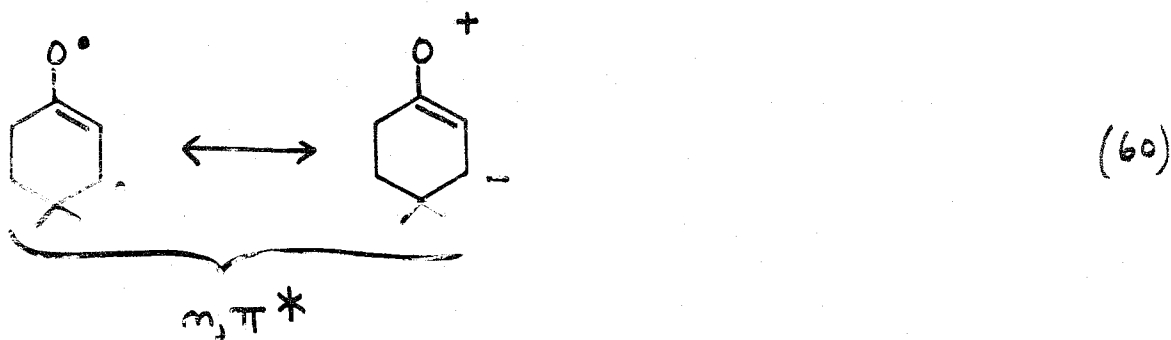
Rev: Sections 5 and 6.9; Org. Photochem., 1, 1 (1968);
Adv. Photochem., 3, 81 (1966)

B. Common in cyclic enones

1. [1,2] Shifts



2. Problem of separating n, π^* and π, π^* reactions



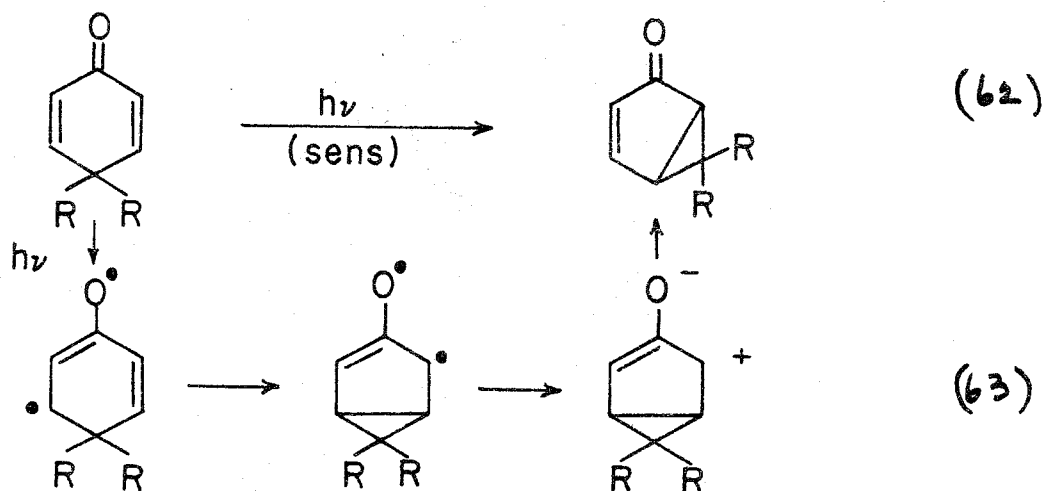
3. Prevails over dimerization for 4,4-disubstituted

4. Efficiency generally ($\phi \approx 0.01$), rate slow ($\sim 10^6 \text{ sec}^{-1}$)

9.9 (continued)

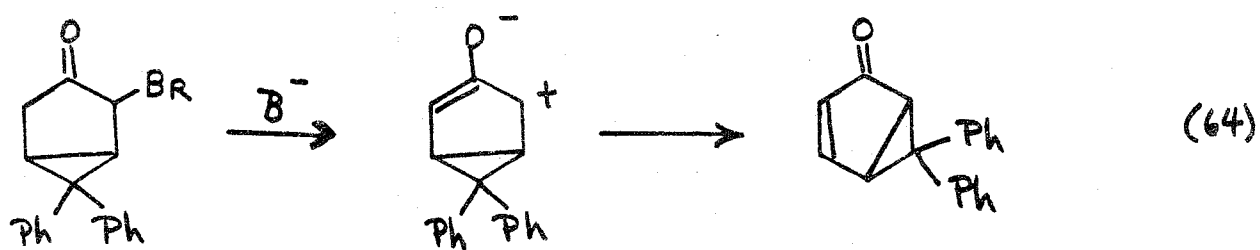
C. 2,5-Cyclohexadienones

Rev: Angew. Chem. Int. ed. Eng., 8, 1 (1969)



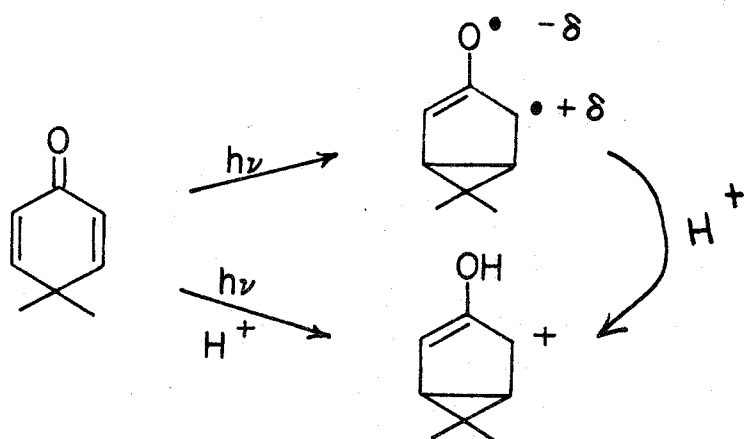
1. Key features: high efficiency ($\phi \sim 0.5$), fast rate ($\sim 10^9 \text{ sec}^{-1}$)

2. Ground state generation of intermediate



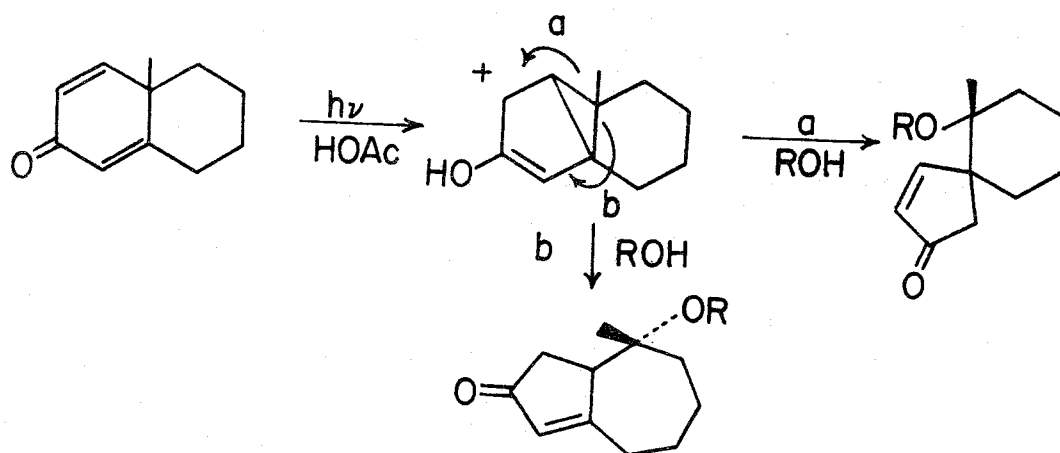
9.9 C. (continued)

3. Solvent effects on product yields



(65a)

(65b)

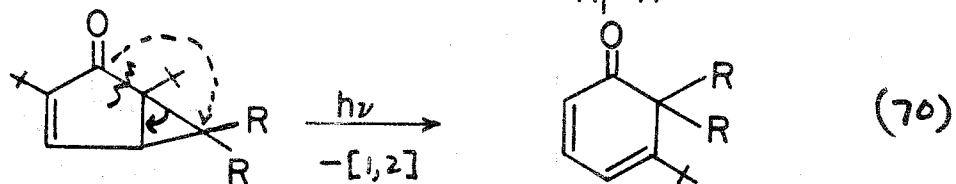
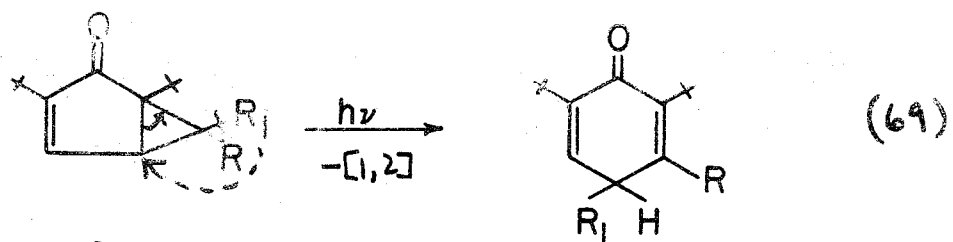
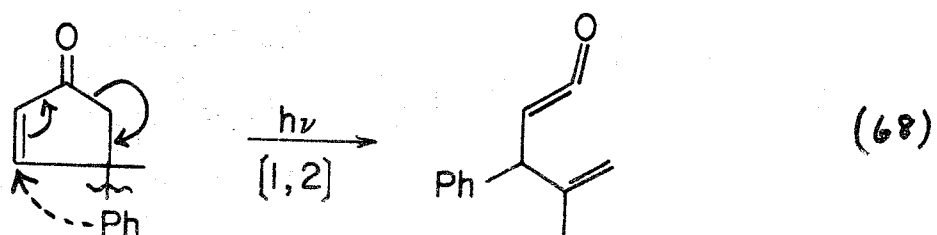
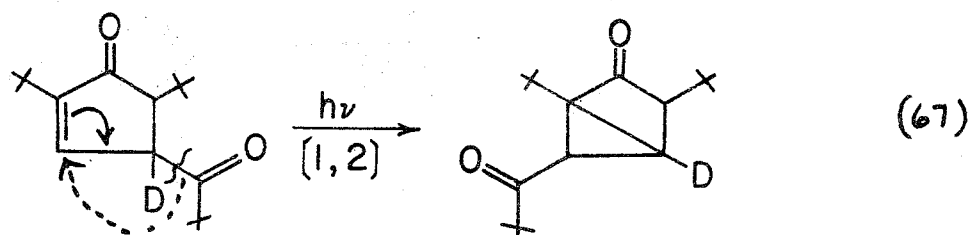


(66a)

(66b)

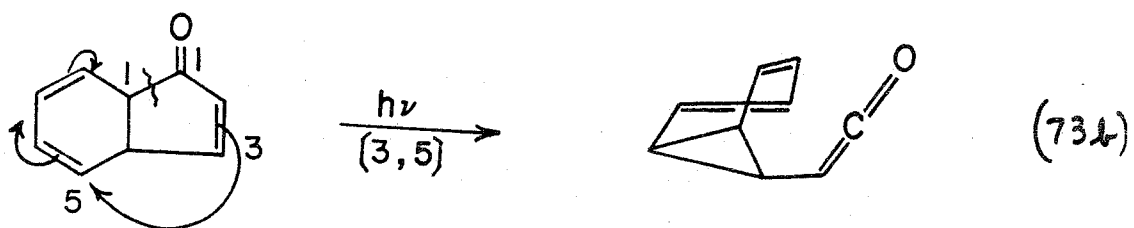
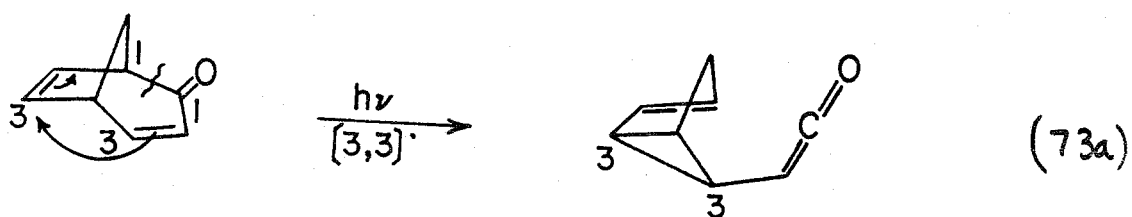
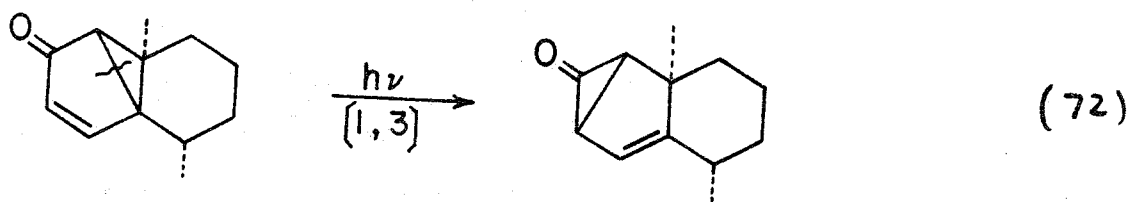
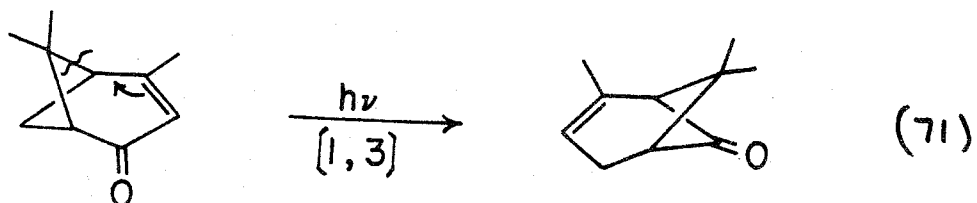
9.9 (continued)

D. Further variations of [1,2] shifts



9.9 (continued)

E. Other sigmatropic shifts



F. Summary

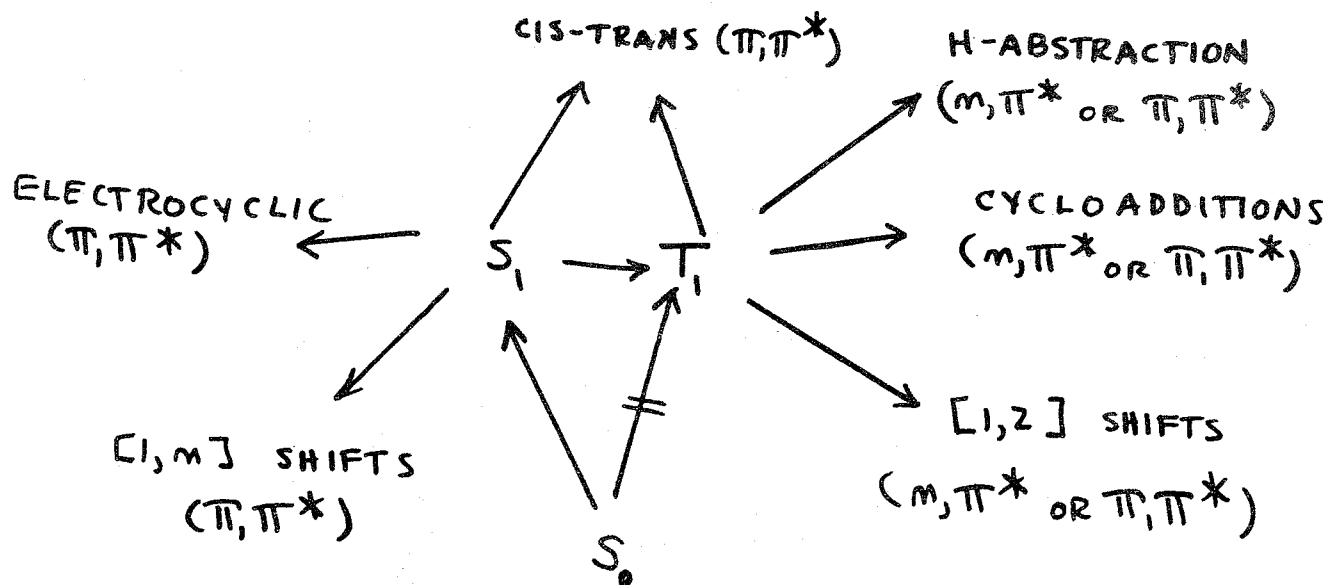
1. Wide variation in product types as function of starting material structure, solvent, acidity and temperature
2. Closeness of energy of n, π^* and π, π^* states makes chemistry rich, but difficult to interpret

9.9 (continued)

G. References

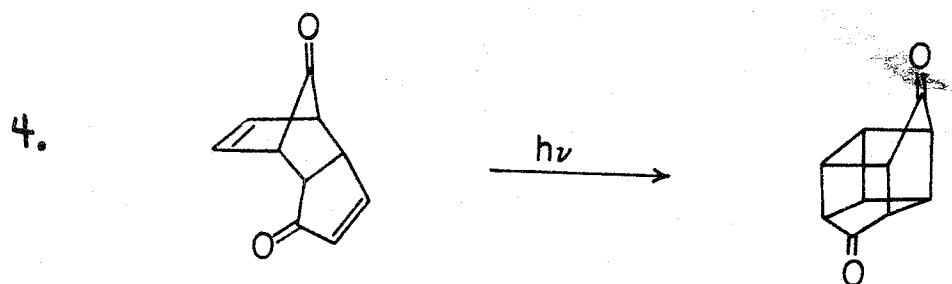
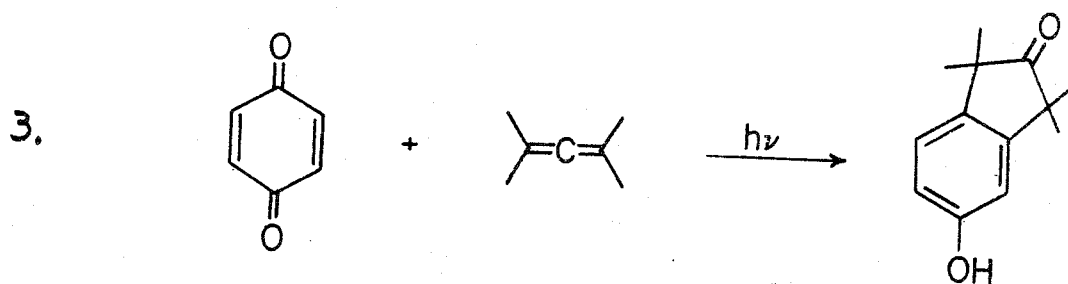
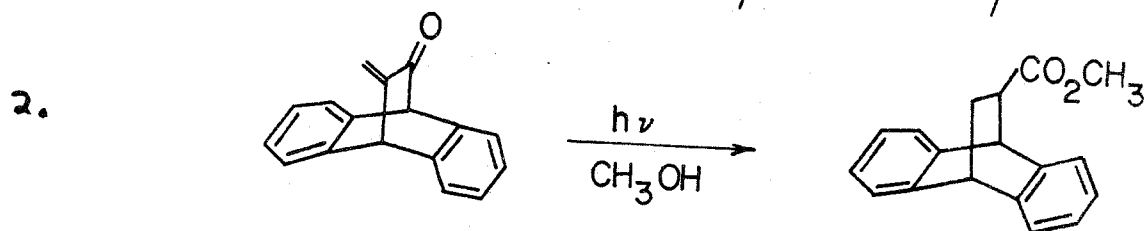
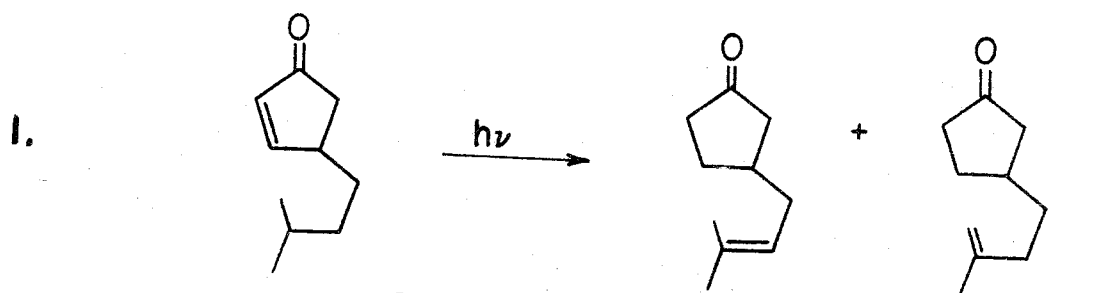
- (58) J. Amer. Chem. Soc., 91, 887 (1969)
- (59) J. Amer. Chem. Soc., 93, 3674 (1971)
- (62) J. Amer. Chem. Soc., 83, 4486 (1961)
- (64) J. Amer. Chem. Soc., 91, 434 (1969)
- (66) J. Amer. Chem. Soc., 85, 3779 (1963)
- (67) Tetrahedron Letters, 4811 (1971)
- (68) Chem. Commun., 698 (1972)
- (69) J. Amer. Chem. Soc., 89, 1690 (1967)
- (70) Chem. Commun., 574 (1971)
- (71) J. Amer. Chem. Soc., 89, 3828 (1967)
- (72) J. Amer. Chem. Soc., 91, 3664 (1969)
- (73) J. Amer. Chem. Soc., 91, 6856 (1969)

9.10 SUMMARY



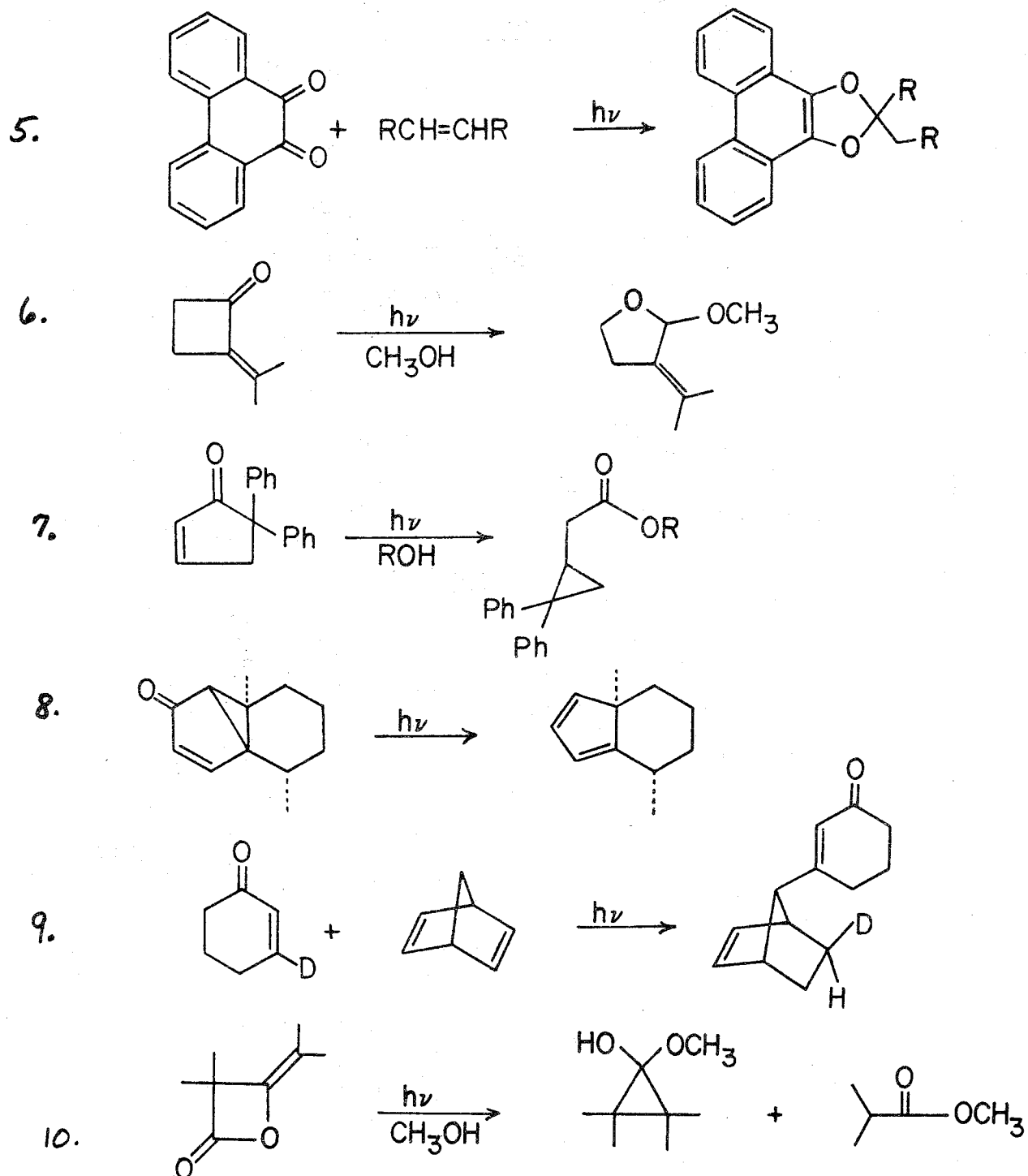
9.11 PROBLEMS

A. Classify the following photoreactions in terms of primary photochemical processes discussed in this chapter or previous chapters. Specify the nature of the excited state (multiplicity and configuration) and, for pericyclic reactions, indicate the number and types of electrons involved.



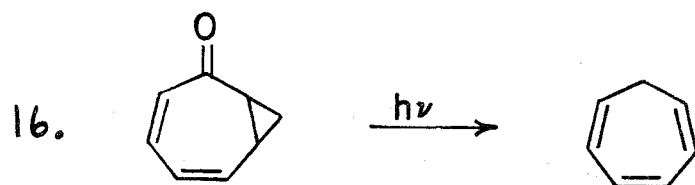
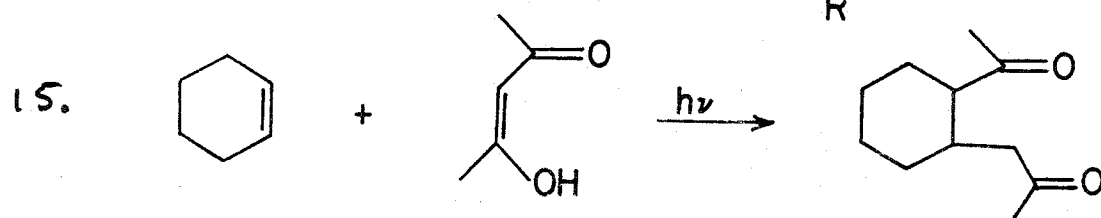
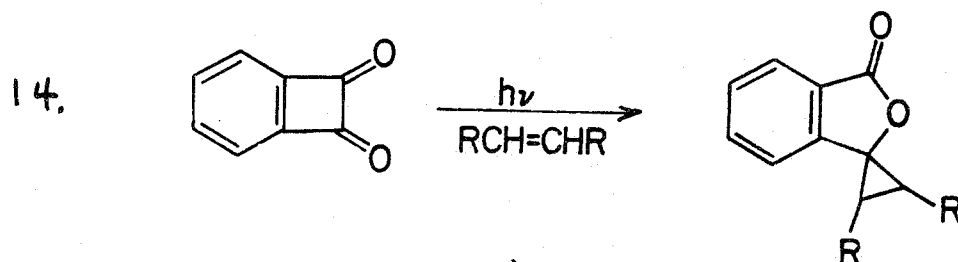
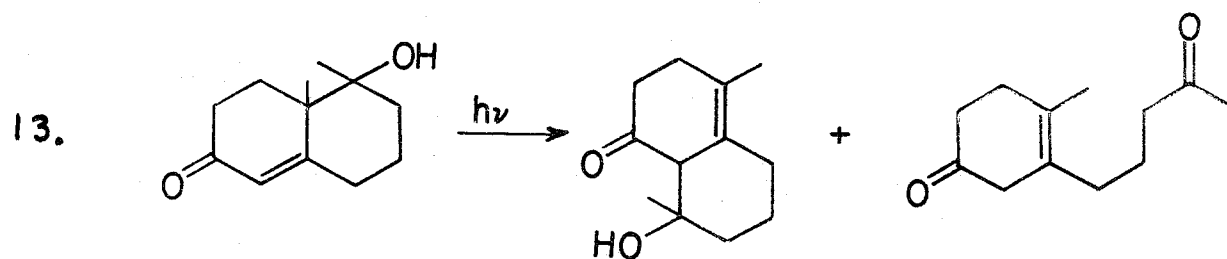
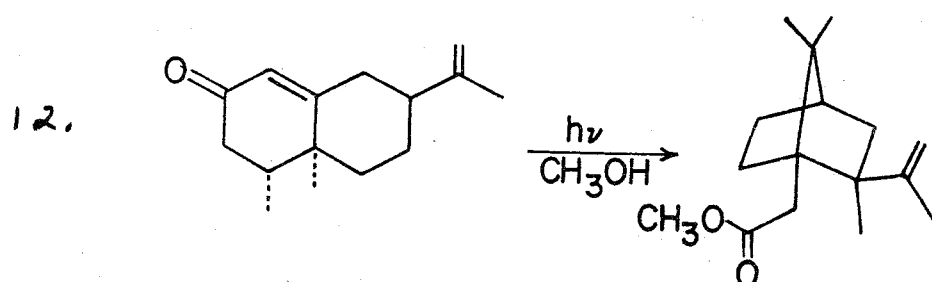
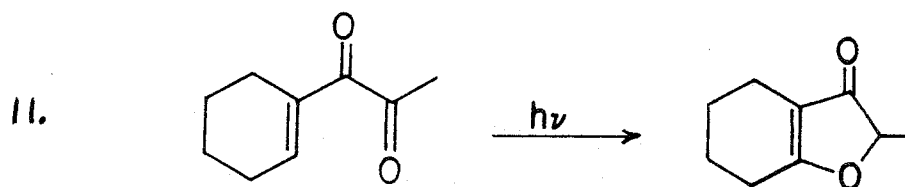
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9.11 A. (continued)



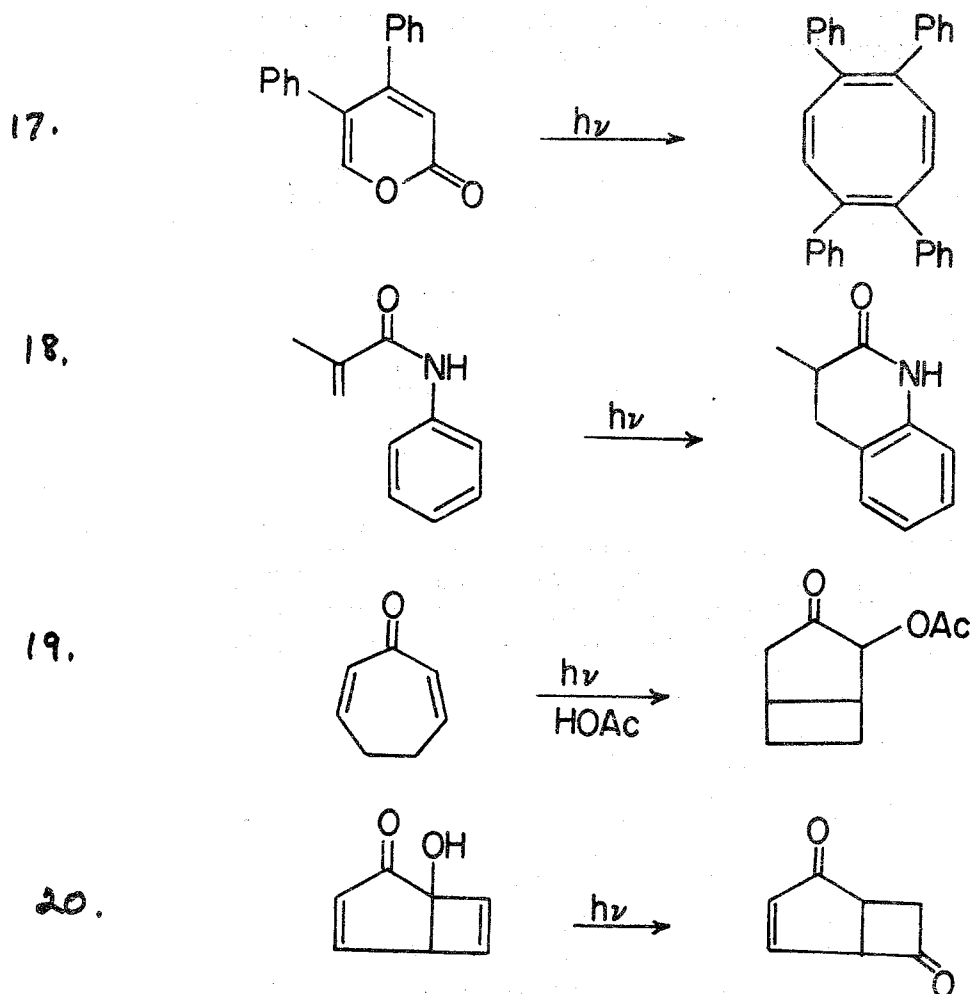
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9.11 A. (continued)

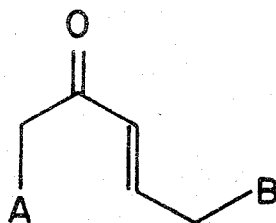


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9.11 A. (continued)

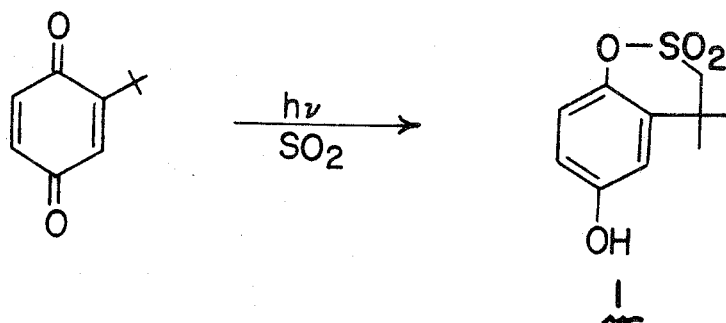


B. Consider the enone shown below. Draw the structures of the [1,2] shift products derived from migration of A and involving an excited carbonyl group, and migration of B and involving an excited carbon-carbon double bond.

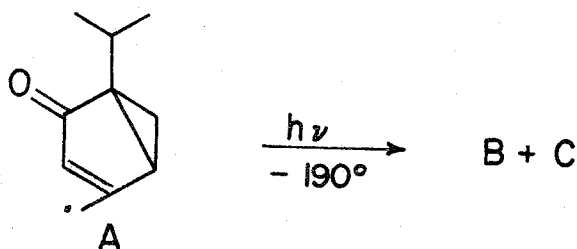


9.11 (continued)

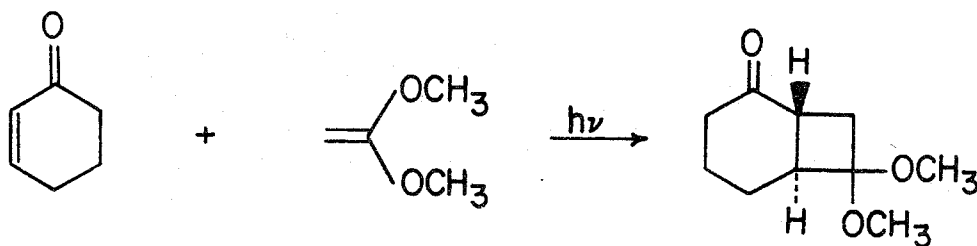
- C. Irradiation of *t*-butylbenzoquinone in liquid SO_2 results in the formation of 1. Propose a mechanism for this transformation.



- D. Irradiation of A at -190°C yields two isomeric compounds, one (B) which possesses a prominent IR band at 2113 cm^{-1} and another (C) which possesses prominent IR bands at 1670 cm^{-1} and 1630 cm^{-1} . Suggest structures for B and C which might result from primary photochemical processes discussed in this chapter.

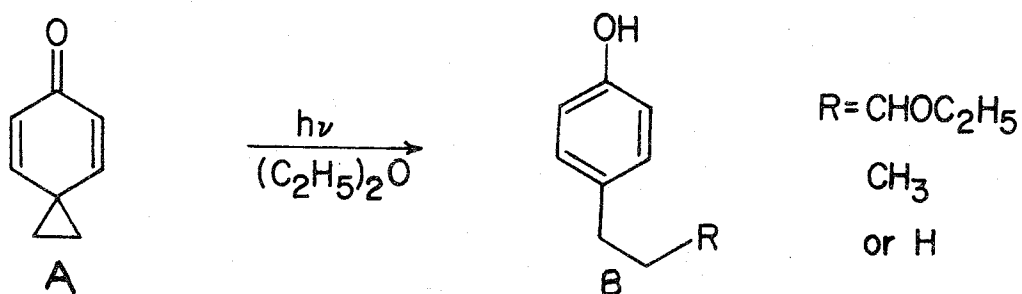


- E. Suggest reasons why the photoaddition of 2-cyclohexenone to 1,1-dimethoxyethylene yields a trans adduct as the major product.

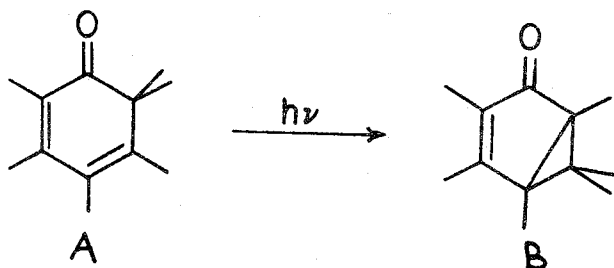


9.11 (continued)

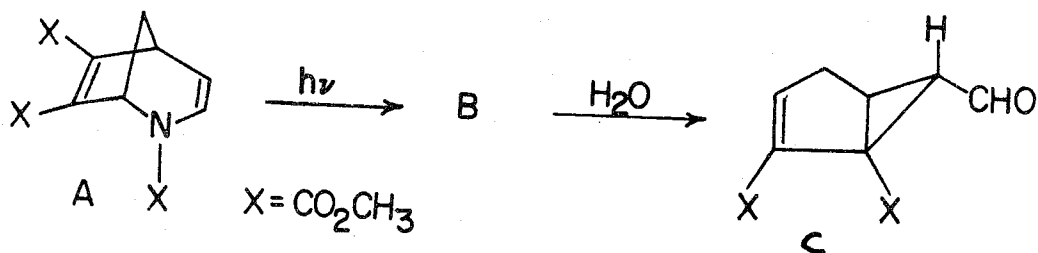
- F. Suggest a rationale to explain why the spirodienone A does not yield the usual [1,2] shift product, but instead yields phenols such as B.



- G. Suggest a rationale for the following rearrangement.

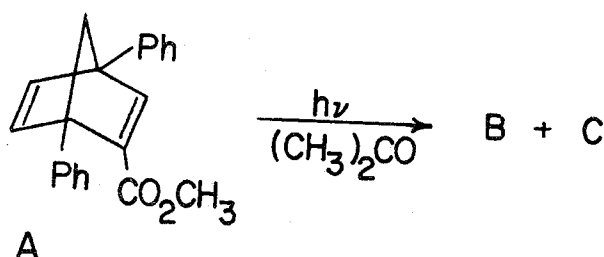


- H. Irradiation of the bicyclic compound A results in the formation of a material B which, upon hydrolysis, yields the aldehyde C. Suggest a structure for B and a mechanism for its formation.

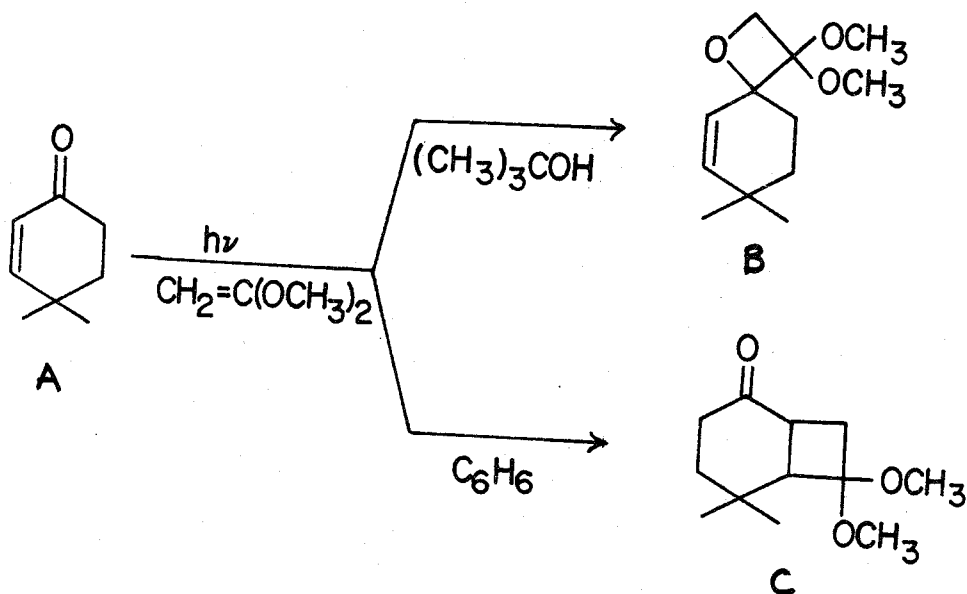


9.11 (continued)

- I. The norbornadiene A yields a quadricyclane upon direct excitation, but acetone induces a [1,2] shift. The latter reaction is unusual for norbornadienes: (a) Two [1,2] shift products are formed. Suggest structures for them; (b) Suggest a reason for the occurrence of the [1,2] shift in this case, rather than the usual ring closure.

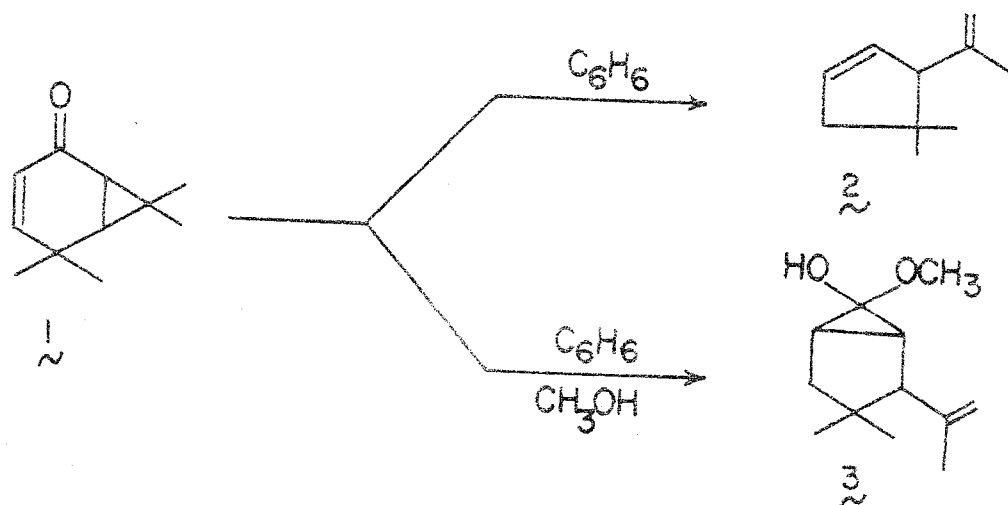


- J. Rationalize the following observations: irradiation of 4,4-dimethylcyclohexenone, A, in t-butanol undergoes oxetane formation, B, with 1,1-dimethoxyethylene but in benzene, A yields a cyclobutane, C, with 1,1-dimethoxyethylene.

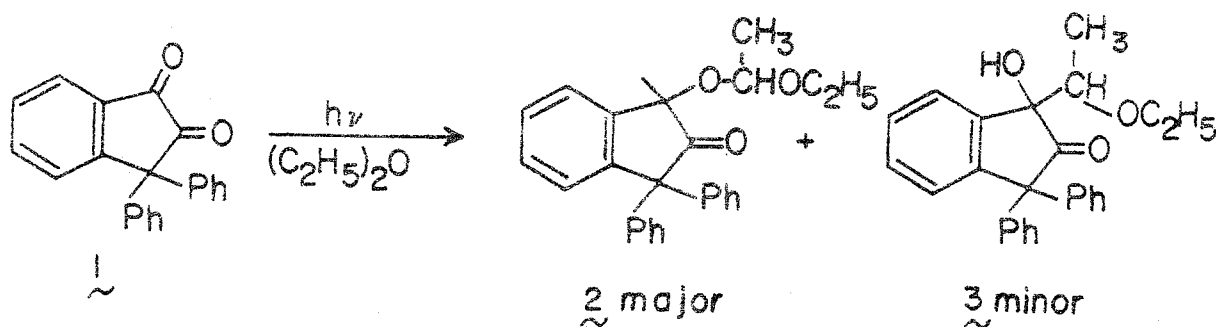


9.11 (continued)

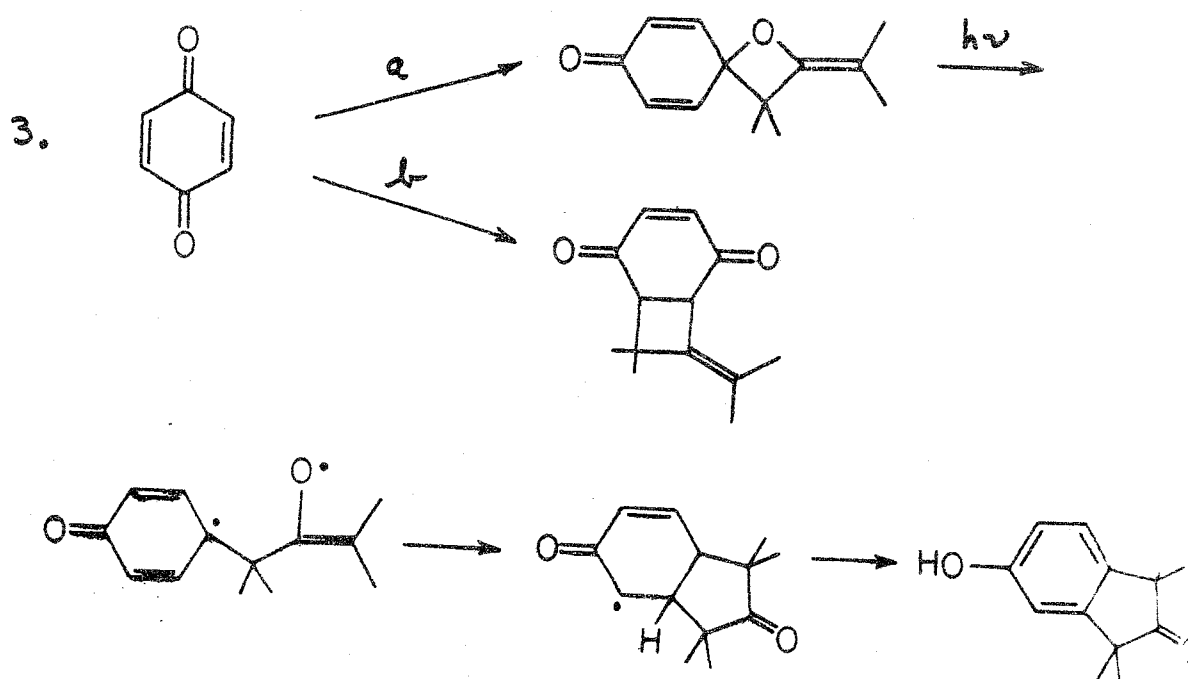
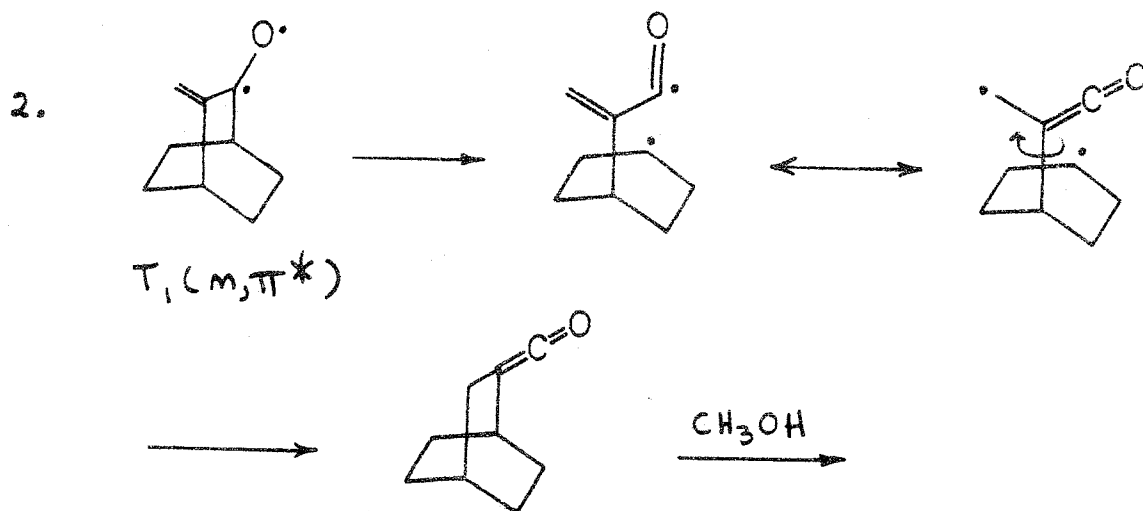
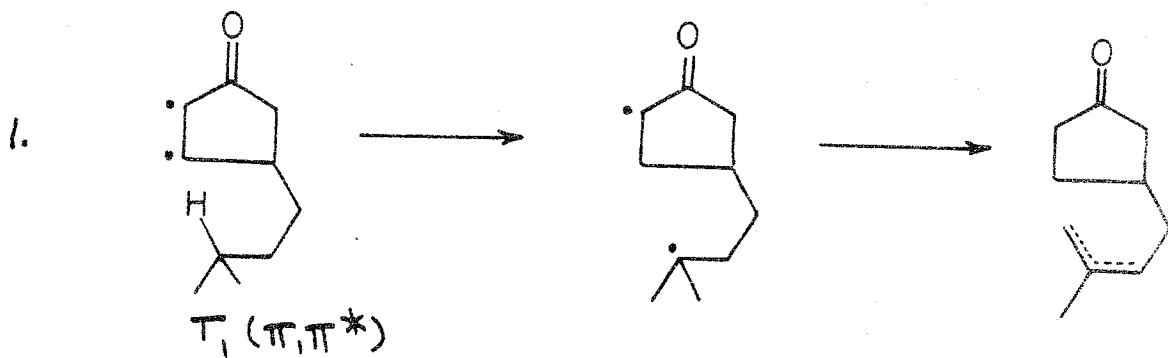
K. Suggest a mechanism to rationalize the following observations.



L. Irradiation of the diketone, 1, results in the formation of products 2 and 3, with 2 being the major product. Suggest a mechanism for formation of 2 and 3.

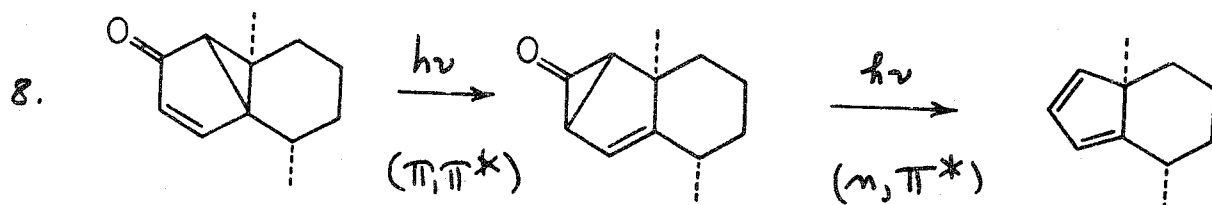
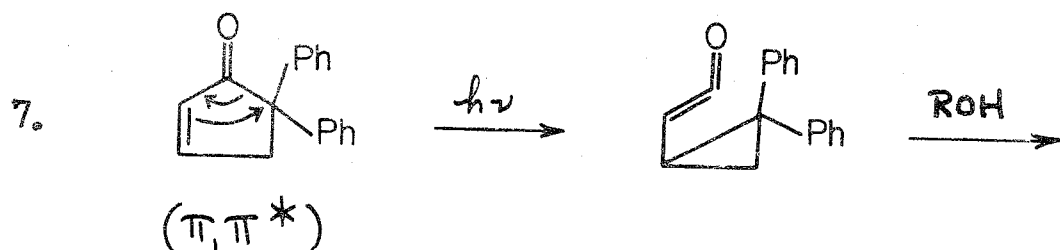
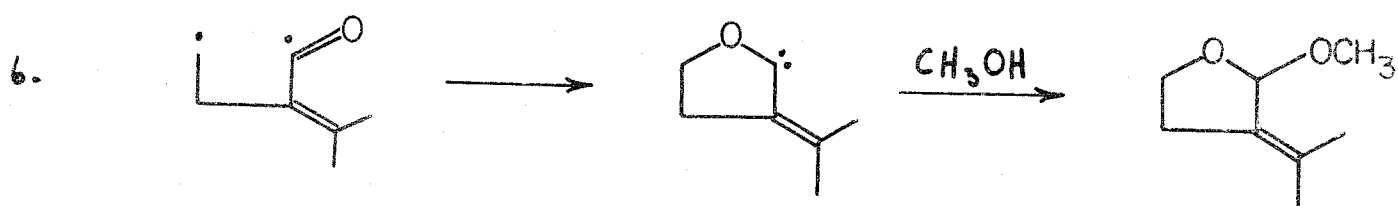
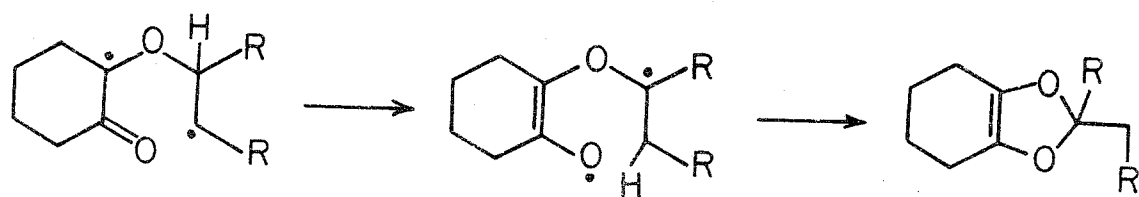
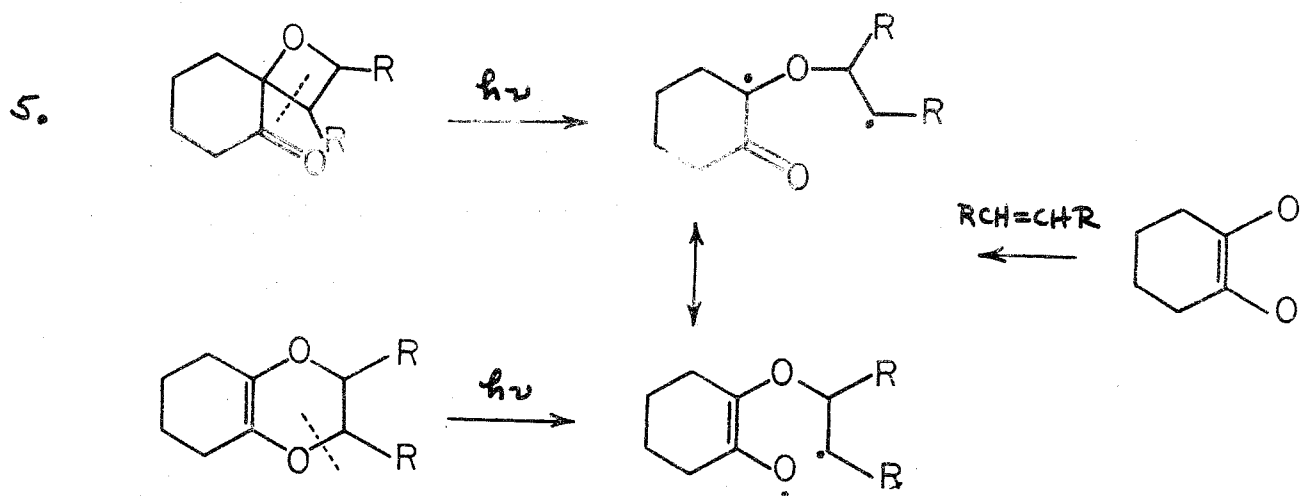


9.12 ANSWERS



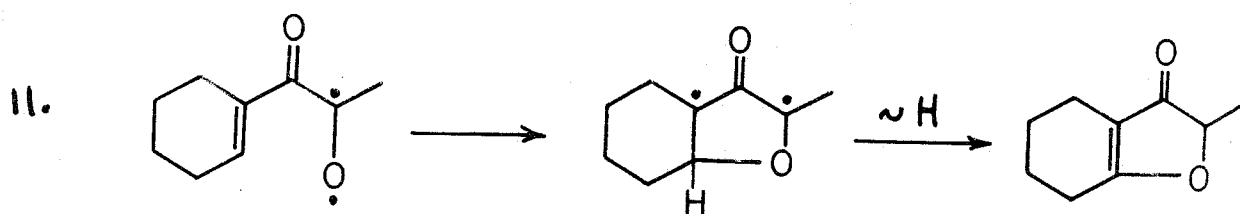
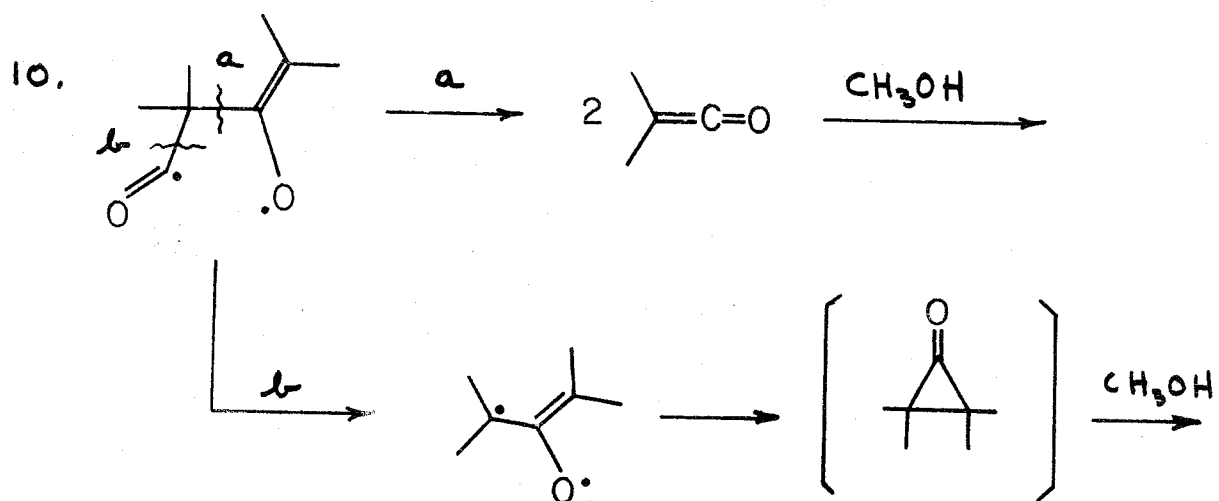
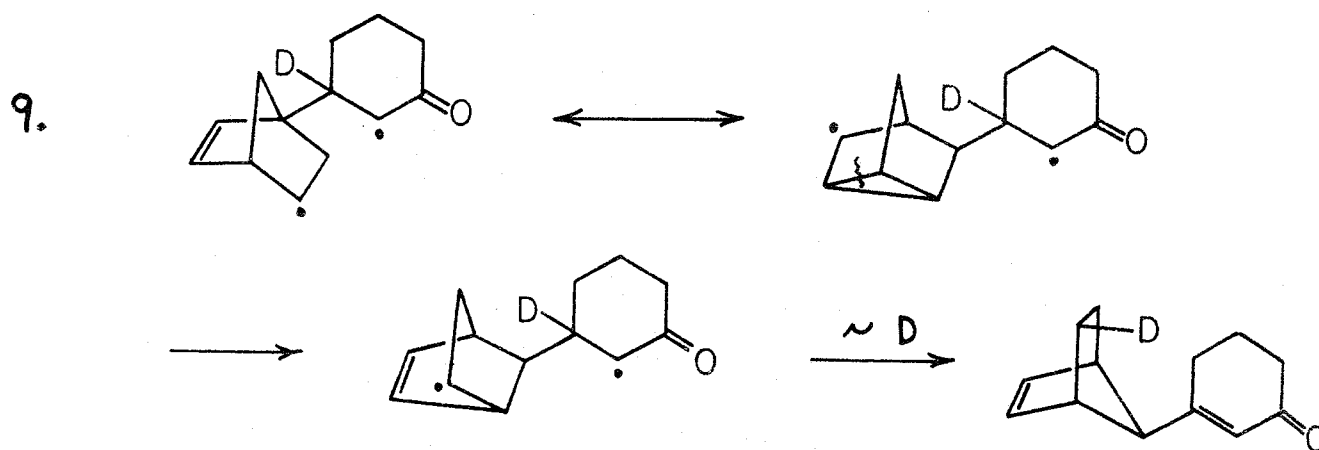
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9.12 A. (continued)



(continued)

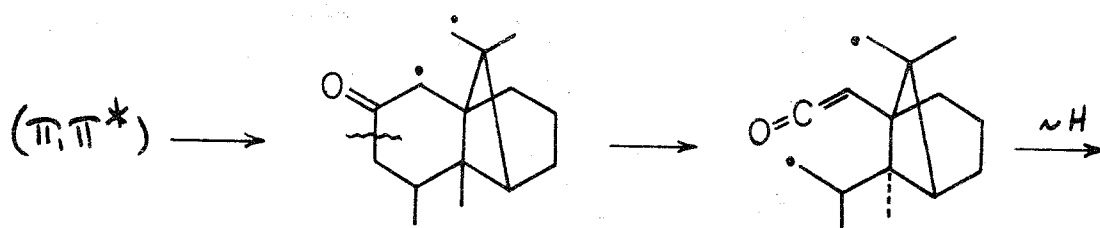
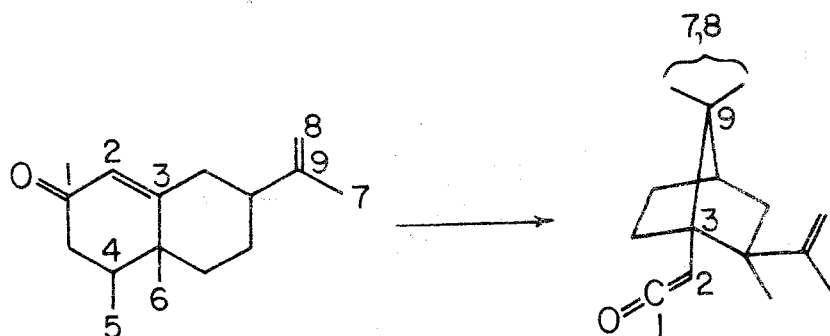
9.12 A. (continued)



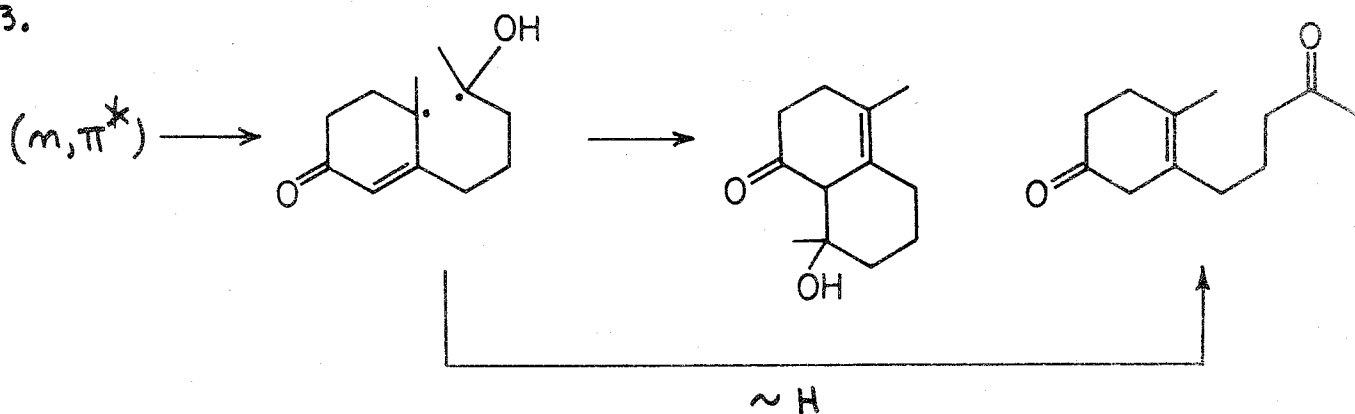
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9.12 A. (continued)

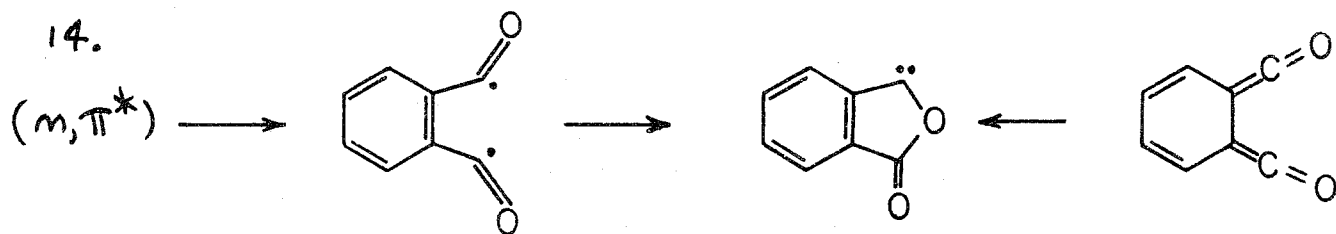
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13.



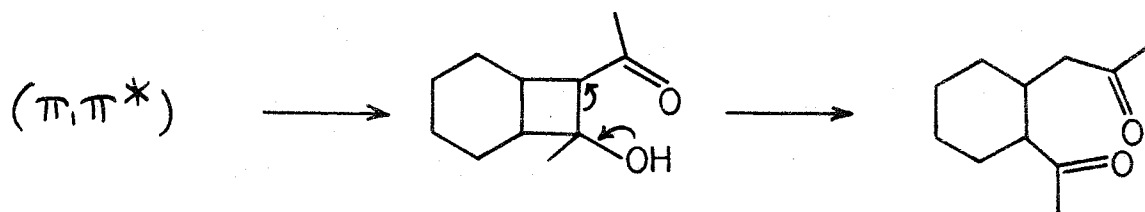
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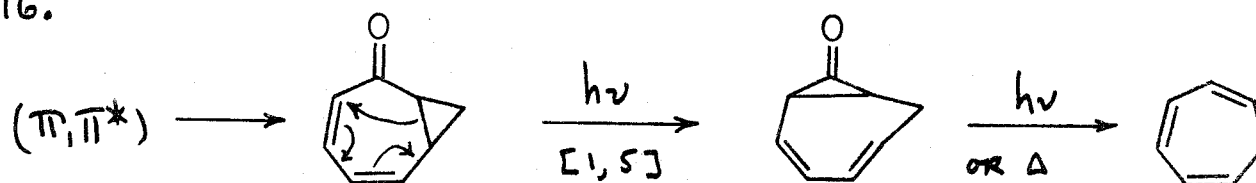
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9.12 A. (continued)

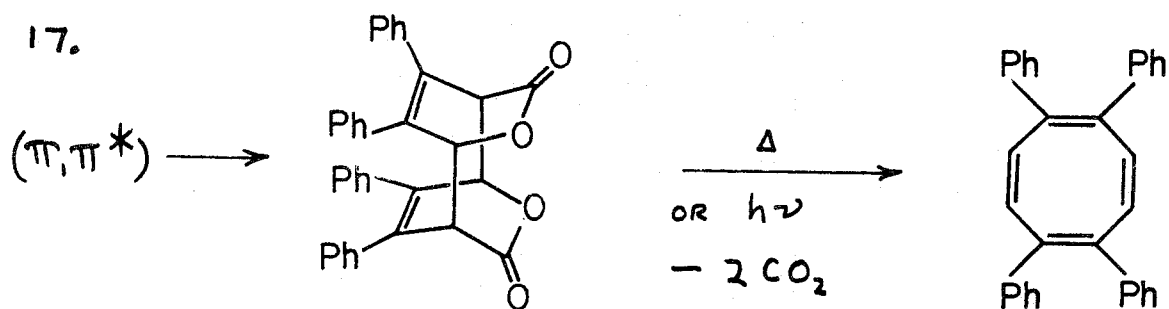
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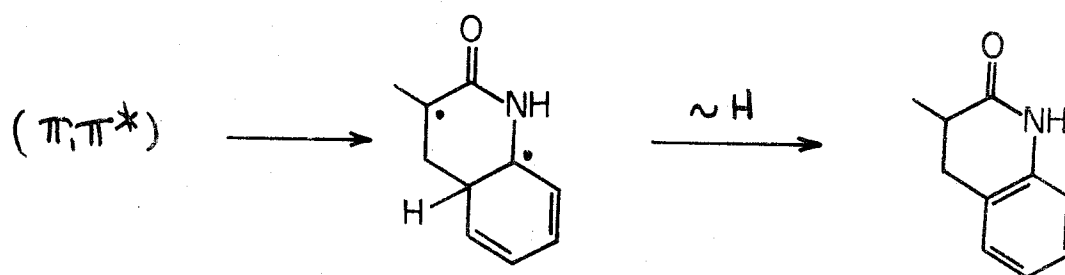
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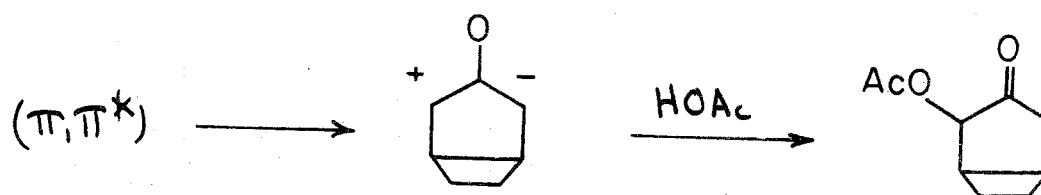
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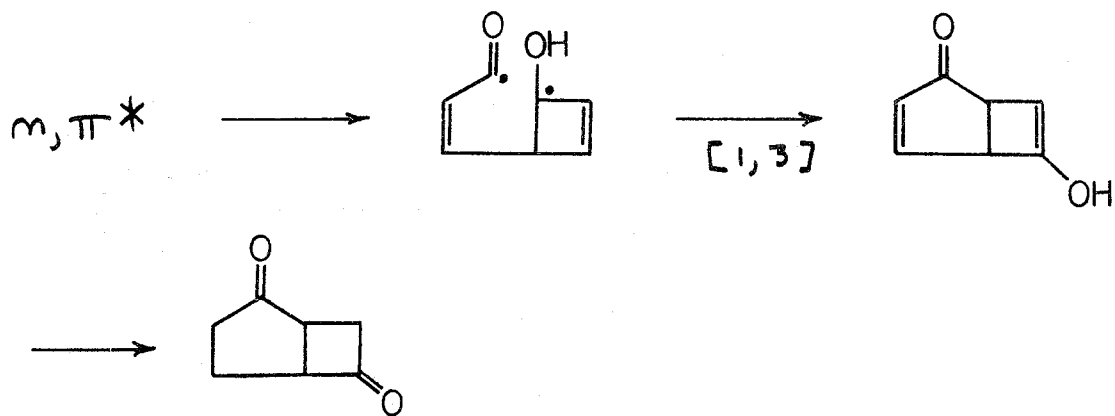
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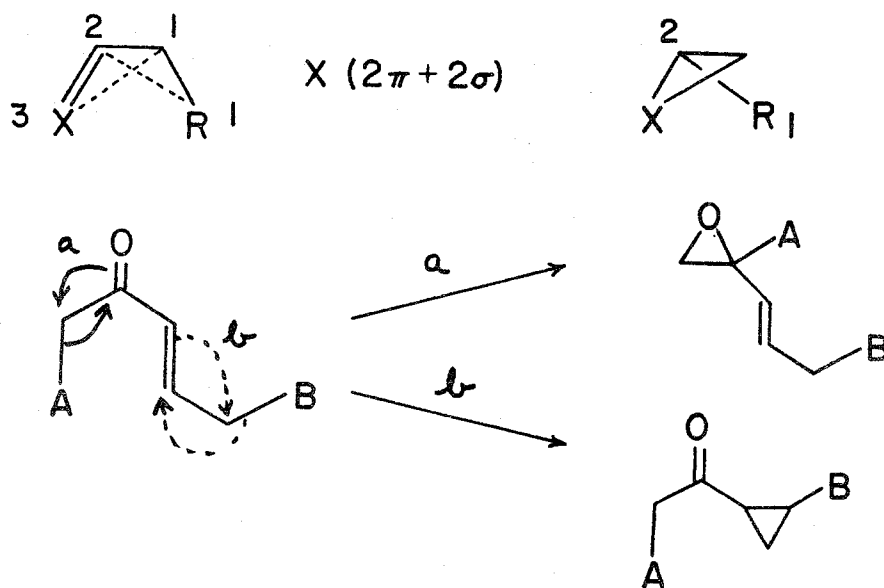
(continued)

9.12 A. (continued)

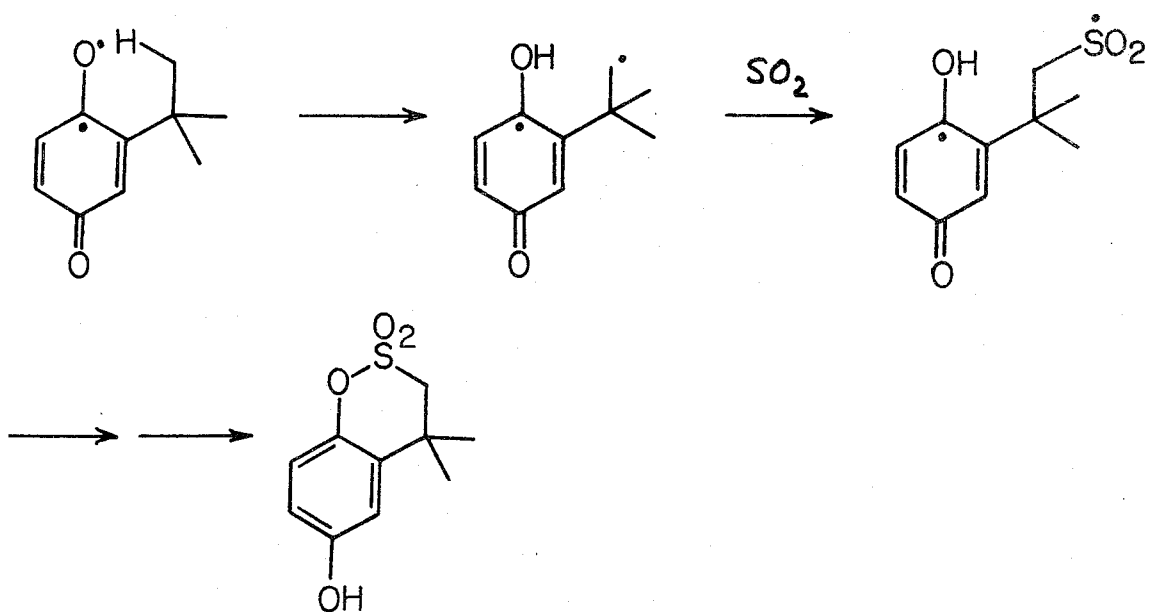
20.



B.

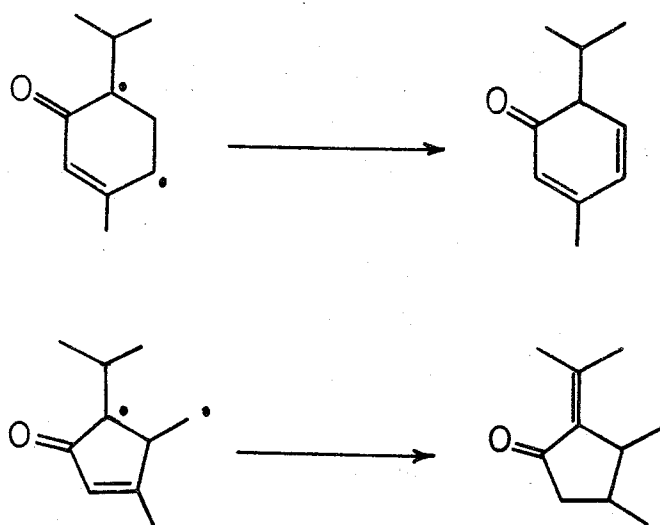


C.

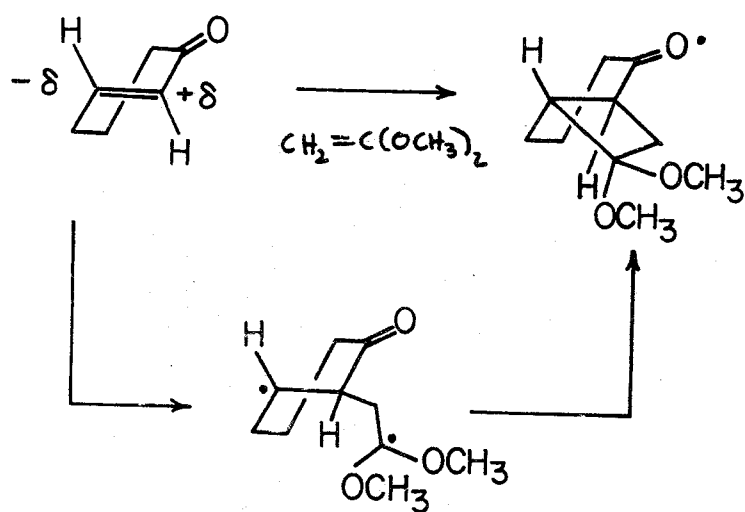


9.12 (continued)

D.

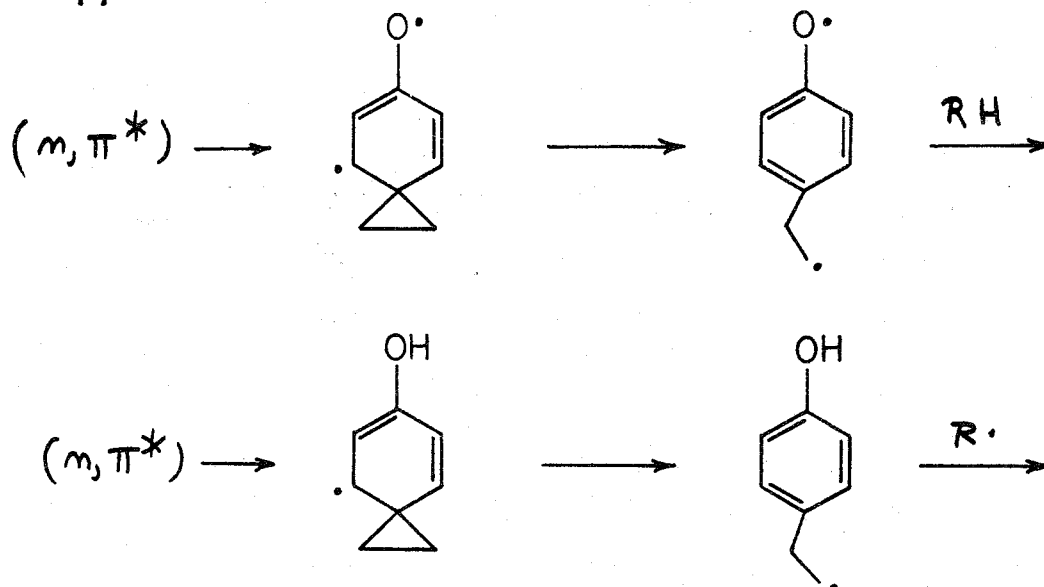


E.

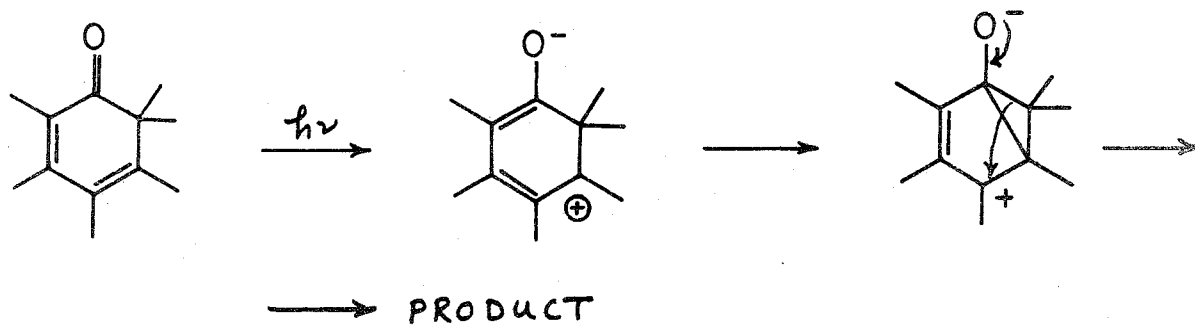


9.12 (continued)

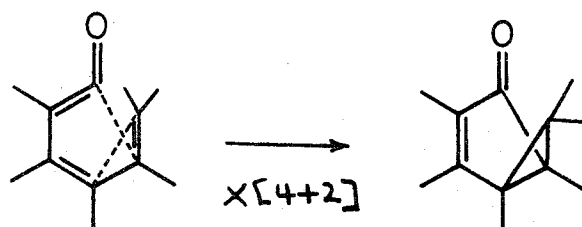
F.



G.

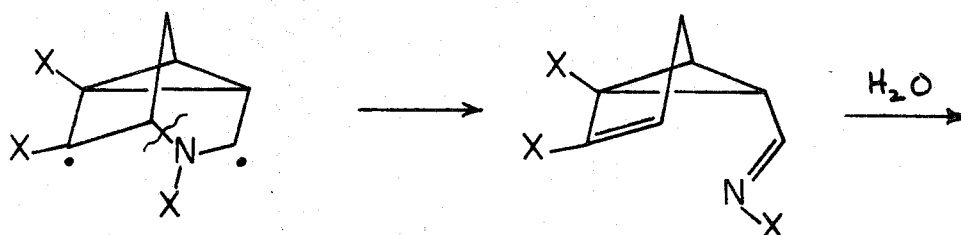


OR



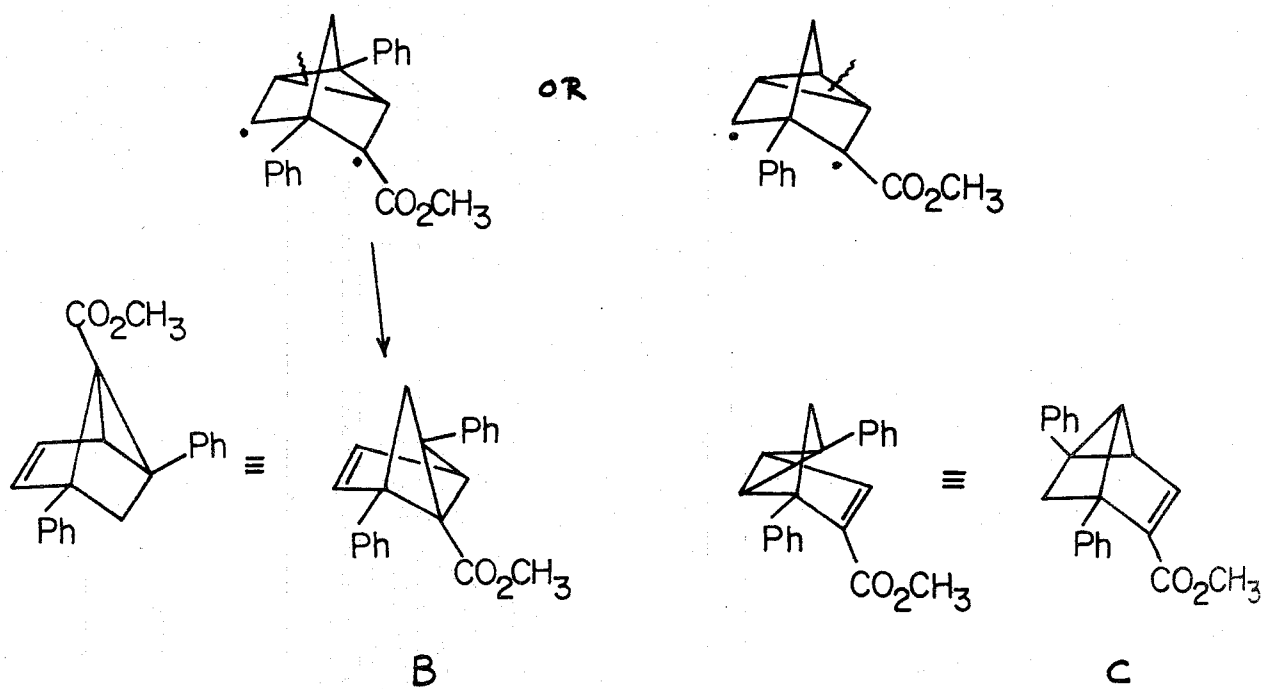
9.12 (continued)

H.



PRODUCT

I.

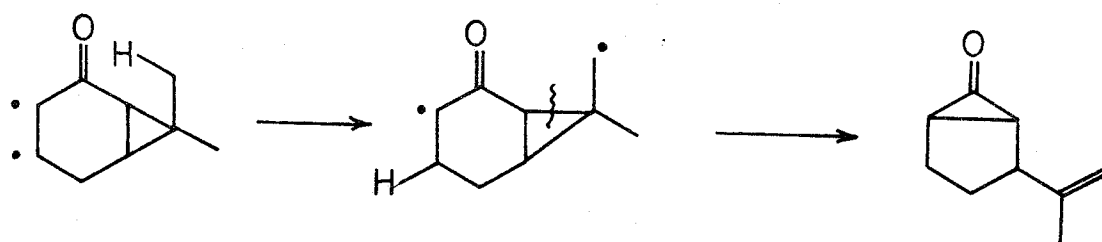
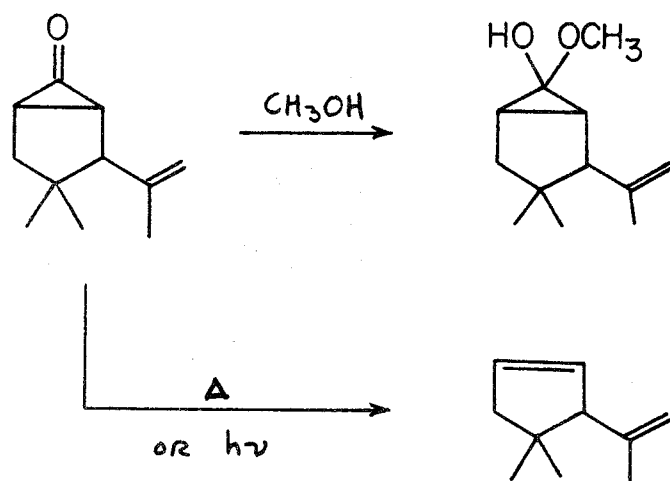


9.12 (continued)

J.

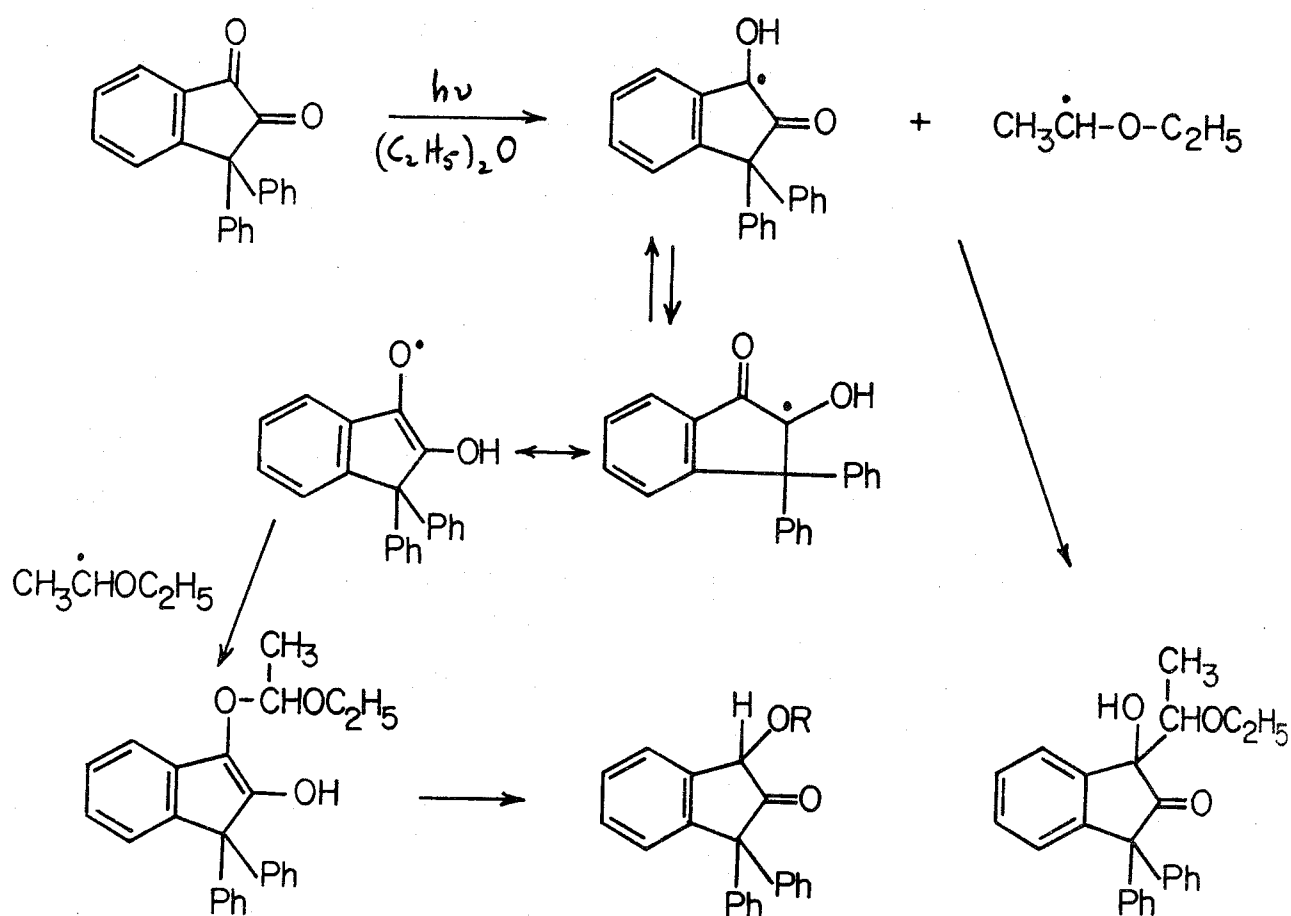


K.



9.12 (continued)

L.



CHAPTER 10
PHOTOCHEMISTRY OF SOME UNSATURATED NITROGEN
CHROMOPHORES AND PHOTOCHEMICAL OXIDATIONS

10.0 UNSATURATED NITROGEN CHROMOPHORES

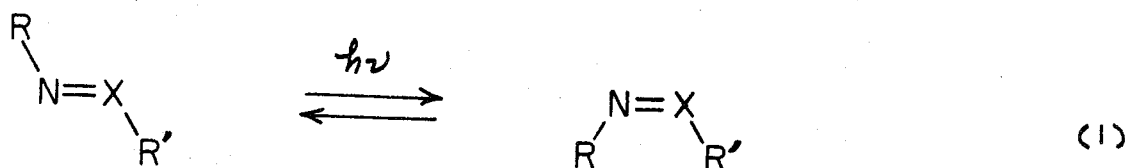
A.



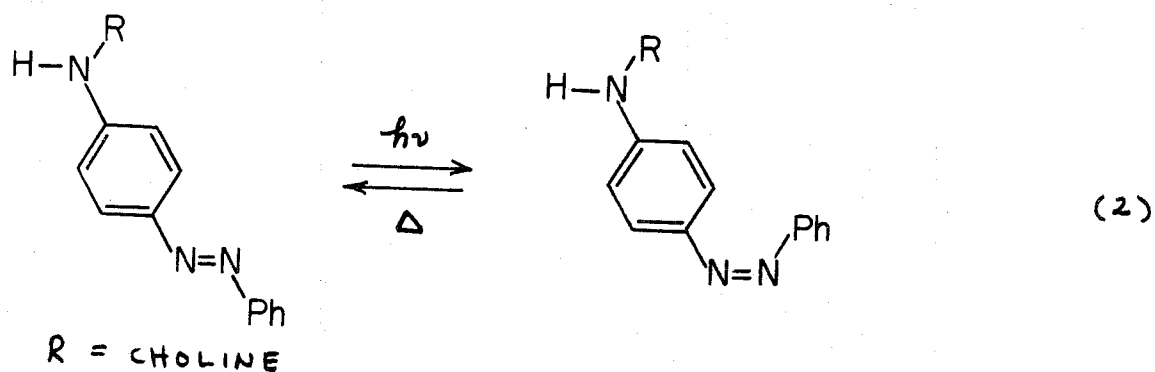
B. Use of analogies

10.1 EXAMPLES OF PHOTOREACTIONS OF UNSATURATED NITROGEN CHROMOPHORES

A. cis-trans-Isomerization



1. Photoregulation of enzymic activity



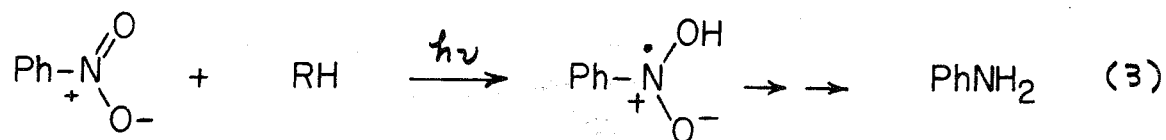
2. Plant growth regulators

3. Ref. to reactions

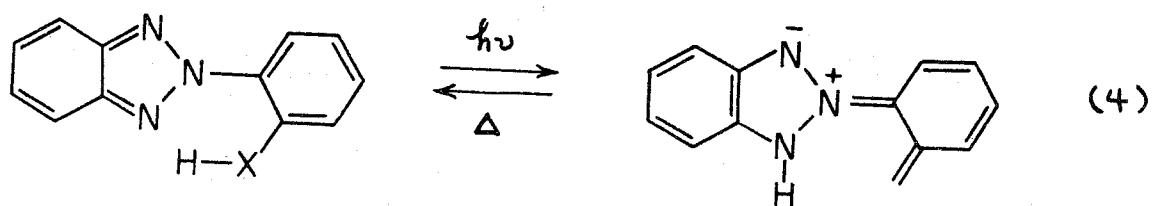
(2) Proc. Natl. Acad. Sci, USA, 66, 850 (1970)

10.1 (continued)

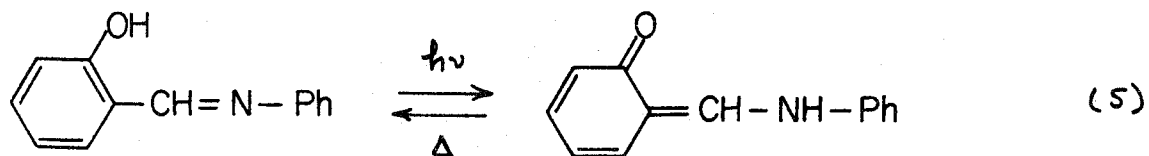
B. Hydrogen abstraction



1. Photostabilizers



2. Photochromic systems



3. References to reactions

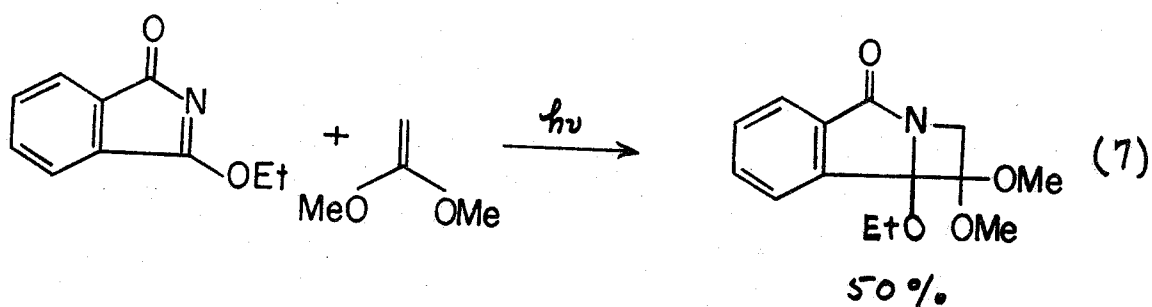
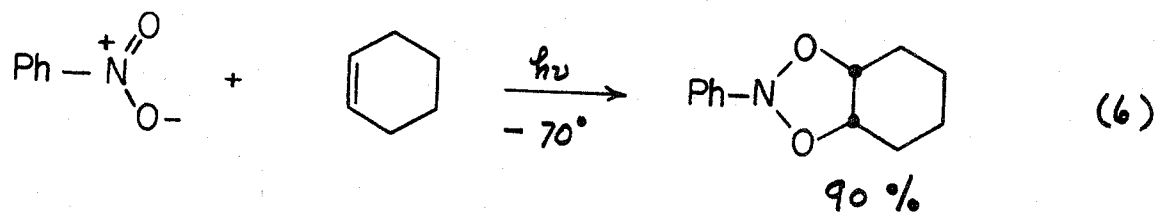
(3) J. Amer. Chem. Soc., 90, 1949, 7044 (1968)

(4) J. Chem. Phys., 43, 1410 (1965)

(5) J. Amer. Chem. Soc., 89, 1298 (1967)

10.1 (continued)

C. Cycloaddition

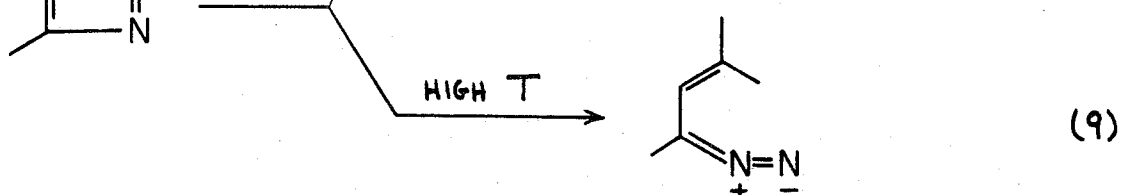
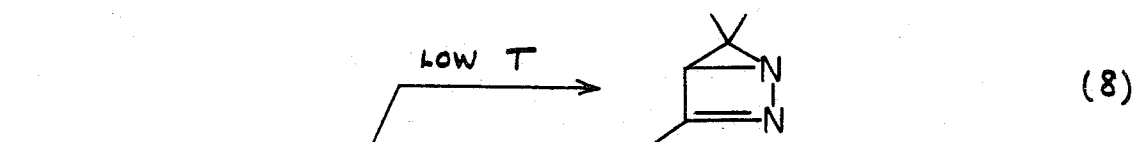


1. Relatively rare
2. References to reactions

(6) J. Amer. Chem. Soc., 93, 2463 (1971)

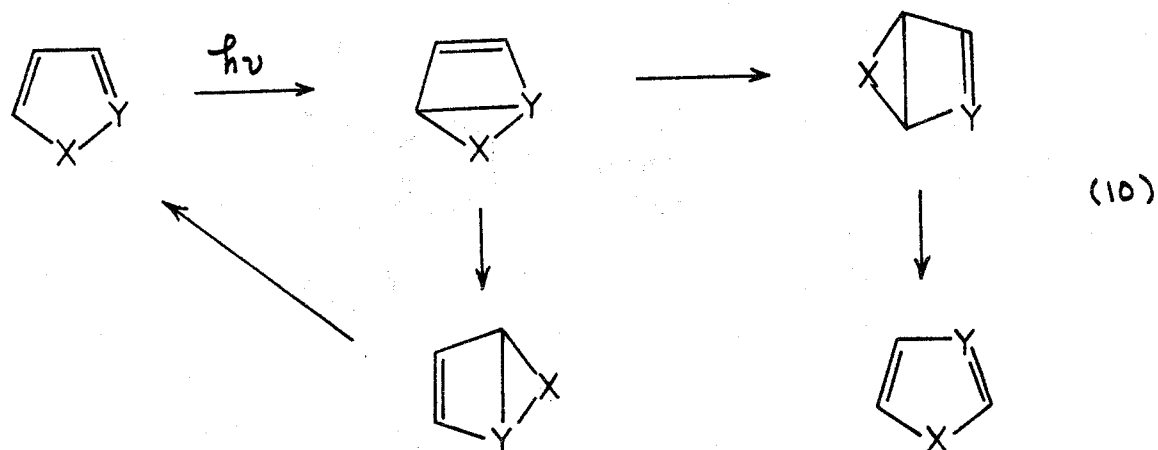
(7) Tetrahedron Letters, 4035 (1972)

D. Electrocyclic

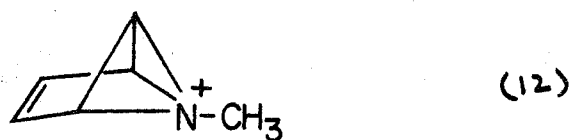
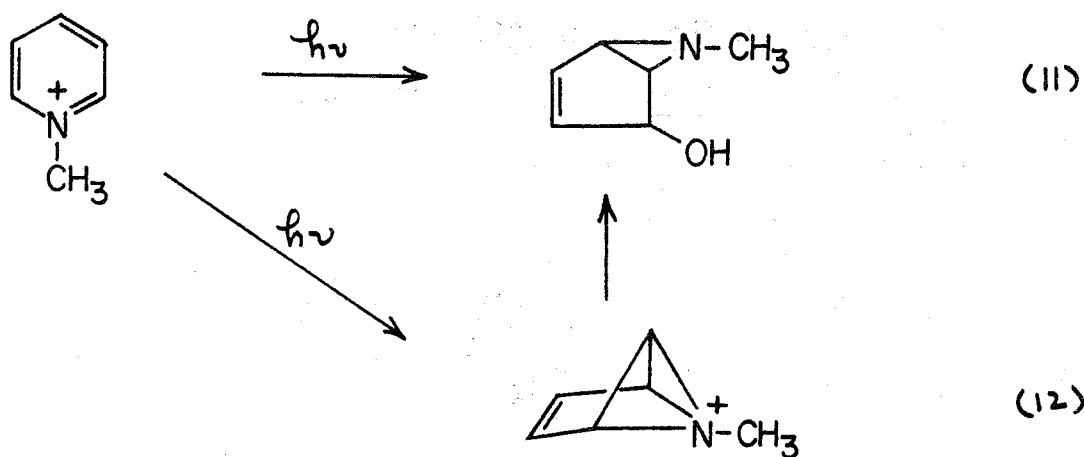


10.1 D. (continued)

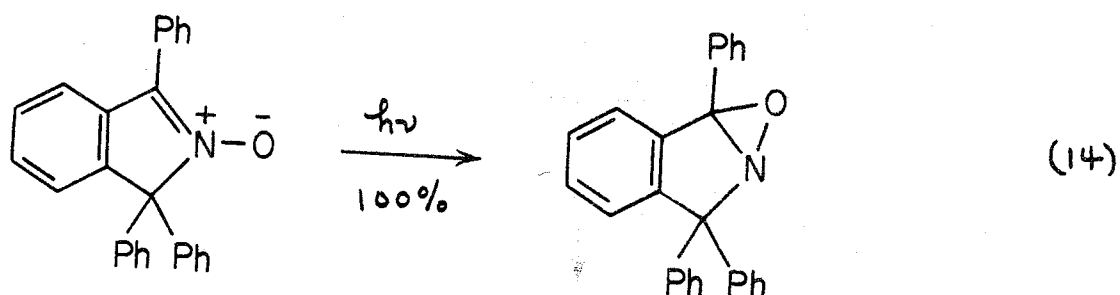
1. Heterocyclic rearrangements



2. Analogy to benzene isomerizations



10.1 D. 2 (continued)



3. References to reactions

(8) and (9) J. Amer. Chem. Soc., 90, 173 (1968)

(10) Rev. of heterocyclic rearrangements: Bull. Soc. Chim. France, 679 (1971)

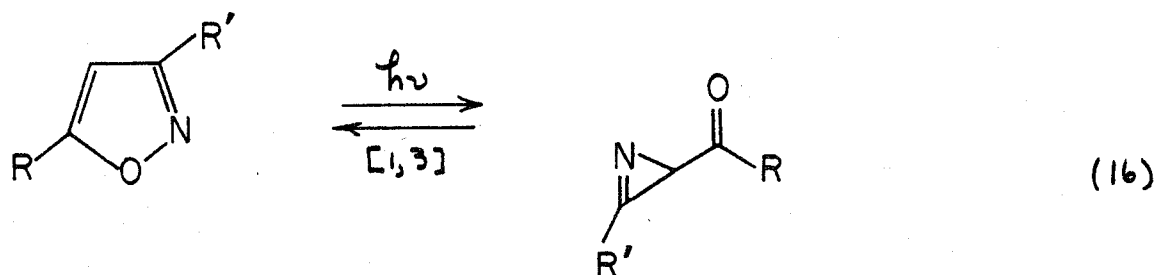
(11) and (12) J. Amer. Chem. Soc., 94, 3283 (1972)

(13) J. Amer. Chem. Soc., 92, 2178 (1970)

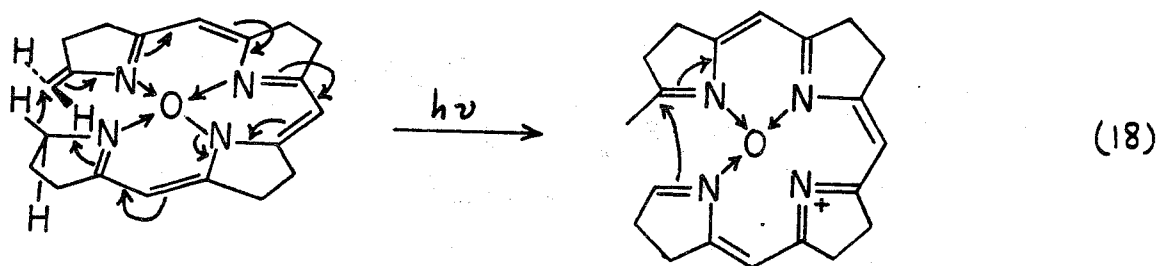
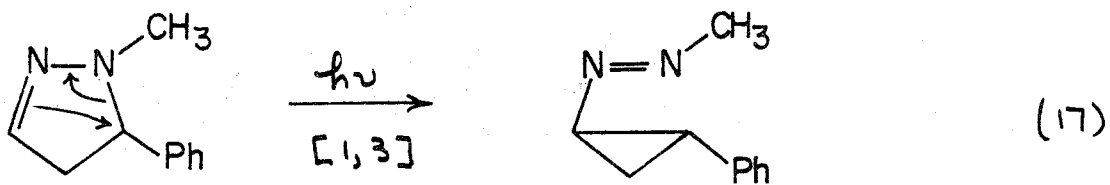
(14) J. Amer. Chem. Soc., 90, 3893 (1968)

E. Sigmatropic rearrangements

1. [1,3] Shifts common



10.1 E. (continued)



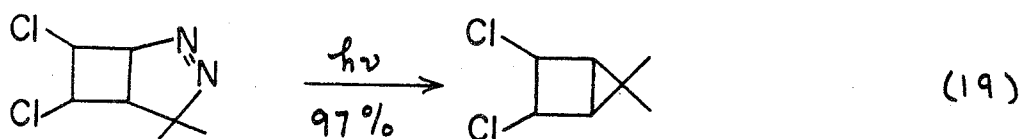
2. References to reactions

(15) Rev. Bull. Soc. Chim. France, 679 (1971)

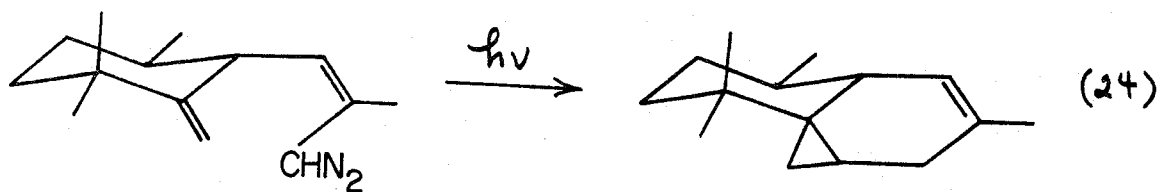
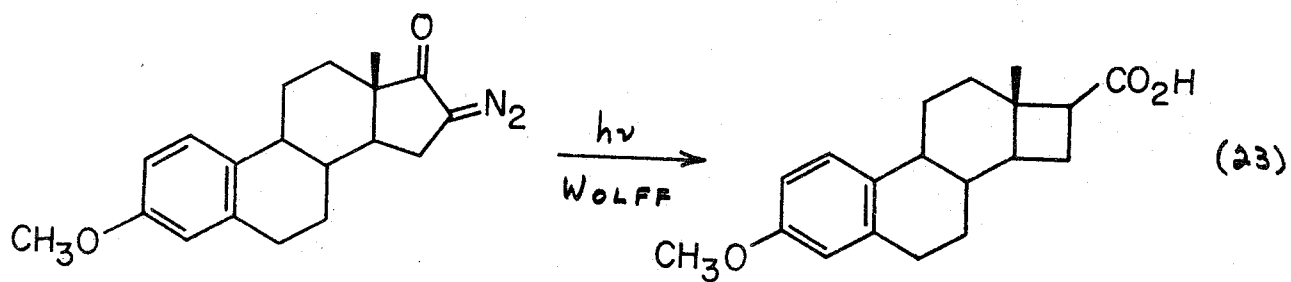
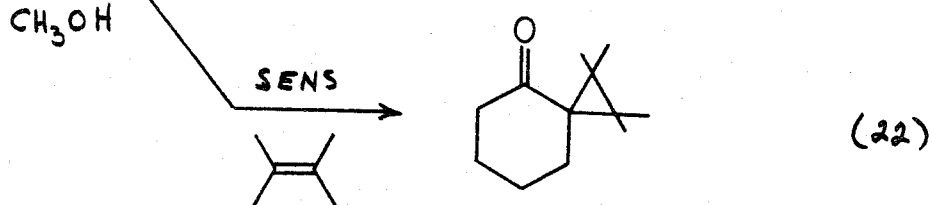
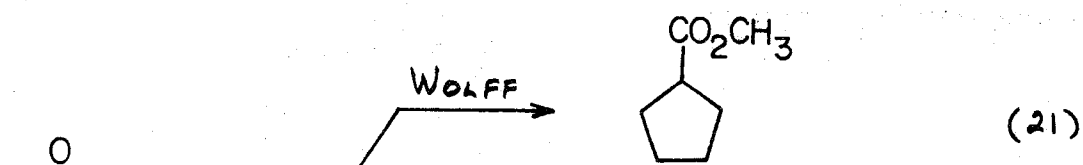
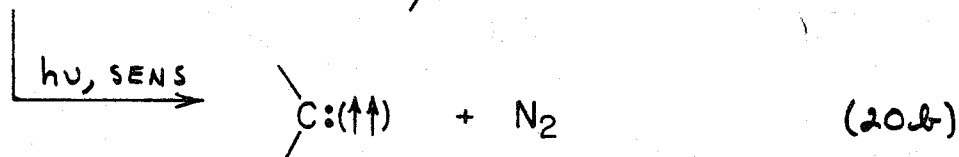
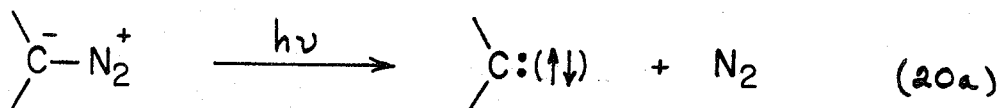
(16) J. Amer. Chem. Soc., 89, 6911 (1967)

(17) Helv. Chim. Acta, 51, 1628 (1968)

F. Fragmentations

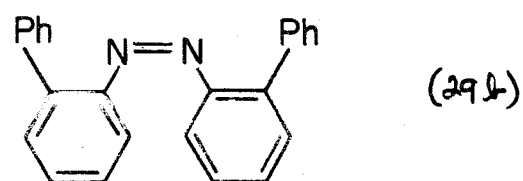
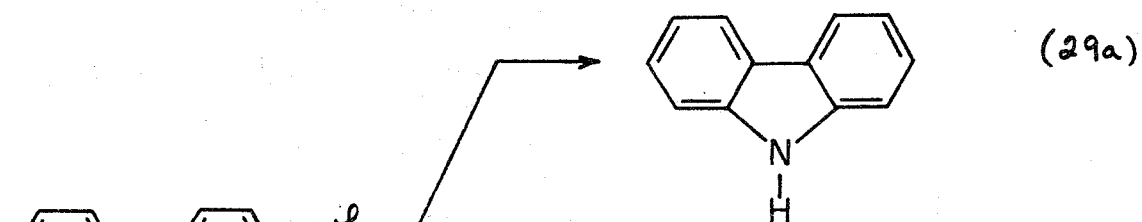
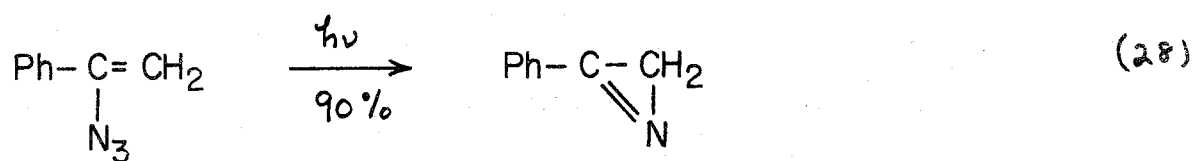
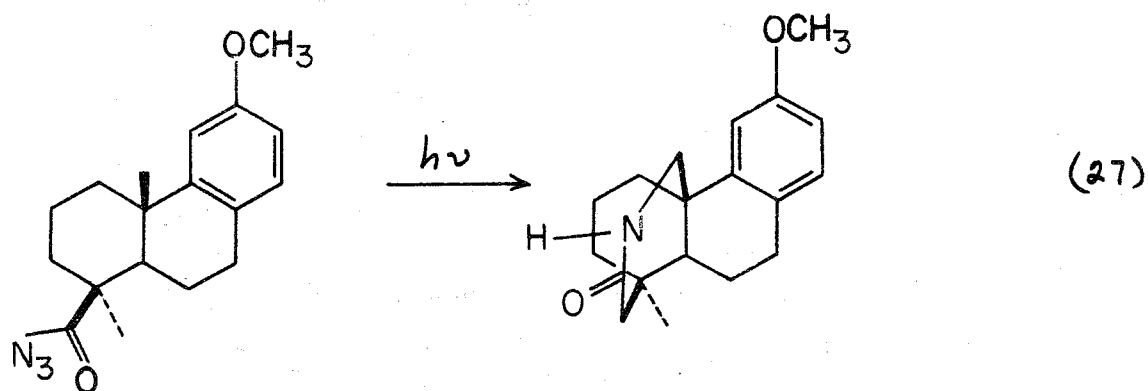
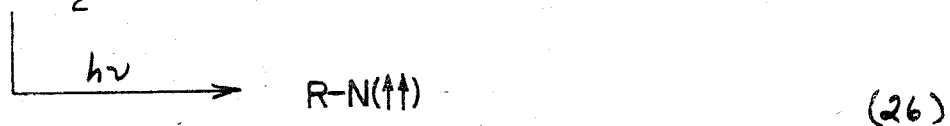
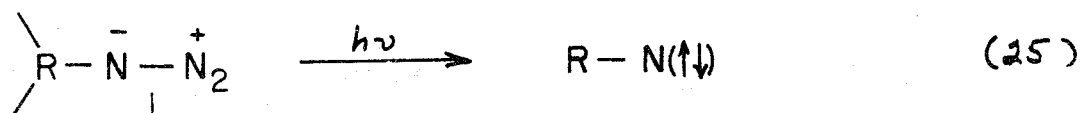


10.1 F. (continued)

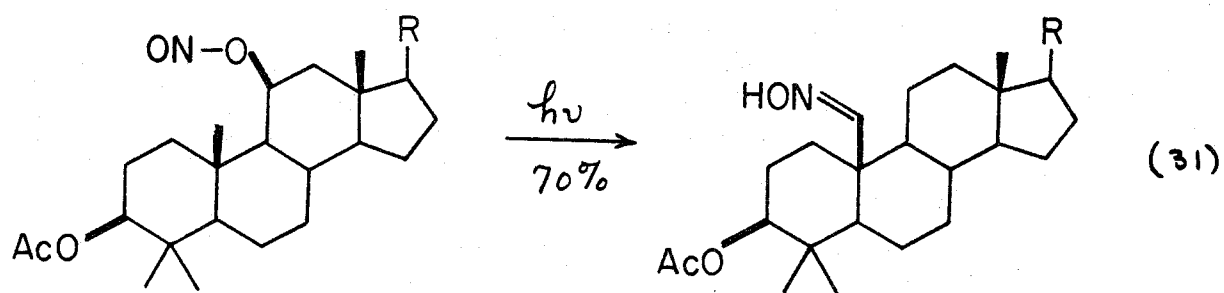
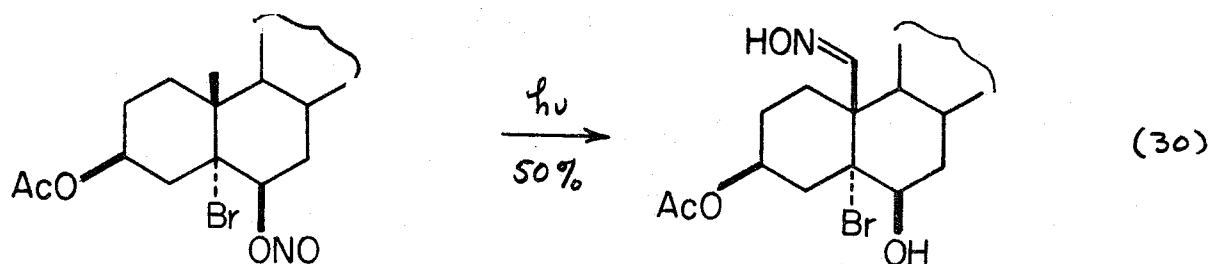


THUJOPSENE

10.1 F. (continued)



10.1 F. (continued)



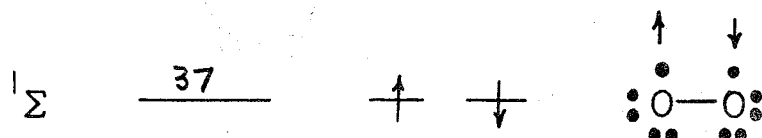
G. References

- (19) Tetrahedron Letters, 2979 (1968)
- (20) Rev: W. Kirmse, "Carbene Chemistry," 2nd ed., Academic Press, New York, New York, 1971.
- (21) and (22) J. Amer. Chem. Soc., 90, 2200 (1968)
- (23) J. Amer. Chem. Soc., 84, 115 (1962)
- (24) J. Amer. Chem. Soc., 86, 2884 (1964)
- (25) and (26) Rev: Angew. Chem., int. ed. Eng., 6, 897 (1966); Chem. Rev., 69, 345 (1969)
- (27) Can. J. Chem., 40, 896 (1962)
- (28) J. Amer. Chem. Soc., 90, 2869 (1969)
- (29) J. Amer. Chem. Soc., 92, 3102 (1970)
- (30) Rev: Nitrite photolyses (Barton reaction): Adv. Free Radical Chem., 3, 83 (1969); Chem. Ber., 102, 643 (1969)
- (31) J. Chem. Soc. C, 336 (1969)

10.2 SINGLET OXYGEN CHEMISTRY

A. Excited states of singlet oxygen.

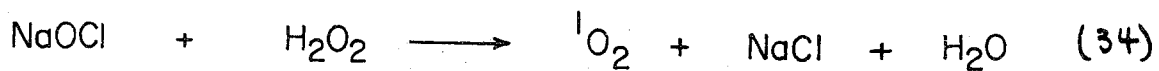
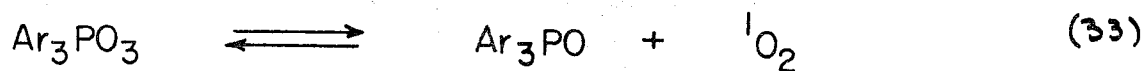
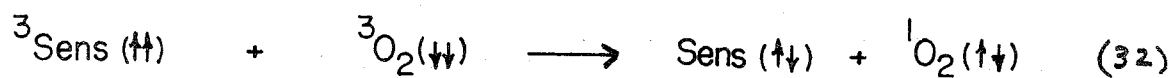
Rev: Chem. Rev., 71, 395 (1971)



1. ${}^1\Delta$: electrophilic, "ethylene like"

2. $\tau \sim 10^{-3}$ sec in CCl_4 ; $\tau \sim 10^{-6}$ sec in H_2O

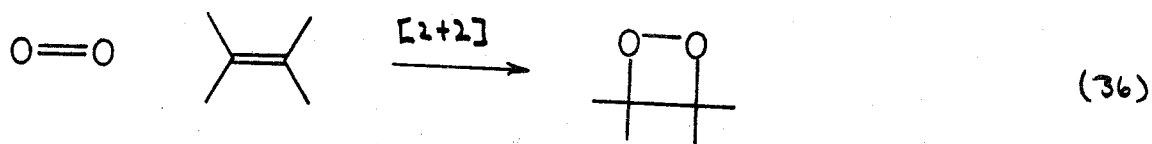
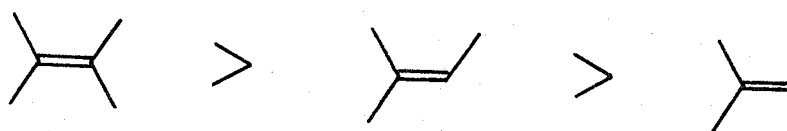
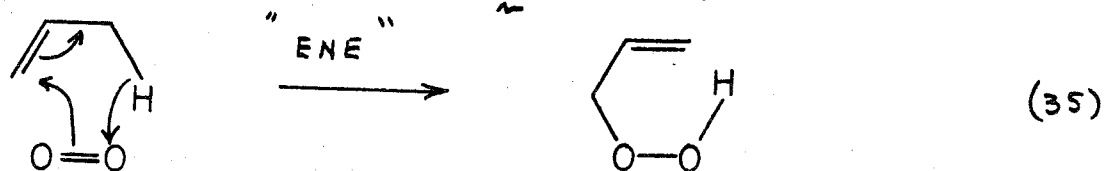
B. Generation of $\text{O}_2({}^1\Delta)$



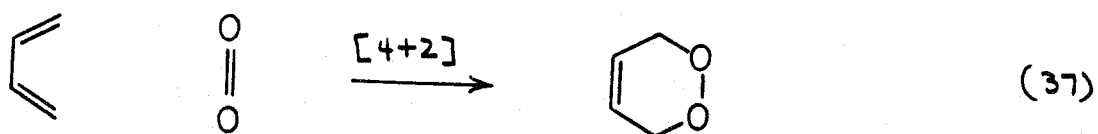
10.2 (continued)

C. Reactions of $^1\text{O}_2$

Rev: Accounts of Chem. Research, 1, 104 (1968)



1. Ene reaction inhibited. Electron-rich ethylene

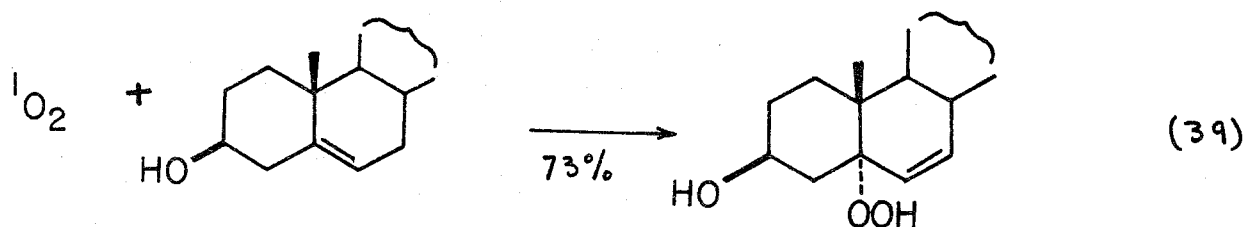
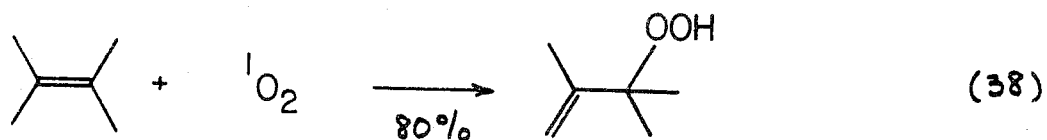


2. Goes best with cis-fused 1, 3-dienes

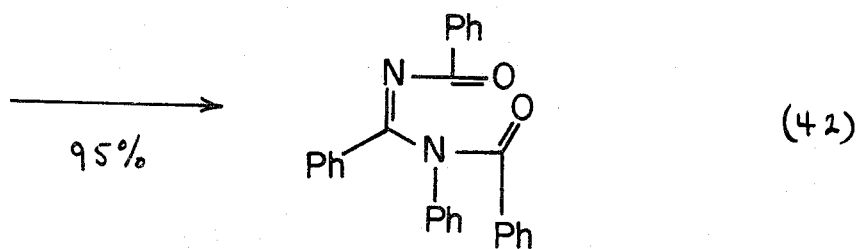
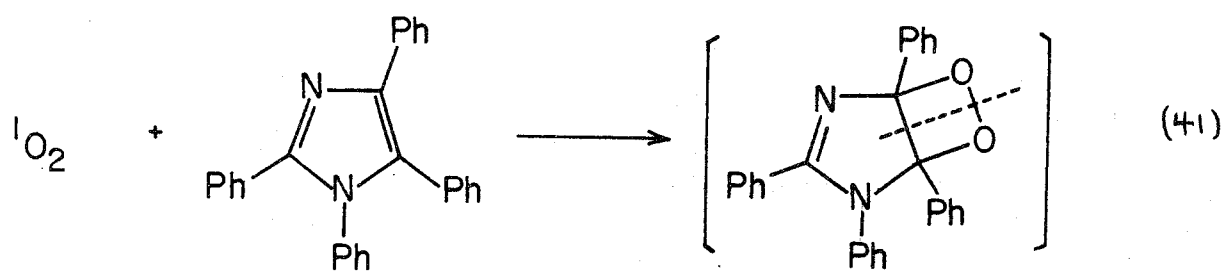
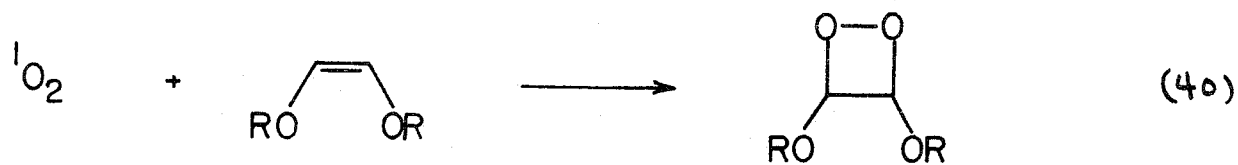
10.2 (continued)

D. Examples

1. Ene reaction

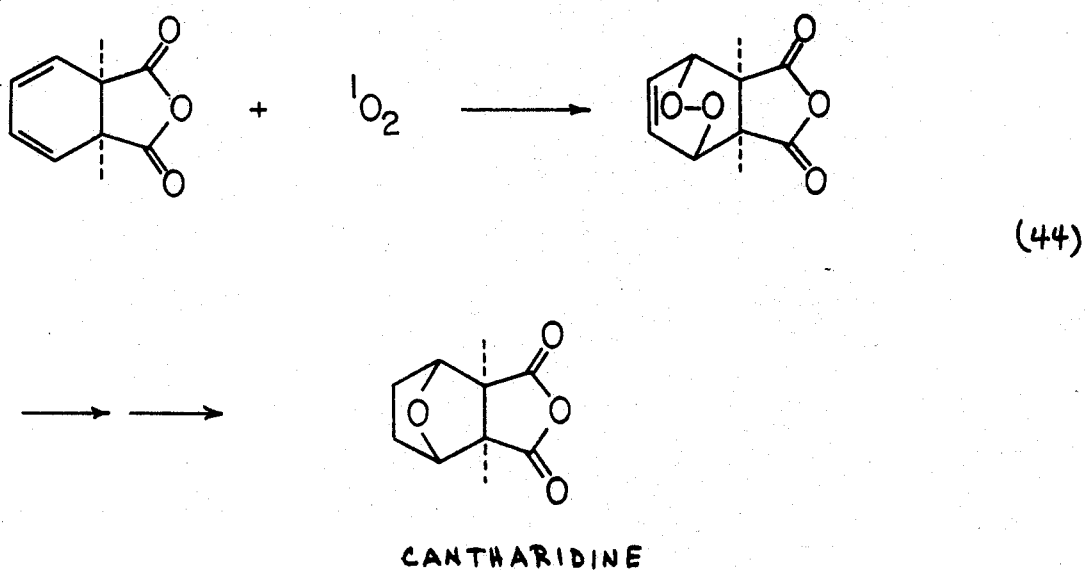
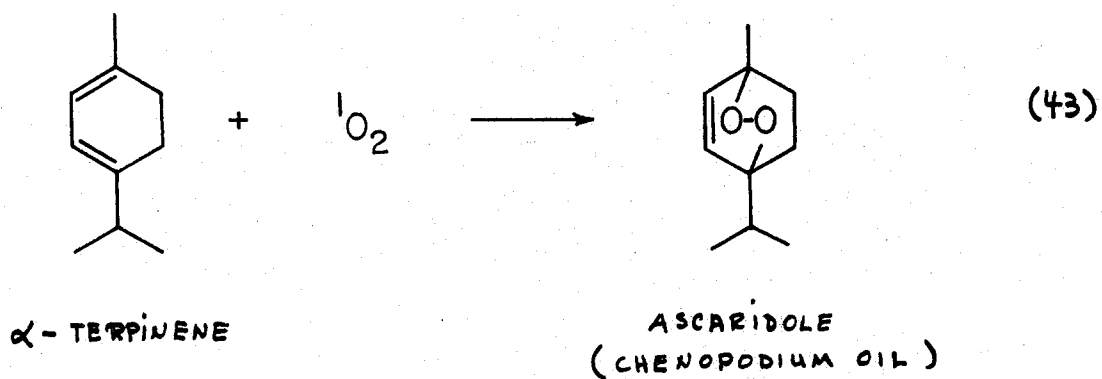


2. [2+2] Cycloaddition



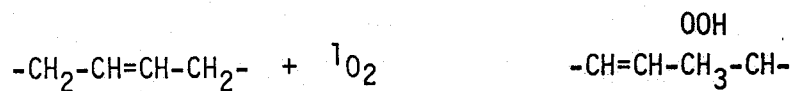
10.2 D. (continued)

3. [4+2] Cycloadditions



E. Role in polymer degradation

1. Production of unsaturated groups
2. Diffusion of oxygen
3. Role of photostabilizers



10.2 (continued)

F. Photodynamic effects on biological systems

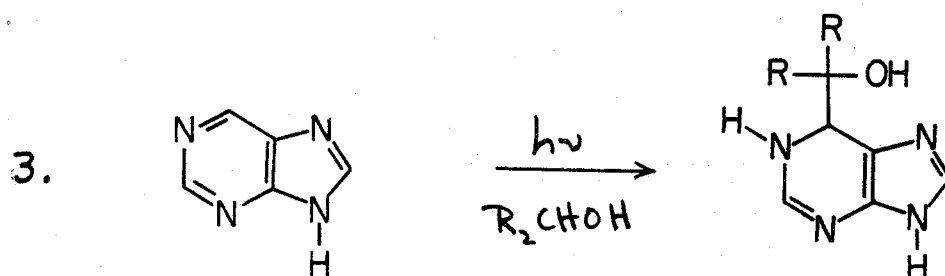
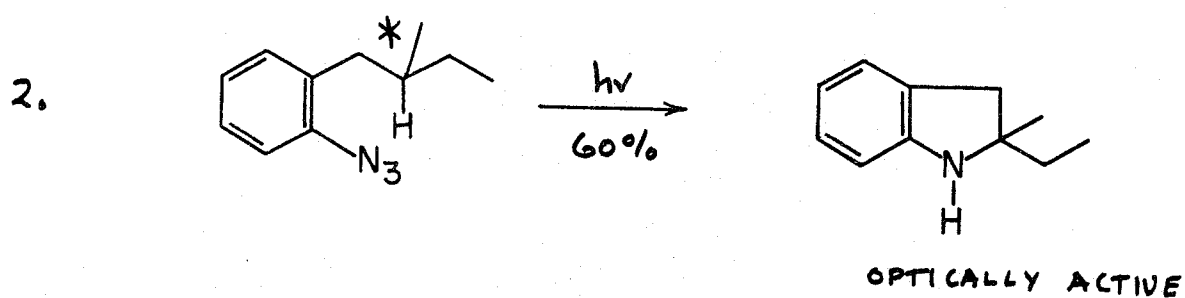
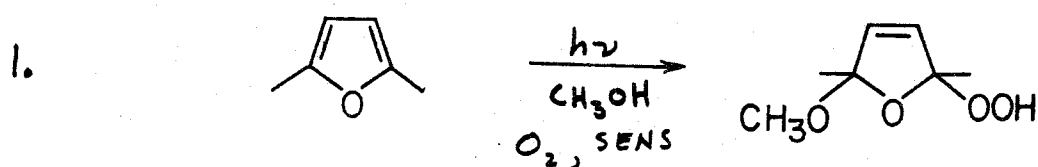
Rev: Photophysiology V, ed. A.C. Guise, 1970, p. 49

G. References

- (32) Rev. A. Schonberg, "Preparative Photochemistry," Verlag Chemie, 1968, p. 373
- (33) J. Amer. Chem. Soc., 92, 1234 (1970)
- (38) J. Amer. Chem. Soc., 92, 210 (1970)
- (39) Liebigs. Ann. Chem., 618, 194 (1958)
- (40) J. Amer. Chem. Soc., 92, 3223, 6055 (1970)
- (41) and (42) Tetrahedron Letters, 3277 (1968)
- (43) Naturwiss., 32, 157 (1944)
- (44) Naturwiss., 40, 581 (1953)

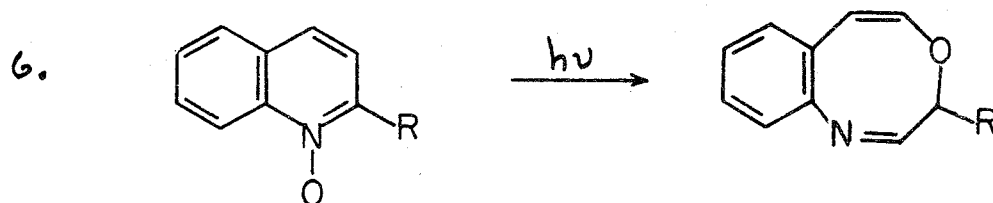
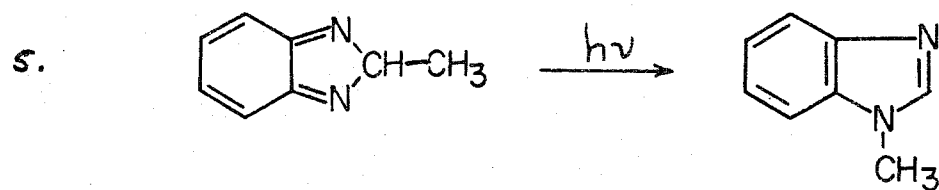
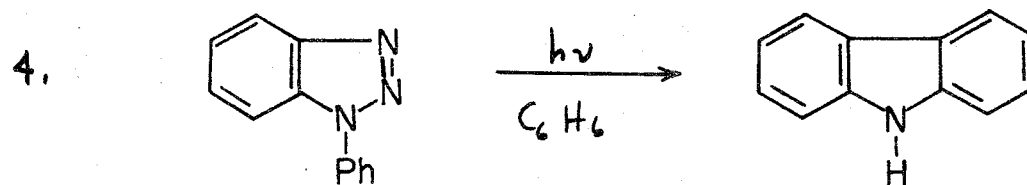
10.3 PROBLEMS

A. Classify the following photoreactions in terms of one of the processes discussed in this chapter.

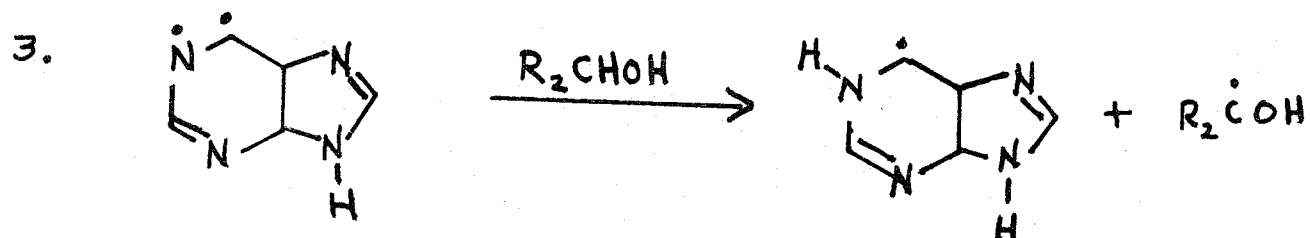
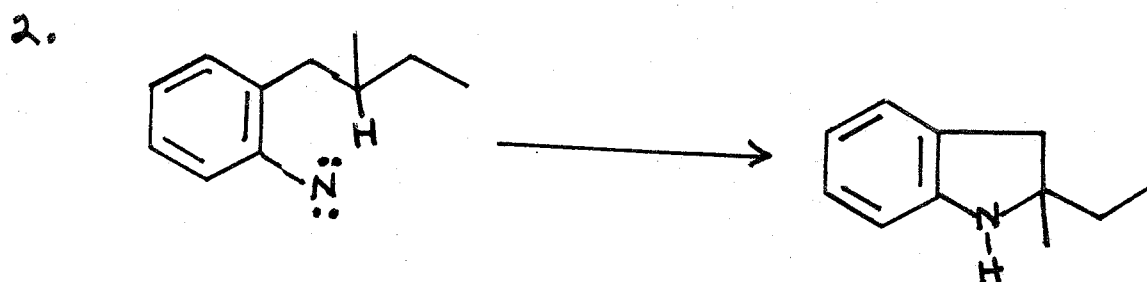
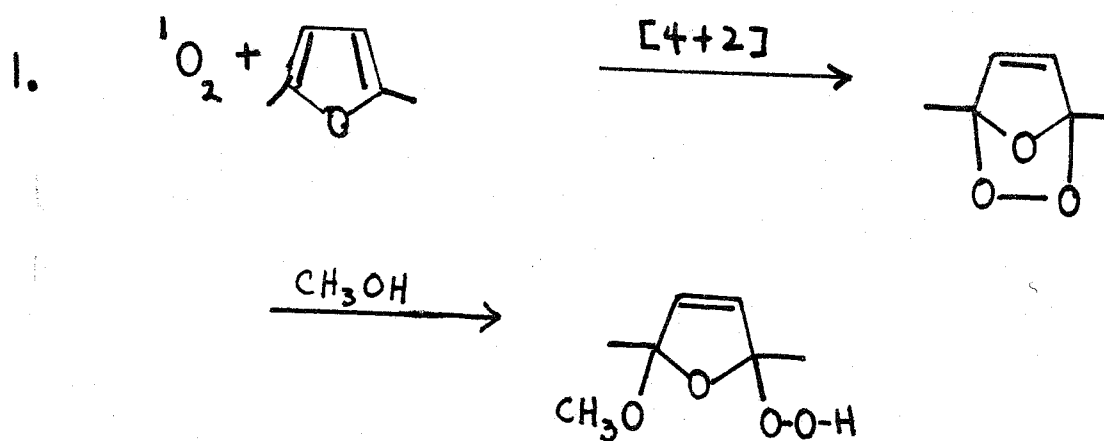


(continued)

10.3 A. (continued)



10.4 ANSWERS TO PROBLEMS



(continued)

10.4 (continued)

