

# OXOCARBONS

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# Contents

List of Contributors	ix
Preface	xi

## 1 HISTORY OF THE OXOCARBONS

Robert West

I. Introduction	1
II. Early History: Croconate and Rhodizonate	2
III. Squaric Acid and the Aromatic Oxocarbons	3
IV. Deltic Acid	5
V. Diamagnetic Anisotropy and Aromaticity in Croconate Ion	6
VI. Oxidation and Reduction Products	8
VII. Theoretical Calculations and Electronic Spectra	10
VIII. Pseudo-Oxocarbons	12
References	13

## 2 THIOXOCARBON DIANIONS AND THEIR DERIVATIVES

Gunther H. R. Seitz

I. Introduction	15
II. Thioxocarbon Dianions	16
III. Mixed C <sub>4</sub> Oxo-Thioxocarbon Dianions	19
IV. Dithiosquaric Acid Diamides	22
V. Thiodeltic Acid Derivatives	36
VI. Mixed C <sub>5</sub> Oxo-Thioxocarbon Dianions	38
References	40

## 3 PHYSICAL CHEMISTRY OF AQUEOUS OXOCARBONS

Lowell M. Schwartz, Robert I. Gelb, and Daniel A. Laufer

I. Introduction	43
II. Survey of Oxocarbon Acid pK Determinations	44
III. Thermodynamic Data	46

IV. Structures of Aqueous Oxocarbons	49
V. A New Type of Aqueous Complex	56
References	57

## 4 NEW BOND-DELOCALIZED (DICYANOMETHYLIDENE)CROCONATE DERIVATIVES: "CROCONATE VIOLET" AND "CROCONATE BLUE"

Alexander J. Fatiadi

I. Introduction	59
II. Reaction of Croconates with Malononitrile	62
III. Electrical Conductivity of Some Bond-Delocalized Salts	73
IV. Summary	76
References	76

## 5 EXCITED STATES OF OXOCARBON DIANIONS

Josef Michl and Robert West

I. Introduction	79
II. The Perimeter Model for $(4N+2)$ -Electron $[n]$ Annulenes	80
III. The Perimeter Model for Oxocarbon Dianions	88
IV. Comparison with Experiment	95
References	99

## 6 THE MYCOTOXIN "MONILIFORMIN" AND RELATED SUBSTANCES

H.-D. Scharf and H. Frauenrath

I. Moniliformin	101
II. Syntheses and Properties of Semisquaric Acid and Its Derivatives	109
III. The Series of Semioxocarbons $\text{CH}(\text{CO})_n^{(-)M^{(+)}}$	114
IV. Naturally Occurring Phenyllog Substances	116
References	117

## 7 RAMAN SPECTRA AND JAHN-TELLER EFFECTS OF OXOCARBON DIANIONS

Mitsuo Ito, Koji Kaya, and Machiko Takahashi

I. Introduction	121
II. Raman Intensity and Electronic States	122
III. Electronic Absorption Spectra of Oxocarbon Ions	127
IV. Raman Spectra of $\text{C}_n\text{O}_n^{2-}$	128
V. Jahn-Teller Effect Suggested by Raman Intensities	133
VI. Jahn-Teller Deformation of Ions	135
VII. Excitation Profile and Jahn-Teller Effect	138
VIII. Conclusion	139
References	140

## 8 THE STRUCTURAL PHASE TRANSITION AND DIELECTRIC PROPERTIES OF SQUARIC ACID

Jens Feder

I. Introduction	141
II. Structural Determinations	143
III. Raman and Infrared Spectra	147
IV. NMR Spectra	149
V. Birefringence, Dielectric, and Elastic Properties	152
VI. Theory	160
VII. Conclusion	165
References	166

## 9 SYNTHESSES OF HIGHLY OXIDIZED CYCLOBUTANES VIA [2+2] CYCLOADDITION REACTIONS OF KETENES

Daniel Belluš

I. Introduction	169
II. Moniliformin	173
III. Alkylmoniliformins	175
IV. Arylmoniliformins	179
V. Squaric Acid	180
References	183

## 10 THE CHEMISTRY OF SQUARAINES

Arthur H. Schmidt

I. Introduction	185
II. Structure and Nomenclature	186
III. Identification of Squaraines	190
IV. Methods of Preparation	190
V. Tables of Squaraines	197
VI. Reactions of Squaraines	197
VII. Final Remarks	229
References	230

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## Preface

Oxocarbons, first synthesized 155 years ago, were little known until the re-birth of the field following the discovery of squaric acid in 1959. Only since then have chemists generally come to appreciate the remarkable structural, chemical, and electronic properties of these polycarbonylated organic species.

This volume represents a collection of chapters by experts on diverse aspects of the science of oxocarbons. Subjects treated include the spectroscopy and chemical physics of oxocarbons, as well as their reaction chemistry. Included also are several chapters on the substituted derivatives of cyclic polycarbonyls now called "pseudooxocarbons." The colors used on the cover of this volume were chosen to match those of the first known oxocarbon anions. The yellow of the lettering matches the color of croconate ion, and the red of the cover itself is similar to that of rhodizonate ion.

It has been a pleasure to work with the authors of these chapters of this, the first book to be published on oxocarbon chemistry.

Robert West

# 1

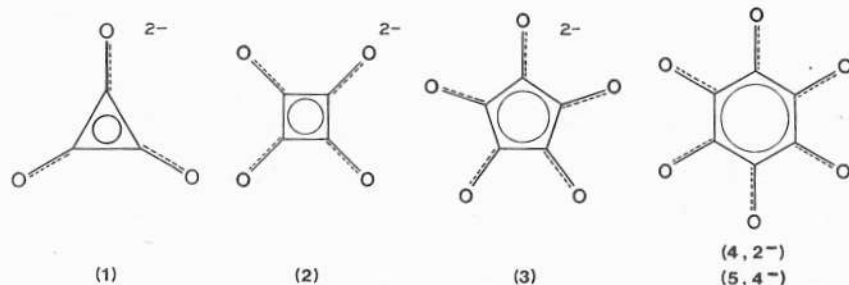
## History of the Oxocarbons

Robert West

I. Introduction . . . . .	1
II. Early History: Croconate and Rhodizonate . . . . .	2
III. Squaric Acid and the Aromatic Oxocarbons . . . . .	3
IV. Deltic Acid . . . . .	5
V. Diamagnetic Anisotropy and Aromaticity in Croconate Ion . . . . .	6
VI. Oxidation and Reduction Products . . . . .	8
A. Neutral Species . . . . .	8
B. Anions and Anion-Radicals . . . . .	8
VII. Theoretical Calculations and Electronic Spectra . . . . .	10
VIII. Pseudo-Oxocarbons . . . . .	12
References . . . . .	13

### I. Introduction

The term "oxocarbon," first suggested in 1963 [1], designates compounds in which all or nearly all of the carbon atoms are bonded to carbonyl or enolic oxygens or their hydrated or deprotonated equivalents. About 20 years ago the cyclic oxocarbon anions were recognized as members of an aromatic series, stabilized by electron delocalization of  $\pi$  electrons around the ring [2]. Known monocyclic oxocarbon anions include deltate (1), squarate (2), croconate (3), rhodizonate (4), and the tetraanion of tetrahydroxy-*p*-benzoquinone (5). This introductory chapter is a brief historical review of oxocarbon chemistry. Its purpose is to set into context the chapters dealing with particular aspects of oxocarbon chemistry which make up the rest of the volume. Two reviews on oxocarbons were published about 10 years ago, one emphasizing physical prop-



erties [3] and one dealing with synthesis [4]. A more recent review mainly covers developments within the past decade [5].

## II. Early History: Croconate and Rhodizonate

Although the special properties of oxocarbons have come to light only recently, their history begins at the very dawn of chemistry and involves many of the great chemists of the early nineteenth century. The first workers to have in hand an oxocarbon were probably Berzelius, Wöhler, and Kindt, who in 1823 observed a black powdery residue formed in the reaction of potassium hydroxide with carbon in what was apparently a pioneer attempt at an industrial synthesis of potassium [6]. Dipotassium croconate and croconic acid (named from the Greek *krokos*, yellow, the color of the acid and its salts) were isolated from this residue by Gmelin in 1825 [7]. This early date is quite significant, for it is the same year in which benzene was obtained from illuminating gas oil by Michael Faraday.\*

These very early experiments on oxocarbons are historically important in another respect. Croconic acid and rhodizonic acid are both known to be products of microbiological oxidation of myoinositol, a compound that is common in plants [8,9]. Gmelin's preparation of croconic acid was therefore a synthesis of a natural product—an "organic" compound in the original sense—from inorganic starting materials. It was perhaps the first such synthesis ever carried out, predating Wöhler's classic synthesis of urea by 3 years.

In 1834, Liebig discovered that a product similar to that from the potassium hydroxide-carbon reaction could be obtained by the reaction of potassium metal with carbon monoxide [10]. A few years later Heller isolated rhodizonic acid (named from the Greek *rhodizein*, rose red) from the products of this reaction and deduced that rhodizonate is the precursor of croconate ion [11].

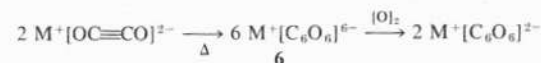
The nature of these transformations has become clear mostly as a result of more recent studies. At low temperatures, alkali metals react with carbon

\*Benzene has usually been assumed to be the first aromatic compound to be isolated, but it is now evident that it must share this distinction with croconate ion.

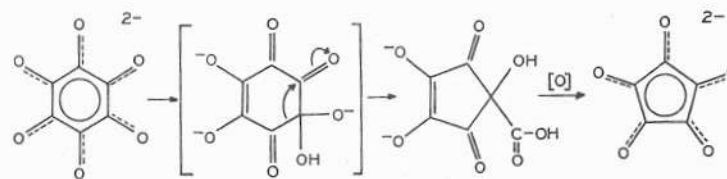
## 1. History of the Oxocarbons

monoxide to give dialkali salts of dihydroxyacetylene  $2M^+[OC\equiv CO]^{2-}$  [12]. This anion can also be regarded formally as an oxocarbon, representing the first member of the oxocarbon series  $C_nO_n^{2-}$ . However, the bond lengths in this dianion, 1.20 Å for C—O, suggest that there is little charge delocalization away from the oxygen [13].

Upon heating, the acetylene diolate salts cyclotrimerize to benzenehexol hexaanion  $C_6O_6^{6-}$  (6). This is the first species that can be isolated when the reaction of metals with CO is carried out at higher temperatures, as in the early studies [10,11]. The anion 6, which can be thought of as species in which the oxocarbon and conventional aromatic series intersect, undergoes oxidation rapidly in air to rhodizonate ion:



However, in Gmelin's early experiment he isolated not rhodizonate but the five-membered ring croconate ion. The latter arises in a rather surprising oxidative ring-contraction reaction, the nature of which was not clarified until many years later. When air or oxygen is bubbled through an alkaline aqueous solution of rhodizonate, the following sequence of changes takes place [13]:

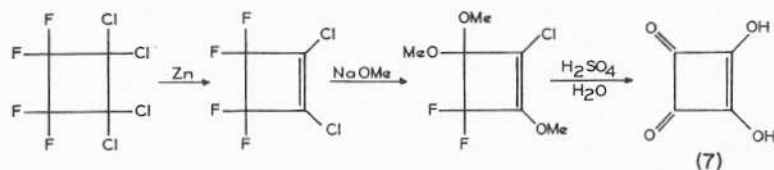


This ring contraction is an example of an  $\alpha$ -oxo alcohol rearrangement, in turn related to the benzilic acid rearrangement. It provides such a convenient method for synthesis of croconates that, to this date, no other preparative method has been developed.

## III. Squaric Acid and the Aromatic Oxocarbons

In the 125 years following the discovery of croconic and rhodizonic acids, these substances were investigated sporadically. Some improved synthesis of rhodizonate (and hence croconate) were developed, and the properties of rhodizonate as an oxidation-reduction indicator were exploited, but no detailed consideration was given to the unusual chemical bonding in these anions. The first suggestion of cyclic delocalization in an oxocarbon was apparently made in 1958 by Yamada [14], but, because this idea appeared only at the end of a lengthy article dealing with other matters, it was overlooked until later.

The modern era of oxocarbon chemistry can be dated from the famous accidental synthesis of squaric acid (7) by Cohen, Lacher, and Park a year later [15]:



Squaric acid was found to be a remarkably strong acid for an enol, having  $pK$  values close to those for sulfuric acid. (The unusual acidity of the cyclic oxocarbons is discussed in Chapter 3.) Cohen *et al.* interpreted the high acid strength as evidence that squarate dianion was greatly resonance-stabilized. The delocalized structure proposed for 2 led to the suggestion that the squarate ion was aromatic and that the oxocarbon anions might constitute a previously unrecognized aromatic series [1]. Evidence from vibrational spectroscopy soon confirmed that squarate and croconate are planar and symmetric ( $D_{4h}$  and  $D_{3h}$ , respectively), with delocalized  $\pi$  bonding around the ring [16]. X-ray crystallographic studies confirmed the delocalized, symmetric nature of 2, 3, and 4. The bond lengths for these species, shown in Table I [17-19] indicate that the carbon-carbon  $\pi$  bonding is substantial in the oxocarbon anions, although weaker than in benzene. All three of the oxocarbon salts in the table have layerlike structures in which the anions are close enough to raise the possibility of interionic charge-transfer interaction in the salts. Such interionic effects may be responsible for the unusual low-energy electronic absorption of some rhodizonate salts [20]. Semiconductivity probably resulting from intermolecular charge transfer in croconate derivatives is discussed in Chapter 4.

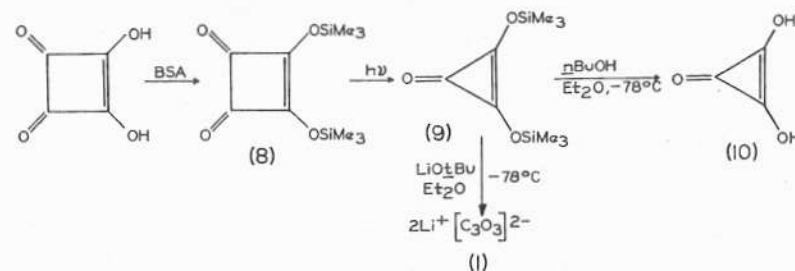
As mentioned above, there are several satisfactory syntheses for 3, 4, and 5, but convenient routes to squaric acid have been lacking. A promising new method is the electrochemical reduction of carbon monoxide in polar aprotic solvents [21], which can be carried out to yield 20 gm of 7 in a single reaction (35% based on CO consumed). It is remarkable that 2 is formed in electrochemical reduction, considering that it has never been observed in chemical reductions of CO. The synthesis of squaric acid and related compounds is treated in Chapter 9, and in a recent review [22].

Table I. Bond Lengths ( $r$ ) and  $\pi$ -Bond Orders ( $\rho$ ) in Oxocarbon Anions

Species	$r_{CC}$ (Å)	$\rho_{CC}$	$r_{CO}$ (Å)	$\rho_{CO}$	Ref.
$K_2C_4O_4 \cdot H_2O$	1.469	0.38	1.259	0.78	17
$(NH_4)_2C_5O_5$	1.457	0.44	1.262	0.78	18
$Rb_2C_6O_6$	1.488	0.27	1.213	1.00	19

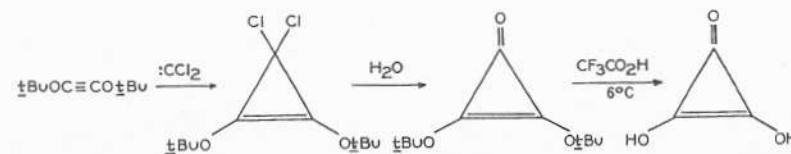
#### IV. Deltic Acid

The possible existence of numerous unknown members of the oxocarbon family was suggested in 1963 [1]. Of the species then unknown, the smallest possible oxocarbon,  $C_3O_3^{2-}$  (1), seemed particularly significant. Attempts in various laboratories to obtain this species were unsuccessful until 1976. The key to the synthesis was formation of bis(trimethylsiloxy)cyclopropenone (9) by photochemical decarbonylation of bis(trimethylsiloxy)cyclobutenedione (8), which can easily be made from squaric acid. Unlike other fully substituted cyclopropenones, 9 undergoes solvolysis without undergoing ring opening to give either deltic acid (10) or the dilithium salt of deltate ion [23]:



Deltic acid and the deltate salts are colorless compounds that slowly decompose in water. As predicted from theory [24], 1 and 10 are less stable than the other monocyclic oxocarbon acids and their anions, but nevertheless deltic acid survives heating to 100°C. Compound 10 is a somewhat weaker acid than the other monocyclic oxocarbons (Chapter 3). For the second dissociation, the greater  $pK$  value for deltic acid is reasonable in view of the larger charge repulsion in 1 than in 2-4.

A second synthesis for deltic acid has been reported, starting with di-*tert*-butoxyacetylene [25]:



An X-ray crystal structure is not yet available for a deltate salt, but a complete vibrational analysis of the Raman and infrared spectra of deltate ion has been carried out [26]. Urey-Bradley force constants (Table II) allow a comparison of bonding in 1 and other aromatic species to be made. The carbon-carbon stretching force constants  $K_{CC}$  for squarate and croconate are between 3.5 and 4.0  $\text{mdyn}/\text{Å}$ , distinctly greater than for C-C single bonds but lower than in ben-



Table II. Urey-Bradley Force Constants for Aromatic Species<sup>a</sup>

Species	$K_{CC}$ (mdyn/Å)	$K_{CO}$ (mdyn/Å)
$C_3O_3^{2-}$ (1)	5.57	5.50
$C_4O_4^{2-}$ (2)	3.95	5.60
$C_5O_5^{2-}$ (3)	3.50	6.72
$C_6H_6$	5.19	
$C_3H_3^-$	5.39	
$C_3H_3^+$	6.59	
$C_3Cl_3^+$	6.22	

<sup>a</sup> From Eggerding *et al.* [26].

zene. For deltate ion  $K_{CC}$  is about 5 mdyn/Å, nearly as large as that for benzene (~5.2). Deltate seems, therefore, to resemble the other three-membered ring aromatic species,  $C_3Cl_3^+$ ,  $C_3H_3^+$ , and  $C_3Ph_3^+$ , which also have exceptionally short and strong C—C bonds.

## V. Diamagnetic Anisotropy and Aromaticity in Croconate Ion

If the oxocarbon anions are in fact aromatic species, they should be expected to sustain a diamagnetic ring current. However, this is difficult to demonstrate by the usual NMR techniques, since compounds 1–4 contain no protons, and the <sup>13</sup>C-NMR chemical shifts are dominated by shielding effects due to the negative charges so that any small contributions from a ring current cannot be easily detected [27].

Some years ago the diamagnetic anisotropy of diammonium croconate  $(NH_4)_2C_5O_5$  was investigated in our laboratories. This salt was chosen because its crystal structure had been determined earlier [18]. The method used was the "flip-angle" method of Krishnan, in which a large single crystal is oriented in a magnetic field and the force required to reorient the crystal to another magnetic axis is measured [28]. This direct method is now seldom used, but it was extensively employed in the 1920's and 1930's to obtain all of the early data that led to the Pauling and London theories of diamagnetic ring current.\*

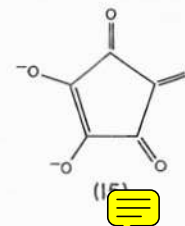
Although we were able to determine the value of the diamagnetic anisotropy ( $\Delta\chi$ ) for 3, at that time it was impossible to separate the total anisotropy into that part resulting from local contributions ( $\Delta\chi_{loc}$ ) and any part due to a diamagnetic ring current ( $\Delta\chi_{arom}$ ). However, more recent studies by Benson, Norris, Flygare,

\*This method has two disadvantages: Rather large single crystals are required, and the crystal structure of the solid must be known. However, now that it is a relatively simple matter to determine crystal structures, the Krishnan method may again come into favor.

## 1. History of the Oxocarbons

and Beak have led to a table of local atom and group anisotropies for planar compounds containing carbon, hydrogen, and oxygen [29]. The data in their table enable one to make at least an approximate calculation of the ring current anisotropy for croconate ion.

Our experiment established the diamagnetic anisotropy of croconate ion to be  $-51.5 \pm 3$  cgs units [30] (the ammonium ions have  $T_d$  symmetry, and hence  $\Delta\chi = 0$ ).<sup>\*</sup> We can now assume a localized structure for croconate. The logical one is **11**, containing five  $sp^2$  carbon atoms, three carbonyl oxygens, and two alkoxide



oxygen. The tables of Benson *et al.* [29] give local  $\Delta\chi$  values of  $-4.4$  for  $sp^2$  carbon,  $-6.5$  for carbonyl oxygen, and  $+2.0$  for ether-type oxygen. The value for the alkoxide oxygens is somewhat uncertain because there are apparently no data on magnetic anisotropies of alkoxides. However, we believe that the value of  $+2.0$  is reasonable. For  $C-O^-$ ,  $\Delta\chi_{loc}$  should in any event be positive, as are the  $\Delta\chi_{loc}$  values for  $C-Cl$  and for the isoelectronic  $C-F$ . Comparison of available data for halogen compounds and analogous hydrocarbons suggests  $\Delta\chi_{loc} \sim +1$  for  $C-Cl$  and  $+1.5-3.0$  for  $C-F$  [31].

Taking the Benson value of  $+2.0$  for the alkoxide oxygens, we calculate for 3,  $\Delta\chi_{loc} = -37.5$ . Subtracting from the measured value of  $-51.5$  for 3 gives  $-14$  as the probable value for  $\Delta\chi_{arom}$ , the diamagnetic anisotropy due to the ring current. The value of  $\Delta\chi_{arom}$  for 3 is compared with that for other cyclic molecules in Table III. The ring current anisotropy in croconate appears to be a little less than that for furan, and about half that of benzene. In contrast, the nonaromatic molecules tropone and  $\alpha$ -pyrone show nearly zero values of  $\Delta\chi_{arom}$  [32]. The result, therefore, confirms other evidence for aromatic behavior in this oxocarbon anion.

\*The torsion constant of the quartz fibers, 1 m in length, was calculated from measurements on crystals of 1,3,5-triphenylbenzene. As a further calibration the magnetic anisotropy of hexachlorobenzene was redetermined, with results in good agreement with those in the literature [30a]. In crystalline diammonium croconate the  $C_5O_5^{2-}$  ions are perpendicular to the  $c$  (needle) axis. Typical azimuths at the flip angle, with  $c$  parallel and  $b$  perpendicular to the magnetic field were  $146^\circ$ ,  $147^\circ$ ,  $146^\circ$ , and  $149^\circ$ ; similarly, for  $c_{||}$  and  $a_{\perp}$ , azimuths were  $150^\circ$ ,  $152^\circ$ ,  $150^\circ$ , and  $150^\circ$ . The anisotropy between the  $a$  and  $b$  axes was too small to be determined. The diamagnetic anisotropy  $\Delta\chi$  ( $c - b = c - a$ ) was calculated as  $-52.5 \pm 3$  cgs units from the usual formula,  $\Delta\chi = Mk(\alpha_c - \pi/4)/mH^2$  [28].

**Table III.** Diamagnetic Anisotropy and Ring Current Anisotropy in Planar Species

Species	$\Delta\chi_{exp}$	$\Delta\chi_{loc}$	$\Delta\chi_{arom}$
Benzene	-59.7	-26	-33
Furan	-38.7	-16	-23
Croconate	-52.5	-37	-15
Tropone	-36.0	-37	0
2-Pyrone	-24.8	-26	0
Cyclopenten-3-one	-16.8	-17	0

## VI. Oxidation and Reduction Products

### A. NEUTRAL SPECIES

The oxidation of croconic and rhodizonic acids leads to compounds that have long been known as leuconic acid ( $C_5H_{10}O_{10}$ ) and triquinoyl octahydrate ( $C_6H_{16}O_{14}$ ), respectively [4]. These substances are obtained by treating the parent acids or their alkali salts with oxidants, such as free halogens or nitric acid. The analogous four-membered ring compound  $C_4(OH)_8$  was synthesized from squaric acid with bromine or nitric acid in 1963 [33]. All of the oxidation products can be reduced back to the parent oxocarbon acids with  $SO_2$ .

The structure of  $C_4(OH)_8$  has been shown both by vibrational spectroscopy [33] and X-ray crystallography [34] to be octahydroxycyclobutane. The infrared spectra of octahydroxycyclobutane, leuconic acid, and triquinoyl are all similar; none of the compounds shows  $C=O$  absorption. It is highly probable that all three compounds have the fully hydroxylated structures shown in Scheme 1.

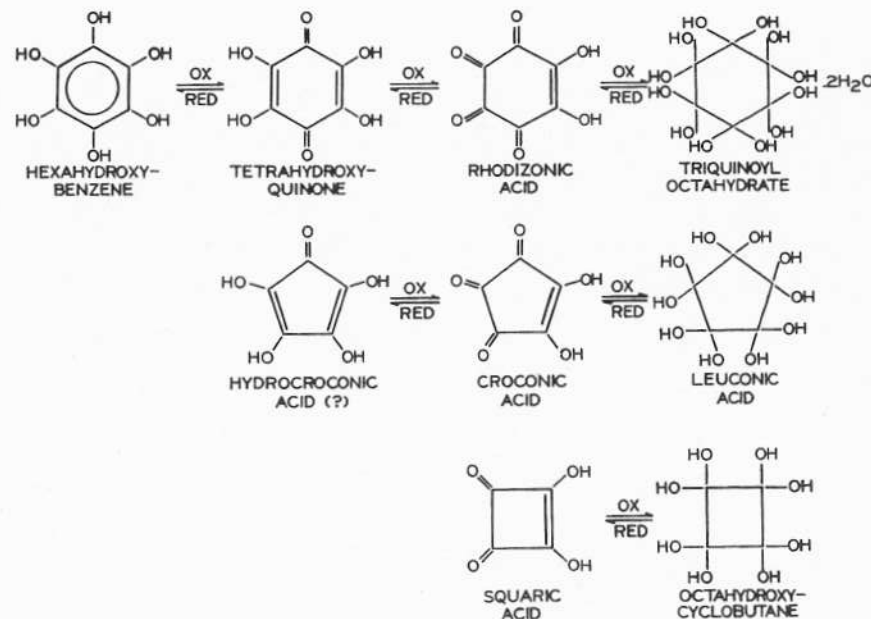
The dehydrated molecules corresponding to the perhydroxycycloalkanes shown in the scheme would be of great interest. These molecules, which would be oligomers of carbon monoxide,  $(CO)_n$ , are almost surely strongly endothermic, and all attempts to prepare them have been unsuccessful.

Reduction of the oxocarbons is well understood only for the six-membered ring compounds. Rhodizone ion or rhodizonic acid can be reduced with  $SO_2$  or other mild reagents, first to tetrahydroxy-*p*-benzoquinone and later to hexahydroxybenzene. The reduction takes place in successive two-electron steps and is essentially reversible.

### B. ANIONS AND ANION-RADICALS

In addition to the oxocarbon anions themselves (1-5), the species  $C_6O_6^{6-}$  and  $C_6O_6^{4-}$  [35] are well established. Formation of anion-monoradicals and anion-triradicals by oxocarbons was predicted some years ago, but, because these

## 1. History of the Oxocarbons



Scheme 1

species are unstable in water, they could not be investigated until salts of oxocarbons with the  $Ph_3PNPPH_3^+$  cation were prepared and found to be soluble in aprotic solvents [36]. Electrolytic oxidation of  $CH_2Cl_2$  solutions of these salts of 2, 3, and 4 led to ESR signals assigned to the anion-monoradicals (Table IV). The  $g$  values increase with increasing ring size, indicating (in agreement with other evidence and with theoretical calculations) that spin density is shifting gradually toward the oxygen atoms, which have larger spin-orbit coupling than carbon. Only for  $C_5O_5^{\cdot-}$  were  $^{13}C$  side bands observed, but the measured splitting constant of 4.1 G for this species is of special interest. From known  $Q$  values for  $\pi$  radicals [37], this splitting indicates a spin density  $\Sigma\rho_c$  of 0.08 on the carbon

**Table IV.** ESR Spectra for Oxocarbon Anion-Radicals<sup>a</sup>

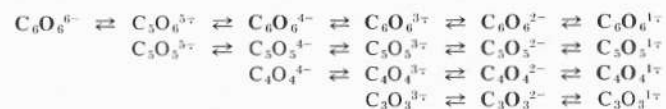
Species	$g$	$a_{13C}$ (G)
$C_4O_4^{\cdot-}$	2.00584	
$C_5O_5^{\cdot-}$	2.00624	4.10
$C_6O_6^{\cdot-}$	2.00652	
$C_6O_6^{3\cdot-}$	2.00457	

<sup>a</sup> From Patton and West [36].

atoms, and hence  $\Sigma\rho_o = 0.92$  on the oxygens. This is in excellent agreement with results from Hückel-McLachlan MO calculations, which predict  $\Sigma\rho_c = 0.10$ ,  $\Sigma\rho_o = 0.90$  [36].

A radical-trianion was obtained upon electrolytic reduction only for the six-membered ring. This finding is consistent with the fact that the tetraanion (**5**) is known for the six-membered ring but not for the smaller ones. The  $C_6O_6^{3-}$  radical has a somewhat lower  $g$  value than the radical-monoanions, suggesting that in this species the unpaired electron is associated more with the carbon atoms and less with the oxygen.

The following scheme shows the possible anions and anion-radicals for the monocyclic oxocarbons. Known species appear in boldface type; the others are possible but have not yet been established:



## VII. Theoretical Calculations and Electronic Spectra

Because of their high degree of symmetry, the oxocarbon anions lend themselves especially well to theoretical studies. The  $\pi$ -electron energy levels for oxocarbons, from early Hückel MO calculations, are shown in Fig. 1. The patterns of the  $\pi$  orbitals can also be predicted qualitatively from symmetry considerations, as explained in Chapter 5. As shown in the figure, each of the oxocarbon dianions possesses a nondegenerate HOMO and a doubly degenerate LUMO. This arrangement is similar to that in two-electron annulenes such as cyclopropenium ion or cyclobutadiene dication.\*

The earliest calculations on oxocarbons were of the simple Hückel type, but more recently theoretical studies have been carried out using more advanced methods, including extended Hückel [38], LCAO-CI [39], semiempirical SCF-CI [40], CNDO and CNDO-CI [41], MINDO/2 and CNDO-CI [42], and unrestricted Hartree-Fock [43]. Several of the more advanced techniques give qualitatively good agreement with observed energies for the first  $\pi$ - $\pi^*$  transition. Of these papers the one by Leibovici [42] is particularly useful because it deals with the entire series of oxocarbons and permits comparisons to be made between theoretical results and experimentally observed quantities. Table V gives results of the MINDO/2 calculations by Leibovici. The calculated heats of formation, normalized for ring size, suggest equivalent stabilization for **2** and **3**,

\*From this orbital arrangement the anion  $C_6O_6^{4-}$  (**5**) is predicted to be a triplet-state species. Magnetic measurements, however, indicate that **5** is diamagnetic [3]; the degeneracy of the partly occupied orbitals is probably removed by Jahn-Teller distortion.

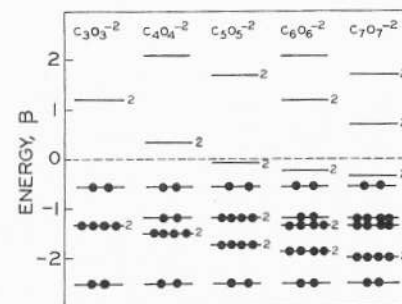


Fig. 1.  $\pi$ -Electron energy levels for oxocarbon dianions, from Hückel LCAO-MO calculations.

slightly less for **4**, and much less for **1**, in agreement with the observed stabilities of these anions. The calculated bond lengths accurately portray the observed trends, which are that the C—C bond length increases and C—O decreases with increasing ring size (see Table I). Unusually short C—C and long C—O bonds are predicted for **1** due to ring strain effects.

Calculations of electronic distribution in the anions indicate that there is a very strong charge separation between oxygen and carbons, which decreases with increasing ring size. The double-bond character is predicted from the  $\pi$ -bond orders (Table V) and associated Wiberg bond indices to increase for C—O and decrease for C—C bonds as the ring size increases. This corresponds very well with the trends in force constants derived from vibrational studies for **1**, **2**, and **3** [16,26] (see Table II). Identical Wiberg bond indices are calculated for C—C and C—O in delatate ion, in good agreement with the nearly identical values of the Urey-Bradley force constants. Even the strong transannular repulsion interaction between carbon atoms in 1,3 positions in squarate, evident from the vibrational studies, is consistent with the high values of Wiberg populations calculated for these nonbonded carbons [42].

For a quantitative treatment of the electronic spectra of oxocarbons, calculations, including configuration interaction, are necessary and, as several workers

Table V. Results of MINDO/2 Molecular Orbital Calculations for Oxocarbon Anions  $C_nO_n^{2-n}$

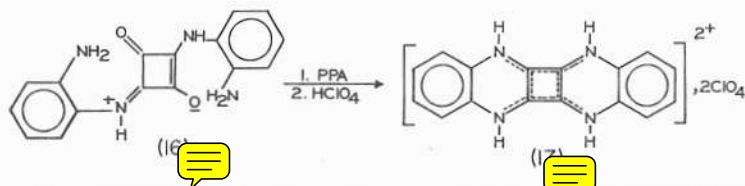
$n$	$d_{CC}$ (Å)	$d_{CO}$ (Å)	$\bar{p}_{CC}$	$\bar{p}_{CO}$	$-\Delta H_f/n$ (kcal/mole)
3	1.396	1.262	0.570	0.470	26.3
4	1.440	1.249	0.427	0.607	40.3
5	1.458	1.243	0.369	0.687	41.2
6	1.471	1.240	0.340	0.736	37.6

<sup>a</sup> From Leibovici [42].

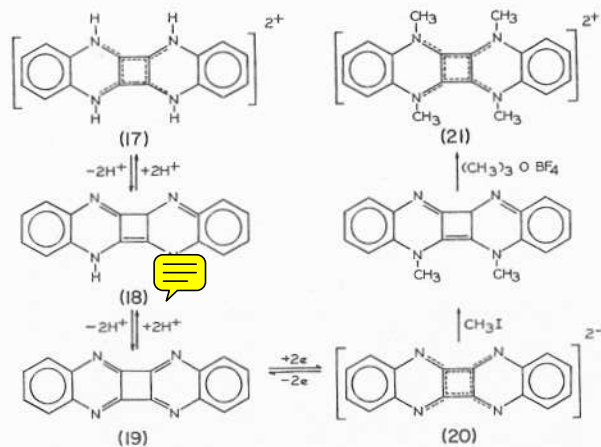
have found, doubly excited as well as singly excited states must be included in the treatment. The VESCF-CI calculations by Sakamoto and I'Haya [40] correspond fairly well to the observed frequencies for the first  $\pi-\pi^*$  transition. The electronic spectra of oxocarbons have been carefully studied and are the subject of Chapters 5 and 7.

### VIII. Pseudo-Oxocarbons

In recent years a number of oxocarbon analogs have been prepared in which one or more of the oxygen atoms are replaced by other groups, such as S, Se, NR, or  $C(CN)_2$ . Because of their resemblance to the oxocarbons, such compounds are sometimes called pseudo-oxocarbons. The remarkable chemistry of the sulfur compounds (thioxocarbons) and that of the dicyanomethylidene derivatives are the subjects of Chapters 2 and 4, respectively. Since they are not covered elsewhere in this volume, some mention should be made of the interesting tetranitrogen derivatives of squaric acid, studied by Hünig and his students [44]. From the reaction of squaric acid with *o*-diaminobenzene they obtained the 1,3-diamide **12**, which can be condensed to form the green dication **13**:



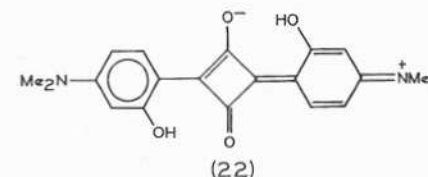
As shown in Scheme 2, **13** can be converted to several other interesting species, including the diamidines **14**, the radicalene derivative **15**, the dianion **16**,



Scheme 2

and the tetramethyl dication **17**. These species show an elaborate oxidation-reduction chemistry; the dication **17** can be reduced to a radical cation, and **15** undergoes reversible oxidation-reduction to **16** through an intermediate electron-delocalized radical-anion.

More complex derivatives of the oxocarbons have also been prepared. Those of squaric acid are especially significant because of their unusual electronic properties. The chemistry of these cyanine-like derivatives, the "squaraines," is discussed in Chapter 10. Special mention should be made of the photoconductivity of compounds such as **18**. Photovoltaic cells constructed of **18** with appropriate contact materials show the highest efficiencies for conversion of sunlight to electrical energy ever recorded for an organic substance [45].



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## 2

# Thioxocarbon Dianions and Their Derivatives

Gunther H. R. Seitz

I. Introduction . . . . .	15
II. Thioxocarbon Dianions . . . . .	16
A. Synthesis and Reactions of the C <sub>4</sub> Thioxocarbon Dianion . . . . .	16
B. Spectroscopic Data . . . . .	18
III. Mixed C <sub>4</sub> Oxo-Thioxocarbon Dianions . . . . .	19
A. Syntheses and Reactions of Monothiosquarate and 1,2-Dithiosquarate Dianions . . . . .	19
B. Reaction of Thiosquarate Esters with Amines . . . . .	21
C. Syntheses and Reactions of 1,3-Dithio- and 1,2,3-Trithiosquarate Dianions . . . . .	22
IV. Dithiosquaric Acid Diamides . . . . .	22
A. Syntheses and Properties of 1,2-Dithiosquaric Acid Diamides . . . . .	23
B. Syntheses and Properties of "1,3-Dithiosquaric Acid Diamides" . . . . .	25
C. Reactions with Nucleophiles . . . . .	28
D. Reactions with Electrophiles . . . . .	33
V. Thiodeltic Acid Derivatives . . . . .	36
VI. Mixed C <sub>5</sub> Oxo-Thioxocarbon Dianions . . . . .	38
A. Synthesis and Properties . . . . .	38
B. Chemical Behavior . . . . .	39
References . . . . .	40

## I. Introduction

In the 20 years since the oxocarbon anions C<sub>n</sub>O<sub>n</sub><sup>2-</sup> were recognized as members of a new class of stabilized carbocyclic nonbenzenoid aromatic compounds [1], knowledge of their chemical and physical properties has been developing rapidly. Their unique electronic structures, high degree of symmetry, and esthet-

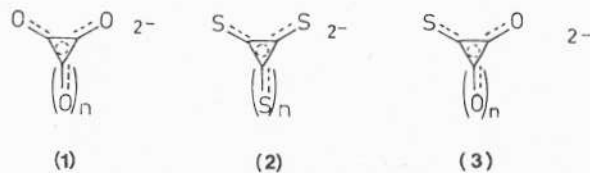
ically beautiful geometry generated a fresh impetus to study the effect of replacing the oxygens by various other functional groups, such as nitrogen [2], sulfur [3-7], selenium [8], phosphorus [9], and the dicyanomethylene group [10-14]. Our interest has been focused on studies pertinent to the aromatic oxocarbon dianions in which the original carbonyl oxygen atoms in  $C_nO_n^{2-}$  are either partially or completely replaced by sulfur. In the meantime a considerable volume of information about these fascinating sulfur-substituted analogs of the oxocarbons has accumulated in numerous publications scattered throughout the chemical literature [3-7]. Their well-known chemical behavior and their potential for further applications make a review of the chemistry of the sulfur derivatives of cyclic oxocarbon anions particularly opportune, especially because no comprehensive publication on these compounds has yet appeared.

## II. Thioxocarbon Dianions

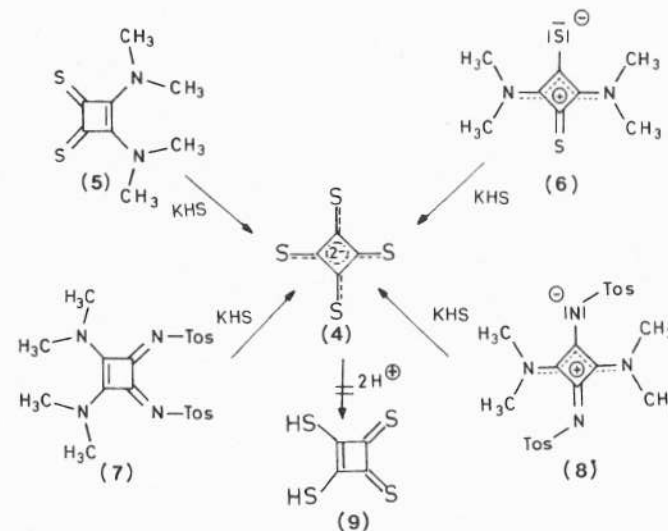
Analogous to the oxocarbon dianions **1**, the thioxocarbon dianions  $C_nS_n^{2-}$  can be characterized by the common formula **2**, in which  $n$  is any positive integer. In the case of only partial replacement, as in formula **3** (see Scheme 1), the dianions have to be termed mixed oxo-thioxocarbons.

### A. SYNTHESIS AND REACTIONS OF THE $C_4$ THIOXOCARBON DIANION

It is well known that addition-elimination reactions of various nucleophiles proceed smoothly with cyclobutenediones bearing leaving groups on the vinyl carbons [1]. This observation provided a convenient route for the synthesis of the first thioxocarbon dianion (**4**), the sulfur analog of the squarate dianion [5,6]. The 1,2-dithiosquaric acid diamide **5** [15,16] serves as a suitable precursor of **4**. Upon treatment with a freshly prepared solution of excess potassium hydrosulfide in dry ethanol, both the amine functions in **5** are replaced by sulfur to give **4** in nearly quantitative yield [5]. Likewise, the 1,3-dithiosquaric acid diamide **6** [17] or the tosyl-substituted bis(amidines) of squaric acid (**7** or **8**) [18,19] serve as easily available starting materials for the synthesis of the  $C_4$  thioxocarbon dianion by a similar reaction sequence, as shown in Scheme 2.



Scheme 1

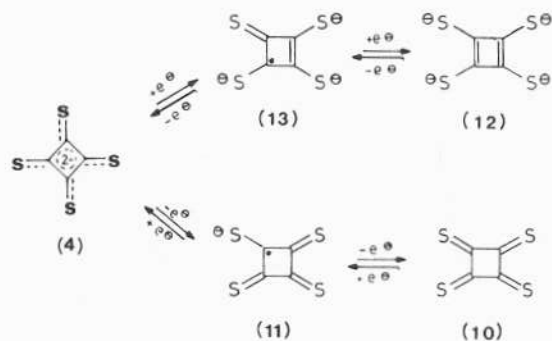


Scheme 2

These syntheses give **4** as the orange-yellow hydrate  $K_2[C_4S_4] \cdot H_2O$ , which can then be recrystallized from ethanol/water. Upon heating of **4** in air above  $120^\circ C$ , the water of crystallization is removed and a dark violet, strongly hygroscopic modification is formed, which is readily reconverted to the hydrated salt when exposed to the air. Compound **4** dissolves readily in water to give stable solutions.

Free tetrathiosquaric acid (**9**) cannot be obtained from the alkali metal salts of **4**, either by ion exchange on the aqueous solution with  $H^+$ -form cation-exchange resins, or by treating with the equivalent amount of sulfuric acid. In both cases an insoluble yellow powder is formed, probably a polymeric product of **9**.

On account of its high degree of symmetry and readily polarizable S atoms,  $C_4S_4^{2-}$  appears to be especially suitable for the production of organometallic catena complexes, which are potential one-dimensional electrical conductors. Thus, the dianion of tetrathiosquaric acid (**4**) formed numerous compounds having bischelate structure with transition metals (Cr, Mo, W, Mn, Au) and various diamagnetic compounds with a chain structure (Ni, Pd, Pt), which exhibit interesting properties pertinent to electrical conductivity [20]. In addition, the search for more effective "organic metals" led to the investigation of some organic charge-transfer complexes prepared from 1,2-dithiolylium derivatives and tetrathiosquarate salts [21]. Redox reactions of **4** are of considerable interest (Scheme 3) because they must ultimately lead either to the neutral tetrathioxocyclobutane **10** via the radical-anion **11** or to the antiaromatic cyclobutadiene tet-



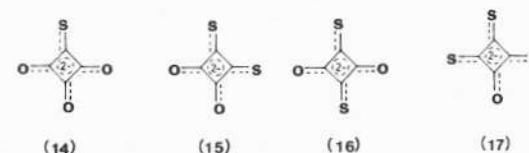
Scheme 3

rathiolate **12** via the radical-trianion **13**. While oxidation of **4** in many cases led to polymeric products, **4** in contrast to the  $C_4O_4^{2-}$  dianion could be smoothly reduced polarographically in two one-electron steps (half-wave potentials  $-1.53$  and  $-1.79$  V) in aqueous solution to the tetraanion  $C_4S_4^{4-}$  (**12**) [20]. Hence, further work on the redox products of the  $C_4S_4^{2-}$  dianion would be especially useful.

### B. SPECTROSCOPIC DATA

Spectroscopic data have contributed much to knowledge of the structure of oxocarbon anions [1]. Also, in the case of the  $C_4$  thioxocarbon dianion **4**, there is no doubt that it has a planar structure with  $D_{4h}$  symmetry, consistent with complete  $\pi$ -electron delocalization and aromaticity [5]. The characteristic orange color of **4** is due to an intense UV absorption at 430 nm. The infrared spectrum is very simple and is dominated by some intense sharp bands around  $1240\text{ cm}^{-1}$ , which can be assigned to  $C\cdots C\cdots S$  vibrational frequencies. The  $^{13}\text{C}$ -NMR spectrum in  $D_2O$  shows one signal at  $\delta = 229.2$  ppm, indicating that all carbon atoms in **4** are equivalent. An X-ray crystal structure determination confirms these findings [5]. Bond lengths for the symmetric and planar anion are  $\langle C-C \rangle = 1.448(6)\text{ \AA}$  and  $\langle C-S \rangle = 1.663(9)\text{ \AA}$ ; the corresponding bond orders of about 1.25 for the  $C-C$  bond and 1.5 for the  $C-S$  bond are calculated from the accepted bond distance-bond order relationship [22,23]. An interesting finding is that bond orders in the  $C_4$  oxocarbon and in the sulfur analog dianion are only slightly different, despite the fact that sulfur, in contrast to the 2p element oxygen, belongs to the third row of the periodic table with an increased radius of covalency (C,  $0.74\text{ \AA}$ ; S,  $1.04\text{ \AA}$ ), decreased tendency to form 2p-3p double bonds, larger polarizability, etc.

## 2. Thioxocarbon Dianions and Their Derivatives



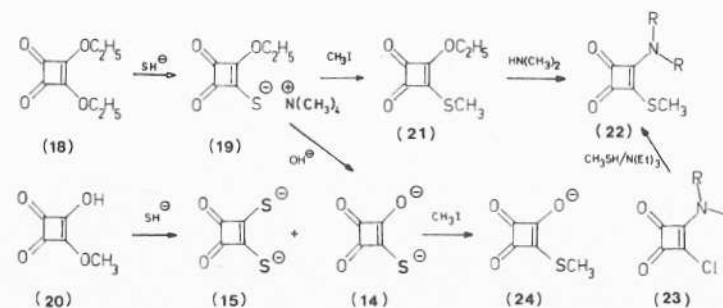
Scheme 4

### III. Mixed $C_4$ Oxo-Thioxocarbon Dianions

A formal, stepwise replacement of the oxygen atoms in the squarate dianion leads to the mixed  $C_4$  oxo-thioxocarbon dianions formulated as **14**, **15**, **16**, and **17** in Scheme 4.

#### A. SYNTHESSES AND REACTIONS OF MONOTHIOSQUARATE AND 1,2-DITHIOSQUARATE DIANIONS

The monothiosquarate ion **14** ( $MTS^{2-}$ ) was first prepared by West and Eggerding from diethyl squarate (**18**) [3], as shown in Scheme 5. With 1 equivalent of potassium or tetramethylammonium hydrosulfide, displacement of only one ethoxy group occurs, yielding the 3-ethoxycyclobutenedione 4-thiolate anion **19**. Hydrolysis of **19** with hydroxide is nearly quantitative, giving  $MTS^{2-}$  (**14**), which has been isolated and characterized as the hygroscopic tetramethylammonium salt ( $Me_4N$ ) $_2$ MTS (**14a**) and as the ternary zinc salt ( $Me_4N$ ) $_2$ Zn( $MTS$ ) $_2$  (**14b**). Another route to  $MTS^{2-}$  starts from the half-ester 1-hydroxy-2-methoxycyclobutenedione (**20**), which is obtained instead of the dimethyl ester when squaric acid is heated with methanol. Sulfhydrylolytic of **20**, however, yields a mixture of the desired  $MTS^{2-}$  and the 1,2-dithiosquarate ion **15** ( $1,2-DTS^{2-}$ ), as indicated by  $^{13}\text{C}$ -NMR spectroscopy [6]. All attempts to separate these two products were unsuccessful.

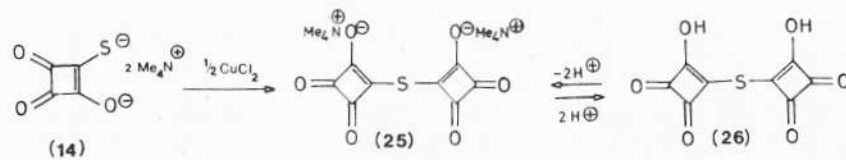


Scheme 5

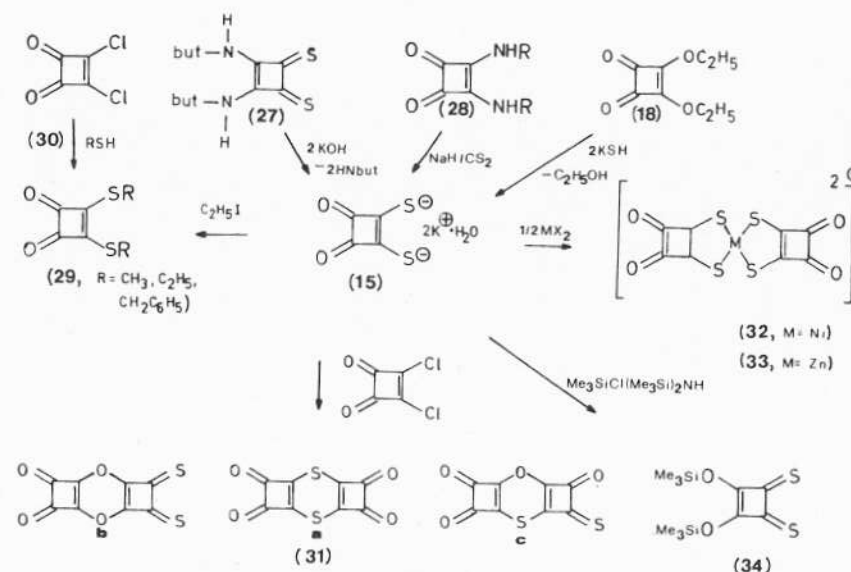
The 3-ethoxycyclobutenedione 4-thiolate ion **19** is easily alkylated, forming 3-ethoxy-4-methylthiocyclobutenedione (**21**) [4]. Reaction of **21** with 1 equivalent of dimethylamine gives only displacement of the ethoxy group, yielding 3-dimethylamino-4-methylthiocyclobutenedione (**22**, R = CH<sub>3</sub>), which is identical with the product obtained from the reaction of methylmercaptan and 4-chloro-3-dimethylaminocyclobutenedione (**23**) in the presence of triethylamine [24]. The MTS<sup>2-</sup> ion reacts only at sulfur with excess iodomethane, to form the *S*-methylated ion **24** [4]. An interesting finding is the synthesis of a sulfur-bridged binuclear oxocarbon acid (**26**) by reaction of MTS<sup>2-</sup> with 0.5 equivalent of copper(II) chloride [25]. The obtained yellow anion (**25**) can be smoothly transformed to its conjugate acid by treatment of a concentrated solution of **25** with cold 12 *N* aqueous hydrochloric acid, as shown in Scheme 6. The resulting 2,2'-thiobis(3,4-dioxocyclobuten-1-ol) (**26**) crystallizes as a dihydrate and decomposes above 125°C. Like squaric acid, **26** is an extremely strong acid with a *pK* less than zero, as indicated by spectrophotometric measurements [25].

Useful starting materials for the synthesis of the 1,2-dithiosquarate ion **15** are either diethyl squarate (**18**), which can smoothly be converted to **15** by treatment with 2 equivalents of potassium hydrosulfide [3,4], or the dithiosquaramide **27** (but = *n*-C<sub>4</sub>H<sub>9</sub>), which is cleanly hydrolyzed with potassium hydroxide [6] (Scheme 7). Disodium 1,2-DTS<sup>2-</sup> (**15a**) has also been prepared in low yield from the bis(cyclohexylamide) of squaric acid (**28**) by the amide cleavage method of Shahak and Sasson [26]. Reaction of 1,2-DTS<sup>2-</sup> (**15**) with alkyl iodides in DMF-water yields *S,S'*-dialkyl 1,2-dithiosquarates (**29**) [4], which have also been prepared by reactions of alkylmercaptans and 3,4-dichlorocyclobutenedione (**30**) [4,27]. Treatment of **15** with equal amounts of **30**, the "acid chloride" of squaric acid [15,28], yields the symmetric red-orange dithiin **31** [6]. The unsymmetric alternative structures (**31b** and **c**) can be ruled out by <sup>13</sup>C-NMR spectroscopy. Two signals at δ = 187.2 and 184.1 ppm are consistent only with structure **31a**, which can also be obtained through an independent route by treatment of **30** with the dimer of *p*-methoxyphenylthionophosphine sulfide [29].

Interesting anionic complexes of 1,2-DTS<sup>2-</sup> as chelating ligand with transition metal cations—for instance, the potassium salts of the bis(dithiosquarato)nickelate(II) (**32**) and bis(dithiosquarato)zincate(II) (**33**)—have been prepared and



## 2. Thioxocarbon Dianions and Their Derivatives

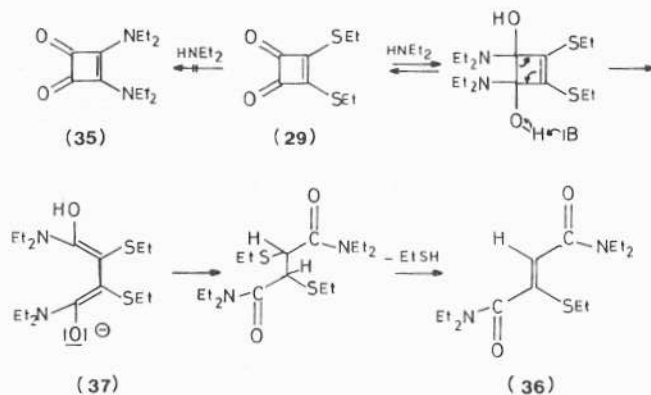


characterized by X-ray crystal structure determination to confirm the intriguing mode of bonding as well as the formulation of the ligand as the 1,2-DTS<sup>2-</sup> [3,30]. Protonation of 1,2-DTS<sup>2-</sup> gave a yellow solid with an S—H band in the infrared spectrum, but rapid decomposition with loss of hydrogen sulfide discouraged further characterization [4]. Silylation of **15** yielded an extremely moisture sensitive red-orange compound (**34**), which readily dissolved in ether and carbon tetrachloride. Spectroscopic data provide evidence that **34** was the *O*-silylated derivative of 1,2-DTS<sup>2-</sup> [4].

### B. REACTION OF THIOSQUARATE ESTERS WITH AMINES

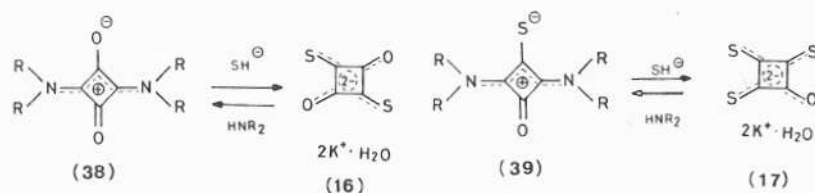
It is well known that reactions of dichlorocyclobutenedione (**30**) and diethyl squarate (**18**) resemble those of carboxylic acid chlorides and esters and that carboxylic thioesters react like esters. In contrast, chemical properties of alkylthiocyclobutenediones cannot be predicted from those of the alkoxy-cyclobutenediones. As shown in the reaction with diethylamine [4] (Scheme 8), the reactivity of **29** is quite different from that of **18**. Not the expected squaramide (**35**), but a fumaramide derivative (**36**) is obtained when **29** is treated with an excess of diethylamine. An obvious mechanism of this reaction via **37** is shown in Scheme 8.





### C. SYNTHESSES AND REACTIONS OF 1,3-DITHIO- AND 1,2,3-TRITHIOSQUARATE DIANIONS

In the same fashion as tetrathiosquarate ion **4**, 1,3-dithiosquarate ion **16**, (1,3-DTS<sup>2-</sup>) and 1,2,3-trithiosquarate ion **17** (TTS<sup>2-</sup>) are smoothly obtained by sulfhydrylolytic of the corresponding amides **38** and **39**, respectively [6].

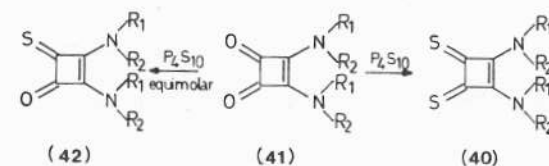


Upon treatment with excess secondary amine, **16** and **17** are reconverted to the corresponding 1,3-squaric acid diamides [6], as shown in Scheme 9. The spectroscopic data of all the mixed oxo-thiocarbon dianions (**14**–**17**) are consistent with a delocalized structure, but  $\pi$ -electron delocalization is less intensive than in the symmetric C<sub>4</sub>O<sub>4</sub><sup>2-</sup> or C<sub>4</sub>S<sub>4</sub><sup>2-</sup> dianions [4,6].

## IV. DITHIOSQUARIC ACID DIAMIDES

Dithiosquaric acid diamides with the sulfur atoms in 1,2 and 1,3 positions have proved useful as starting materials for the synthesis of various pseudo-oxocarbons [5,6].

## 2. Thiocarbon Dianions and Their Derivatives

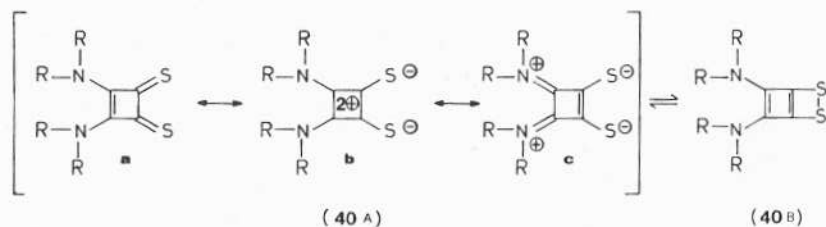


### A. SYNTHESSES AND PROPERTIES OF 1,2-DITHIOSQUARIC ACID DIAMIDES

The 1,2-dithiosquaric acid diamides **40** (1,2-DTSD) are easily obtained in a stepwise sequence via **42** (Scheme 10) by reaction of the corresponding diamides **41** [15] with convenient sulfur transfer reagents such as phosphorus(V) sulfide [31] (method A), the dimer of *p*-methoxyphenylthionophosphine [32,33], or the recently discovered alkoxy-carbonyl isothiocyanate [17] (method B). The yields of and some data for 1,2-DTSD are summarized in Table I. All of these compounds are high melting and stable, and their properties and spectra are in agreement with the open  $\alpha$ -dithione structure **40A** (Scheme 11). The initially

Table I. Yields of and Data for 1,2-DTSD's (**40**) from the Corresponding Diamides with P<sub>4</sub>S<sub>10</sub> (Method A) or Alkoxy-carbonyl Isothiocyanate (Method B)

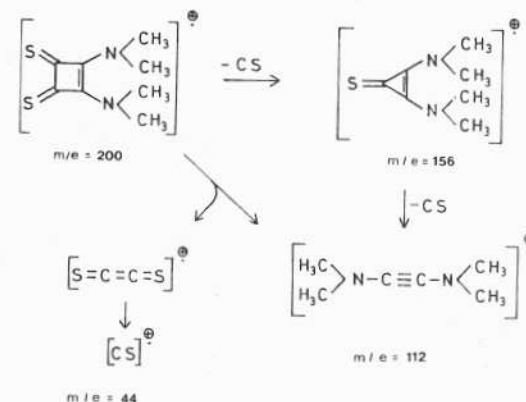
Compound	N <sup>1</sup>		N <sup>2</sup>		mp (°C)	Yield (%)	
	R <sup>1</sup>	R <sup>2</sup>	R <sup>1</sup>	R <sup>2</sup>		Method A	Method B
<b>40a</b>	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	235 (dec.)	70	54
<b>40b</b>	(CH <sub>2</sub> ) <sub>2</sub> -O-(CH <sub>2</sub> ) <sub>2</sub>	(CH <sub>2</sub> ) <sub>2</sub> -O-(CH <sub>2</sub> ) <sub>2</sub>	(CH <sub>2</sub> ) <sub>2</sub> -O-(CH <sub>2</sub> ) <sub>2</sub>	(CH <sub>2</sub> ) <sub>2</sub> -O-(CH <sub>2</sub> ) <sub>2</sub>	240 (dec.)	35	70
<b>40c</b>	-(CH <sub>2</sub> ) <sub>5</sub> -	-(CH <sub>2</sub> ) <sub>5</sub> -	-(CH <sub>2</sub> ) <sub>5</sub> -	-(CH <sub>2</sub> ) <sub>5</sub> -	243 (dec.)	72	78
<b>40d</b>	-(CH <sub>2</sub> ) <sub>4</sub> -	-(CH <sub>2</sub> ) <sub>4</sub> -	-(CH <sub>2</sub> ) <sub>4</sub> -	-(CH <sub>2</sub> ) <sub>4</sub> -	249 (dec.)	68	75
<b>40e</b>	H	(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	H	(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	225 (dec.)	76	—
<b>40f</b>	H	C(CH <sub>3</sub> ) <sub>3</sub>	H	C(CH <sub>3</sub> ) <sub>3</sub>	345 (dec.)	78	—
<b>40g</b>	H	CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	H	CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	228 (dec.)	81	—
<b>40h</b>	-(CH <sub>2</sub> ) <sub>5</sub> -	-(CH <sub>2</sub> ) <sub>5</sub> -	-(CH <sub>2</sub> ) <sub>4</sub> -	-(CH <sub>2</sub> ) <sub>4</sub> -	229 (dec.)	46	—
<b>40i</b>	(CH <sub>2</sub> ) <sub>2</sub> -O-(CH <sub>2</sub> ) <sub>2</sub>	CH <sub>3</sub>	CH <sub>3</sub>	CH <sub>3</sub>	198 (dec.)	52	—



Scheme 11

surprising stability of the intriguing  $\alpha$ -dithione system [34] is in good accord with LCAO-MO calculations [35], which predict that conjugative electron release by the substituents stabilizes the  $\alpha$ -dithione structure relative to the valence tautomeric 1,2-dithiete form (40B). In the case of 1,2-DTSD (40), the unfavorable 1,2-dithiete structure is additionally destabilized by the considerable angle strain of the bicyclic system, but primarily by the antiaromatic character of the resulting cyclobutadiene. As anticipated, spectroscopic evidence excludes the bicyclic valence tautomeric 1,2-dithiete structure (40B) for all these compounds [36]. In a first approximation the molecules may be described as hybrids of three resonance forms (a-c) and are probably best represented as zwitterionic (40Ac) with a high contribution to the actual electronic structure of 40A. This corresponds to the high melting points and slight solubility in nonpolar aprotic solvents and is moreover strongly supported by spectroscopic data. The unusually high stretching vibration frequencies of the  $\text{>N}^{\oplus}\text{---C---C---N}^{\oplus}$  system around 1680 and 1580  $\text{cm}^{-1}$  indicate a relatively high  $\pi$ -bond order of the semicyclic C—N bond. In addition, strong preference for the polar resonance structure 40Ac follows unambiguously from an X-ray structure determination of 40d [37]. The atomic distances of the C—N bond [C—N = 1.313(4) Å] as well as of the C—S bond [C—S = 1.645(3) Å] fall between the known values for single and double bonds [C—N = 1.47 Å; C=N (from oximes) = 1.27 Å; and C—S = 1.81 Å; C=S = 1.60 Å, respectively] and demonstrate a degree of delocalization similar to that found in the closely related thioamides [38].

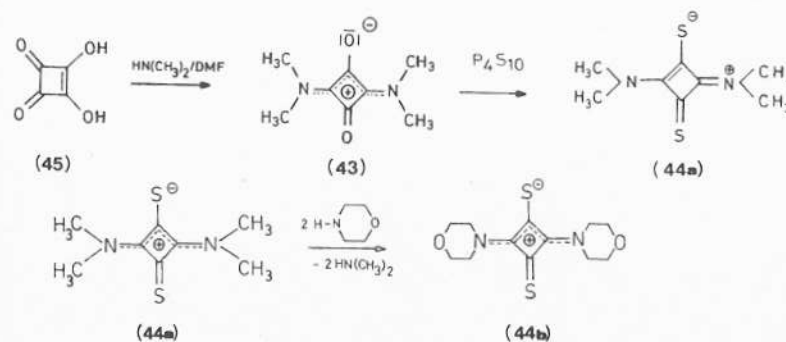
All the 1,2-DTSD's have a bright yellow color, whereas their oxygen analogs are colorless. The electronic spectra exhibit two intense absorptions around 290 and 400 nm, with a shoulder around 370 nm. The intense long-wavelength bands can probably be assigned to the  $\pi \rightarrow \pi^*$  transition. An expected absorption of low intensity at about 450 nm due to the  $n \rightarrow \pi^*$  transition cannot be detected and is perhaps hidden under the long-tailing, broad absorption around 400 nm. The mass spectra of all 1,2-DTSD's [36] are dominated by intense parent ion peaks, which are also the base peaks. Characteristic features of the fragmentation are the elimination of carbon monosulfide and ring contraction besides a scission of two parallel C—C bonds of the four-membered ring, as outlined in Scheme 12.



Scheme 12

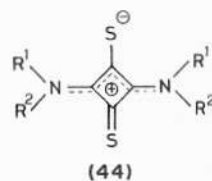
## B. SYNTHESSES AND PROPERTIES OF "1,3-DITHIOSQUARIC ACID DIAMIDES"

In contrast to the facile synthesis of 1,2-DTSD's, reaction of "1,3-squaric acid diamides" with convenient sulfur transfer reagents in most cases yields mixtures of mono- and dithiosquaric acid diamides that are difficult to separate. Fortunately, this is not the case with the hitherto unknown dimethylamide 43, which proved to be the most appropriate starting material for the synthesis of a great variety of secondary "1,3-dithiosquaric acid diamides" (44, 1,3-DTSD) [36]. Compound 43 can be prepared from squaric acid (45) [36], as outlined in Scheme 13. Upon treatment of 1,3-DTSD (44a) with excess secondary amines, replacement of the dimethylamine functions occurs (Scheme 13), as expected for an all-trans vinamidinium system [2], to yield the 1,3-DTSD's (44b-d) listed in



Scheme 13

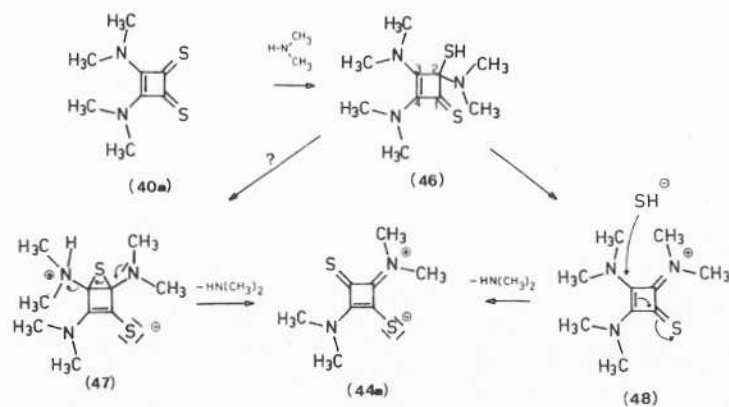
**Table II.** Yields of and Data for 1,3-DTSD's Synthesized via 1,3 Displacement (A) from **44a** or via Rearrangement (B) from **40e**



Compound	R <sup>1</sup>	R <sup>2</sup>	Yield (%)	mp (°C)
<b>44b</b>	(CH <sub>2</sub> ) <sub>2</sub> -O-(CH <sub>2</sub> ) <sub>2</sub>		70 (A)	304
<b>44c</b>	-(CH <sub>2</sub> ) <sub>5</sub> -		97 (A)	290
<b>44d</b>	-(CH <sub>2</sub> ) <sub>4</sub> -		78 (A)	295
<b>44e</b>	H	CH <sub>3</sub>	67 (B)	218 (dec.)
<b>44f</b>	H	(CH <sub>2</sub> ) <sub>3</sub> CH <sub>3</sub>	70 (B)	165 (dec.)
<b>44g</b>	H	CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	85 (B)	260 (dec.)

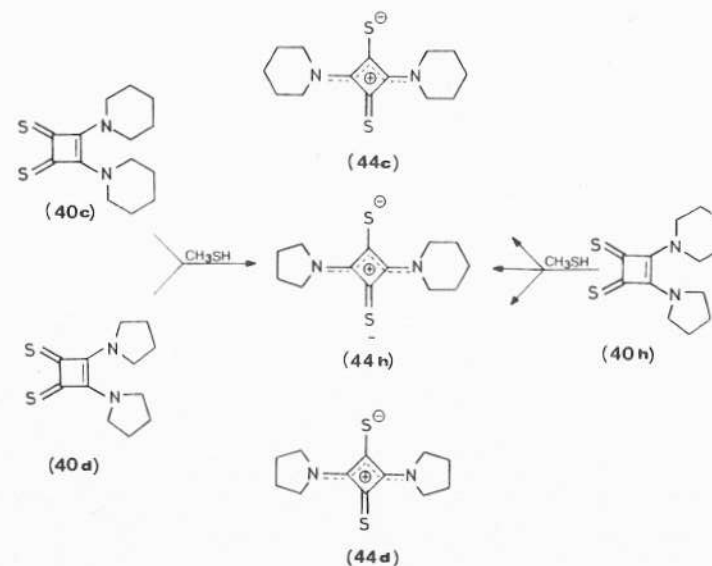
Table II. Attempts to convert **44a** to primary diamides by the same method were not successful [36]. Moreover, various 1,3-DTSD's (**44**) could be synthesized in a most surprising way. Upon treatment of 1,2-DTSD (**40a** or **d**) with excess primary or secondary amine, the expected nucleophilic displacement of the amine is accompanied by rearrangement. The starting material is readily converted to the isomeric, thermodynamically more stable 1,3-DTSD (**44a** or **f**), summarized in Table II. The rearrangement is also achieved when 1,2-DTSD's are treated with traces of methylmercaptan as a very efficient catalyst in acetonitrile as solvent, yielding the corresponding 1,3-DTSD (**44**) quantitatively [7,36].

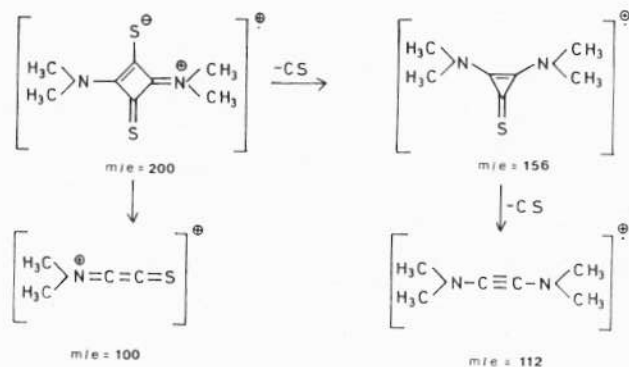
An obvious route of this interesting rearrangement is outlined in Scheme 14. In



the first step of the reaction, the nucleophilic reactant attacks the thiocarbonyl carbon atom of **40a**, yielding the intermediate *N,S*-acetal **46**. The migration of the sulfur atom from position 2 to 3 may proceed by an inter- or intramolecular mechanism via **47** or **48**, respectively, as intermediate. In both cases elimination of dimethylamine follows, and the 1,3 isomer (**44a**) of the starting material is the only reaction product in nearly quantitative yield.

Two crossover experiments, outlined in Scheme 15, produced evidence for an intermolecular mechanism for this arrangement [7]. Upon heating of equal molar amounts of two differently substituted 1,2-DTSD's (**40c** and **40d**) in the same acetonitrile solution in the presence of traces of methylmercaptan, three reaction products were detected—two symmetric and one mixed 1,3-DTSD—proving intermolecular migration at least of the amine functions. These findings were confirmed by a second experiment in which the starting material was the mixed 1,2-DTSD **40h**, which was treated under the same conditions as before, yielding the same three products. The formation of the two symmetric crossover products again indicates an intermolecular migration mechanism. Criteria for discriminating between 1,2- and 1,3-DTSD depend on the different constitution of these two structures [36]. Thus, the 1,3-DTSD's have an intramolecular salt structure and exhibit higher melting points. Because of the higher degree of symmetry, their IR spectra are simpler and dominated by an intense, broad band around 1600 cm<sup>-1</sup>, which can be assigned to stretching vibrations of the [ $\text{>N}\cdots\text{C}\cdots\text{C}\cdots\text{C}\cdots\text{N}<$ ] <sup>+</sup> system. In contrast to the bright yellow 1,2-DTSD's, the 1,3-DTSD's are





orange-yellow. Their electronic spectra exhibit strong absorption maxima at about 430 nm and a band of lower intensity in the region of longer wavelengths at 490 nm, which can be assigned to the  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions, respectively. The mass spectra show a very intense parent ion peak, which is also the base peak, indicating the high stability of these compounds. The main fragmentation pattern can be represented by Scheme 16. The parent ion may break down via two paths, either by the successive loss of two molecules of carbon monosulfide or by fragmentation in two identical ions with a pronounced peak at  $m/e = \frac{1}{2}M^+$ .

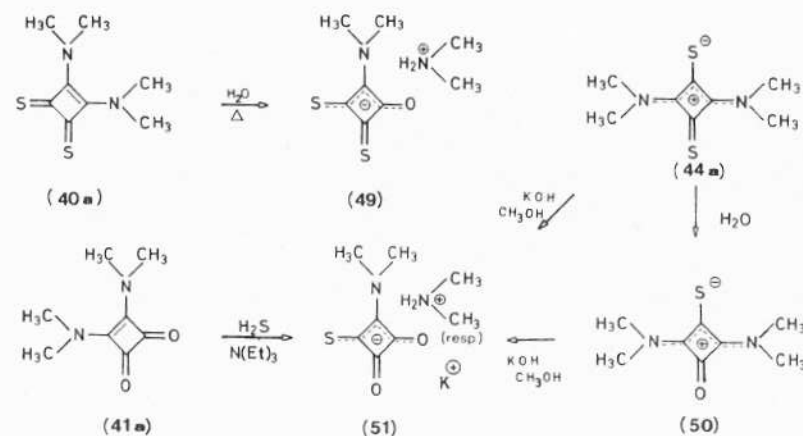
### C. REACTIONS WITH NUCLEOPHILES

Because of their amphoteric character, dithiosquaric acid diamides can react with electrophiles and nucleophiles as well. Various nucleophiles prefer reaction on the vinylic carbon atoms of the four-membered ring and displace the substituents via an addition-elimination mechanism. These general remarks can be confirmed by some typical examples.

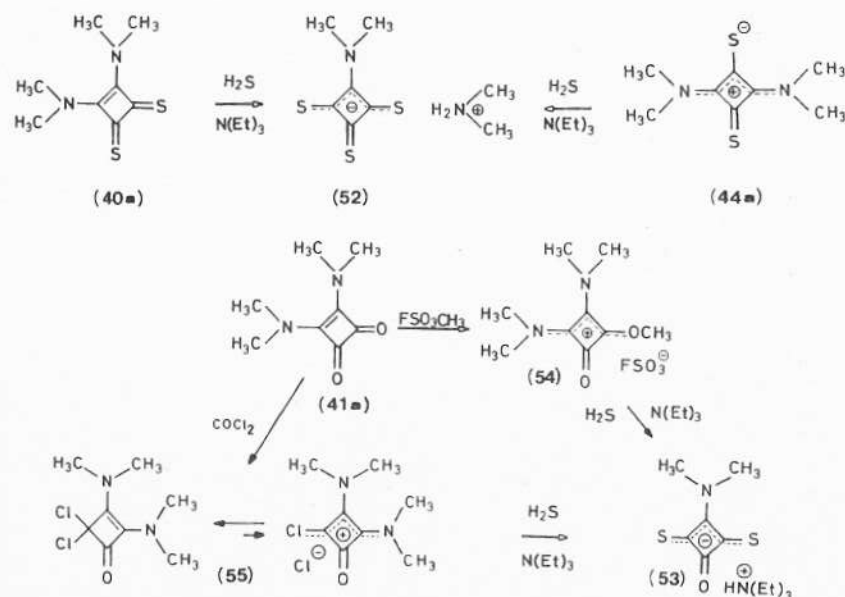
#### 1. Sulfur-Containing Squarate Anions from Hydrolysis or Sulphydrolysis of 1,2- or 1,3-DTSD

In view of their potential applicability as contact herbicides, new synthetic routes to variations of the recently discovered mycotoxin "moniliformin" [39], the potassium or sodium salt of semisquaric acid, have been extensively investigated [40]. Hydrolysis or sulphydrolysis of 1,2- or 1,3-DTSD has provided important pathways to novel variations of this natural product, in which the vinylic hydrogen of the mycotoxin is replaced by a dimethylamino group [41]. Heating of 1,2-DTSD (40a) in water yields a new anion (49) with two vicinal sulfur atoms. Surprisingly, the corresponding 1,3-DTSD (44a) is not converted to the expected product under the same conditions; instead, the monothiosquaric

### 2. Thioxocarbon Dianions and Their Derivatives



acid diamide **50** is obtained, which upon treatment with potassium hydroxide in methanol gives the anion (**51**) with only one sulfur atom. Treatment of 1,2-squaric acid bis(dimethylamide) (**41a**) with  $H_2S/N(Et)_3$  yields the same anion by an independent synthetic route as its dimethylammonium salt (see Scheme 17). The anion (**52**) with three adjacent sulfur atoms is obtained by sulphydrolysis of either **40a** or **44a** (Scheme 18), whereas the synthesis of **53** with two sulfur atoms



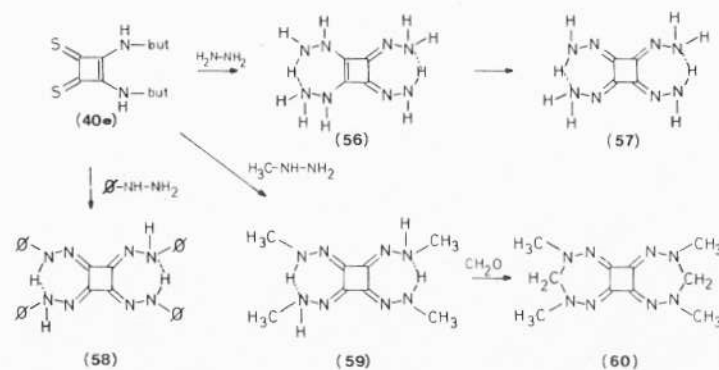
in positions 1 and 3 can easily be achieved by sulfhydrylolytic of the cations **54** or **55** [13,41]. All these derivatives of moniliformin have proved inactive in various pharmacological tests [36].

### 2. Reaction of 1,2-DTSD with Hydrazines

The reaction of 1,2-DTSD (**40e**) with the strongly nucleophilic hydrazines surprisingly leads to sulfur-free products [36,42], as shown in Scheme 19. Apparently all functional groups of the 1,2-DTSD are replaced by the excess nucleophile. However, the resulting compound is not the expected bishydrazidine (**56**), but its oxidation product (**57**), the tetrahydrazone of the hitherto unknown cyclobutatetraone. Under the same conditions the corresponding tetrahydrazones (**58** or **59**) are obtained upon treatment of **40e** with excess phenyl- or methylhydrazine, respectively. Thus far, all the experiments to reduce **59** to the corresponding bis(hydrazidine) have been unsuccessful. Formaldehyde, for instance, does not reduce (**59**); instead, ring closure to the novel tricyclic rings system **60** is observed. Further work pertinent to the redox properties of these tetrahydrazones (**57-60**) would be useful.

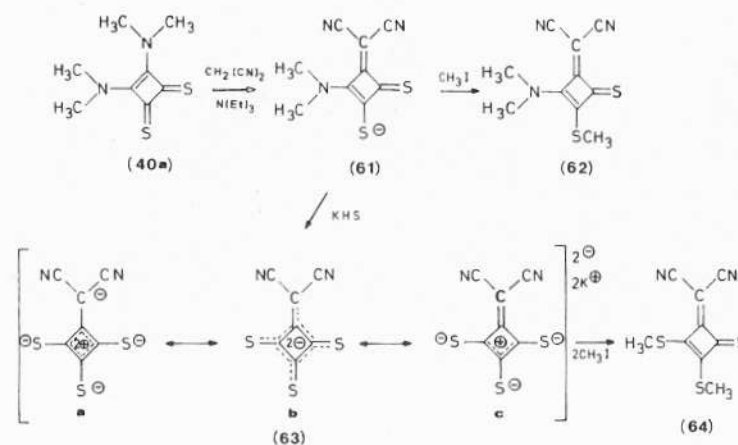
### 3. Reaction of 1,2-DTSD with Malononitrile or Cyanamide

Despite the fact that dicyanomethylene analogs of the deltatate [43], squarate [10-13], and croconate dianions [14] have recently been reviewed [44], sulfur-containing derivatives of these most interesting variations of the oxocarbon dianions so far remained unexplored. The first example of this new class of pseudo-oxocarbons was obtained in the thiosquarate series [45]. In a two-step reaction sequence (see Scheme 20), the anion of malononitrile first reacts with 1,2-DTSD (**40a**) with replacement of only one dimethylamino group. The resulting salt (**61**) can be characterized by alkylation with methyl iodide to the neutral **62**. In the second step, **61** is treated with potassium hydrogen sulfide in dry ethanol to form



Scheme 19

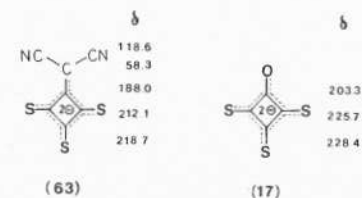
## 2. Thioxocarbon Dianions and Their Derivatives



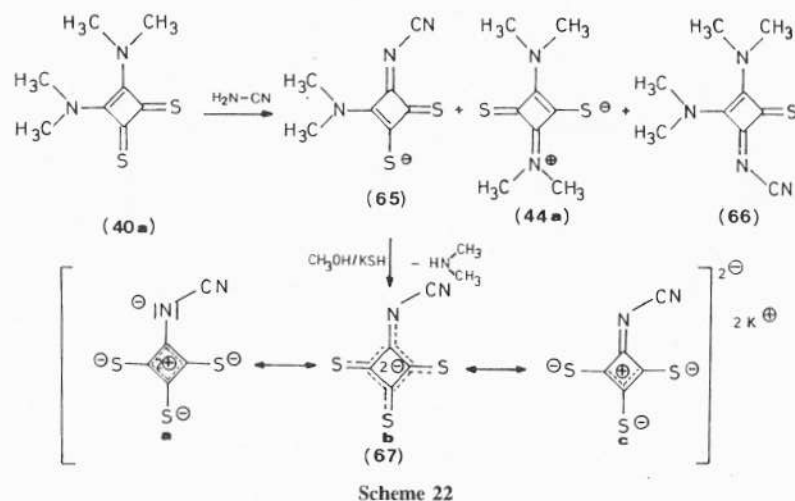
Scheme 20

the ochre-colored dipotassium salt **63**, which can be alkylated to **64**. The dianion of **63** is assigned a symmetric bond-delocalized structure comparable with that of the trithiosquarate dianion (**17**). The resonance forms (**63a-c**) are three of several possible forms contributing to the ground state of **63**. It receives considerable stabilization from the electron-withdrawing exocyclic substituent. However,  $\pi$ -electron delocalization among ring thiocarbonyl groups and the dicyanomethylene group is not as intensive as in the oxygen analog dianion **17**. This is indicated by the  $^{13}\text{C}$ -NMR data shown in Scheme 21 and the relatively high frequency absorption of the semicyclic C—C bond at  $1594\text{ cm}^{-1}$  in the IR spectrum of **63**.

A high yield of a similar novel pseudo-oxocarbon dianion is smoothly obtained from the reaction of 1,2-DTSD (**40a**) with 1 equivalent of the anion of cyanamide as nucleophilic reagent (Scheme 22). The main product of the first step of the replacement reaction is the intermediate anion **65**, which is accompanied by traces of two by-products, such as 1,3-DTSD (**44a**) and the neutral species **66**. In the latter, surprisingly one sulfur atom is substituted. Anion **65** can be cleanly transformed to a novel type of sulfur-containing oxocyanocarbon (**67**) by sulf-



Scheme 21

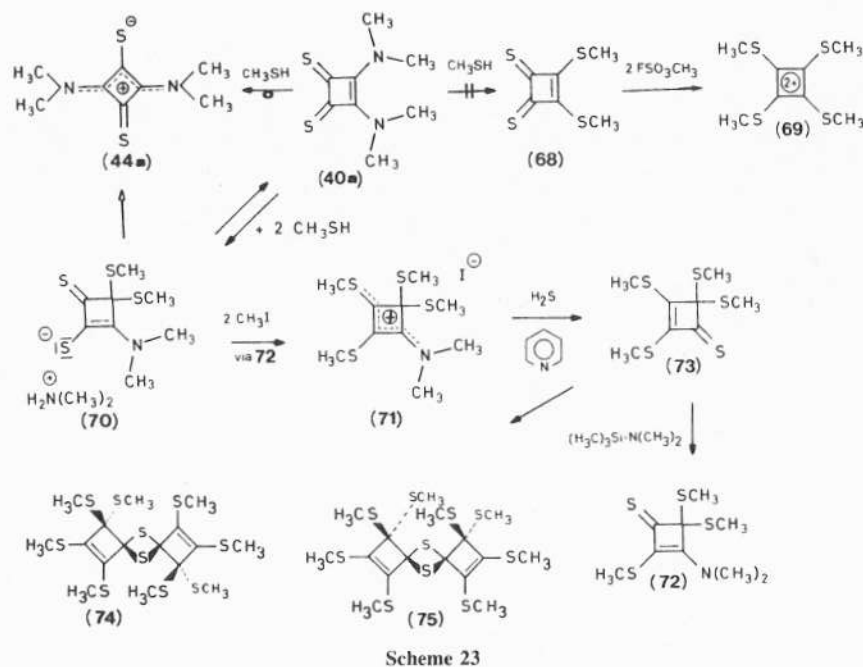


hydrolysis, as shown in Scheme 22. Close examination of this orange-red dianion by spectroscopic methods revealed that it can also be regarded as a member of the aromatic pseudo-oxocarbons with a bond-delocalized electronic system. Structure 67a-c are three of several resonance forms contributing to the ground state of 67.

#### 4. Reaction of 1,2-DTSD with Methylmercaptan

The results of most reactions of 1,2-DTSD with nucleophiles, which proceeded by loss of both the dimethylamino groups, suggested that the reaction with methylmercaptan might provide an attractive synthetic approach to the hitherto unknown tetrathiosquaric ester 68, a potent precursor of the aromatic cyclobutadiene dication 69. Surprisingly, reaction of 1,2-DTSD (40a) with excess methylmercaptan at elevated temperature did not lead to the desired product; instead, the 1,3 isomer (44a) of the starting material was obtained in quantitative yield via intermolecular rearrangement [7], as already mentioned. At room temperature, however, we succeeded in isolating an intermediate. Structure elucidation indicated that 2 equivalents of the nucleophile had been added to the same vinylic carbon atom. Via substitution of one dimethylamino group, the salt 70 is obtained, which is in reversible equilibrium with the starting material. Upon heating of a solution of the salt 70 in chloroform, 1,3-DTSD (44a) is obtained irreversibly. The anion 70 proved to be suitable starting material at least for a precursor of the desired tetrathiosquaric ester.

In a two-step reaction sequence, outlined in Scheme 23, the anion 70 could be converted to the cation 71 via the neutral 72. Sulfhydrylification of 71 in pyridine yielded a dark red crystalline product, which proved to be the thioketal (73) of

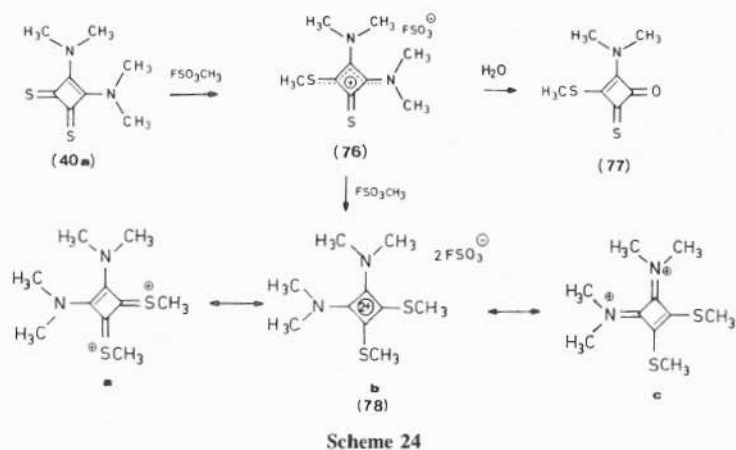


tetrathiosquaric ester. The structure of this interesting precursor of 68 was established by its reaction with  $(\text{CH}_3)_3\text{SiN}(\text{CH}_3)_2$  to regenerate 72 and furthermore by its spectroscopic data. Thus, the IR spectrum exhibits a strong absorption band at  $1272 \text{ cm}^{-1}$ , which probably can be assigned to the  $\text{C}=\text{S}$  stretching vibration. The UV spectrum shows three absorptions at  $\lambda_{\text{max}}$  ( $\log \epsilon$ ) 274 (3.9), 395 (3.9,  $\pi \rightarrow \pi^*$  transition), and 507 nm (2.2,  $n \rightarrow \pi^*$  transition), which are typical of a vinyl dithio ester system. At least the presence of a thiocarbonyl group in 73 was unambiguously indicated by a signal at  $\delta = 219 \text{ ppm}$  in the  $^{13}\text{C-NMR}$  spectrum. Compound 73 is sensitive to light both in solution and in the crystalline state, suggesting that the tetrathiosquaric ester 68 is not a very stable compound. When exposed to daylight the red solution of 73 in dichloromethane turned bright yellow; evaporation of the solvent gave a yellowish product, which turned out to be a dimer of 73 with one of the alternative structures 74 or 75 [7].

#### D. REACTIONS WITH ELECTROPHILES

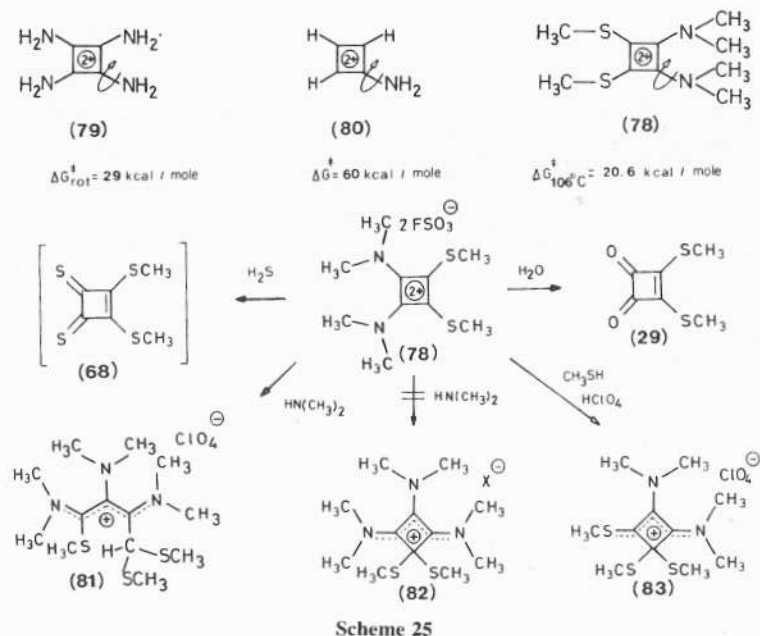
##### 1. Synthesis and Properties of a Stable Cyclobutadiene Dication

As already pointed out, electrophiles can also react with DTSD and attack predominantly at the sulfur atoms. Thus, "magic methyl" ( $\text{FSO}_3\text{CH}_3$ ) alkylates



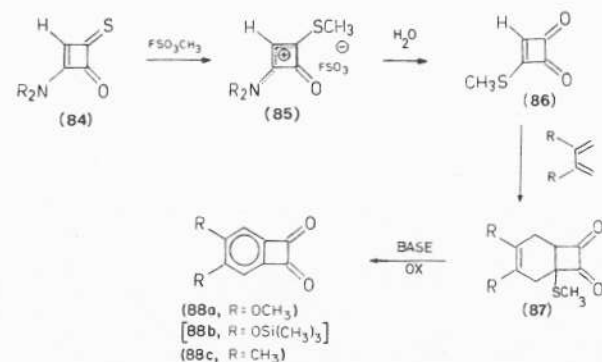
1,2-DTSD (**40a**) in a two-step reaction via the cation **76** which is smoothly hydrolyzed to **77** at both the sulfur atoms, yielding the first isolable cyclobutadiene dication (**78**) [27,46] (Scheme 24). This interesting "Hückel aromatic" system containing  $4n + 2$  ( $n = 0$ )  $\pi$  electrons obtains a strong stabilizing influence from the substituents [47-49]. On the one hand, delocalization of the positive charge occurs from the sulfur atoms into the ring; on the other hand, the amino groups strongly back-donate electron density to the carbons of the four-membered ring, as illustrated by the hybrid structures **78a-c**; the contribution by **78c** is expected to be most important. This is strongly supported by the spectroscopic data, which give insight into the electronic structure of the dication **78**. The C—N stretching frequency in the IR spectrum at  $1758\text{ cm}^{-1}$  indicates an unusually high  $\pi$ -bond order for this semicyclic bond. Thus, the dication **78** undergoes relatively infrequent rotation about the C=N bond at room temperature, giving rise to nonequivalent methyl groups in the  $^1\text{H-NMR}$  spectrum. Variable-temperature study showed coalescence of the *N*-methyls at  $106^\circ\text{C}$ , corresponding to a free activation enthalpy  $\Delta G^\ddagger = 20.6\text{ kcal/mole}$  [50]. This rotational barrier seems to be relatively small compared to calculated values of other amino-substituted dications (**79** and **80**) [47] (Scheme 25). Steric hindrance of the adjacent dimethylamino groups certainly lowers the rotational barrier and thus can account for this discrepancy between theory and experiment.

The dication **78** is stable at room temperature in the absence of moisture and is, as anticipated, very sensitive to nucleophiles [27,46]. Some of the interesting chemical behavior [51] is outlined in Scheme 25. Hydrolysis yields the dithioquaric acid *S,S'*-dimethyl ester **29**. Upon treatment with hydrogen sulfide, a deep red solution was obtained, but the expected tetrathiosquaric ester **68** could not be isolated. Reaction of **78** with dimethylamine leads to the ring-opened product **81**

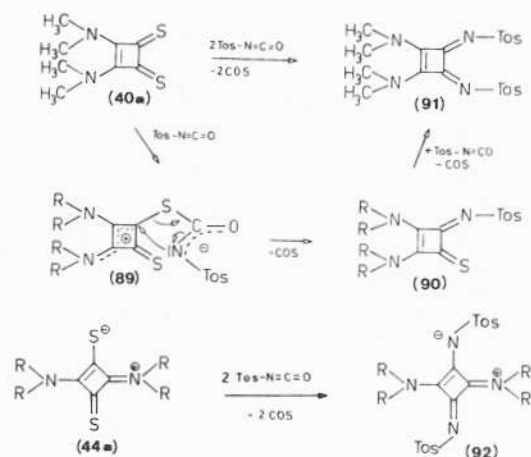


and not to the vinamidinium cation **82**. With methylmercaptan the dication **78** surprisingly reacts to give the cation **83**.

In the same fashion as described above thioamides of semisquaric acid (**84**  $\text{R} = \text{CH}_3$ ) are alkylated by "magic methyl" [52]. The resulting cation **85** is readily hydrolyzed to yield the corresponding thioester **86**, which has proved to be a potent reagent in [4+2] cycloadditions [53], as shown in Scheme 26. Reaction



(**88a**,  $\text{R} = \text{OCH}_3$ )  
 (**88b**,  $\text{R} = \text{OSi}(\text{CH}_3)_3$ )  
 (**88c**,  $\text{R} = \text{CH}_3$ )



Scheme 27

with substituted butadienes leads to the cycloaddition products **87**, which on treatment with base eliminate methylmercaptan. Promoted by aromatization, subsequent oxidation yields the most interesting benzenoid vinylog of squaric acid esters [**88a**, R = OCH<sub>3</sub> [54]; **88b**, R = OSi(CH<sub>3</sub>)<sub>3</sub>] or other benzocyclobutenediones (**88c**, R = CH<sub>3</sub>).

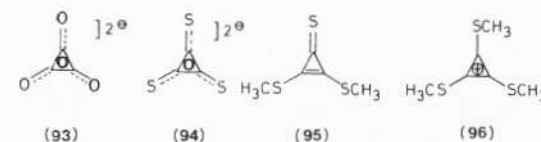
## 2. Reaction of 1,2- and 1,3-DTSD with Tosyl Isocyanate

Although well known in the thioamide series [38], acylation reactions of DTSD have not yet been reported. In contrast, the reaction with tosyl isocyanate has been extensively investigated. As shown in Scheme 27, the reaction of DTSD with this electrophilic reagent probably proceeds via initial attack at the sulfur atom, yielding a dipolar intermediate (**89**), which in the course of an S<sub>N</sub>i reaction or after cyclization to a 1,3-thiazetidin-2-one spontaneously eliminates carbon oxysulfide [55,56]. Treatment of the resulting amidine with excess tosyl isocyanate leads to the interesting bis(amidine) of squaric acid (**91**) in very good yield [19]. The corresponding 1,3 isomer (**92**) is prepared in the same fashion with 1,3-DTSD (**44a**) as starting material.

## V. Thiodeltic Acid Derivatives

Since the successful synthesis of the fascinating deltate dianion **93** [57,58] (see Scheme 28), all our efforts to synthesize the corresponding sulfur analog (**94**), the three-carbon member of the thioxocarbon dianions [59], have proved unsuccessful. Only some interesting derivatives of the thiodeltate dianion **94**

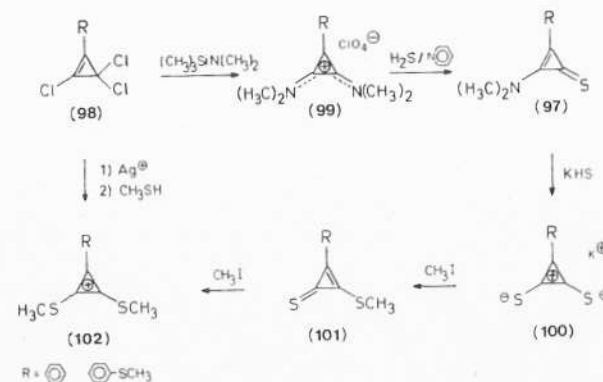
## 2. Thioxocarbon Dianions and Their Derivatives



Scheme 28

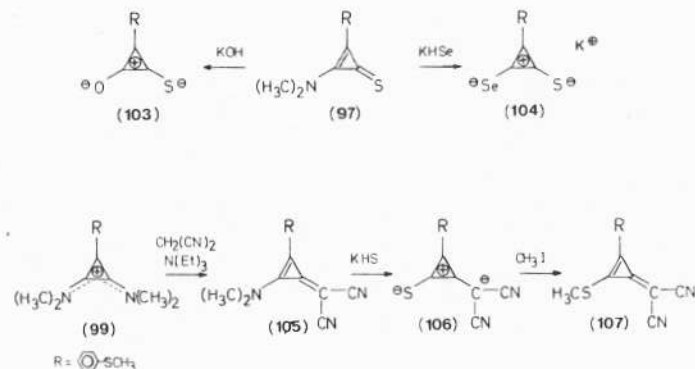
have recently been reported, such as the thiodeltic acid dimethyl ester **95** [60] and the aromatic trimethylthiocyclopropenyl cation **96** [60-62]. However, new sulfur-containing pseudo-oxocarbons in the aryl-substituted deltate series are easily obtained from the corresponding vinylog thioamides (**97**) [63,64]. These can be prepared in a two-step reaction from aryltrichlorocyclopropene (**98**) via the intermediate vinamidinium cation **99** (Scheme 29). Reaction with hydrogen sulfide in pyridine gives the thioamide **97** in high yield [64,65]. Upon treatment with potassium sulfide the aryl-substituted pseudo-oxocarbon **100** is obtained and can be isolated as the yellow, not very stable potassium salt. Compound **100** is best characterized by successive alkylation with methyl iodide, which leads to the aromatic cation **102** via the yellowish-brown dithioester **101** and by <sup>13</sup>C-NMR spectroscopy [59]. In addition, **102** can be obtained by an independent route from **98** upon treatment with silver fluoroborate and excess methylmercaptan.

In the same fashion as described above, reaction of **97** with potassium hydroxide or hydrogen selenide leads to the mixed pseudo-oxocarbons **103** and **104**, respectively (Scheme 30), which are stable enough to be characterized by <sup>13</sup>C-NMR spectroscopy in D<sub>2</sub>O solution [63]. The corresponding malononitrile pseudo-oxocarbon anion (**106**) with one sulfur atom can be attained by the reaction sequence **99**→**106** [59]. The anion **106** is a stable compound, which can easily be characterized by spectroscopic data and alkylation to the trifulvene derivative **107**.



Scheme 29



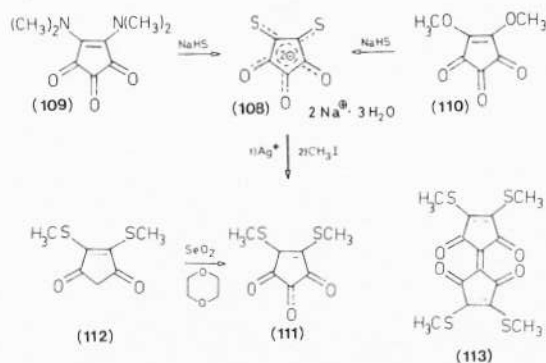


Scheme 30

## VI. Mixed C<sub>5</sub> Oxo-Thiocarbon Dianions

### A. SYNTHESIS AND PROPERTIES

Although sulfur derivatives of the croconate dianion, the dinosaur among the oxocarbon dianions, were mentioned about 100 years ago [66,67], they remained uninvestigated until recently [68,69]. The synthesis of the dithiocroconate dianion **108**, the first C<sub>5</sub> pseudo-oxocarbon with two adjacent sulfur atoms, was easily achieved by reaction of either dimethyl croconate (**110**) [68] or croconic acid 1,2-bis(dimethylamide) (**109**) [69] with alcoholic alkali hydrogen sulfide (Scheme 31). The structure of this mixed C<sub>5</sub> oxo-thiocarbon was established on the basis of spectroscopic data, especially of the <sup>13</sup>C-NMR spec-



Scheme 31

## 2. Thioxocarbon Dianions and Their Derivatives

trum, which exhibited three signals at  $\delta = 184.7$  and  $187.5$  ppm (C—O) and  $\delta = 204.8$  ppm (C—S). Visible-UV studies in aqueous solutions at different acidities demonstrate that the dithiocroconate spectrum exhibits recognizable alteration as the pH is lowered from 4 to 3, whereas the croconate spectrum is unchanged down to pH 2.7. This leads to the conclusion that dithiocroconate **108** is a stronger proton acceptor than is croconate and suggests that resonance stabilization in the croconate dianion must be substantially greater than in dithiocroconate [68] since simple thiols are more acidic than their oxygen counterparts in the absence of resonance effects. These findings are confirmed by investigation of the IR spectrum of K<sub>2</sub>C<sub>5</sub>O<sub>3</sub>S<sub>2</sub> in KBr, which exhibits strong absorption bands at 1658(s), 1602(m), 1564 cm<sup>-1</sup> (vs, broad), indicating an increased C—O bond order compared with that of the croconate dianion.

### B. CHEMICAL BEHAVIOR

Some of the interesting chemical reactions of the dark red dithiocroconate dianion **108** are summarized in Scheme 31. The black silver salt, which is quantitatively precipitated from aqueous solution, dissolves in potassium iodide or sodium thiosulfate solutions to regenerate the dithiocroconate dianion. Treatment of dry silver dithiocroconate with excess methyl iodide yields the intensely red "dithio ester" of croconic acid (**111**). The observation of one singlet in the <sup>1</sup>H-NMR spectrum at  $\delta = 3.07$  ppm is consistent only with structure **111**, which can be additionally confirmed by an independent synthetic route. Thus, 4,5-bis(methylthio)-4-cyclopentene-1,3-dione (**112**) can be oxidized by selenium dioxide in dioxane, yielding a red reaction product identical with that from alkylation of the silver salt of **108** [69]. Under these conditions condensation of the starting material with the oxidation product leads to the intriguing by-product **113**, a possible precursor of a sulfur-substituted "diaryl," consisting of two C<sub>5</sub> pseudo-oxocarbon rings [69]. Solutions containing the dithiocroconate dianion react to form intensely colored complexes of various hues with several transition metal ions, which have been investigated by spectral and ESR measurements [68]. These studies suggest that the 1,2-dithiocroconate is functioning as a bidentate ligand, with four coordination preferred for Ni(II) and Cu(II).

### Acknowledgments

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# 3

## Physical Chemistry of Aqueous Oxocarbons

Lowell M. Schwartz, Robert I. Gelb, and Daniel A. Laufer

I. Introduction . . . . .	43
II. Survey of Oxocarbon Acid $pK'$ Determinations . . . . .	44
III. Thermodynamic Data . . . . .	46
IV. Structures of Aqueous Oxocarbons . . . . .	49
A. Deltic Acid . . . . .	49
B. Squaric Acid . . . . .	50
C. Croconic Acid . . . . .	52
D. Rhodizonic Acid . . . . .	53
V. A New Type of Aqueous Complex . . . . .	56
References . . . . .	57

### I. Introduction

This chapter surveys the current state of understanding of the physical chemistry of aqueous oxocarbon species and equilibria. The study focuses on the oxocarbon acids deltic, squaric, croconic, and rhodizonic and their anions and only mentions the existence of derivatives of these made by replacing hydroxyls with other functional groups or by replacing oxygens with sulfur or selenium atoms. Nor is any consideration given here to crystalline substances or to solutions or oxocarbons in mixed or nonaqueous solution.

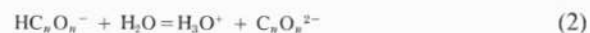
For convenience several abbreviations are used:  $Sq^{2-}$  for squarate,  $Cr^{2-}$  for croconate (this cannot be confused with the element chromium which is never involved in these reactions), and  $R^{2-}$  for rhodizonate. It is expected that discrimination between the latter symbol and the gas constant should be obvious from context. Protonated forms of these dianions are written by attaching appropriate H's.

Virtually all reactions in this chapter involve transfer of protons and hence are acid ionizations. Normally, the equilibrium constants for such reactions are subscripted, i.e.,  $K_a$  or  $pK_a$ , to designate "acid," but in this chapter the subscripts are omitted for conciseness. The term "ionization" is preferred here because some ionizations are accompanied by other forms of fragmentation of the principal species, and the term "dissociation" would be ambiguous in such cases. Finally, because our readers are likely to be more familiar with the traditional thermodynamic units, we do not use the SI system and abbreviate cal mole<sup>-1</sup> K<sup>-1</sup> as e.u. for entropy units.

The parent series of oxocarbon acids having nominal formulas  $H_2C_nO_n$  are dibasic as aqueous solutes yielding monoanions  $HC_nO_n^-$  and dianions  $C_nO_n^{2-}$  upon proton ionization. The strength of an acid is commonly understood to refer to the magnitude of the ionization equilibrium constant. The primary ionization constant  $K_1$  or  $pK_1$  corresponding to



is a measure of the parent acid strength, and the secondary ionization constant  $K_2$  or  $pK_2$  corresponding to



is a measure of the monoanion acid strength. Recent studies have shown however, that these reactions written as uncomplicated proton transfers do not adequately reflect structural changes that occur in the oxocarbon species in several cases. These changes are discussed in Section IV.

## II. Survey of Oxocarbon Acid $pK$ Determinations

A survey of oxocarbon acid ionization constant determinations is summarized in Table I. This survey is restricted to reports that give some indication of the methodology used and to those published within the previous two decades. References to earlier works can be found in papers by Alexanderson and Vannerberg [1] and Patton and West [2]. Table I includes only the parent series  $H_2C_nO_n$  with  $n = 3-6$ . Acidities have been found for several derivatives formed by replacing one of the parent hydroxyls with some other functional group, and Patton and West [3] list those reported to 1973. Each entry in the second column of Table I is the  $pK$  value at ambient temperature and the investigator's estimate of the statistical uncertainty if quoted. Equilibrium constants are variously reported as "thermodynamic" values by extrapolation to zero ionic strength or "conditional" values appropriate to a fixed nonzero ionic strength medium. The third column of Table I gives the ionic strength corresponding to the  $pK$ , and the fourth column states the method used to extrapolate to zero ionic strength or the solvent medium if a conditional constant is reported. A number of substances

Table I. Oxocarbon Acid Strengths at 25°C

Ionization	$pK$	Ionic strength $\mu$ (M)	Medium/extrapolation <sup>a</sup>	Experimental technique <sup>b</sup>	Ref.
Primary, $pK_1$					
$H_2C_3O_3$ , deltic acid	$2.57 \pm 0.04$	0	D-H	Pot.	12
$H_2C_4O_4$ , squaric acid	$1.7 \pm 0.3$	0.1	KCl	Pot.	13
	$1.2 \pm 0.2^c$	0	Davies	Pot.	14
	$0.55 \pm 0.15$	0	Davies	Pot.	15
	$0.51 \pm 0.02$	0	Davies	Cond.	17
	$0.54 \pm 0.06$	0	Davies	Cond.	16
	$0.96 \pm 0.03$	3	NaClO <sub>4</sub>	Pot.	1
$H_2C_5O_5$ , <sup>d</sup> croconic acid	0.68	?		Spect.	18
	0.32	2	HCl, NaCl	Spect.	19
	$0.50 \pm 0.05$	0	H <sub>2</sub> SO <sub>4</sub> /a.f.	Spect.	20
	$0.7 \pm 0.03$	0	HCl/H-E	Pot.	21
	$0.80 \pm 0.08$	0	HCl/H-E	Spect.	21
	$0.75 \pm 0.02$	0	HCl, KCl/D-H	Color. <sup>e</sup>	22
$H_2C_6O_6$ , <sup>d</sup> rhodizonic acid	4.20	?		Spect.	23
	$4.25 \pm 0.05$	0	KCl/D-H	Spect.	2
	$4.02 \pm 0.05$	?		Spect.	24
	$3.9 \pm 0.5^f$	3	NaClO <sub>4</sub>	Spect.	1
	$3.45 \pm 0.11$	3	NaClO <sub>4</sub>	Pot.	1
	$4.378 \pm 0.009$	0	D-H	Pot.	25
Secondary, $pK_2$					
$HC_3O_3^-$	$6.03 \pm 0.06$	0	D-H	Pot.	12
$HC_4O_4^-$	3.21	0.1	KCl	Pot.	13
	$3.48 \pm 0.02$	0	Davies	Pot.	14
	2.89	0.5	NaCl, NaClO <sub>4</sub>	Pot.	26
	$3.48 \pm 0.02$	0	Davies	Pot.	15
	$3.19 \pm 0.01$	3	NaClO <sub>4</sub>	Pot.	1
$HC_5O_5^-$	1.97	?		Spect.	18
	1.51	2	HCl, NaCl	Spect.	19
	$1.65 \pm 0.10$	0.5	H <sub>2</sub> SO <sub>4</sub> , Na <sub>2</sub> SO <sub>4</sub>	Spect.	20
	$2.28 \pm 0.14$	0	HCl/H-E	Pot.	21
	$2.24 \pm 0.01$	0	HCl/H-E	Spect.	21
$HC_6O_6^{2-}$ <sup>d</sup>	4.65	?		Spect.	23
	5.06	0.1	NaClO <sub>4</sub>	Pot.	27
	$4.72 \pm 0.07$	0	KCl	Spect.	2
	$4.62 \pm 0.05$	?		Spect.	24
	$3.1 \pm 0.09^f$	3	NaClO <sub>4</sub>	Spect.	1
	$3.58 \pm 0.11$	3	NaClO <sub>4</sub>	Pot.	1
	$4.65 \pm 0.01$	0	D-H	Pot.	25

<sup>a</sup> Extrapolation methods: D-H, Debye-Hückel activity coefficient correlation [28]; Davies, activity coefficient [29]; H-E, Harned-Ehlers activity coefficients of HCl [30]; a.f., activity function.

<sup>b</sup> Experimental techniques: Pot., potentiometric; Cond., conductimetric; Spect., spectrophotometric; Color., colorimetric.

<sup>c</sup> Miscalculation of  $pK_1$  (private communication).

<sup>d</sup> Nominal formula.

<sup>e</sup> Cresol red indicator.

<sup>f</sup> Note  $pK_1 > pK_2$ .

that are not members of the cyclic  $H_2C_nO_n$  series might be classified as oxocarbon acids if the definition is extended to include those acidic compounds having a carbon-oxygen skeleton and whose anions are believed to be stabilized by  $\pi$ -electron delocalization. Ionization constants for some of these are as follows: carbonic acid  $H_2CO_3$ :  $pK_1 = 3.88$  [4],  $pK_2 = 10.329$  [5]; oxalic acid  $H_2C_2O_4$ :  $pK_1 = 1.271$  [6],  $pK_2 = 4.266$  [7]; acetylenedicarboxylic acid  $H_2C_4O_4$  (an isomer of squaric acid):  $pK_1 = 0.656$ ,  $pK_2 = 2.336$  [8]; and tetrahydroxy-*p*-benzoquinone  $H_4C_6O_6$ :  $pK_1 = 4.8$ ,  $pK_2 = 6.8$  [7,9].

Although it is widely held that oxocarbon acids are quite strong, Table I shows that only squaric and croconic acids have  $pK_1$  values less than unity, but these are greater than zero. In comparison, the "strong" mineral acids  $HNO_3$  and  $HClO_4$  have  $pK$  values of  $-1.45$  and  $-1.59$ , respectively [10]. Several organic cyanocarbon acids, such as cyanoforn,  $pK = -5.1$ , and hexacyanoisobutylene,  $pK_1 < -8.5$ ,  $pK_2 = -2.5$  [11], also are much stronger than the strong oxocarbon acids. Therefore, the descriptor "moderately strong" applied to squaric, croconic, and acetylenedicarboxylic acidities puts these in a more appropriate perspective. These three acids are much stronger than enols and most carboxylic acids, which, of course, are "weak," having acid ionization  $pK$  values ranging upward from about 2.

It is clear from Table I that neither  $pK_1$  nor  $pK_2$  of the cyclic  $H_2C_nO_n$  series varies in a regular way as  $n$  changes from 3 to 6. Such a trend might be expected if the energetics of the acids and anions varied in a simple way with the size of the ring skeleton and if the proton dissociations took place *in vacuo* in the absence of solvent interactions. Clues to the role of solvent in the irregularity of oxocarbon acid  $pK$  values can be found by comparing the thermodynamic parameter values of ionization, by  $^{13}C$ -NMR structural studies, and to some extent by the ultraviolet-visible spectra of the aqueous oxocarbon species.

### III. Thermodynamic Data

Structural information about the species involved in a reaction can be inferred from the thermodynamic parameters  $\Delta H^0$  and  $\Delta S^0$  associated with the reaction. Values for these parameters are obtained either by temperature variation of the equilibrium constants or by direct calorimetry. The former method depends on the fact that each  $K$  or  $pK$  for Eq. (1) or (2) is measured for an equilibrium mixture at fixed temperature and pressure so that the following well-known thermodynamic relationships apply:

$$\Delta G^0 = -RT \ln K = 2.303RT pK \quad (3)$$

$$\Delta G^0 = \Delta H^0 - T \Delta S^0 \quad (4)$$

$$-R \left[ \frac{\partial \ln K}{\partial (1/T)} \right]_p = 2.303R \left[ \frac{\partial pK}{\partial (1/T)} \right]_p = \Delta H^0 \quad (5)$$

$$R \left[ \frac{\partial (T \ln K)}{\partial T} \right]_p = -2.303R \left[ \frac{\partial (T pK)}{\partial T} \right]_p = \Delta S^0 \quad (6)$$

The temperature variation of the equilibrium constant at some given temperature thus is used to calculate  $\Delta H^0$  from the appropriate slope via Eq. (5) and  $\Delta S^0$  from Eq. (6). Alternatively, either parameter can be combined with  $K$  at that same temperature to find the other parameter by eliminating  $\Delta G^0$  from Eqs. (3) and (4). When the direct calorimetric method is used to measure  $\Delta H^0$ ,  $\Delta S^0$  is calculated in this way.\*

Those determinations of  $\Delta H^0$  and  $\Delta S^0$  for oxocarbon acid dissociations made to date are listed in Table II. Before making deductions about the structures of species involved in a reaction from  $\Delta H^0$  and  $\Delta S^0$  data, it is important to recognize the following principle, which has been quoted many times [32,33]. These enthalpy and entropy changes reflect energetic and configurational differences, respectively, of the reacting system as a whole, i.e., the solvent medium as well as the reacting solutes. Consequently, a given  $\Delta H^0$  datum reflects both the difference in energies between product and reactant species *in vacuo* and the difference of energetic interaction between the product-solvent system and the reactant-solvent system. Similarly, a given  $\Delta S^0$  value can be attributed to several effects: (a) the intrinsic configurational differences between product and reactant species *in vacuo*, (b) the configurational changes induced in these species by the solvent environment, and (c) the configurational difference between the solvent surrounding the product species and that of the reactant species. Although many statistical mechanical and semiempirical theories [34] have been applied to the understanding of these phenomena, this discussion takes a completely empirical approach. Thermodynamic data for oxocarbon systems are compared to corresponding data for other systems, and structural explanations are offered which are consistent with results of nonthermodynamic experiments. In adopting this empirical approach, no attempt is made to explain why, for example, a given oxocarbon acid ionization has the specific  $\Delta S^0$  value observed, but rather why this  $\Delta S^0$  is similar to or different from the corresponding value of some reference acid. The reference chosen for this purpose is not a specific molecule but rather the average of all comparable carboxylic acids for which thermodynamic data of aqueous ionization are conveniently available. Ebersson and Wadsö [35] compiled such a list of about 60 ionizations in 1963, and Larson and Hepler [31] gathered about 90 in 1967 and listed these in their Tables 1-2 and 1-3. Neither list

\*Larson and Helper [31] have noted that  $\Delta H^0$  values for the same reaction measured by calorimetry and by temperature variation of  $K$  are frequently in conflict even though the two methods are equally valid in principle. Both experimental methods are subject to sources of systematic error, and so only when utmost care is taken in both experiments can agreement be expected.

Table II. Thermodynamic Data<sup>a</sup> for Oxocarbon Acid Ionizations

Acid	Primary ionization		Secondary ionization		Ref.
	$\Delta H_1^0$	$\Delta S_1^0$	$\Delta H_2^0$	$\Delta S_2^0$	
Deltic acid	~0	-12	~0	-27	12
Squaric acid	-1.5 ± 0.1	-7.5 ± 0.7	-3.0 ± 0.5	-26 ± 2	16
Croconic acid	3.46	8.9 (pK <sub>1</sub> = 0.60) <sup>c</sup>	-1.75 ± 0.05	-19.8 (pK <sub>2</sub> = 3.05) <sup>c</sup>	15
	3.9 ± 0.2	9.5 ± 0.7	-2.39	-16.2 (pK <sub>2</sub> = 1.80) <sup>c</sup>	36
	3.9 ± 0.3 <sup>d</sup>	9.8 ± 0.7	-3.0 ± 0.1	-20.1 ± 0.4	36
Rhodizonic acid	4.6 ± 0.3	-4.6 ± 0.8	9.6 ± 0.3	11 ± 1	21
					25

<sup>a</sup> The  $\Delta H^0$  values are in kilocalories mole<sup>-1</sup>;  $\Delta S^0$  in calories mole<sup>-1</sup> K<sup>-1</sup> (entropy units); all data at 25°C.

<sup>b</sup> Abbreviations: T.V., temperature variation of  $K$  using technique designated; Cal., calorimetric at ionic strength designated. For other abbreviations, see footnote b, Table I.

<sup>c</sup> Calorimetric  $\Delta S^0$  values calculated from pK values in parentheses.

<sup>d</sup> Calculated from data given in the reference.

is up to date, but there is little likelihood that additions would be so abnormal as to change the averages very much. The Larson and Hepler tables include data for 14 dibasic acids ranging in size from oxalic to suberic acid and some including hydroxy, aromatic, or unsaturated functionality. Using these 14 as a basis, the ranges of variability are  $-1.3 < \Delta H_1^0 < 0.8$  and  $-1.6 < \Delta H_2^0 < 0.3$  kcal/mole and  $-22 < \Delta S_1^0 < -8$  and  $-36 < \Delta S_2^0 < -19$  e.u. These ranges also may be expressed as excursions from the midpoint:  $\Delta H_1^0 = -0.2 \pm 1.1$ ,  $\Delta H_2^0 = -0.6 \pm 1.0$  kcal/mole and  $\Delta S_1^0 = -15 \pm 7$ ,  $\Delta S_2^0 = -27 \pm 9$  e.u. A hypothetical typical acid, which shall be called "typic acid" and written H<sub>2</sub>Ty, will be assigned thermodynamic data corresponding to the midpoints of the ranges, and so, by Eqs. (3) and (4), typic acid has pK<sub>1</sub> = 3.1 and pK<sub>2</sub> = 5.5 at 25°C.

A cursory examination of the same tables indicates that  $\Delta H^0$  values exist in a narrow range about zero, but  $\Delta S^0$  values are more correlated with the large variation of observed pK values. These observations led Ebersson and Wadsö [35] to develop the empirical relationship

$$\Delta S^0 = -(0.3 + 4.94 \text{ pK}) \quad (7)$$

to fit their tabulated data, which included both primary and secondary ionizations and spanned the range  $1.9 < \text{pK} < 8.3$ . The quality of the fit of the data to this correlation is  $\pm 2$  e.u. It is significant that Ebersson and Wadsö could not find a similar relationship between  $\Delta H^0$  and pK. Thus, in addition to "typic" acid being used for a reference level,  $\pm 2$  e.u. deviation about Eq. (7) will serve as a rough range of normal variability for  $\Delta S^0$ , and similarly  $-0.4 \pm 1.2$  kcal/mole will serve for  $\Delta H^0$ .

#### IV. Structures of Aqueous Oxocarbons

It appears that the aqueous equilibria involving the oxocarbon acid systems becomes progressively more complicated as the ring size increases from three to six carbon atoms. Each system is discussed separately.

##### A. DELTIC ACID

Relatively little work has been done on the physical chemistry of deltic acid. Both the parent and monoanion are weak acids (pK<sub>1</sub> = 2.6, pK<sub>2</sub> = 6.0) [12], somewhat similar in strength to the reference acid H<sub>2</sub>Ty (pK<sub>1</sub> = 3.1, pK<sub>2</sub> = 5.5). Little temperature variation of the pK values was observed, and, because the scatter of data plotted versus temperature was relatively large, only rough thermodynamic values could be estimated. Nevertheless, each datum listed in Table II for deltic acid is well within the corresponding range for typical carboxylic acids mentioned in Section III. Thus, the simplest picture for the deltic acid

system is that no unusual changes occur as deltatate dianion protonates to monoanion and then to parent acid. If, on the other hand, deltatate dianion is hypothesized to be more stabilized by  $\pi$ -electron delocalization than the protonated forms, this effect must be small or must be offset by some other factor tending to increase the stabilities of the protonated forms.

### B. SQUARIC ACID

With  $pK_1 = 0.5$  and  $pK_2 = 3.5$ , squaric acid and its monoanion are each stronger than the reference acid, having  $pK_1 = 3.1$  and  $pK_2 = 5.5$ . Comparisons are more conveniently made using the magnitude of the standard Gibbs free-energy change of ionization, which, like  $pK$ , is an inverse measure of the acid strength. This parameter more directly reflects the relative contributions of energetic and configurational factors to the acid strength. At any given temperature  $\Delta G^0$  is composed of  $\Delta H^0$  and  $-T \Delta S^0$ , and Table III shows the magnitudes of these quantities for both the oxocarbon acids and the reference acid. The superior strength of  $H_2Sq$  relative to " $H_2Ty$ " is clearly seen by the difference of 3.6 kcal/mole in  $\Delta G_1^0$ . Contributing to this difference are 1.3 from  $\Delta H_1^0$  and 2.3 from  $-T \Delta S_1^0$ . Thus,  $H_2Sq$  is as strong as it is for both energetic and configurational reasons, with the latter dominating. The thermodynamic data for the primary dissociation are, nevertheless, not unusual. The  $\Delta H_1^0$  value is somewhat low but is within the normal range, and the observed  $\Delta S_1^0$  is some 4.5 e.u. more negative than predicted by Eq. (7) for  $pK_1 = 0.5$ , but, since no other acids of moderate strength were included in the correlation, the explanation is uncertain. An explanation for the dominant role played by  $T \Delta S^0$  in determining acid strengths can be given by quoting Ebersson and Wadsö [35], who in turn were reflecting earlier statements by others: "The strength of a given acid is determined to a large extent by the change in orientation and compression of solvent molecules around

Table III. Thermodynamic Contributions<sup>a</sup> to Acid Strengths

Ionization	$\Delta G_1^0$	$\Delta H_1^0$	$-T \Delta S_1^0$	Ref.
Primary				
" $H_2Ty$ " reference	4.3	-0.2	4.5	—
$H_2Sq$	0.7	-1.5	2.2	16
$H_2Cr$	1.1	3.9	-2.8	21
$H_2R$	6.0	4.6	1.4	25
Secondary				
" $HTy$ "	7.4	-0.6	8.0	—
$HSq^-$	4.7	-3.0	7.7	15
	4.2	-1.7	5.9	36
$HCr^-$	3.0	-3.0	6.0	21
$HR^-$	6.3	9.6	-3.3	25

<sup>a</sup> All entries in kilocalories per mole.

the solute which is appreciable even before ionization." Considering that entropic effects are so important in making  $H_2Sq$  moderately strong, this explanation seems appropriate.

There is some discrepancy in the enthalpy of secondary ionization of squaric acid. If the data of Schwartz and Howard [15] are correct, the monoanion is stronger than the reference " $HTy^-$ ," primarily for energetic reasons. Of the difference of 2.7 kcal/mole in  $\Delta G_2^0$ , 2.4 is due to  $\Delta H_2^0$  and only 0.3 is due to  $\Delta S_2^0$ . At variance with these are the calorimetric results of Orebaugh [36], which give more weight to entropic factors in causing the enhanced strength of  $HSq^-$  and which, if correct, would negate the following interpretations. It is hoped that future experimentation will resolve this discrepancy. The observed  $\Delta H_2^0 = -3.0$  kcal/mole of Schwartz and Howard [15] is substantially more negative than normal, but the observed  $\Delta S_2^0$  of  $-26$  e.u. is quite similar to that of the reference "typic" acid. It is therefore clear that energetic factors must be responsible for the strength of  $HSq^-$ . A reasonable and attractive explanation is that the stability of  $Sq^{2-}$  is enhanced relative to  $HSq^-$  due to  $\pi$ -electron delocalization, although another possibility is that the solvent interaction with  $Sq^{2-}$  is atypically stronger than with  $HSq^-$ . It may be significant that  $\Delta H_2^0$  for the ionization of  $HCr^-$  is also  $-3.0$  kcal/mole, and the coincidence of these two results suggests that the same factors are responsible for both ionizations.

The ultraviolet-visible spectra of aqueous oxocarbon species should be sensitive to differences in the  $\pi$ -electron structures and thus should shed light on this problem. As shown in Table IV the lowest-energy part of the spectrum of each of the oxocarbon dianions [1,2,18,19,21,37] is characterized by two overlapping peaks the maxima of which are separated by 20–30 nm. It is observed in aqueous

Table IV. Low-Energy Electronic Spectra of  $H_2Sq$ ,  $H_2Cr$ ,  $H_2R$ , and Their Anions

Species	Peak 1		Peak 2	
	$\epsilon_{max} \times 10^{-4}$	$\lambda_{max}$ (nm)	$\epsilon_{max} \times 10^{-4}$	$\lambda_{max}$ (nm)
$H_2Sq^a$	1.34	230	1.90	251
$HSq^-$	2.08	241	1.81	263
$Sq^{2-}$	2.27	251	2.31	272
$H_2Cr^b$	1.46	286	0.31	341
$HCr^-$	1.93	309	1.88	355
$Cr^{2-}$	2.48	334	3.61	365
$H_2R^c$				
$HR^{-d}$				
$R^{2-}$		~430	3.3	483

<sup>a</sup> Schwartz and Howard [37].

<sup>b</sup> Schwartz *et al.* [21].

<sup>c</sup> Single peak at 320 nm,  $\epsilon_{max} = 1.1 \times 10^4$  [2].

<sup>d</sup> Probable single peak near 370 nm.

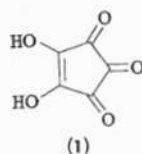
squaric acid that protonation of  $\text{Sq}^{2-}$  to  $\text{HSq}^-$  and then to  $\text{H}_2\text{Sq}$  shifts the two-peak system to slightly higher energies and diminished intensities [37]. If the two-peak system results from  $\pi$ -electron delocalization around the ring skeleton, then it is clear that some changes occur upon successive protonation of  $\text{Sq}^{2-}$ , but it is not clear how to correlate such spectral perturbations with enthalpic changes.

Carbon-13 NMR studies [22,38] have shown only a single resonance for squaric acid containing various proportions of the three species. This indicates that the four carbons are equivalent on the NMR time scale, showing (a) that proton exchange with the solvent is rapid and (b) that there are no hydration equilibria similar to those observed in croconic and rhodizonic acid systems.

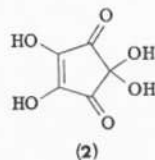
### C. CROCONIC ACID

Both ionizations of croconic acid are substantially stronger ( $\text{p}K_1 = 0.8$ ,  $\text{p}K_2 = 2.2$ ) than those of the reference acid ( $\text{p}K_1 = 3.1$ ,  $\text{p}K_2 = 5.5$ ). The thermodynamic data shown in Table II indicate that both ionizations are grossly abnormal. Whereas typical  $\Delta H^\circ$  values are in the range  $-0.4 \pm 1.2$  kcal/mole, the  $\Delta H_1^\circ$  of croconic acid is 3.9 and  $\Delta H_2^\circ$  is  $-3.0$  kcal/mole. Also, the observed  $\Delta S_1^\circ$  of about 9.5 e.u. and  $\Delta S_2^\circ$  of  $-20$  e.u. are each far from predictions based on Eq. (7). As mentioned above,  $\Delta H_2^\circ$  of  $\text{HCr}^-$  ionization is the same as  $\Delta H_2^\circ$  of  $\text{HSq}^-$ , but  $\text{HCr}^-$  is stronger as an acid because  $\Delta S_2^\circ$  is less negative than  $\Delta S_2^\circ = -26$  e.u. for  $\text{HSq}^-$  ionization. If  $\pi$ -electron delocalization upon ionization explains the abnormally negative  $\Delta H_2^\circ$  values, then perhaps the greater extent of charge distribution about the larger croconate dianion ring is less effective than the squarate ring in orienting solvent molecules. This would explain the differences in entropies observed.

The thermodynamic data for the primary ionization of  $\text{H}_2\text{Cr}$  are so abnormal that the reaction is not believed to be given by Eq. (1), which implies structure 1



for the parent acid. There is firm evidence that the diprotonated species is covalently attached to one water molecule and has structure 2. Carpentier *et al.*



[20] first deduced this fact from the similarity of the UV spectrum of related compounds, and Gelb *et al.* [22] provided confirmation by observing three

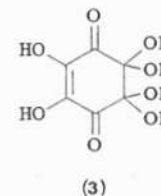
$^{13}\text{C}$ -NMR resonances attributable to un-ionized croconic acid and arising from the three nonequivalent carbons of 2. It was concluded from both these investigations that the monoanion  $\text{HCr}^-$  is not hydrated, so that the primary ionization also involves a dissociation of water. The net reaction is given by Eq. (8).



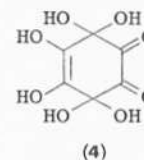
Actually, Gelb *et al.* [22] combined the  $^{13}\text{C}$ -NMR resonance displacements with the measured ionization constant to calculate that the equilibrium partition ratio of species 2 to species 1 is about 9 : 1 and that  $\text{p}K_1$  for unhydrated 1 ionizing to  $\text{HCr}^-$  is nearly zero. Therefore, when 1 mole of croconic acid ionizes yielding the thermodynamic data values given in Table II, the reaction is effectively 0.9 mole by Eq. (8) and 0.1 mole by Eq. (1). Dehydration of aqueous aldehydes and ketones typically involves  $\Delta H^\circ$  values of  $\sim 5$  kcal/mole [39], and similarly the dehydration of the  $\alpha$ -keto acid pyruvic acid has  $\Delta H^\circ = 5.5$  kcal/mole and  $\Delta S^\circ = 16$  e.u. [40]. Therefore, by analogy, a reaction according to Eq. (8) is expected to have  $\Delta H_1^\circ$  some 5 kcal/mole more positive than according to Eq. (1) and  $\Delta S_1^\circ$  some 16 e.u. more positive. These clearly account for the observed anomalous thermodynamic results and also suggest that the primary ionization of unhydrated  $\text{H}_2\text{Cr}$  would be quite similar to that of  $\text{H}_2\text{Sq}$ .

### D. RHODIZONIC ACID

The aqueous dissociation of rhodizonic acid is, like that of croconic acid, complicated by hydration, and several investigators have studied the phenomenon recently [2,24,25]. All agree that  $\text{R}^{2-}$  dianion is unhydrated at equilibrium but that both the monoanion and neutral acid are dihydrated. Patton and West [2] assumed that the dihydrated system had an ortho geometry, i.e.,



but Gelb *et al.* [25] interpreted  $^{13}\text{C}$ -NMR evidence given in Tables V and VI to suggest that the ortho dihydrate system isomerizes slowly to the more stable para dihydrate 4. Because of rapid proton exchange between the enols and carbonyls,





**Table V.**  $^{13}\text{C}$ -NMR Spectra of Rhodizonic Acid and Its Anions in 5%  $\text{D}_2\text{O}/\text{H}_2\text{O}$  at  $25^\circ\text{C}$ <sup>a</sup>

Mole ratio $\text{LiOH}/\text{R}^b$	$^{13}\text{C}$ -NMR (ppm relative to $\text{Me}_4\text{Si}$ )			Acquisition time (hr)
0	191.2	142.8	95.0	0.1
0.15	191.1	143.3	94.9	0.1
0.57	191.3	~144 <sup>c</sup>	95.1	0.4
0.75	191.3	~145 <sup>c</sup>	95.1	0.6
1.05	191.3		95.1	2.6
1.29	191.3	177.88	95.0	1.6
1.51	191.2	177.87	95.0	2.1
2.00		177.88		2.5

<sup>a</sup> From Gelb *et al.* [25]. Reprinted with permission. Copyright (1978) American Chemical Society.

<sup>b</sup> Here R represents total rhodizionate species in solution.

<sup>c</sup> Broad peak.

this structure has only two NMR-equivalent carbons and so is consistent with the two resonances that are observed after solutions of  $\text{H}_2\text{R}$  and  $\text{HR}^-$  are allowed to equilibrate for several days.

The existence of two isomeric forms of aqueous  $\text{H}_2\text{R}$  and  $\text{HR}^-$  introduces the additional complication as to which of these forms is present in any of the solutions examined in the various spectrophotometric or pH potentiometric studies reported to date. This ambiguity can be resolved by the following observations, however. First, the data in Table V indicate that little or no para dihydrate species are formed for ~2 hr when solid  $\text{H}_2\text{R} \cdot 2\text{H}_2\text{O}$  is used in solution preparation. Second, Gelb *et al.* [25] found essentially identical  $\text{p}K_1$  values when

**Table VI.**  $^{13}\text{C}$ -NMR Spectra of  $\text{H}_2\text{R}$  and Its Anions in 5%  $\text{D}_2\text{O}/\text{H}_2\text{O}$  at  $30^\circ\text{C}$  with Prior Equilibration<sup>a</sup>

Mole ratio $\text{LiOH}/\text{R}^b$	$^{13}\text{C}$ -NMR (ppm relative to $\text{Me}_4\text{Si}$ )				Equilibration time <sup>c</sup> (hr)
0	191.1	142.8	95.0		0
0	191.3	172.7	142.9	95.1	92.7
0.07	191.2	172.8	142.9	95.0	92.6
0.07		172.4			92.6
0.10		172.7			92.7
0.27		173.0			92.8
0.50		173.9			93.1

<sup>a</sup> From Gelb *et al.* [25]. Reprinted with permission. Copyright (1978) American Chemical Society.

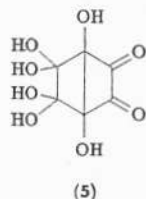
<sup>b</sup> Here R represents total rhodizionate species in solution, which was ~0.5F throughout.

<sup>c</sup> The equilibration times correspond to standing times at ~21°C after solution preparation until the start of data acquisition, which required about 20 hr.

solutions of  $\text{H}_2\text{R}$  and  $\text{K}_2\text{R}$  were titrated: replicates  $4.377 \pm 0.005$ ,  $4.372 \pm 0.007$ ,  $4.391 \pm 0.008$  for  $\text{K}_2\text{R}$  titrations with HCl and  $4.372 \pm 0.004$  for  $\text{H}_2\text{R}$  titrated with NaOH. These observations seem to indicate that the ortho dihydrated species are kinetically favored when  $\text{R}^{2-}$  solutions are acidified and that the stable para dihydrated species form only after several days of standing. Thus, it appears that studies reported in the literature to date deal with the ortho dihydrated  $\text{H}_2\text{R}$  and  $\text{HR}^-$  species since the general experimental practice has involved acidification of  $\text{R}^{2-}$  solutions and prompt measurement.

Visible spectral evidence summarized in Table IV also suggests that substantial changes in  $\pi$ -electron structure accompany protonation and hydration of  $\text{R}^{2-}$ . The dianion spectrum shown by Patton and West [2] has two overlapping peaks near 430 and 480 nm, which are characteristic of  $\pi$ -electron delocalization around the ring, but these two peaks diminish in intensity without shifting to higher energy as the pH decreases. This is in contrast to the corresponding spectral behavior observed in the squarate and croconate systems. The double hydration of  $\text{R}^{2-}$  evidently perturbs the ring molecular orbitals into a more localized configuration, which yields a spectrum of substantially higher energy for the monoanion. Thus, decreasing the pH of a solution of  $\text{R}^{2-}$  simply diminishes the characteristic  $\text{R}^{2-}$  peak intensities in the visible, but decreasing the pH of a solution of, say,  $\text{Sq}^{2-}$  not only diminishes the  $\text{Sq}^{2-}$  spectrum but increases the  $\text{HSq}^-$  spectrum amplitude, which is only slightly shifted to higher energy.

From Table I it can be seen that the apparent  $\text{p}K$  values of rhodizonic acid are quite close. The thermodynamic  $\text{p}K_1$  found by Patton and West [2] is 4.25, whereas that measured by Gelb *et al.* [25] is slightly different at 4.38. Both groups of investigators measured  $\text{p}K_2$  values agreeing within statistical uncertainty near 4.7. Only a single thermodynamic study has been made [25], and that showed very unusual results, as seen in Table II. The secondary ionization enthalpy change is approximately 10 kcal/mole more positive than normal and no doubt reflects the energetically unfavorable dissociation of two water molecules along with the proton. The corresponding entropy change is also abnormally positive, and this also reflects the double dehydration which is entropically favorable, perhaps by as much as 30 e.u. However, the thermodynamic data for the primary ionization are more difficult to interpret. The observed  $\Delta H_1^0$  of 4.6 kcal/mole shows that the reaction is energetically unfavorable, but in this case dehydration cannot be the source. The  $\Delta S_1^0$  of -4.6 e.u. is much less negative than would be expected from the correlation of Eq. (7). These discrepancies may result from changes in bonding caused by the ionization reaction. Thus, bonding in neutral rhodizonic acid might involve a structure (5) having a bond across the ring, similar to that suggested many years ago by Carpeni [41]. The existence of such a bond would impart energetic stability and rigidity to the neutral molecule such that its disruption upon ionization would tend to make both enthalpy and



entropy changes more positive. Structure 5 is also consistent with the three  $^{13}\text{C}$ -NMR resonances observed for the neutral acid with ortho dihydration.

The physical chemistry of rhodizonic acid in solution is far from being well understood, and it is hoped that other studies will be undertaken at least to verify the thermodynamics if not the kinetics involved. The experiments are difficult not only because the solutions are sensitive to air oxidation but because the reactions of hydration and isomerization are slow, so that attainment of equilibrium is difficult to ascertain.

## V. A New Type of Aqueous Complex

In Section IV,B thermodynamic data led to the suggestion that the enhanced acid strength of  $\text{H}_2\text{Sq}$  could be attributed to the orientation of solvent molecules around the neutral but polar acid before ionization. Other important configurational evidence about aqueous  $\text{H}_2\text{Sq}$  was the discovery of complexes formed between this molecule and unprotonated forms of the colorimetric acid-base indicators cresol red and 4-phenylazodiphenylamine (PDPA) [42]. The visible spectra of these complexes are virtually the same as those of the protonated indicators, which indicates that, as far as its reaction with the unprotonated indicator species is concerned, the squaric acid molecule is essentially indistinguishable from an aqueous proton. This further implies that one of the protons on  $\text{H}_2\text{Sq}$  is virtually transferred to a neighboring solvent molecule, and so aqueous  $\text{H}_2\text{Sq}$  probably has a structure resembling an associated ion pair  $\text{H}_3\text{O}^+\text{HSq}^-$ . Such an ion pair dipole would interact strongly with the solvent, and hence the configuration of solvent water around the  $\text{H}_2\text{Sq}$  molecule has an unusually high degree of ordering compared to carboxylic acids.

Gelb and Schwartz [42] measured the formation constants of these  $\text{H}_2\text{Sq}$ -indicator complexes and found values of  $\sim 30$  and  $\sim 10$  for the complexes with cresol red and PDPA, respectively. These values compare with protonation constants of  $\sim 19$  and  $\sim 7$  for the two indicators, respectively, and show that the affinities of both indicators are stronger for  $\text{H}_2\text{Sq}$  than for  $\text{H}_3\text{O}^+$ . These investigators searched for similar complexes in aqueous solutions of a few other moderately strong acids. Oxalic acid solutions showed a slight discrepancy between  $\text{p}K_1$  measured conductometrically and colorimetrically, and this discre-

pancy might be due to a very weak complex or might result from another minor source of experimental error [42]. On the other hand, it was shown unambiguously [21] that croconic acid does not form such a complex. It is now understood, as discussed in Section IV,C, that croconic acid is moderately strong not so much because the neutral acid is highly polar but because of the entropic factors associated with the removal of hydrated water. It is conceivable that unhydrated neutral  $\text{H}_2\text{Cr}$  forms such complexes with indicators but this species cannot reach a sufficiently high concentration to detect it. This assertion is a consequence of the hydration equilibrium of  $\text{H}_2\text{Cr}$ , which at  $25^\circ\text{C}$  leaves only about 7–14% of the acid in the unhydrated form. This concentration of  $\text{H}_2\text{Cr}$  corresponds to only 1–3% of the  $\text{H}^+$  concentration in the solutions reported by Gelb *et al.* [22], so that a complex between unhydrated  $\text{H}_2\text{Cr}$  and cresol red might easily have gone undetected.

Recently, a complex has been found between the moderately strong acetylenedicarboxylic acid and cresol red [43]. This discovery indicates that the phenomenon with squaric acid is not an isolated example. The use of colorimetry in solutions containing un-ionized, moderately strong acids is now open to question, and further experimentation to characterize these complexes is likely to be undertaken in the future.

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## 4

## New Bond-Delocalized (Dicyanomethylidene)croconate Derivatives: "Croconate Violet" and "Croconate Blue"

Alexander J. Fatiadi

I. Introduction . . . . .	59
II. Reaction of Croconates with Malononitrile . . . . .	62
A. 1,3-Bis(dicyanomethylidene)croconate Salts: Croconate Violet . . . . .	62
B. 2-(Dicyanomethylidene)croconate Salts . . . . .	65
C. 1,2,3-Tris(dicyanomethylidene)croconate Salts: Croconic Acid Blue . . . . .	68
D. Attempted Condensation of Six-Carbon Oxocarbons with Malononitrile . . . . .	72
III. Electrical Conductivity of Some Bond-Delocalized Salts . . . . .	73
IV. Summary . . . . .	76
References . . . . .	76

### I. Introduction

The first oxocarbons, croconic acid (**1**) and the dipotassium salt of croconate anion (**2**), were obtained by Gmelin as early as 1825 [1]. Recognition that the oxocarbons  $C_nO_n^{m-}$  were members of a class of hitherto unknown aromatic substances in the 1960's [2] led to greatly renewed interest in this area [3]. In recent years several species have been synthesized in which the carbonyl oxygen atoms have been partially or completely replaced by other atoms; these are called pseudo-oxocarbons. They include nitrogen [4], sulfur [5,6], and selenium [7], analogs of squarate ion and a sulfur analog of croconate [8] (Fig. 1). This chapter

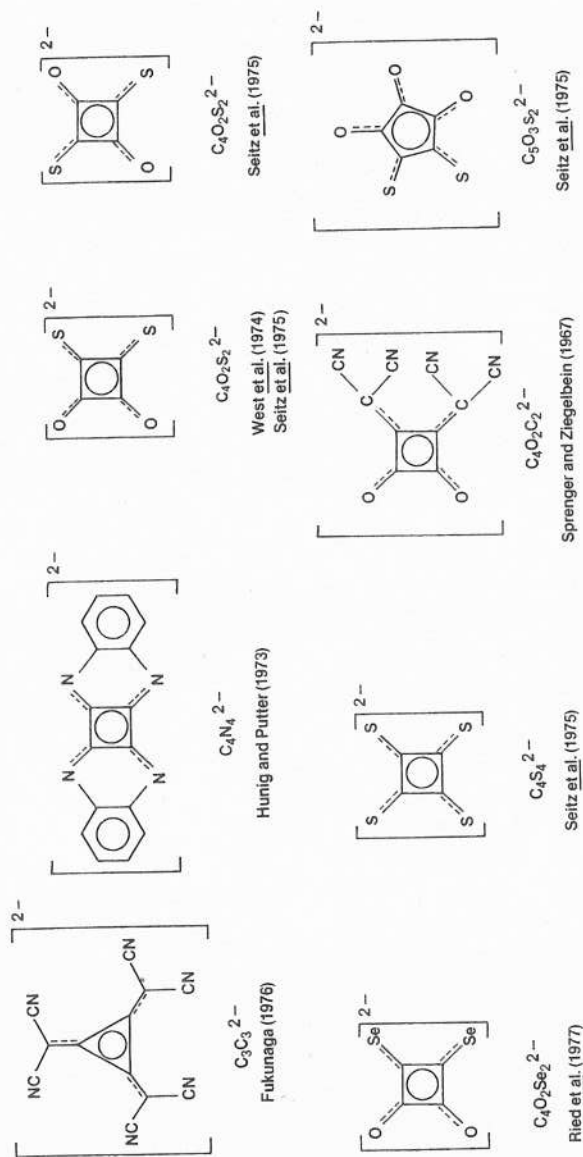
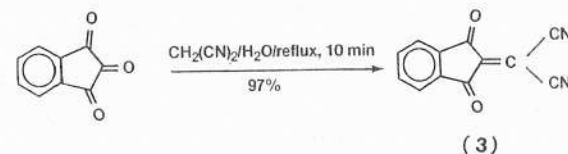


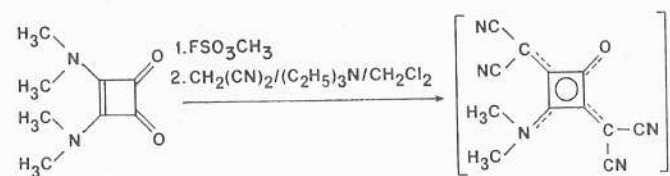
Fig. 1. Some aromatic pseudo-oxocarbon dianions.

is concerned with new oxocarbon derivatives in which one or more of the oxygen atoms are replaced with dicyanomethylidene groups  $=C(CN)_2$ .

Our interest in these substances grew from the observation that 1,2,3-indanetrione reacts readily with malononitrile, with replacement of the most reactive 2-carbonyl oxygen [9,10]. Brief refluxing (5–10 min) of indanetrione with malononitrile in aqueous solution produced 2-(dicyanomethylidene)-1,3-indanedione (3) in almost quantitative yield [11].



The reviews on oxocarbons [3] or vincinal polyketones [12] discuss only briefly the reaction with malononitrile, and a literature survey showed only three reports on this topic. When dibutyl squarate was treated with malononitrile in the presence of sodium butoxide in butanol, Sprenger and Ziegenbein [13] obtained a deep yellow disodium salt of 1,2-bis(dicyanomethylidene)-3-cyclobutene-3,4-dione, a new analog of the squarate dianion (Fig. 1). On treatment of the bis(dimethylamide) of squaric acid with malononitrile in the presence of triethylamine in dichloromethane, Seitz *et al.* [14] isolated a red triethylammonium salt of 2,4-bis(dicyanomethylidene)-3-(dimethylamino)-1-oxo-3-cyclobutene; the bond-delocalized salt is a new example of an aromatic pseudo-oxocarbon. A salt of

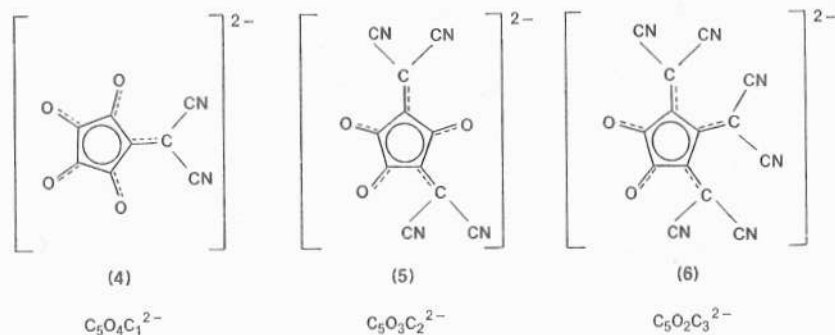


1,2,3-tris(dicyanomethylidene)deltate has also been synthesized by Fukunaga [15] using an indirect method. When tetrachlorocyclopropene was treated with 3 equivalents of malononitrile in 1,2-dimethoxyethane in the presence

of 6 equivalents of sodium hydride, hexacyanotrimethylenecyclopropanediide (Fig. 1) was obtained in almost quantitative yield. The product was isolated as the bis(tetrabutylammonium) salt.

Still another recent report [15a] described a synthesis of a nitrogen analog of deltic acid, a new addition to the pseudo-oxocarbon family.

The most interesting and best studied dicyanomethylidene derivatives to date are derivatives of croconic acid and the croconate dianion. We have found that one, two, or three oxygens in  $C_5O_5^{2-}$  can be replaced by  $=C(CN)_2$  groups to give the dianions **4**, **5**, and **6** respectively [11,16,17]. Salts of these anions are

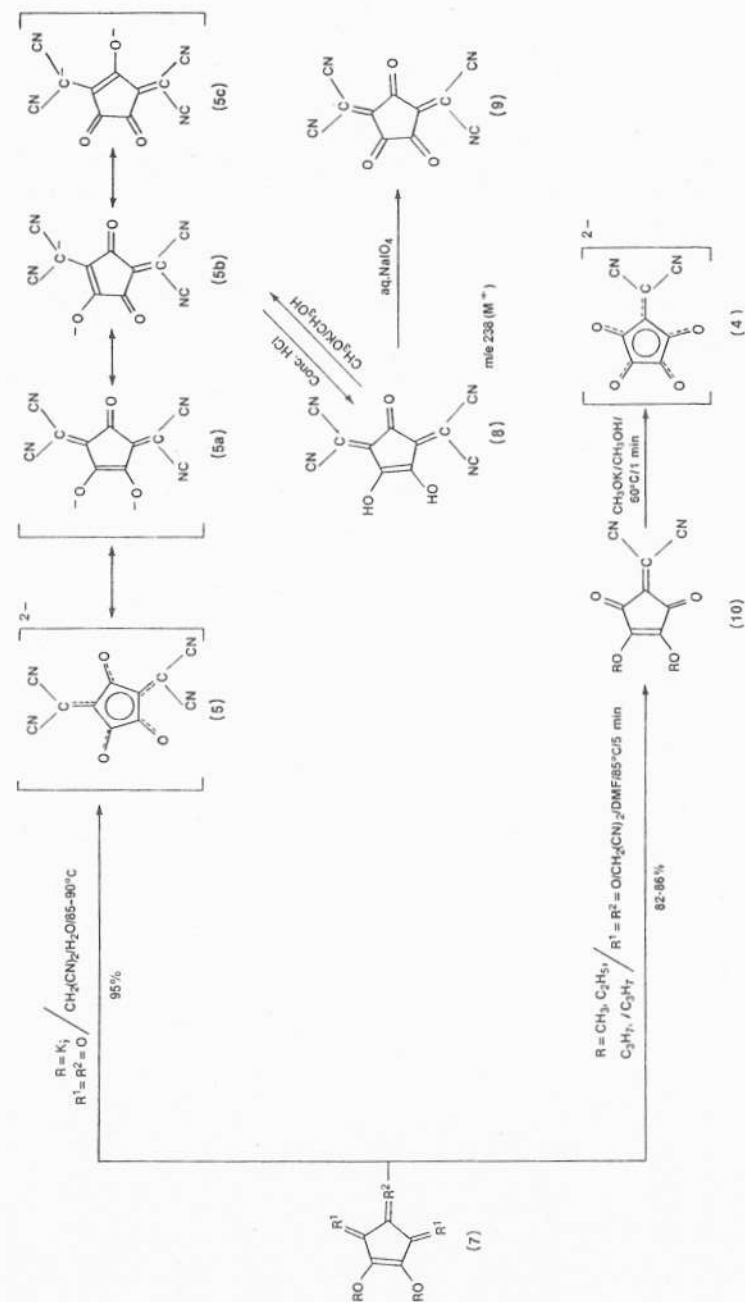


brilliantly colored and show remarkable electrical conductivity. These species and the few mentioned above are members of a new class of pseudo-oxocarbons containing dicyanomethylidene groups with the general formula  $C_nO_m[C(CN)_2]_{n-m}^{2-}$ .

## II. Reaction of Croconates with Malononitrile

### A. 1,3-BIS(DICYANOMETHYLIDENE)CROCONATE SALTS: CROCONATE VIOLET

Treatment of dipotassium croconate (**7**,  $R = K$ ;  $R^1 = R^2 = O$ ) [18] with a 1-2 molar excess of malononitrile in aqueous solution at  $85^\circ-90^\circ C$  yields the dipotassium salt of 1,3-bis(dicyanomethylidene)-2-oxo-4-cyclopentene-4,5-diol (**5**) (Scheme 1) [16]. Recrystallization from hot water gives the salt of **5** as deep blue metallic needles of the dihydrate. This dipotassium salt of **5** is a dye for which we have suggested the name "croconate violet" because of its intense violet color in solution [ $\lambda_{max}(H_2O)$  533 nm ( $\epsilon = 100,000$ )]. The infrared spectrum of the dipotassium salt of **5** is relatively simple, consistent with a symmetric structure for the dianion of the salt. Four strong bands are observed at 1680, 1620, 1580,



Scheme 1

and  $1520\text{ cm}^{-1}$ , probably due to combinations of  $\text{C}=\text{O}$ ,  $\text{C}=\text{C}$ , and  $\text{C}=\text{C}(\text{CN})_2$  vibrations.

The  $^{13}\text{C}$ -NMR spectrum of **5** shows three  $^{13}\text{C}$  resonances for the ring carbon atoms at  $\delta = 181.4$  ( $\text{C}=\text{O}$ ),  $172.0$  ( $\text{C}=\text{O}$ ), and  $147.8$  ppm [ $\text{C}=\text{C}(\text{CN})_2$ ], as well as resonances assigned to exocyclic carbons at  $119.5$  (CN) and  $51.4$  [ $\text{C}=\text{C}(\text{CN})_2$ ].\* This spectrum is also consistent with a symmetric structure for the dianion.

A nearly complete ionization of the dipotassium salt of **5** in aqueous solution is evidenced from the specific conductance of **5** ( $235.7147\ \mu\text{S}/\text{cm}$ ) ( $1\ \text{mM}$ ,  $22.8^\circ\text{C}$ ), as compared to potassium chloride ( $147\ \mu\text{S}/\text{cm}$ ) ( $1\ \text{mM}$ ,  $22.8^\circ\text{C}$ ). Subtraction of the ionic conductance of the dipotassium ions ( $2\text{K}^+ \times 73.5\ \mu\text{S}/\text{cm}$ ,  $25^\circ\text{C}$ ) leaves the ionic conductance ( $\sim 88\ \mu\text{S}/\text{cm}$ ) of the bulky 1,3-bis(dicyanomethylidene)croconate ion, and it is only slightly higher from the ionic conductance ( $76.3\ \mu\text{S}/\text{cm}$ ,  $25^\circ\text{C}$ ) of the chloride ion.

The structure of **5** has been definitely established by an X-ray crystallographic study [19]. As shown in Fig. 2, compound **5** has the 1,3 structure with  $D_{2d}$  symmetry. The dianion is planar, with mean  $\text{C}-\text{O}$  and ring  $\text{C}-\text{C}$  bond lengths of  $1.244$  and  $1.450\ \text{\AA}$ , respectively. These can be compared with the  $\text{C}-\text{O}$  and  $\text{C}-\text{C}$  distances for croconate ion (in diammonium croconate) of  $1.262$  and  $1.457\ \text{\AA}$  [20]. The internal CCC bond angles are all within 1 standard deviation of  $108^\circ$ , the internal angle for a regular pentagon. Thus, the dicyanomethylidene groups do not greatly change the electronic distribution or disturb the  $D_{5h}$  symmetry of the croconate ring.

Dianion **5** can be represented in resonance terms as the hybrid of canonical forms **5a** ↔ **5b** ↔ **5c** (Scheme 1). The bond lengths in Fig. 2 suggest that, consistent with the very high electronegativity of the dicyanomethylidene group, forms such as **5b** and **5c** make a slightly greater contribution than **5a**.

When the dipotassium salt of **5** is treated with strong aqueous acid, the purple color of the solution gradually changes to orange as protonation to the acid form **8** takes place [16]. Brief warming of dipotassium **5** with concentrated HCl produces orange crystals of the free acid **8** (Scheme 1). In water, **8** undergoes immediate ionization to **5**. Compound **8** is perhaps the strongest acid yet known in the oxocarbon or pseudo-oxocarbon series, having an immeasurably large  $\text{p}K_1$  and  $\text{p}K_2$  of  $0.07 \pm 0.02$  [21]. Careful neutralization converts **8** back to **5**, and such neutralization is the best way of making the other alkali metal salts of **5**. Oxidation of **8** with aqueous sodium periodate followed by extractions with ethyl

\*The unusual high-field  $^{13}\text{C}$  chemical shift at  $51.4$  ppm, assigned to the exocyclic olefinic carbon atoms in **5**, can be explained as being due to shielding by the triple bond of the cyano group. Similar resonances are observed for other compounds in this series (**4** and **6**) and for model compounds. The peak assigned to cyano-group carbons at  $119.5$  is a probable multiplet, consistent with structure **5**, which contains two nonequivalent kinds of CN groups.

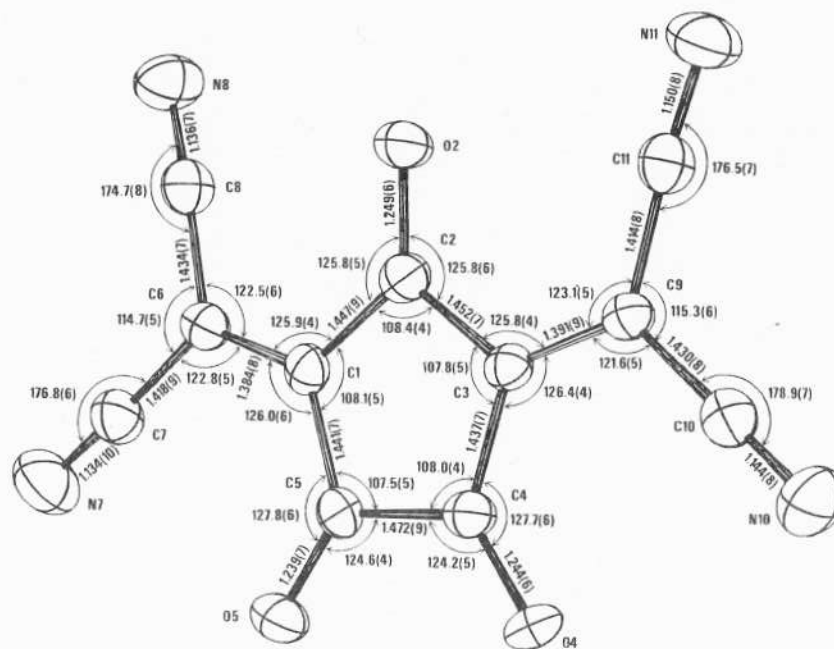


Fig. 2. Bond distances (angstroms) and angles for the dianion of **5**.

acetate gave an orange product ( $\lambda_{\text{max}} 430\text{--}440\ \text{nm}$ ), which may have the unprecedented structure **9** (Scheme 1).

Cyclic voltammetry of the salt of **5** in water revealed an irreversible oxidation potential at  $+0.52\ \text{V}$  versus SCE. (However, a reversible oxidation process for the salt of **5** was observed on a glassy carbon electrode.) The dianion **5** (and its conjugate acid **8**) apparently both undergo two-electron reduction showing two irreversible peak potentials at  $-0.88$  and  $-1.33\ \text{V}$  (Fig. 3). The two-electron reduction probably involves a dicyanomethylidene group and a keto group, e.g.,  $\text{C}=\text{C}(\text{CN})_2 + \text{C}=\text{O} \rightarrow \text{HO}-\text{C}=\text{C}-\text{CH}(\text{CN})_2$ . The redox reaction is pH dependent; the reduction step proceeds faster in alkaline media, as stepwise hydrolysis of **5** takes place via the intermediate dianion **4** to croconate ion (**2**) (see Fig. 4). The oxidation and reduction potentials of **5** are rather similar to those of croconate ion, which shows an oxidation at  $E_1 = +0.59\ \text{V}$  and reduction steps at  $-0.48$  and  $-1.33\ \text{V}$ .

#### B. 2-(DICYANOMETHYLIDENE)CROCONATE SALTS

When esters of croconic acid are allowed to react with malononitrile, only one of the oxygens is replaced by a dicyanomethylidene group. When dimethyl, diethyl, or di-*n*-propyl croconate is warmed with malononitrile in DMF, golden

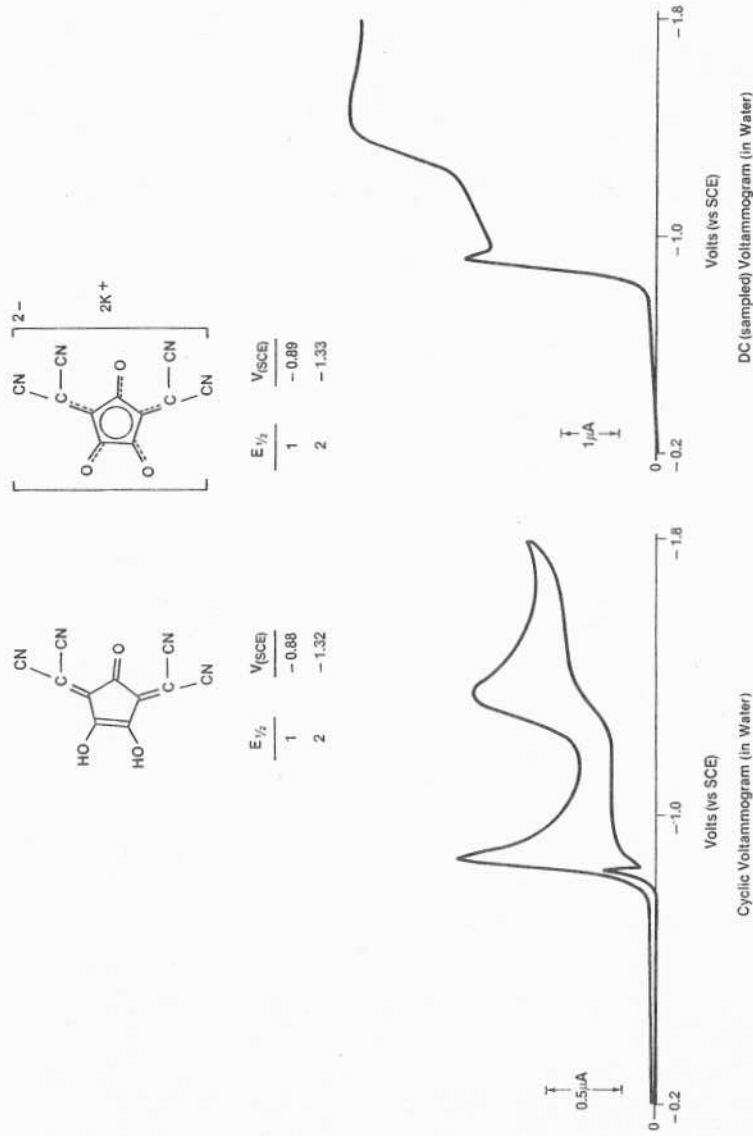


Fig. 3. Cyclic voltammograms of an aqueous solution containing 230 mM of **5** or **8** and 0.1 M NaClO<sub>4</sub> at a dropping mercury electrode. Scan rate 50 mV/sec.

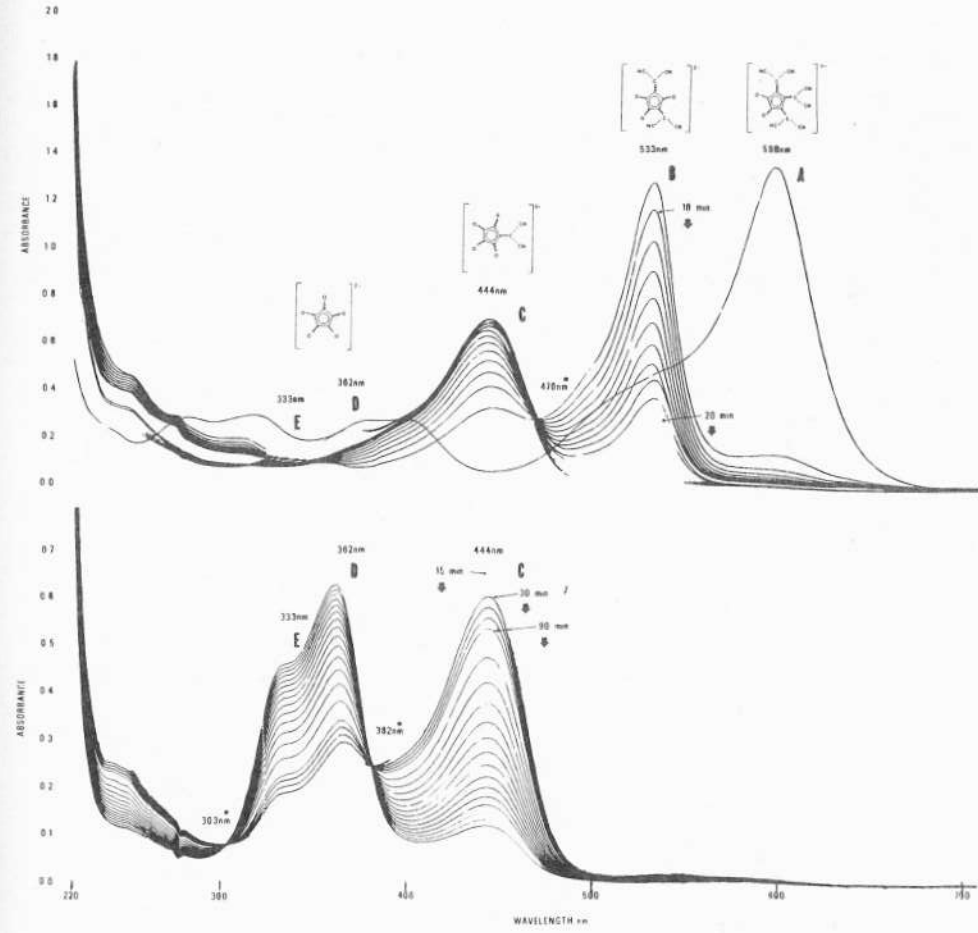
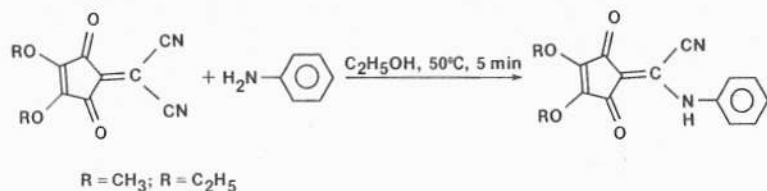


Fig. 4. Spectrophotometric monitoring of the rate of alkaline (pH 13.2) hydrolysis of the bis(tetramethylammonium) salt of **6** (croconate blue). Concentration 22.9 mM; asterisks indicate isosbestic point.

plates of the corresponding 2-(dicyanomethylidene)dialkyl croconates (**10**) are produced. The <sup>13</sup>C-NMR spectra of these compounds are consistent with the symmetric *D*<sub>2d</sub> structures shown in Scheme 1. These compounds are efficient electron acceptors, forming deeply colored charge-transfer complexes with polycyclic aromatic hydrocarbons such as pyrene, benzo[*a*]pyrene, or anthracene.

The crystal structure of the red 1 : 1 complex (pyrene-**10**, R = C<sub>2</sub>H<sub>5</sub>) has been determined [22]; a novelty of the structure is that its crystal unit cell contains two

pyrene molecules differing in symmetry. However, with tetrathiafulvalene as the donor, 2-(dicyanomethylidene)alkyl croconates (**10**, R = CH<sub>3</sub>, C<sub>2</sub>H<sub>5</sub>, *n*-C<sub>3</sub>H<sub>7</sub>, *i*-C<sub>3</sub>H<sub>7</sub>) form charge-transfer salts that are semiconductors [11] (see Section III). Chemically, 2-(dicyanomethylidene) alkyl croconates react readily with aniline in warm alcohol to give deep red dyes with structures similar to that described for the product of reaction of 2-(dicyanomethylidene)-1,3-indanedione with aniline [23].



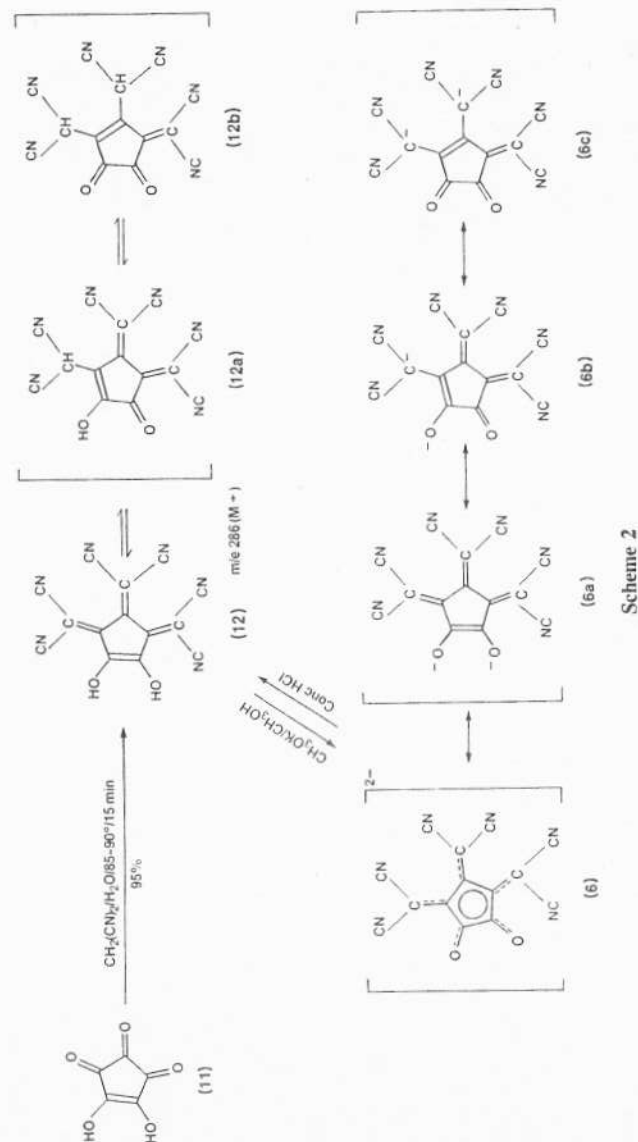
When the esters (**10**) are carefully hydrolyzed with potassium methoxide in methanol, the dipotassium salt of **4** can be isolated. Recrystallization from water yields cherry red crystals of the dihydrate. The infrared spectrum of **4** is similar to that of **5**, which suggests that **4** may also be represented as the hybrid of resonance structures resembling those for **5** (Scheme 1). Anion **4** gives intensely red-violet solutions in water, with  $\lambda_{\max}$  533 ( $\epsilon = 70,000$ ). When the dipotassium salt is warmed with HCl, it forms orange crystals of the conjugate acid (**10**, R = H).

### C. 1,2,3-TRIS(DICYANOMETHYLIDENE)CROCONATE SALTS: CROCONIC ACID BLUE

In Sections II, A and B we have seen that croconate anions and esters give quite different products upon reaction with malononitrile. Yet another result is observed when croconic acid (**11**) (Scheme 2) is treated with malononitrile. In this case *three adjacent* carbonyl groups are replaced to give the new oxocyanocarbon acid **12** [1,2,3-tris(dicyanomethylidene)-4-cyclopentene-4,5-diol] [17]. Shining purple plates of **12** crystallize from solution when croconic acid is simply warmed briefly with malononitrile in aqueous solution at 85°–90°C. The product, obtained in over 90% yield, is intensely blue in water ( $\lambda$  600 nm;  $\epsilon = 55,000$ ), and we have termed it croconic acid blue. However, **12** is very strongly solvatochromic, giving red solutions with  $\lambda$  475–480 nm in anhydrous acetone or alcohol. As expected, **12** is a strong oxocarbon acid; its  $pK_2$  value is  $\sim 1$ , placing it intermediate in acid strength between **8** and croconic acid [21].

The infrared spectrum (KBr) of **12** shows strong bands at 1755, 1700(sh), 1650, 1590, and 1520 cm<sup>-1</sup>. The band at 1755 cm<sup>-1</sup> suggests that tautomers with C—H structure (**12a** or **12b**) may be present in the solid.

As shown in Scheme 2, neutralization of **12** with potassium methoxide in





methanol gives the dipotassium salt of **6**, croconate blue [17]. The salt is obtained as shining blue-green crystals of the trihydrate upon recrystallization from water. Dianion **6** has its principal absorptions in water at 599 ( $\epsilon = 54,600$ ) and 538 nm [ $\epsilon = 32,000(\text{sh})$ ]. The 1,2,3 structure is confirmed by the  $^{13}\text{C}$ -NMR spectrum, which shows resonances at  $\delta = 178.0$  ppm assigned to  $\text{C}=\text{O}$ , 147.3 and 139.1 ppm [ $\text{C}=\text{C}(\text{CN})_2$ ], 120.2, 118.7, and 118.6 ppm (CN), and 53.1 ppm [ $\text{C}=\text{C}(\text{CN})_2$ ]. The three CN peaks are expected for structure **6**, which has three intrinsically different cyano groups. Additional fine structure may also be present in this cluster, possibly reflecting different conformations in solution. The single peak at 53.1 probably results from accidental overlap of resonances for the two kinds of  $\text{C}=\text{C}(\text{CN})_2$  groups.

The properties of **6** resemble generally those of **4** and **5**, suggesting that the croconate blue anion also has a bond-delocalized structure. The probable contributors to the resonance hybrid structure for **6** are shown as **6a** ↔ **6b** ↔ **6c** in Scheme 2. However a stereomodel of **6** indicates that, in order to relieve steric crowding, a staggered conformation of the dicyanomethylidene groups is required. The twist angle for the central dicyanomethylidene group sufficient to relieve steric strain is estimated to be about  $30^\circ$  [17]. The  $^{13}\text{C}$ -NMR spectrum for the central  $\text{C}\equiv\text{N}$  groups may show evidence for this lowered symmetry.

The acid **12** in water at room temperature (sensitive to UV irradiation) hydrolyzes slowly (95% in 85 days) to yield the more thermodynamically stable croconic acid violet **8** [ $\lambda_{\text{max}}(\text{H}_2\text{O})$  534 nm]. In warm ( $95^\circ\text{C}$ ) 10 *M* hydrochloric acid, the acid **12** hydrolyzes completely in a few minutes to **8**. However, excessive heating of **12** in water causes apparent polymerization to give as product deep green, lustrous plates.

Sever crowding and lowered symmetry in **6** compared to **5** may be responsible for the fact that **6** is more easily reduced than **5**. Cyclic voltammetry of **6** revealed the first reduction wave at  $-0.69$  V versus SCE (Fig. 5) compared with  $-0.88$  V for **5**.\* Crowding in **6** is probably also associated with its relative instability in aqueous alkaline media. At pH 13.2 the 2-dicyanomethylidene group is split from **6** within 2–3 sec, giving the croconate violet anion **5** (Fig. 4). This rapid change is followed by much slower, stepwise hydrolysis of the remaining 1,3-bis(dicyanomethylidene) groups to give, first, the orange dianion **4** (band at 444 nm, a change from B to C in 4 hr, Fig. 4) and then, as the final product, yellow croconate dianion **2** [bands at 362 and 333(sh) nm, a change from C to D in 40 hr]. The decomposition of **6** and formation of new products are indicated by three isosbestic points, at 303 ( $\epsilon = 3800$ ), 382 ( $\epsilon = 11,400$ ), and 470 nm ( $\epsilon = 13,000$ ). Note the large bathochromic shift in the visible spectrum of the dianion **2** (363 → 600 nm) due to consecutive addition of the dicyanomethylidene chromophores.

\*Further electrochemical study of both **5** and **6**, including isolation and identification of their redox products, is in progress.

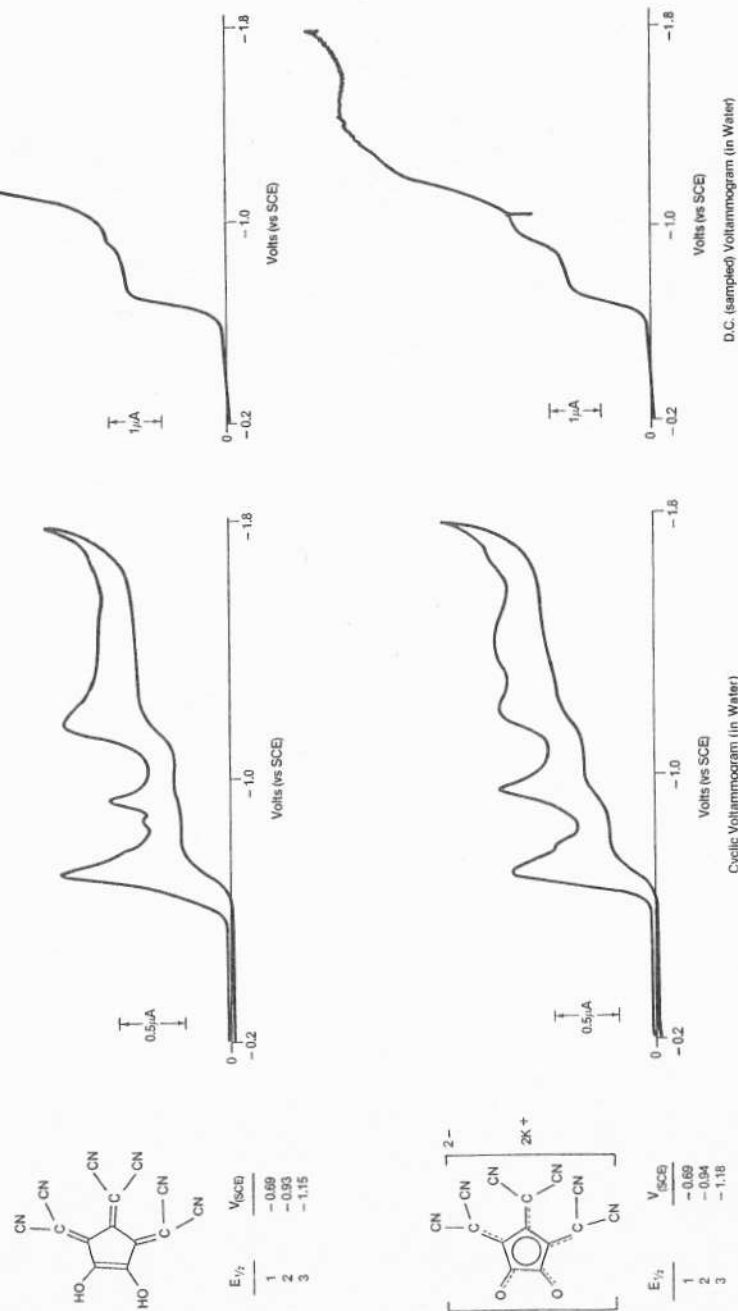
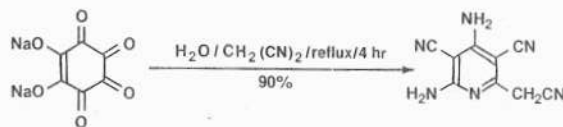


Fig. 5. Cyclic voltammograms of an aqueous solution containing 240 mM of **12** or **6** and 0.1 *M*  $\text{NaClO}_4$  at a dropping mercury electrode. Scan rate 50 mV/sec.

The kinetics of alkaline hydrolysis of the bis(tetramethylammonium) salt of **6** are first order, with an apparent rate-constant of  $K_b = 0.0136 \text{ min}^{-1}$  from B to C (Fig. 4); the rate was 10 times slower going from C to D (e.g.,  $K_c = 0.00135 \text{ min}^{-1}$ ).

#### D. ATTEMPTED CONDENSATION OF SIX-CARBON OXOCARBONS WITH MALONONITRILE

Unlike the reaction of croconic acid or its salts with malononitrile to give crystalline products (Sections IIA, B, and C), treatment of six-carbon oxocarbons, e.g., tetrahydroxy-*p*-benzoquinone (THQ), rhodizonic acid (1,2-dihydroxy-1-cyclohexene-3,4,5,6-tetrone) or their alkali salts with malononitrile in aqueous media produces colored products, the structures of which are under study [24]. For example, THQ [25] and malononitrile in *N,N*-dimethylformamide (DMF) (or water) at 80° yielded a benzodifuran derivative ( $\lambda_{\text{max}}^{\text{DMF}}$  626–642 nm) [25a]. However, a gentle treatment [24] (50° for 10–15 min) of 1 mole of the disodium salt of THQ with 2 moles of malononitrile gave a somewhat differently colored product, with  $\lambda_{\text{max}}^{\text{DMF}}$  562–565 nm. Prolonged treatment of the same salt with an excess of the reagent under reflux yielded a colorless trimer of malononitrile (2-cyanomethyl-4,6-diamino-3,5-dicyanopyridine) in high yield. Similar treatment of disodium rhodizonate or disodium squarate with an excess of malononitrile also gave a trimer of malononitrile, but formation of colored products was again observed under milder reaction temperature. The mechanism of the trimerization reaction can be explained as being due first to the hydrolysis of the salt, followed by a base-catalyzed aldol reaction of malononitrile [11].



Also: Na-THQ  
Na-squarate

A dark green compound is also formed on treatment of benzenehexol with malononitrile, presumed to be a benzodifuran derivative. Controlled reaction of triquinoyl (cyclohexanone octahydrate) or leuconic acid (cyclopentanepentone pentahydrate) [18] with the reagent gave lustrous black microcrystalline products that showed identical infrared spectra different from that of the product from benzenehexol [24].

For the monomeric series of the six-carbon oxocarbons, a direct route for the preparation of the malononitrile adducts should be avoided, unless the reaction is

thoroughly controlled. Instead, an indirect method similar to that described for the synthesis of the 1,2,3-tris(dicyanomethylidene)deltate salt [15] (Fig. 1) should be explored. The synthesis of novel, six-carbon pseudo-oxocarbons wherein the original carbonyl oxygen atoms are either partially or completely substituted with nitrogen, sulfur, selenium, phosphorus, etc., offers an attractive area of study.

### III. Electrical Conductivity of Some Bond-Delocalized Salts

The charge-transfer salts of the  $\pi$  donor tetrathiafulvalene (TTF) [26] or its analog tetraselenafulvalene [27] with tetracyanoquinodimethane (TCNQ) as the acceptor are the best known examples of a new class of organic solids having high electrical conductivity (the quasi-one-dimensional "organic metals") [28]. The search for more effective organic metals has led to the production of a vast number of TTF-TCNQ derivatives that differ primarily in the nature of substituents on either the donor (TTF) or the acceptor (TCNQ) unit. However, only a limited number of such charge-transfer salts show high conductivity. Despite extensive recent work, it is still difficult to specify detailed molecular requirements that would give rise to, and increase conductivity in, organic metals [27–29]. High symmetry, high polarizability, small molecular size, and molecular planarity [26,29] are among the factors that are generally considered to favor high conductivity. However, equally important factors for such conducting salts appear to be (a) an alternating, donor-acceptor stacking arrangement [26], (b) crystal packing [30], and (c) molecular volume [30,31].

Using TTF as a model symmetric  $\pi$  donor in reactions with unsymmetric acceptors (e.g., croconic acid and its esters) in acetonitrile (or methanol-acetonitrile), we have prepared a series of new TTF salts that show all of the properties of semiconductors, having a conductivity of  $2.5 \times 10^{-3}$  to  $10^{-4} \Omega^{-1} \text{ cm}^{-1}$  (pellet, 300 K) [11].

Dipotassium tetrathiosquarate [6] (Fig. 1) has been reported [32] to react with 1,2-dithiolonium salts to give shining black 2 : 1 complexes; these have, however, been found to be insulators, with a room-temperature compaction conductivity of  $10^{-10} \Omega^{-1} \text{ cm}^{-1}$ . The metathesis between donor and acceptor salts probably involves almost complete electron transfer, leading to considerable electrostatic repulsion in the solid state, which may partially explain the low conductivity of these salts [32]. Indeed, the most recent report [33] described the preparation of the squaric acid complex bis(squarato)platinum(II) salt, a new example of a one-dimensional electrical conductor. We have found that the 1 : 1 adduct between dimethyl sulfoxide and tetrahydroxyquinone (which is a proton-transfer complex) is also a poor conductor with a conductivity of  $10^{-9} \Omega^{-1} \text{ cm}^{-1}$  (pellet, room temperature) [24].

However, croconate violet, the dipotassium salt of **5** (Table I, entry 2) has a room temperature single-crystal conductivity of  $2 \times 10^{-6} \Omega^{-1} \text{cm}^{-1}$ , comparable to that of the potassium salt of the TCNQ anion-radical (Table I, entry 1). Measurements of magnetic susceptibility indicate that the salt of **5** is diamagnetic, and the salt exhibits no ESR spectrum. An unusually large increase in the

**Table I.** Electrical Conductivities of Some Oxocarbons and Pseudo-Oxocarbons

Entry	Salt	Conductivity ( $\Omega^{-1} \text{cm}^{-1}$ )	Entry	Salt	Conductivity ( $\Omega^{-1} \text{cm}^{-1}$ )
1		$2 \times 10^{-4}{}^a$	5		$8 \times 10^{-8}{}^a$
2		$2 \times 10^{-6}{}^b$	6		$5 \times 10^{-9}{}^a$
3		$1.5 \times 10^{-7}{}^a$	7		$4 \times 10^{-9}{}^a$
4		$1 \times 10^{-7}{}^a$	8		$6 \times 10^{-10}{}^a$ (Rhodizone)
			9		$2 \times 10^{-10}{}^a$ (THQ)

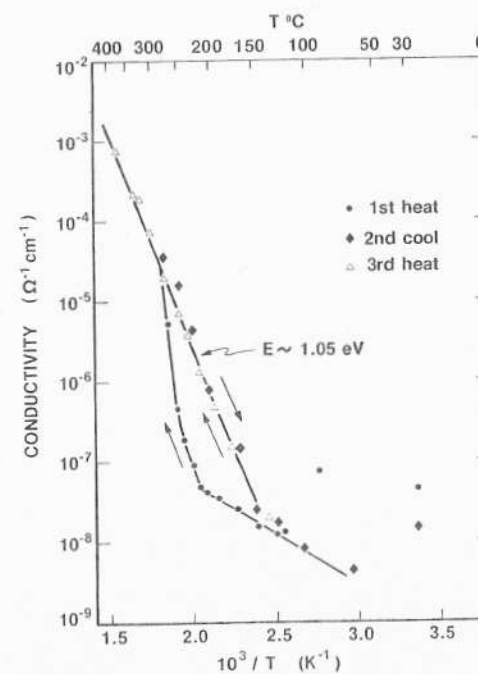
<sup>a</sup> Compressed pellet, 300 K.

<sup>b</sup> Single crystal, 300 K.

electrical conductivity, by a factor of  $10^4$ – $10^5$ , was observed on heating the dipotassium salt of **5** from 25° to 400°, and this is typical behavior of a semiconductor. The dipotassium salt of **5** showed a remarkable thermal stability since the conductivity was not altered appreciably on repeating the heating-cooling cycle (25°–400°) (Fig. 6) [22].

The intrinsic conductivity of the dipotassium salts of **4**, **5**, and **6** (Table I, entries 2–4) is partially due to the electronic conductivity that is associated with polarizability (via the strongly electronegative dicyanomethylene groups), structural symmetry, extensive electronic delocalization, and appreciable aromatic character of the dianion. However, in the case of the dipotassium salt of **5**, the ionic contribution to the conductivity may be due to the unique crystal structure and crystal packing. Structurally there are columns of the cyclopentane ring anions parallel to the cation columns, with only 3.32 Å separation between adjacent molecular sites [19] (as compared to 3.30 Å found for the interplanar spacing for TTF-TCNQ). Hence, the (potassium) cation, by virtue of partial occupancy of sites in a channel, is capable of relatively high ionic conductivity.

Much lower conductivities are found for oxocarbons containing no di-



**Fig. 6.** Rise in the electrical conductivity on heating of the dipotassium salt **5** (croconate violet) from 25° to 400°.

cyanomethylene group. The diamagnetic dipotassium salts of croconic, squaric, and rhodizonic acids and of tetrahydroxyquinone (Table I, entries 6–9) are all poor conductors, and the single-crystal (four-probe), room-temperature ionic conductivity of dilithium croconate trihydrate [18] was found to be  $1 \times 10^{-8} \Omega^{-1} \text{ cm}^{-1}$ , a value within the semiconductor range [24]. However, metal complexes of oxocarbons may be much better conductors. A recent report [33] described the preparation of the bis(squarato)platinum(II) salt  $\text{K}_2[\text{Pt}(\text{C}_4\text{O}_4)_2] \cdot 2\text{H}_2\text{O}$ , a new example of a one-dimensional electrical conductor. The observed conductivity of the salt at  $25^\circ\text{C}$  was  $5 \times 10^{-3} \Omega^{-1} \text{ cm}^{-1}$ , suggesting a metallic state. Metal complexes of **4**, **5**, and **6**, when they are prepared, may also show higher conductivity.

#### IV. Summary

Either partial or complete replacement of the original carbonyl oxygen atoms in three-, four-, five-, or six-membered oxocarbon anions  $\text{C}_n\text{O}_n^{m-}$  with the  $\text{C}=\text{O}$  equivalent,  $\pi$ -isoelectronic groups  $\text{C}=\text{C}$ ,  $\text{C}=\text{N}$ ,  $\text{C}=\text{P}$ ,  $\text{C}=\text{S}$ ,  $\text{C}=\text{Se}$ , etc., yields a series of unusual oxocarbon analogs, the pseudo-oxocarbons. Many of these new oxocarbons may be of considerable interest to the theoretical chemist with regard to their molecular symmetry, the planarity of their anions, and their novel, nonbenzenoid aromaticity. Studies of their chemistry (e.g., esters, amides, and salts), their physical properties (e.g. electronic, vibrational, and NMR spectroscopic, dipole moment, force constant, X-ray crystal structure, and coordinate analysis, and MO + LCAO + MO calculations), their analytical applications (e.g., electrochemistry, photolysis, and solution chemistry), and their biomedical applications offer new directions in the chemistry of oxocarbons. In their 1969 review on oxocarbons, West and Niu [3] stated that the chemistry of the more complex oxocarbons was only beginning and that hundreds of possible stable structures awaited synthesis by the organic chemists of tomorrow. This prediction seems valid today.

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