

# Oxocarbons and Pseudooxocarbons

Gunther Seitz\* and Peter Imming

Department of Pharmaceutical Chemistry, University of Marburg, Marbacher Weg 6, D-3550 Marburg/Lahn, Germany

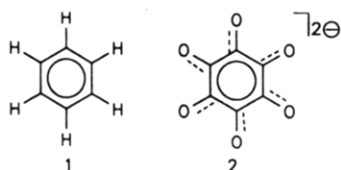
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## I. Introduction

Times are changing and so do space and taste. A creative science like organic chemistry especially suffers and profits from our changing outlook and interests. Aromaticity—electronic interactions *within* a molecule—and the beauty of two-dimensional symmetry seem to have been replaced in the minds of many organic chemists by electronic interactions *between* molecules and the usefulness of three-dimensional complicatedness. But as mathematicians cannot dispose of Euclidean geometry, we cannot do without molecules like benzene **1** or rhodizonate **2**. But we also must not forget



Gunther Seitz was born in Hamburg, Germany, on March 8, 1936. Having studied pharmacy and chemistry he received his Dr.rer.nat. degree with H. Böhme in 1965 in pharmaceutical chemistry at the University of Marburg, Germany. In 1972 he took a Chair of Chemistry of the veterinary High School of Hannover, where he became full professor before he returned to the University of Marburg in 1978, where he is currently the head of the Institute of Pharmaceutical Chemistry. His research interests include non-benzenoid aromatic compounds such as heterosquifulvalenes and pseudoazulenes, oxo- and pseudooxocarbons and inter- and intramolecular [4 + 2]-cycloadditions with inverse electron demand.

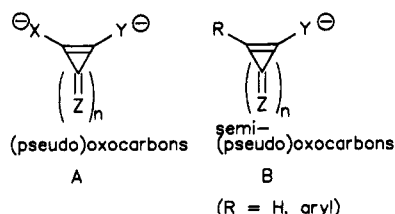


Peter Imming was born in 1958. He studied pharmacy and chemistry in Marburg, Germany, where he also got his Dr.rer.nat. degree with Prof. Seitz in 1987. He then spent a year in Oxford, U.K., with J. E. Baldwin, investigating penicillin biosynthesis. Currently, he is a junior lecturer in the Pharmaceutical Chemistry department, working on the preparation of  $\beta$ -lactam analogues.

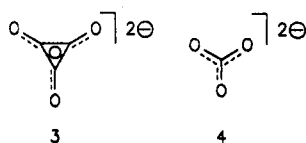
what we know about their properties and reactions and also that there is still a great number of hidden beauties waiting for synthesis. Even in applied chemistry, two-dimensional molecules are often irreplaceable. So this review tries to sum up the knowledge that was acquired about oxocarbons and pseudooxocarbons between 1979 and 1991. They are perhaps the best example of a class of molecules having symmetric  $\pi$ -systems with heteroatoms being responsible for delocalization—just as benzenoid systems are the standard example of delo-

## Scheme 1

Anions:



calized carbon perimeters. Oxocarbons (e.g. deltate 3) may also be regarded as constituting a link between delocalized inorganic molecules such as, for example, carbonate 4 with cross conjugation (this was conceptualized under the term of "Y aromaticity"<sup>1</sup>) and the aforementioned "pure carbon" perimeters that prefer cyclic conjugation.



This review will be concerned with chemical methodology in the field of oxocarbons and will provide an overview both of substances synthesized during the past years and of the emerging field of applications of oxocarbon derivatives. The following classes of compounds will be considered (Scheme 1): (pseudo)-oxocarbons, represented by general formula A, with X, Y, and Z designating chalcogen-, nitrogen-, or carbon-bonded electron acceptors; semi-(pseudo)oxocarbons B; zwitterions C and D; radicalenes E (not including carbon-bonded substituents); cations F-H (hetero-substituents only). Also included are a few vinylogous analogues of the Scheme 1 formulae.

Not included are benzo derivatives, alkyl-substituted cyclo-alkenediones, alkyne 1,2-diethers, and simple functional derivatives of the oxocarbon acids.

Previous reviews of this topic have appeared. Above all, the substantial monograph edited by West<sup>2</sup> has to be mentioned; the present review will not cover material included in that book. Also there have been a few treatments on part of the material: on the chemistry of oxocarbons;<sup>3</sup> on pseudooxocarbons;<sup>4</sup> on acetylene

diethers<sup>5</sup> (that may be regarded as esters of a first member of the oxocarbon family,  $C_2O_2^{2-}$ ); on cyclopropenyl cations, cyclopropenyl radicals and anions, and cross conjugated derivatives of cyclopropene;<sup>6</sup> on highlights of oxocarbon chemistry;<sup>7</sup> on sulfur-containing derivatives of deltate and squaric acid.<sup>8</sup>

In the organization of this review, the main headings will be according to ring size, derivatives of deltate acid ( $C_3$ ) coming first. Within the headings, syntheses will be discussed first, followed by reactions of the respective compounds. Physicochemical properties, theoretical studies, and applications and uses of all oxocarbon derivatives are presented in three final chapters.

We hope that readers will enjoy the symmetry of the oxocarbons and discover the many aspects of comparison they provide—both synthetically and theoretically. Also there remains the challenge to prepare the many "missing pearls" of this chain of symmetrical beauties—a challenge that in the authors' opinion would have to involve the development of new methodology or the invention of new synthetic schemes, just as the preparation of each of the oxocarbon acids themselves (deltate, squaric, croconic, rhodizonic acid) has its own characteristic.

## II. $C_3$ Derivatives of Deltate Acid

### A. Syntheses

#### 1. Deltate Acid

Deltate acid 3a (2,3-dihydroxycycloprop-2-ene-1-one) and its dianion, deltate 3b, were synthesized in 1975 for the first time.<sup>9a,b</sup> The next higher homologue, squaric acid, was the starting point of this synthesis, whereas another preparation<sup>9c</sup> started from an alkyne 1,2-diether (Scheme 2).

Recently a preparation of 3 in low yield was published,<sup>10</sup> mimicking the last-century syntheses<sup>11</sup> of croconic and rhodizonic acids by reduction of carbon monoxide with alkali metals. Deltate 3 was formed when carbon monoxide was led through a solution of the crown ether complexes of alkali metal anions in tetrahydrofuran (Scheme 2).

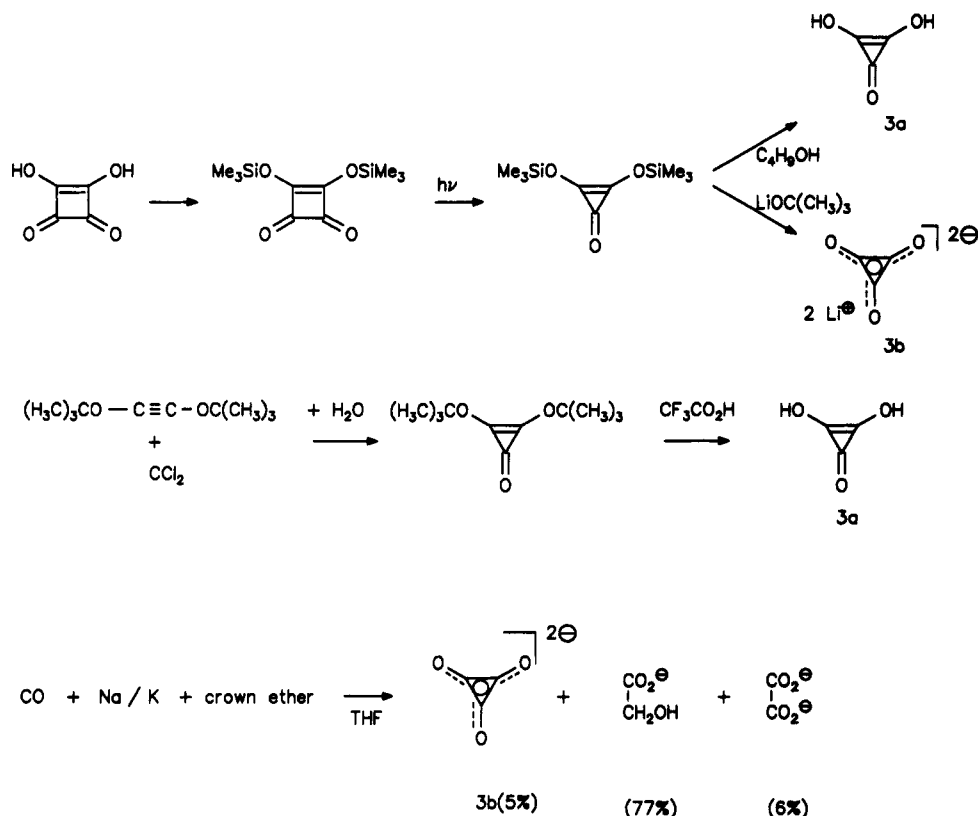
#### 2. $C_3$ Pseudooxocarbons

The complete or partial replacement of oxygen in the deltate dianion 3 by analogous<sup>12</sup> substituents, viz., sulfur, cyanamide, dicyanomethylene, and related ones, leads to a series of compounds with delocalized  $\pi$ -systems that are called "pseudooxocarbons",<sup>13</sup> according to a proposal by Fatiadi.<sup>13</sup> The main achievement in this field was the completion of the series of trisubstituted (pseudo)oxocarbons. They are shown in Scheme 3. The trithiodeltate 6 escaped synthetic efforts for an especially long time.<sup>2,8</sup>

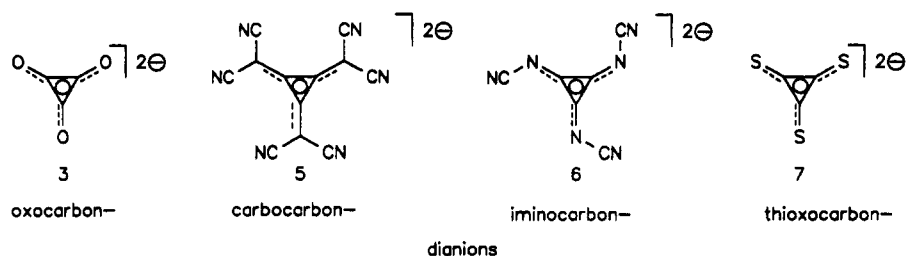
Fukunaga<sup>14</sup> published the synthesis of the symmetrically substituted carbocarbon dianion 5 in 1976 (Scheme 4). Tris(cyanoimino)deltate (6), the first nitrogen-substituted analogue of deltate 3, was obtained<sup>15</sup> from tetrachlorocyclopropene (8) through the mesoionic deltaine 9 as depicted in Scheme 4.

This scheme exemplifies a general method of approach to acceptor-donor- or mixed-substituted cyclopropenes, viz. cations, anions, or mesoionic compounds. The preparation starts from the uncharged,

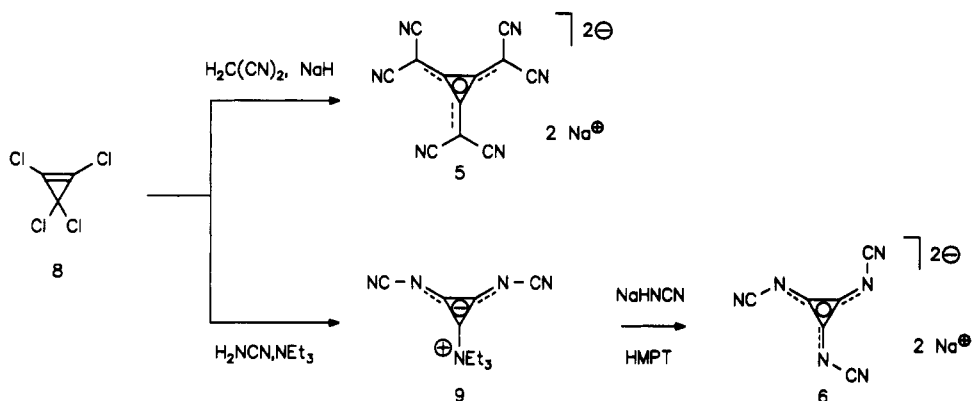
Scheme 2



Scheme 3



Scheme 4

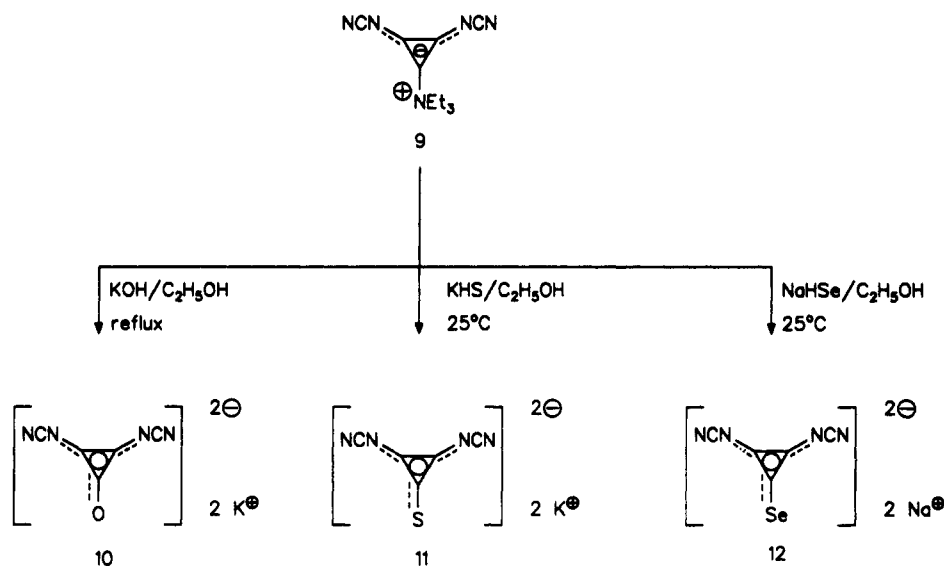


readily accessible<sup>16</sup> tetrachlorocyclopropene (**8**) which is reacted with carbon, nitrogen, or sulfur nucleophiles under basic or (Lewis) acidic conditions, leading to zwitterions or cations, respectively. In a second step, the cationic substituent(s) may be replaced by (usually) an anionic nucleophile. It has proved to be good strategy to prepare symmetrical anions of this class via non-symmetrical, electrically neutral intermediates, as can also be seen in the syntheses of deltate (see section II.A.1) and trithiodeltate (see below).

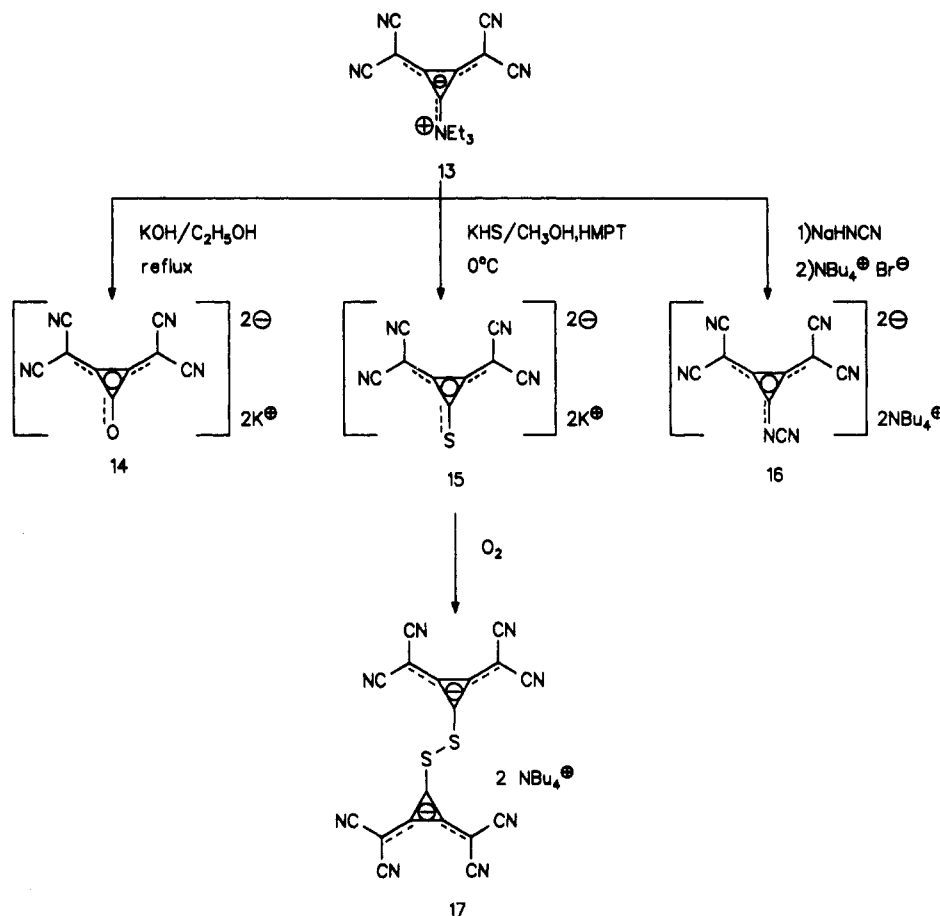
The symmetric iminocarbon dianion **6** was isolated as its sodium salt, an other-colored powder that is stable to air and may be purified by filtration through silica gel with a mixture of methanol and dichloromethane. Some of its spectroscopic features will be discussed together with those of the other  $\text{C}_3$  (pseudo)oxocarbons of Scheme 3 at the end of this chapter.

The zwitterionic intermediate **9** from Scheme 4 was also reacted<sup>17</sup> with nucleophiles other than sodium cyanamide, thus illustrating the versatility of the

## Scheme 5



## Scheme 6



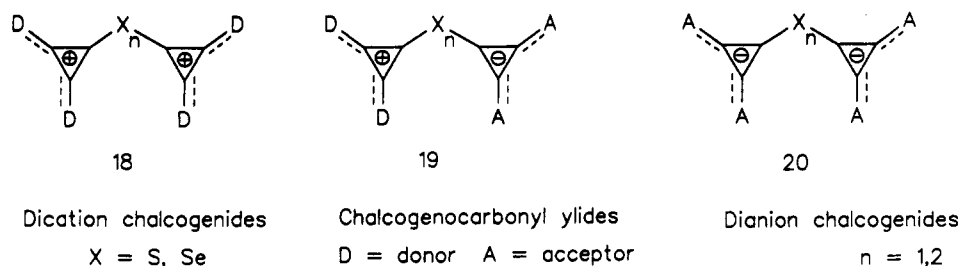
aforementioned synthetic strategy (Scheme 5). Scheme 6 shows a related set of transformations of the dicyanomethylene-substituted zwitterion **13**.<sup>18</sup>

Again, a mesoionic intermediate (**13**)<sup>14</sup> opened up access to several dianions.

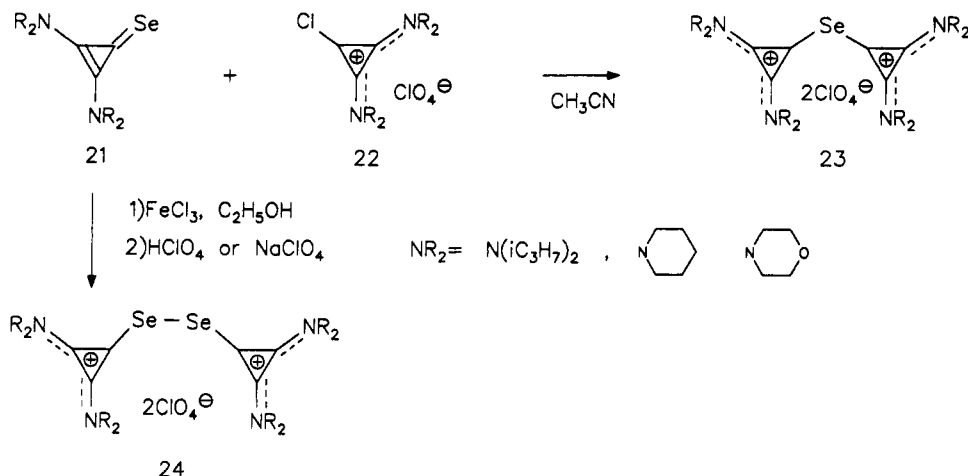
These reactions have to be run between 0 and  $100^\circ\text{C}$  in a solvent having about the polarity of ethanol. Purification is done simply by washing with ethanol and less polar solvents, by recrystallization from an alcohol or an aqueous mixture, or by filtration through silica gel with a methanolic eluent. Yields are generally

good or very good. The size of the counterion is critical: if it is too small, isolation and purification may become impossible. In such a case, tetraalkylammonium, -phosphonium, or even -arsonium salts have to be added so as to precipitate the product (e.g., **16** in Scheme 6; other examples to follow). The presence of the cyclopropene ring system betrays itself by a strong vibrational absorption between  $1820$  and  $1900\text{ cm}^{-1}$  (important because nucleophiles sometimes open the ring). Thio- and especially selenocarbons are, of course, sensitive to light and oxygen. The selenocarbon **12**, for example,

Scheme 7



Scheme 8



has to be prepared under an argon atmosphere and is stable for only a few days. If, on the other hand, the reaction of the thioxocarbon 15 with potassium hydrogen sulfide is run without exclusion of air, a well-characterized product, the disulfide 17, is isolated<sup>18</sup> (Scheme 6). This interesting finding initiated the investigation of sulfur- and selenium-bridged  $\text{C}_3$  pseudooxocarbons, viz., dication (di)chalcogenides 18, ylides 19, and dianions 20 (Scheme 7). In terms of Scheme I (see Introduction), these classes of pseudooxocarbons should be regarded as bridged derivatives of the anions A, of the cations F, or of both. Dication sulfides (18,  $\text{X} = \text{S}$ ,  $n = 1$ ) are well-known stable substances.<sup>19</sup>

Dication selenides (18,  $\text{X} = \text{Se}$ ,  $n = 1$ ) were prepared<sup>20,21</sup> from diaminocyclopropeneselones (21) by a nucleophilic displacement reaction. Selones 21 were also oxidized to dication diselenides 24<sup>21</sup> (Scheme 8), which are examples of the general formula 18 in Scheme 7 ( $\text{X} = \text{Se}$ ,  $n = 2$ ).

The perchlorate salts of the dications 23 and 24 are stable against light and air. Similarly substituted derivatives of 23 and 24 gave rise to very similar spectra. The carbon atoms  $\alpha$  to nitrogen appear at different ppm values, indicating hindered rotation due to a bond order higher than one of the semicyclic carbon–nitrogen bonds.

It was also possible to obtain thiocarbonyl ylides<sup>22</sup> and—to our surprise—even selenocarbonyl ylides,<sup>20</sup> both corresponding to the general formula 19 in Scheme 7. These were the first selenocarbonyl ylides to be isolated at all. Scheme 9 depicts the synthetic pathways.

Both thio- and selenocarbonyl ylides are conveniently prepared, first, by the reaction of acceptor-substituted deltains 26 with thiones or selones 25 or second, by the reaction of thio- or selenodeltates 27 with donor-substituted chlorocyclopropenium perchlorates 22. The

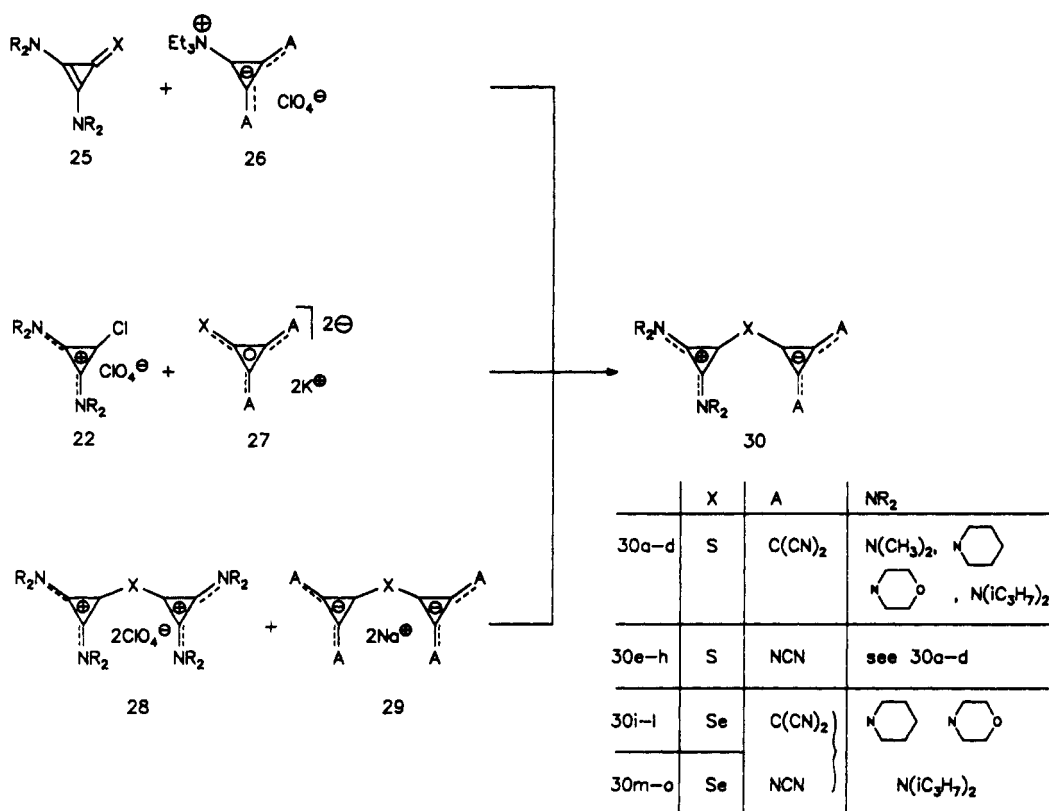
third approach to the stable crystalline ylides is somewhat unusual. It consists of a randomization reaction that rearranges one molecule each of the dication 28 and the dianion 29 to two molecules of the ylide 30 which is formed due to its low solubility and precipitates in boiling acetonitrile. A comparison of the spectroscopic properties of the colorless crystalline selenocarbonyl ylides 30i–o ( $\text{X} = \text{Se}$ ) with dication selenides 23 and the dianion selenide 31d (see below) revealed that the cyclopropene termini seem to be completely isolated from each other electronically, retaining the features of the cationic and anionic termini in compounds 23 and 31d. The two three-membered rings in the ylide 30i ( $\text{X} = \text{Se}$ ,  $\text{NR}_2 = \text{N}(\text{iC}_3\text{H}_7)_2$ ,  $\text{A} = \text{C}(\text{CN})_2$ ) are almost perpendicular to each other, as was shown by X-ray crystallographic analysis.<sup>20</sup> The C–Se–C bond angle is  $92.8^\circ$ , the C–Se bond lengths amount to 188 and 190 pm, corresponding to a bond order of  $n = 1.0$ .

The synthesis of the dianion dichalcogenides 20 of Scheme 7 remains to be discussed. They were also prepared in our group for the first time, as summarized in Scheme 10.<sup>22</sup>

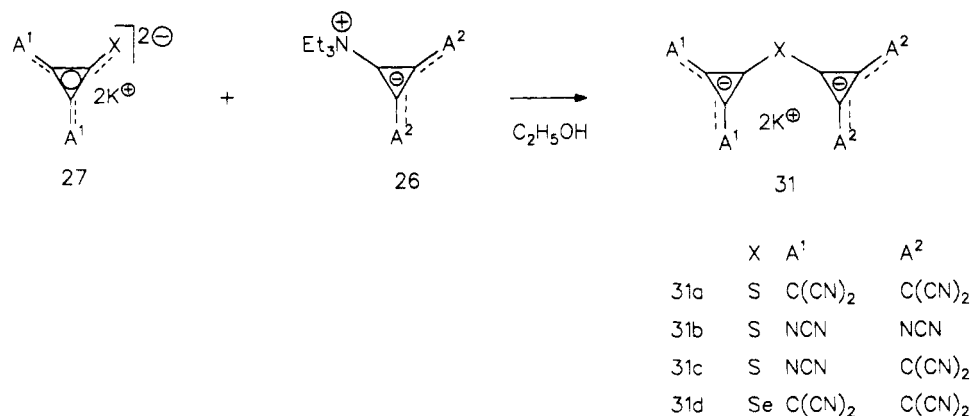
In the synthesis of trithiodeltate (7), the usual approaches failed (nucleophilic displacement of substituents in suitably activated deltic acid derivatives).

Finally, a pathway (Scheme 11) was elaborated<sup>23</sup> that involved the preparation of a symmetrically thioalkyl-substituted cyclopropenylium salt (32) which contains alkyl functions capable of undergoing elimination reactions, leaving the sulfur atoms attached to the three-membered ring. Direct fluoride-promoted conversion of 32 into trithiodeltate (7) failed. But after reductive removal of one of the alkylsilyl groups, the intermediate thione 33, on treatment with tetrabutylammonium fluoride, fragmented to give the desired pseudooxo-

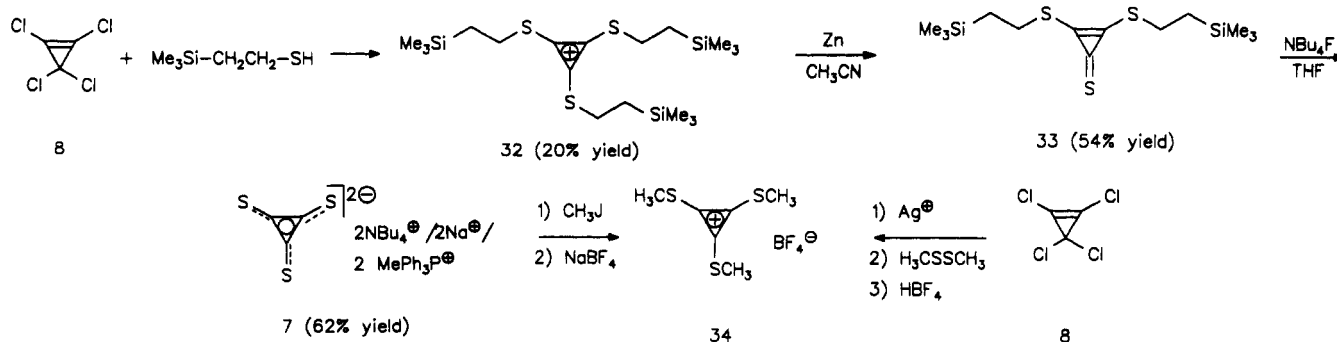
Scheme 9



Scheme 10



Scheme 11

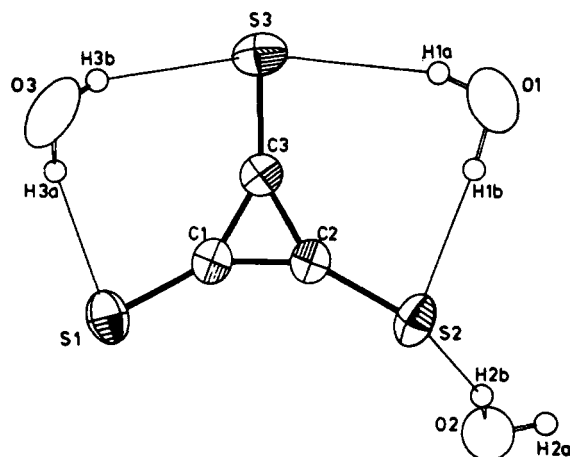


carbon dianion **7** that was characterized as its sodium and methyltriphenylphosphonium salt.<sup>23</sup>

Chemical proof of the structure was easily accomplished by treating the sodium salt of **7** with methyl iodide, followed by sodium tetrafluoroborate (Scheme 11). This gave the known tris(methylthio)cyclopro-

penium salt (**34**), identical with a sample prepared from tetrachlorocyclopropene **8** by the method of Weiss.<sup>24</sup>

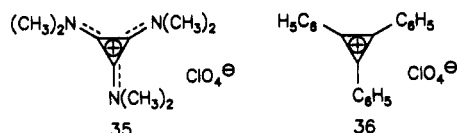
The spectroscopic data of **7** are in agreement with a planar symmetrical structure. The <sup>13</sup>C NMR spectrum consists of a single signal at  $\delta = 176.5$  ppm. The Raman and IR spectra show that the dianion has the



**Figure 1.** ORTEP plot of the dianion of 7 [(MePh<sub>3</sub>P)<sub>2</sub>C<sub>3</sub>-S<sub>3</sub>·3H<sub>2</sub>O].

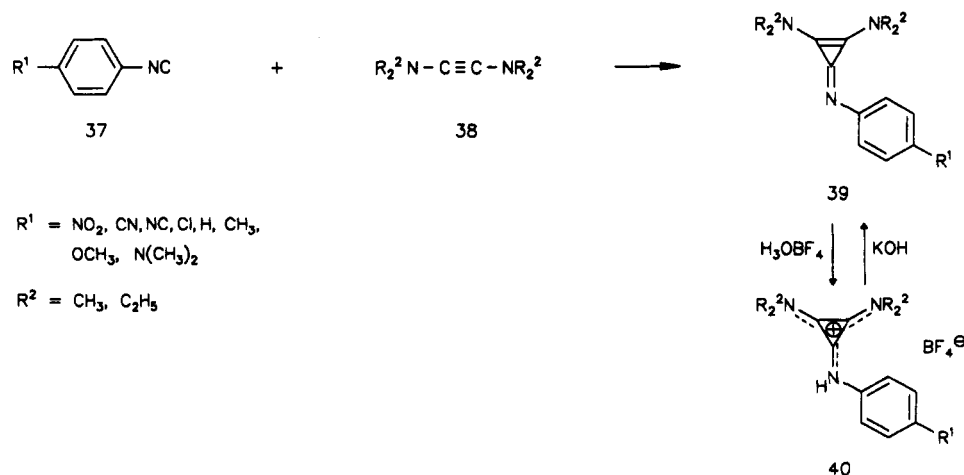
proposed  $D_{3h}$  symmetry. This is also confirmed by the X-ray crystal structure determination. Figure 1 presents the ORTEP plot of the methyltriphenylphosphonium salt of 7. The C-C bond distances are equal within experimental error; their value of 140.5 pm is virtually similar to those in tris(dimethylamino)cyclopropenylum perchlorate<sup>25</sup> (35) (136.3 pm) and triphenylcyclopropenylum perchlorate<sup>26</sup> (36) (137.3 pm). The C-S distance hardly differs from that in the next higher homologue, tetrathiosquarate<sup>27</sup> (166.4 pm) and corresponds to a partial double bond, such as observed in thiocarboxylic acids.<sup>28</sup> Therefore it seems reasonable to regard the trithiodeltate dianion as a symmetrically substituted cyclopropenylum cation. Resonance formulae displaying C=S character contribute only to a very small extent to its ground state.

Some of the spectroscopic data of trithiodeltate 7 are

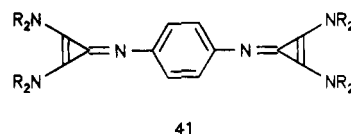


summarized in Table 1, together with data of its relations, the oxo-, carbo-, and iminocarbon dianions 3, 5, and 6 (cf. Scheme 3). A more general presentation of the physical properties of the (pseudo)oxocarbons will follow in section VIII. By using quite different

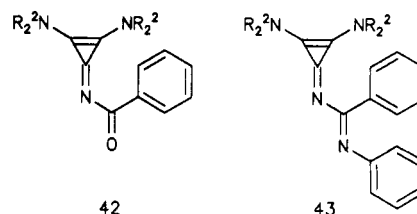
### Scheme 12



methodology, a facile entry into diaminocyclopropenimines and tris(alkylamino)cyclopropenylum cations was provided by an extension of Serratosa's method of deltate synthesis (see section II.A.1) from the [2 + 1]-cycloaddition of a carbene to an alkene 1,2-diether. Krebs et al.<sup>40</sup> reached arylisocyanides 37 with alkyne-1,2-diamines 38 and obtained cyclopropenimines 39 and their corresponding iminium salts 40 (Scheme 12). By this method, they also observed a 2:1 addition with 1,4-diisocyanobenzene, yielding 41. 42 and 43 resulted



from the cycloaddition reactions with benzoyl- and benzimidoylisocyanide.



Alkyl isocyanides, on reaction with ynediamines, did not give cyclopropenimines. The authors<sup>40</sup> ascribe this to the low stability of the latter that probably decompose under the reaction conditions.

### 3. C<sub>3</sub> Semloxocarbons

This class of molecules is represented by formula 44, corresponding to the more general formula B of Scheme 1.

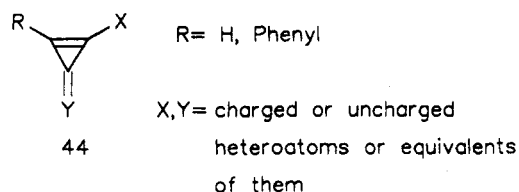
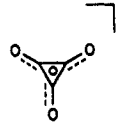
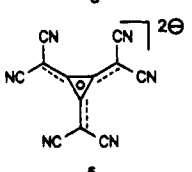
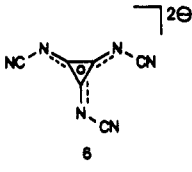
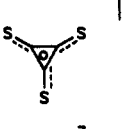
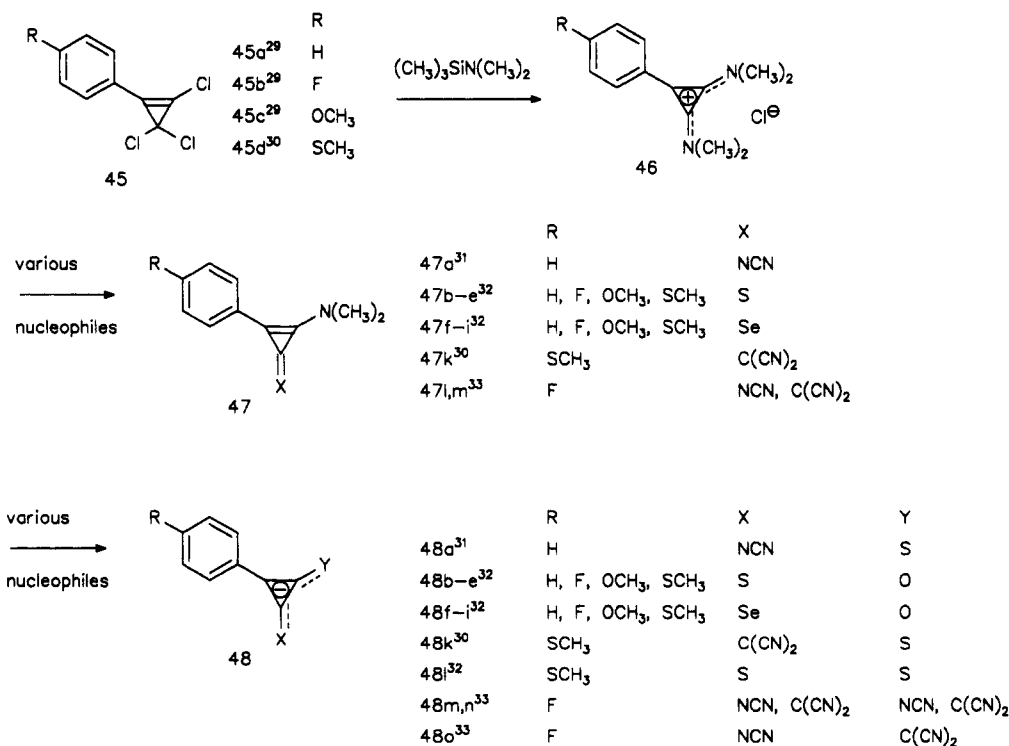


Table 1. Symmetric C<sub>3</sub> (Pseudo)oxocarbons

compd		<sup>13</sup> C ring carbons (ppm)	C-C bond distance, ring carbons (ppm)	C-hetero bond distance (pm)	IR (most prominent bands) (cm <sup>-1</sup> )
3		140.0 <sup>e</sup>	no X-ray published		1445, <sup>a</sup> 965
5		124.5 <sup>f</sup>	no X-ray published		2197, <sup>f</sup> 2150, 1420
6		133.0 <sup>b</sup>	no X-ray published		2170, <sup>b</sup> 1470
7		176.5 <sup>c</sup>	140.5 <sup>c</sup>	167.6 <sup>c</sup>	1223, <sup>d</sup> 694, 157

<sup>a</sup> K salt (ref 162). <sup>b</sup> Na salt (ref 15). <sup>c</sup> MePh<sub>3</sub>P salt (ref 23). <sup>d</sup> Na salt (ref 23). <sup>e</sup> Li salt in D<sub>2</sub>O (ref 9b). <sup>f</sup> NBu<sub>4</sub> salt (ref 14).

Scheme 13



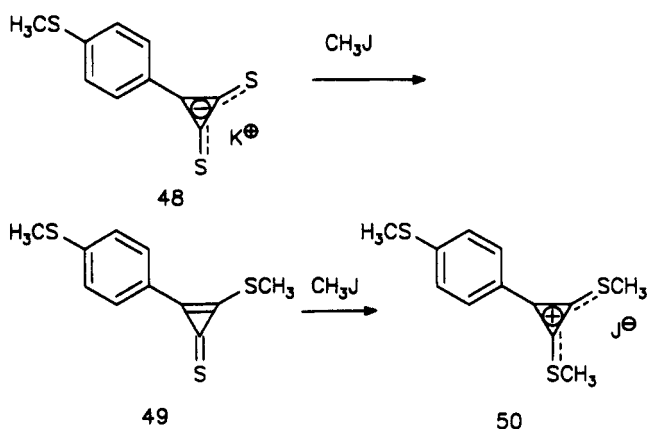
Work on hydrogen-substituted derivatives of 44 (R = H) was published only recently; phenyl derivatives (R = phenyl) have been known for a longer time.

Just as tetrachlorocyclopropene (8) served as a facile entry into pseudooxocarbons (previous section), so the trichlorophenylcyclopropenes 45 were used as starting materials for a number of phenyl(pseudo)oxocarbons (Scheme 13).

In each case,<sup>30-33</sup> the vinamidinium chlorides 46 were reacted with a suitable nucleophile (e.g., H<sub>2</sub>C(CN)<sub>2</sub>/NEt<sub>3</sub>, NaHSe) to give the amides 47. These, in turn, contained a dimethylamino group that underwent replacement on reaction with oxygen, nitrogen, sulfur, selenium, or carbon nucleophiles, yielding the semi-(pseudo)oxocarbons 48. Chemical proof of the structures 48 could also be obtained from the characteri-

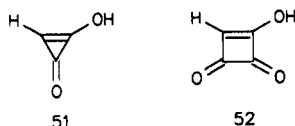


zation<sup>30-32</sup> of alkylated derivatives, e.g.:<sup>32</sup>



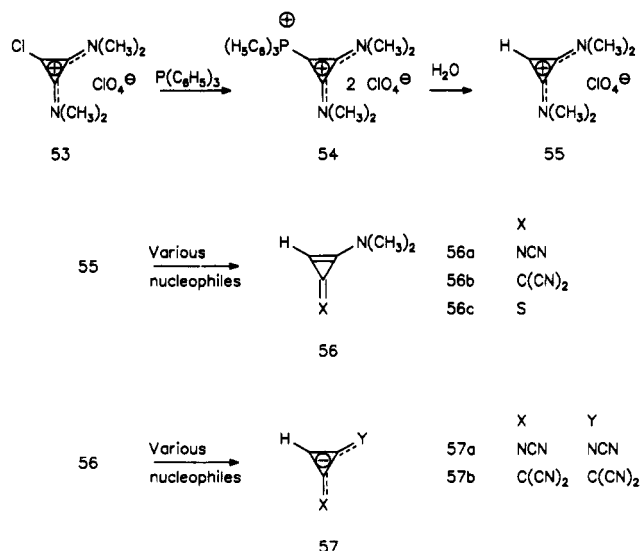
Comparison of the <sup>13</sup>C NMR data of 48, 49, and 50 showed<sup>32</sup> that the distribution of electron density in the phenyl ring is hardly affected by the cyclopropene moiety.

Semideltic acid (2-hydroxy-2-cyclopropenone) 51 is an interesting unknown compound. It was recently



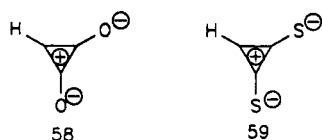
detected IR spectroscopically in an argon matrix after UV irradiation of its homologue, semisquaric acid (52).<sup>34</sup> Very few derivatives of semideltic acid are known. Their synthesis (Scheme 14) followed the same strategy that

Scheme 14



was used for their phenyl analogues.

The amides 56 and semipseudooxocarbon anions 57 represent the—as yet—only examples of derivatives of semideltic acid (51). Neither the anion of 51, 58, nor its sulfur analogue 59 could be obtained by various routes.<sup>35</sup>



Semideltates easily open the ring on reaction with nucleophiles. For instance, in the reaction of the triafulvene 56b with malononitrile and potassium ethoxide, the pentadienide 61 was isolated as a byproduct.<sup>35</sup> It most probably results from the addition of malononitrile to C-3 of the cyclopropene ring and subsequent rearrangement (Scheme 15), C-3 being sterically the least hindered electrophilic center.

Another interesting feature of semipseudooxodeltates was the easy quantitative exchange of the hydrogen atom for deuterium, see Scheme 16 for an example.<sup>35</sup> This behavior was also shown for *donor*-stabilized cyclopropenium systems,<sup>36</sup> see section IX (Scheme 74). The rapid electrophilic substitution reaction is good proof for the aromatic cationic character of the three-membered ring, and should be compared with the electronic structure of trithiodeltate as inferred from its X-ray data (see above).

## B. Reactions

Many reactions of derivatives of deltac acid involve a transformation into another representative of the same class by a nucleophilic replacement reaction, so most of the material was covered in the previous section.

There are, of course, a lot of reactions involving cyclopropenium ions with carbon substituents. These are not going to be reviewed here (see Introduction), but some surprising findings from the reaction of sulfur-substituted cyclopropenium cations will be mentioned.

It was found that sulfonium methylides 63 react with tris(alkylthio)cyclopropenium perchlorate (or tetrafluoroborate) 62 to give mixtures of bis(alkylthio) ketenes 64 and tetrakis(alkylthio)allenes 65. The latter one was formed in low yield in the case of the tris(*tert*-butylthio) derivative only (Scheme 17).<sup>37</sup>

The authors could also obtain the sulfonium salts 66 from the same educts at lower temperature. They propose them to be intermediates for the formation of the ketenes and allenes, but give no evidence for this—they do not even report the transformation of isolated sulfonium salts into 64 or 65.

There have also been reports of cycloaddition reactions with the tris(isopropylthio)cyclopropenium cation (67) (Scheme 18).<sup>38,39</sup> Quinolines substituted at position 7 or 5 (68 and 69, respectively) and pyrrolizines (70 and 71) were obtained in acceptable yields.

Finally, tetrachlorocyclopropene (8) itself was utilized in many cycloaddition reactions. Since neither 8 nor the reaction products can be counted as oxocarbons, they will not be reviewed here. The reader is referred to the literature on the subject.<sup>41</sup>

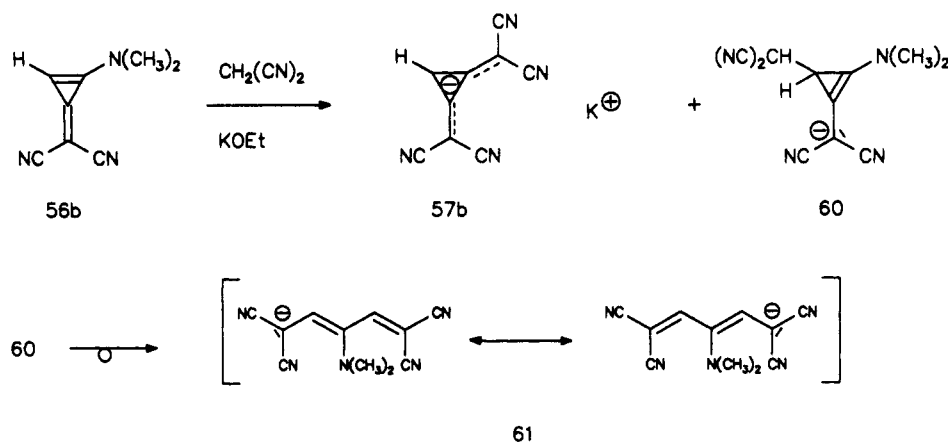
## III. C<sub>4</sub> Derivatives of Squaric Acid

### A. Syntheses

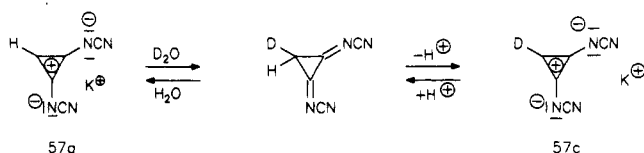
#### 1. Squaric Acid

Oxocarbons, first synthesized more than 160 years ago (croconate and rhodizionate; see sections IV and V), were little known until the rebirth of this field following the discovery of 3,4-dihydroxycyclobut-3-en-1,2-dione 77 (commonly called "squaric acid") in 1959<sup>42</sup> (Scheme 19).

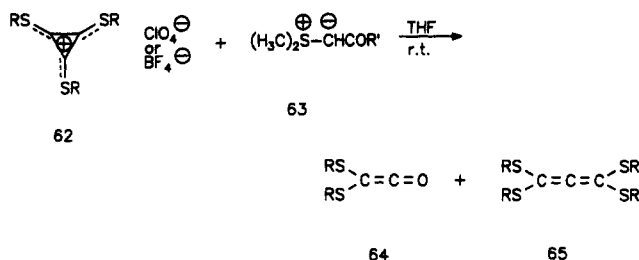
## Scheme 15



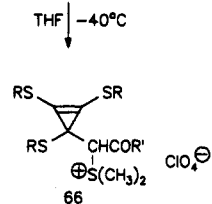
## Scheme 16



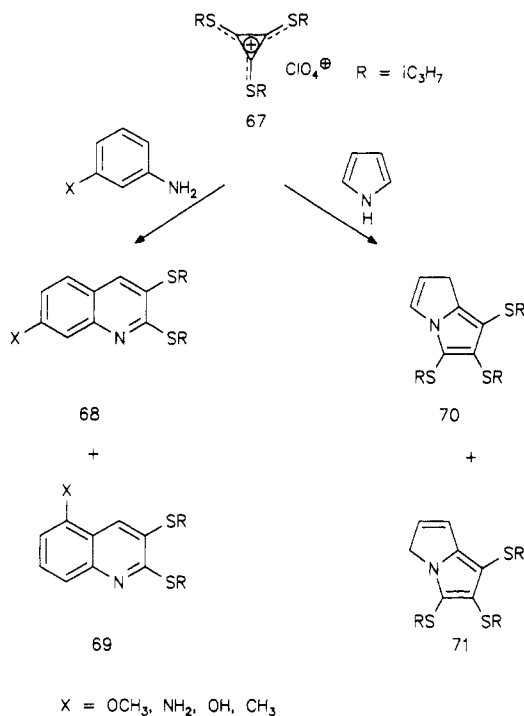
## Scheme 17



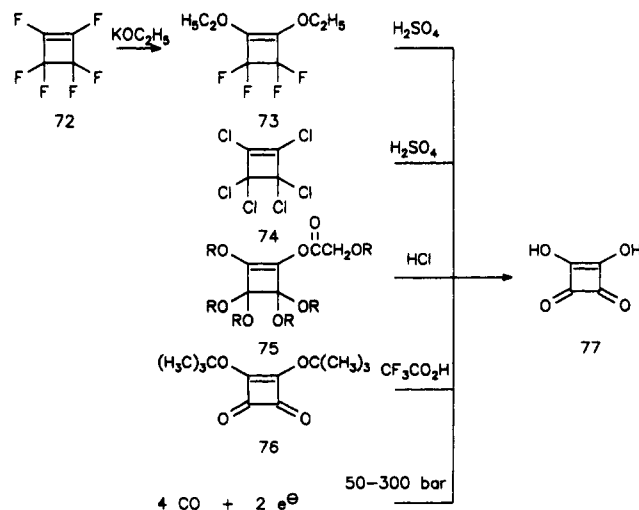
$\text{R} = \text{Et}, \text{C}(\text{CH}_3)_3, 4-(\text{CH}_3)_3\text{CC}_6\text{H}_4, \text{R}' = \text{EtO}; \text{C}_6\text{H}_5, \text{EtS}$



## Scheme 18



## Scheme 19



Only after this did West and Powell<sup>43</sup> recognize the series of polycarbonylated aromatic ring systems that have come to be known as "oxocarbons".

Today, squaric acid is produced on a small industrial scale by hydrolysis, not of perfluorocyclobutene (72) as in the original preparation, but of perchlorocyclobutene (74) in one step.<sup>44</sup> Scheme 19 also lists other cyclobutene derivatives that were converted into squaric acid.<sup>45,9c,46</sup> A promising newer method is the electrochemical reduction of carbon monoxide in polar aprotic solvents,<sup>47</sup> which can be carried out to yield 35% of 77 (based on CO consumed). It mimicks the chemical reduction of CO with alkali metals which yields croconate, rhodizone, and even deltate (see section II.A.1), but no squarate.

2.  $\text{C}_4$  Pseudooxocarbons

As in the case of  $\text{C}_3$  pseudooxocarbons (see section II.A.2), numerous derivatives of squarate were prepared with carbon, nitrogen, sulfur, and selenium substituents

in place of oxygen. Since the four-membered ring allows an even greater variability, we have subdivided

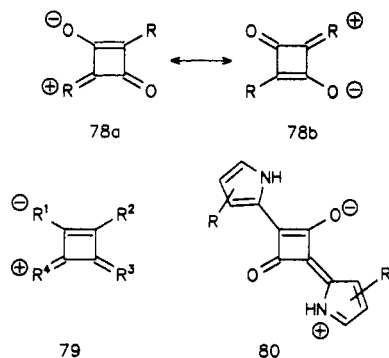
Table 2. Representatives of Zwitterions 87

$  \begin{array}{c}  \oplus \\  R_nX \\  \diagup \quad \diagdown \\  \text{C} = \text{C} \\  \diagdown \quad \diagup \\  \text{O} \quad \text{Z}  \end{array}  \quad Y^-  $					87	
$R_nX$	Y	Z	obtained according to Scheme	ref(s)		
$(H_5C_2)_3N$	O	O	20	50		
	O	O	20, 21	50, 51, 53		
	NCN	O	20, 21	55		
	O	O	20	54		
	O	O	20	54		
$(H_5C_6)_3P$	O	O	20	52		
$(H_5C_6)_3P$	NCN	O	20	55		
$(H_5C_6)_3As$	O	O	20	52		
	O	O	20	52		
$(H_5C_6)_3P$	S		20	52		
$NC-\text{pyrrole}$	O		20	50		

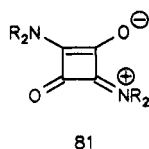
this heading according to the net charge of the respective derivatives into zwitterionic, cationic, and anionic oxocarbons. In many instances, of course, these may be converted into each other, and indeed several synthetic paths leading to dianions—true “pseudooxocarbons”—start from squaric acid esters or amides with the intermediate conversion of the latter into zwitterions, cations, or monoanions.

There will also be separate headings for radialenes, for semisquarates, and for reactions not covered in reviewing the syntheses.

*a. Zwitterionic Derivatives.* Squaraines 3d are mesoionic derivatives of squaric acid, represented by formula 78 or, more generally, by formula 79. The first examples of this class were prepared in 1965 from pyrroles and squaric acid, yielding the intensely colored condensation products 80.<sup>48</sup>



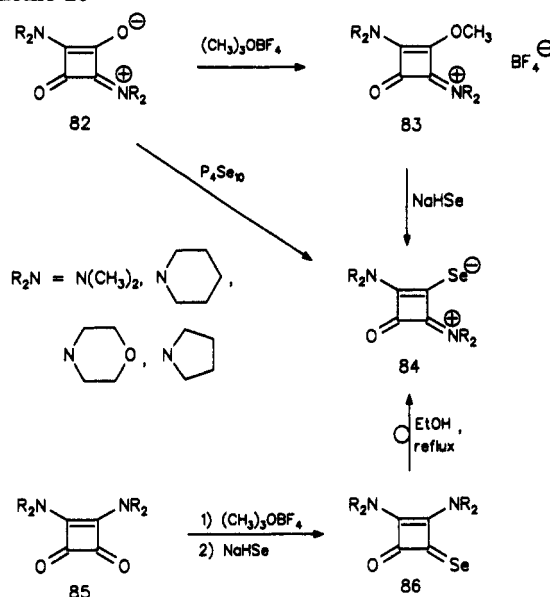
The major part of the work in this field was carried out on squaraines of type 81. A review on the chemistry of squaraines by Schmidt (whose group contributed most of the compounds) appeared in 1980,<sup>49</sup> and the



reader is referred to it as for earlier work and basic features of the molecules in question.

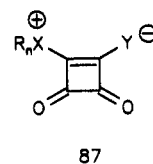
Recently, there was a report on pseudosquaraines, namely, on selenosquaraines, the first of which was synthesized in 1976.<sup>56</sup> Scheme 20 depicts the pathways that were found to selenosquaraines 84.<sup>57</sup>

Scheme 20



They could be obtained from the reaction of phosphorus selenide with squaraines 82, through the conversion of the latter to the vinamidinium salts 83 and subsequent reaction with hydrogen selenide, or alternately, from the rearrangement of the selones 86. Crossover experiments indicated an intermolecular migration of the amino functions of 86.<sup>57</sup>

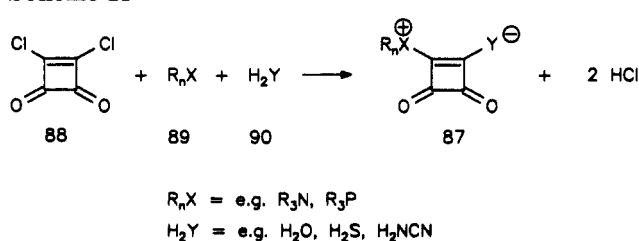
A further class of zwitterionic derivatives of squaric acid is represented by formula 87.



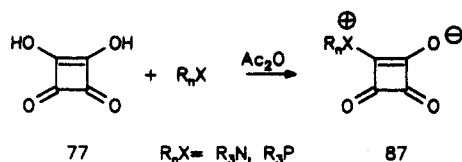
During the past 10 years, a large number of compounds corresponding to the general formula 87 have been prepared. They can be obtained by the reaction of squaric dichloride (88) with two different nucleophiles (89 and 90), one of which will bear the positive, the other one the negative charge in the product, as outlined in Scheme 21. Yields for this process are generally not very good (40% on the average).

Another process which permits of less variation of the reaction components is shown in Scheme 22. Table 2 lists some zwitterionic representatives of formula 87.

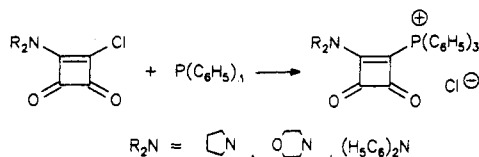
Scheme 21



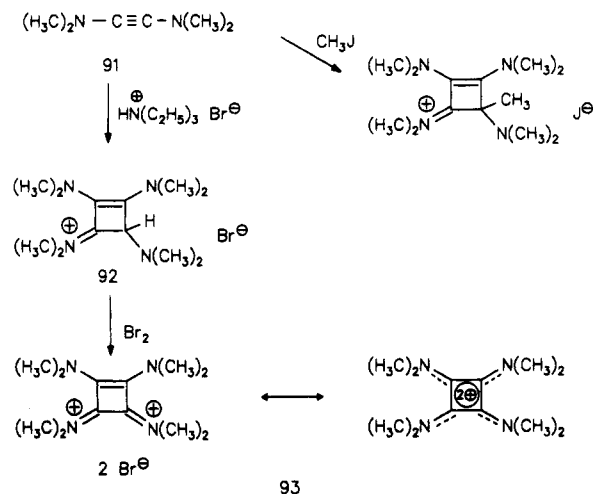
Scheme 22



Scheme 23



Scheme 24

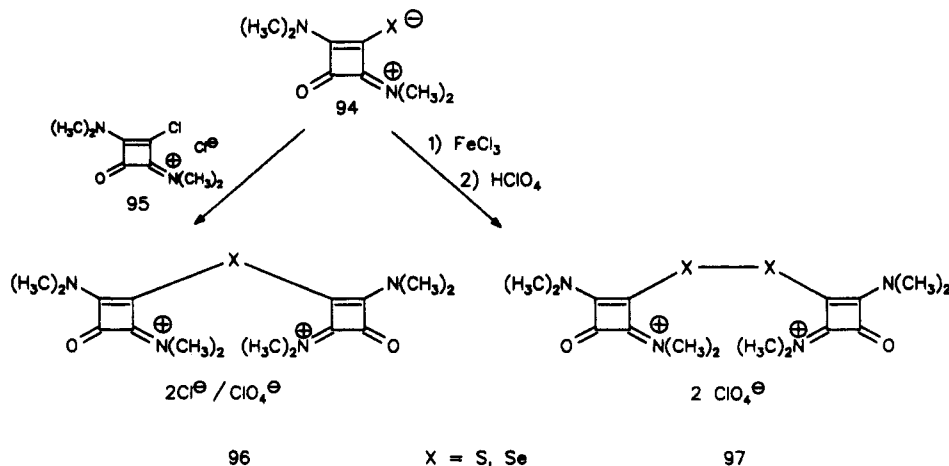


The method by which they were obtained is indicated in a separate column. Also included are hydrazones of some zwitterions 87. For complete lists of the numerous but essentially similar derivatives, readers are referred to the original publications in the final column of Table 2.

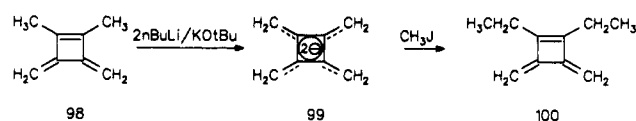
*b. Cationic Derivatives.* These may be obtained generally from substitution reactions on suitable squaric acid derivatives, as was exemplified in a newer synthesis (Scheme 23).<sup>58</sup>

Other examples of cationic squaric acid derivatives will be found under the previous and following headings, when they were formed as intermediates for zwitterions or squarates.

Scheme 25



Scheme 26



A different approach to squaric acid amidinium salts was found in the dimerization of 1,2-bis(dimethylamino)ethyne (91), promoted by acidic or methylating agents (Scheme 24).<sup>59</sup>

The resulting vinamidinium cation 92, in turn, was oxidized to the aromatic cyclobutene dication 93, isolated as its dibromide, an orange powder. Only more complex analogues of 93 where the nitrogen atoms are included in a cyclic system were previously known.<sup>60</sup>

As in the case of deltic acid derivatives, it was also possible to obtain sulfur- and selenium-bridged cations 96 and 97 from mesoionic cyclobutenes 94 (Scheme 25).<sup>61</sup>

Dications of cyclobutene derivatives— $2\pi$  Hückel aromatics—may be classified as oxocarbon dications, although this means taking the definition of oxocarbons quite far.

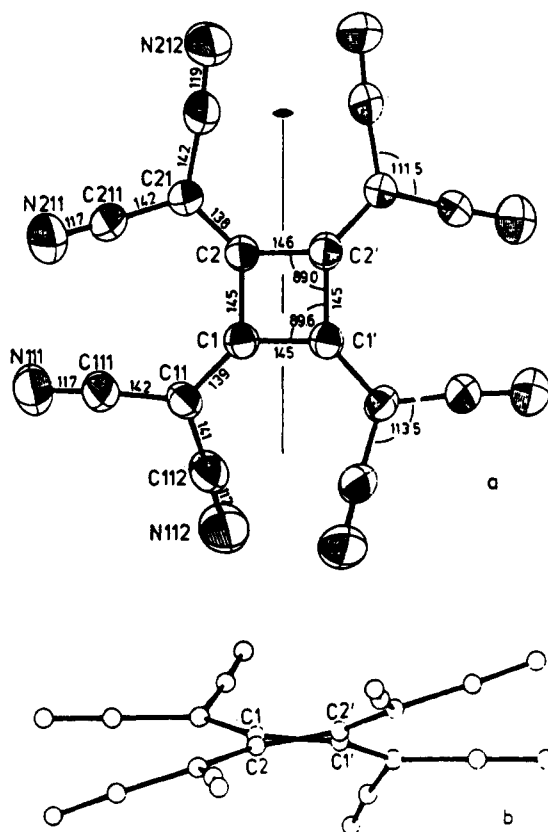
Monocations are mentioned only because they played important roles in some oxocarbon syntheses (and, of course, in other fields). Otherwise, the chemistry of cyclobutenium cations and that of squarate analogues do not really go together under the same heading. In light of this, we will leave this topic and turn again to “true” (pseudo)oxocarbons, namely anionic systems.

*c. Anionic Derivatives (“Pseudosquarates”).* Most of the work in this field was dedicated to the preparation of acceptor-substituted analogues of squarate, but there was also a report on the hydrocarbon analogue 99, which shall be considered first (Scheme 26). The dianion 99 of 1,2-dimethyl-3,4-bis(methylene)cyclobutene (98) was prepared<sup>62</sup> by metalation with *n*-butyllithium and potassium *tert*-butoxide. 99 was characterized by quenching with, e.g., methyl iodide, which yielded the diethylcyclobutene 100, and by <sup>1</sup>H NMR spectroscopy, which showed a singlet at 1.71 ppm in THF. From a comparison of the chemical shift with the charge density on the terminal carbons, the authors propose (without presenting calculations) that 99 is closely related to aromatic systems like the cyclopentadienyl anion, rather than to nonaromatic linear delocalized anions. After the successful synthesis<sup>63</sup> of the sulfur analogue of squarate, tetrathiosquarate (101), our group further

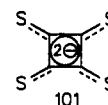
Table 3. Pseudooxocarbons of the C<sub>4</sub> Series

102    n = 1 or 2

	A	B	C	D	counterion(s)	ref(s)
a	C(CN) <sub>2</sub>	N(CH <sub>3</sub> ) <sub>2</sub>	S	S	H <sub>2</sub> N <sup>+</sup> (CH <sub>3</sub> ) <sub>2</sub>	30
b	C(CN) <sub>2</sub>	S	S	S	2K <sup>+</sup>	30
c	NCN	N(CH <sub>3</sub> ) <sub>2</sub>	S	S	HN <sup>+</sup> Et <sub>3</sub>	64
d	NCN	S	S	S	2K <sup>+</sup>	64
e	C(CN) <sub>2</sub>	O	O	O	2K <sup>+</sup>	65
f	C(CN) <sub>2</sub>	C(CN) <sub>2</sub>	O	O	2Na <sup>+</sup>	65
g	C(CN) <sub>2</sub>	O	O	O	2Na <sup>+</sup>	65
h	C(CN) <sub>2</sub>	C(CN) <sub>2</sub>	C(CN) <sub>2</sub>	O	2K <sup>+</sup>	65
i	C(CN) <sub>2</sub>	C(CN) <sub>2</sub>	C(CN) <sub>2</sub>	C(CN) <sub>2</sub>	2Na <sup>+</sup>	65, 69
k	C(CN) <sub>2</sub>	NR <sub>2</sub>	C(CN) <sub>2</sub>	O	2H <sub>2</sub> N <sup>+</sup> (CH <sub>3</sub> ) <sub>2</sub>	65
l	NCN	O	O	O	2K <sup>+</sup>	66
m	NCN	O	NCN	O	2Na <sup>+</sup>	66
n	NCN	NCN	NCN	O	2K <sup>+</sup>	66
o	NCN	NCN	NCN	NCN	2Na <sup>+</sup>	66
p	NCN	N(CH <sub>3</sub> ) <sub>2</sub>	NCN	O	HN <sup>+</sup> Et <sub>3</sub>	66
q	C(CN) <sub>2</sub>	S	C(CN) <sub>2</sub>	O	2Na <sup>+</sup>	67
r	C(CN) <sub>2</sub>	Se	C(CN) <sub>2</sub>	O	2K <sup>+</sup>	67
s	C(CN) <sub>2</sub>	NCN	C(CN) <sub>2</sub>	O	2Na <sup>+</sup>	67
t	NCN	S	NCN	O	2K <sup>+</sup>	67
u	NCN	Se	NCN	O	2K <sup>+</sup>	67
v	NR <sub>2</sub>	Se	O	O	Na <sup>+</sup>	57
w	C[PO(OEt) <sub>2</sub> ] <sub>2</sub> CN	O	C[PO(OEt) <sub>2</sub> ] <sub>2</sub> CN	O	2Na <sup>+</sup>	68
x	CHNO <sub>2</sub>	CHNO <sub>2</sub>	O	O	2Na <sup>+</sup>	68
y	CHNO <sub>2</sub>	N <sup>-</sup> O	O	O	Na <sup>+</sup>	68

Figure 2. ORTEP plot of the dianion of 102i [[H<sub>2</sub>N-(CH<sub>3</sub>)<sub>2</sub>]<sub>2</sub>C<sub>4</sub>[C(CN)<sub>2</sub>]<sub>2</sub>].

pursued the preparation of mono- and dianionic pseudosquarates of the type 102. Table 3 lists the various acceptor or push-pull substituted salts that were characterized. Of these, the tetrakis-substituted dianions 102i and 102o deserve special attention. Scheme



27 shows their synthesis.<sup>65,66,69,70</sup>

Several uncharged or mesoionic derivatives of squaric acid were found to be suitable educts in preparation of the two pseudooxocarbons, 102i and 102o. They completed a series related to squarate 77b (Scheme 28).

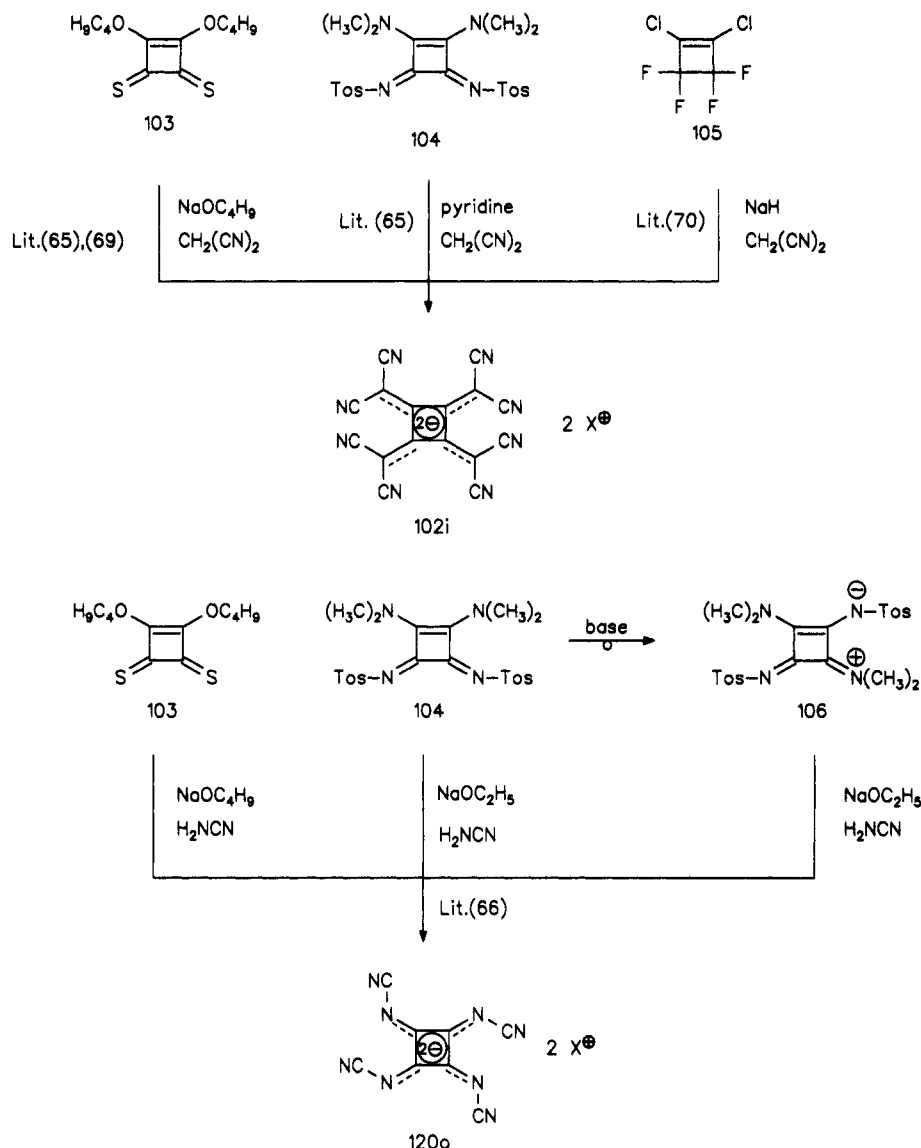
The available spectroscopic data indicate that all four dianions have got a fully delocalized  $\pi$ -system. Above all, the X-ray diffraction analyses should be mentioned. 102i<sup>66</sup> shows C<sub>2</sub> symmetry, the axis of symmetry lying in the plane of the molecule. The four-membered ring is folded by 162.5° at the diagonal axes (see Figure 2).

The dicyanomethylene side chains are almost planar. They are distorted from the plane of the four-membered ring, not consecutively (like a propeller), but alternately (quasitetrahedrally).

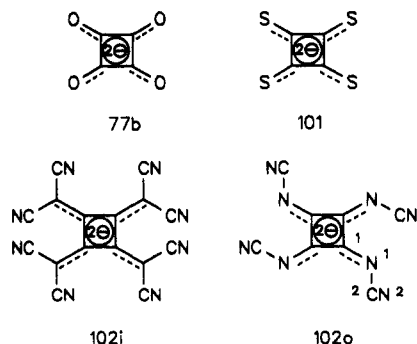
The bond lengths of the endocyclic C-C bonds of 102i (145.3 pm) are almost the same as in 102o<sup>66</sup> (145.0 pm) and very similar to those of squarate<sup>71</sup> (145.7 pm) and of tetrathiosquarate<sup>63</sup> (144.8 pm). This indicates a similarity in bonding with a  $\pi$ -bond order of 0.2 for the ring bonds in 102i. From the X-ray analysis<sup>66</sup> of the iminocarbon 102o, the high degree of delocalization becomes also apparent, e.g. in the shortening of the bonds between N-1 and C-2 (see Scheme 28) to 132.7 pm and the lengthening of the C-1-N-1 bonds to 131.3 pm.

Going back to Table 3, we would also like to point out the successful preparation of two series of carbo- and iminocarbons the final members of which (102i and 102o) were just discussed (Scheme 29).

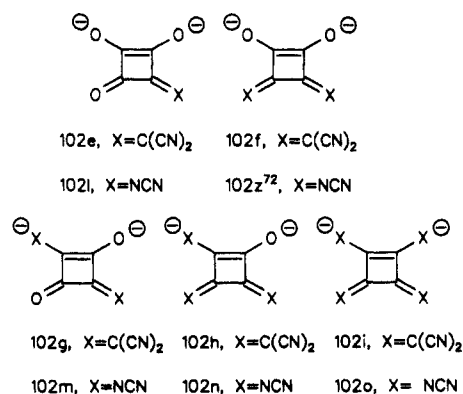
Scheme 27



Scheme 28



Scheme 29

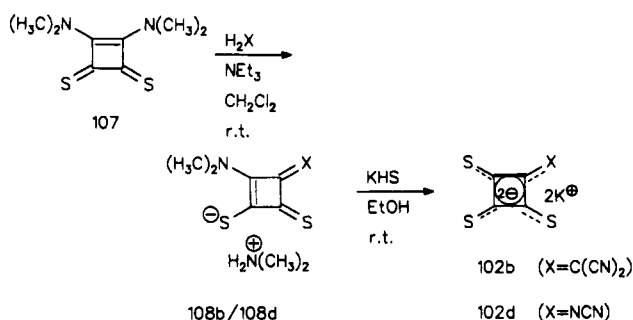


These were also prepared from squaric acid diesters, amino hydrazones, or other suitably activated derivatives.<sup>65,66,72</sup> The introduction of the dicyanomethylene and cyanoimino groups leads to a continual bathochromic shift of the absorption of highest wavelength. The  $^{13}\text{C}$  NMR data reveal that—as was to be expected—the dicyanomethylene function has much weaker acceptor properties than oxygen. The chemical shift of, for example, the carbonyl carbons of squarate (204.2 ppm) and of 102h (171.2 ppm) differ by 33 ppm.  $^{13}\text{C}$  NMR data also show that the negative charge is

mainly located on the atoms directly connected to the ring, whether they be oxygen, nitrogen, or carbon.

Concerning some general hints on the preparation of pseudooxocarbons, the authors refer the reader to the previous section on pseudodeltates. It should just be pointed out that for a successful synthesis of a specific compound the choice of educt is very critical. Sometimes several will do, but if the “wrong” educt is taken, the product may form, but it will not be possible to

## Scheme 30

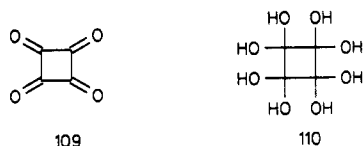


isolate and identify it because of byproducts having similar properties. Otherwise, most of the pseudooxocarbons of Table 3 were isolated in good yield. As an example, Scheme 30 outlines the preparation of dipotassium 2-(dicyanomethylene)-4-thioxocyclobutene-1,3-dithiolate (102b)<sup>30</sup> and of dipotassium 3-(cyanomimino)-4-thioxocyclobutene-1,3-dithiolate (102d).<sup>64</sup>

In both cases, one dimethylamino group of dithiosquarate bis(dimethyl amide) (107) was substituted by the anions of malononitrile and cyanamide. 108b was isolated in 71% and 108d in 50% yield as yellow crystals after chromatography with dichloromethane on silica gel or after recrystallization from water. Potassium hydrogen sulfide in ethanol displaces the second dimethylamino group. 102b (93% yield) and 102d (95% yield), ocher-colored powders, were washed with ethanol and ether and recrystallized from a mixture of water and ethanol. For further experimental and spectroscopic details, we refer to the literature.<sup>30,64</sup>

3.  $\text{C}_4$  Radialenes

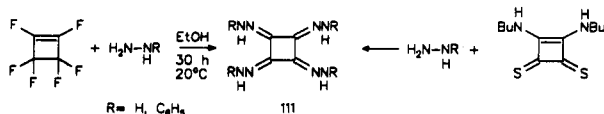
In the past, attempts to prepare electrically neutral oxocarbons  $\text{C}_n\text{O}_n$  (e.g.,  $\text{C}_4\text{O}_4$ , 109) proved unsuccessful and resulted in the isolation of the fully hydrated derivatives only (e.g.  $\text{C}_4(\text{OH})_8$ , 110).<sup>73</sup> Attempts to



obtain oxocarbons  $\text{C}_n\text{O}_n$  from silylated oxocarbon acids were also unsuccessful.<sup>74</sup>

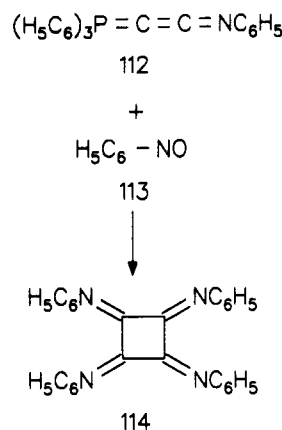
Apart from substituted methylene analogues of oxocarbons  $\text{C}_n\text{O}_n$ , which shall not be considered in this review, it has been possible to prepare some heteroanalogues of 109. During the time under review, a new synthetic pathway to the tetrakis-hydrazones 111 was discovered,<sup>75</sup> some of which had been prepared from a dithiosquarate diamide previously<sup>76</sup> (Scheme 31).

## Scheme 31



Another route to tetraaza[4]radialenes, which did not start from a prefigured cyclobutene ring, consisted<sup>77</sup> in the addition reaction between [(phenylimino)vinylidene]triphenylphosphorane 112 and nitrosobenzene (113) (Scheme 32).

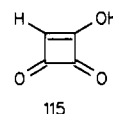
## Scheme 32



The very interesting electrochemical behavior of tetraaza[4]radialenes will be considered in the chapter on physicochemical properties.

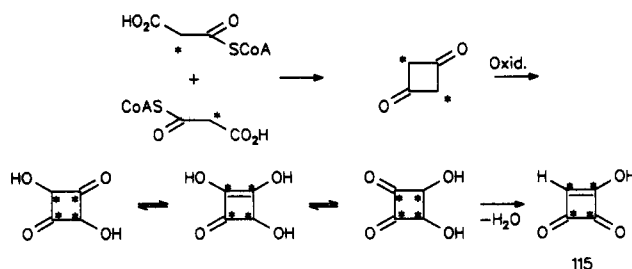
4.  $\text{C}_4$  Semioxocarbons

Semisquaric acid 115 is a naturally occurring mycotoxin. It was given the trivial name of moniliformin because of its isolation from the mold *Fusarium moniliforme*. Its chemistry was reviewed in 1980.<sup>78</sup>



During the time under review, a paper on the biosynthesis of 115 appeared.<sup>79</sup> From feeding experiments with radioactively labeled possible biogenetic precursors, it was concluded that 115 is made up of acetate units as shown in Scheme 33. This possible pathway

## Scheme 33



could also be imitated by a total synthesis.<sup>79</sup>

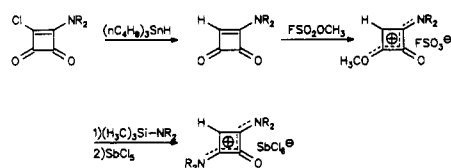
A few papers on the synthesis of moniliformins also appeared. One of them reported on cationic derivatives, namely on vinamidinium salts that were obtained through the known<sup>80</sup> reduction of squaric acid amide chlorides with tributyltin hydride, subsequent methylation, and reaction with silylated amines (Scheme 34).<sup>81</sup>

Two other contributions dealt with new syntheses of semisquaric acid, its amide and ammonium salts. Scheme 35 summarizes one of the papers.<sup>82,87</sup>

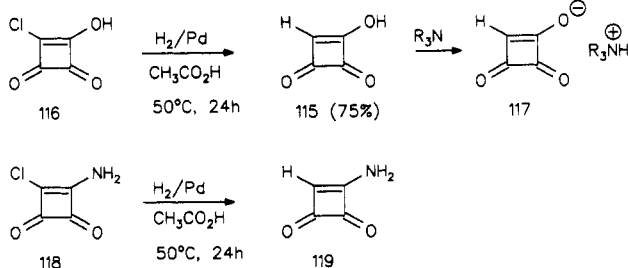
The catalytic reduction of squaric acid monochloride (116) adds to the various known<sup>83</sup> preparations of 115.

Either this method or the hydrolysis of tetraalkoxycyclobutanones<sup>84</sup> (from the cycloaddition of ketene to a tetraalkoxyethene) are to be recommended if one wants to prepare moniliformin.

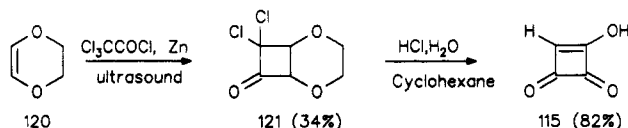
## Scheme 34



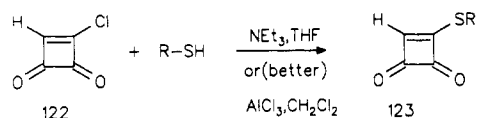
## Scheme 35



## Scheme 36



## Scheme 37



R = Me, Pr, Bu, Ph

On reaction with ammonia and several amines, the ammonium salts 117 were isolated, in contrast to an earlier report<sup>85</sup> which claimed amides of 115 to be the products. This could not be confirmed; instead, the amide of moniliformin 118 was obtained in low yield from the catalytic reduction of 3-amino-4-chloro-3-cyclobutene-1,2-dione (118). Moniliformin also resulted from the hydrolysis of the dioxanocyclobutenone 121 that was formed by the addition of dichloro ketene to 2,3-dihydro-1,4-dioxin (120) (Scheme 36).<sup>86</sup>

Finally, the preparation of *S*-alkyl and *S*-aryl thiosemisquarates 123 from semisquaric chloride 122 and thiols was reported. Yields were better with aluminum chloride as a catalyst than with triethylamine (Scheme 37).<sup>87</sup>

What was stated for semidelates holds also true for semisquarates: very few "true", i.e. anionic semioxocarbons are yet known. In the time under review, no report appeared on an anionic pseudosemisquarate.

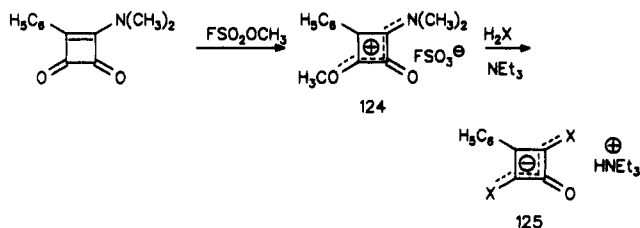
The Scheme 38 presents the preparation of some *phenyl* analogues of moniliformin with dicyanomethylene and cyanoimino acceptor substituents.<sup>65,66</sup>

The semipseudooxocarbons 125 and 127 resulted from the base-catalyzed reaction of suitably di- (124) or mono-activated (124 and 126, respectively) phenylcyclobutenedione derivatives with malononitrile and cyanamide.

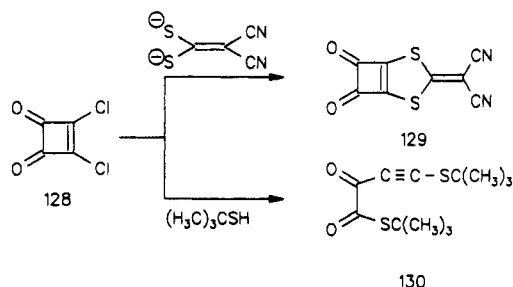
## B. Reactions

There are many uses of squaric acid derivatives for the preparation of other cyclobutenes, of five- and six-membered rings, and of open-chain compounds. Strictly speaking, this does not exactly fall under (pseudo)-

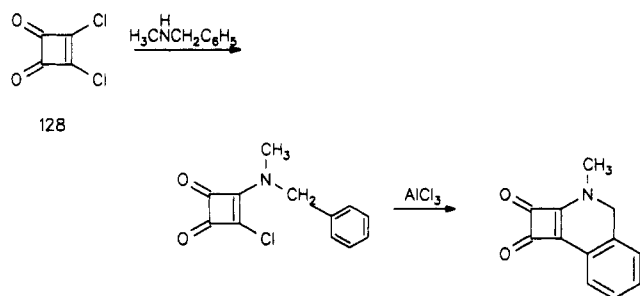
## Scheme 38



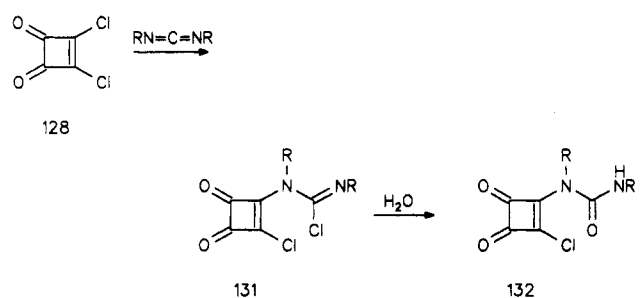
## Scheme 39



## Scheme 40



## Scheme 41



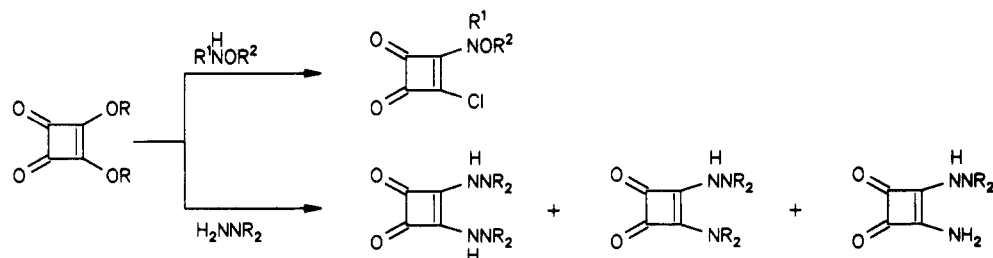
oxocarbon chemistry, also because it is not the oxocarbon ions, but simply squaric dichloride and diesters that mainly serve as synthetic units. Nevertheless, we feel that a review on oxocarbons would not be complete without an even short survey of this field.

During the time under review, squaric acid derivatives were reacted with several sulfur, nitrogen, and (most important) carbon nucleophiles, also with some "isobolals"<sup>88</sup> of carbon nucleophiles to give organometallic compounds.

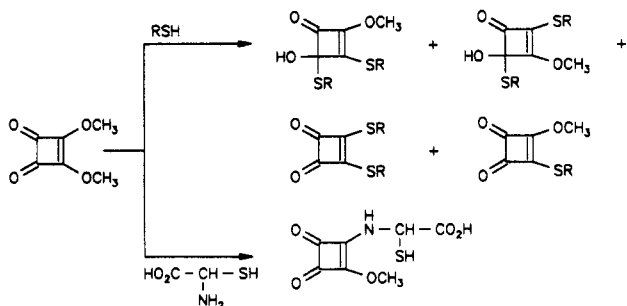
Scheme 39 lists two examples of the reaction of squaric dichloride 128 with thiols.<sup>89</sup> In the one case, the expected disubstitution takes place, leading to the annelated ring system 129. With *tert*-butyl thioalcohol, on the other hand, ring opening to the ethyne 130 occurs. Some other thiols reacted without cleavage of the four-



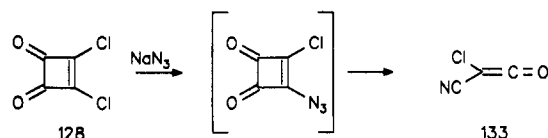
## Scheme 42



## Scheme 43



## Scheme 44



membered ring to give dithiines.<sup>89</sup> If squaric dichloride is reacted with 1 mol of an amine or silylated amine, squaric amide chlorides result. This was investigated by several groups,<sup>90-92</sup> leaving aside earlier syntheses of this class of compounds.<sup>93</sup> Scheme 40 shows an example of this and the intramolecular annelation reaction of the primary product.<sup>92</sup>

With carbodiimides, squaric dichloride 128 was shown to yield chloroformamidines 131 which could be hydrolyzed to the ureas 132 (Scheme 41).<sup>94</sup>

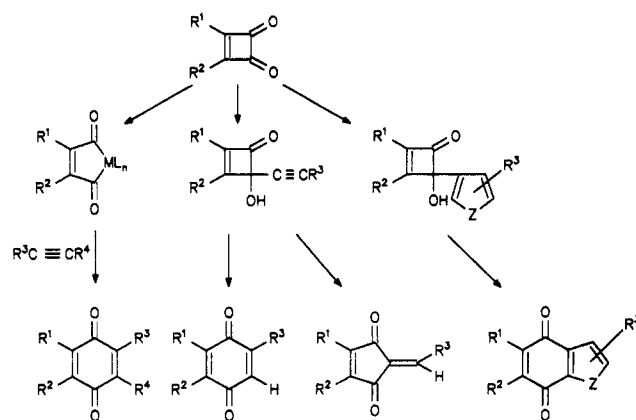
The two reaction schemes last mentioned illustrate that, in squaric dichloride, the second chlorine atom is much more difficult to replace; in other words, squaric dichloride does not behave as oxalyl dichloride does.

Squaric diesters gave monosubstitution with hydroxylamines,<sup>95</sup> but disubstitution and partial decomposition (depending on the hydrazine and the temperature) with hydrazines<sup>96</sup> (Scheme 42). From squaric dimethyl ester and thiols, a number of products resulted via 1,2- or 1,4-addition. The product distribution depended on the nature of the substituent R of the thiol. With amino thiols, substitution by nitrogen occurred (Scheme 43).<sup>97</sup>

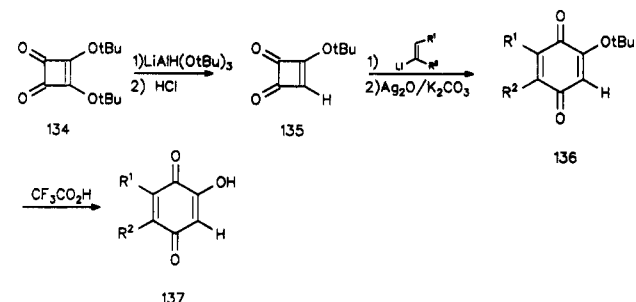
Squaric dichloride 128, on reaction with the azide ion, served as a precursor to chlorocyanoketene 133 (Scheme 44).<sup>98,99</sup> The large field of the use of squaric diesters and related cyclobutenediones for the preparation of various quinones and cyclopentenones remains to be mentioned. Scheme 45 gives an outline of this.<sup>100</sup>

The syntheses usually involve the initial reaction of an organometallic reagent with the cyclobutenedione derivative. It would be far beyond the scope of this review to give an account of these transformations. A few leading references will have to do: for the reaction with lithium and magnesium organyls see refs 100-

## Scheme 45



## Scheme 46



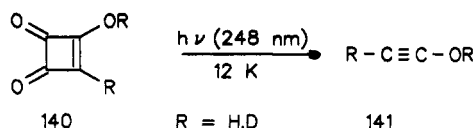
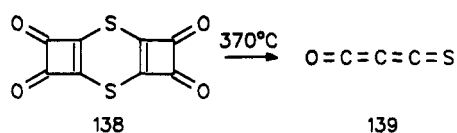
103; with organocopper reagents (ultimately leading to cyclo[n]carbons), ref 104; with alkylstannanes, refs 100 and 105; with metal complexes, leading to metallacycles, refs 100 and 106, or to metal-substituted cyclobutenediones, ref 107. Some of the usefulness of squaric acid derivatives for this kind of reaction sequence is due to the fact that either the two carbonyl groups or the two vinylic substituents may be differentiated (cf. the monosubstitution reaction of squaric dichloride and diesters toward oxygen and nitrogen nucleophiles, above). (Also compare with the use of diethyl squarate as a coupling reagent, section X.) If one of them becomes changed during the reaction, the other one, because of steric and conjugative effects, will have lower reactivity, thus avoiding double reaction.

During the investigation of regiospecific syntheses of hydroxy quinones, Heerding and Moore<sup>102a</sup> reduced di-*tert*-butyl squarate 134 with lithium tri-*tert*-butoxyaluminum hydride, thus providing a facile synthesis of the semisquaric ester 135 (Scheme 46).

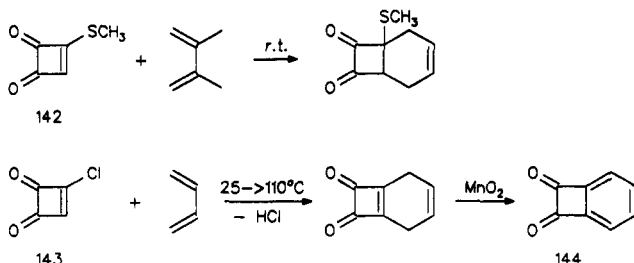
Reaction of 135 with vinyl- and aryllithium compounds, followed by oxidation and hydrolysis, formed the desired hydroxyquinones 137.

Not only did squaric acid derivatives serve as a precursor for the labile chlorocyanoketene 133 (see

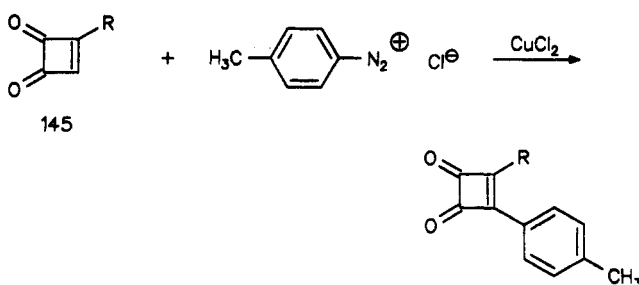
Scheme 47



Scheme 48



Scheme 49



Scheme 44), but also for the carbon subsulfide 139<sup>108</sup> and for ethynol 141,<sup>109</sup> as outlined in Scheme 47.

Moniliformin 140 and its deuterated analogue) is the prototype of semisquarates. Some derivatives of semisquaric acid show dienophilic character, the thiol ester 142 being the first example of this.<sup>110</sup> Semisquaric chloride 143 was reacted in the same manner,<sup>111</sup> in spite of an earlier failure.<sup>112</sup> Scheme 48 depicts two examples of [4 + 2] cycloaddition reactions with semisquarate derivatives. In the latter case the primary Diels-Alder adduct was not isolated, only the product after hydrogen chloride elimination. Subsequent oxidation with manganese dioxide yielded benzocyclobutenedione 144 in good yield.<sup>111</sup>

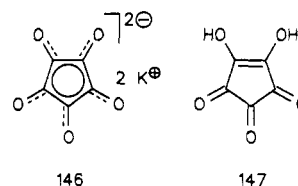
Finally, the Meerwein arylation of semisquaric acid and amides 145 is outlined in Scheme 49.<sup>113</sup>

#### IV. C<sub>5</sub>. Derivatives of Croconic Acid

##### A. Croconic Acid

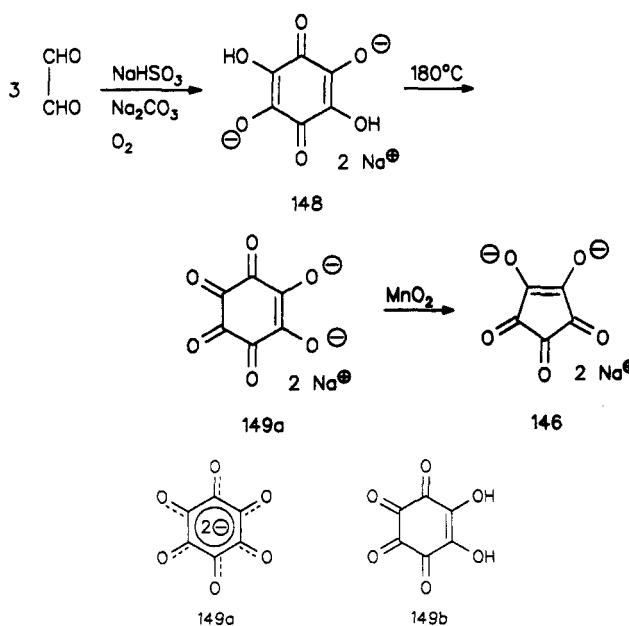
Although the special properties of oxocarbons have come to light only recently, their history begins at the very dawn of modern chemistry and involves many of the great chemists of the early nineteenth century.

The first worker to have in hand an oxocarbon was probably Gmelin,<sup>114</sup> who isolated dipotassium croconate (146) and croconic acid (147) from a black residue formed in the reaction of potassium hydroxide with carbon. 4,5-Dihydroxy-4-cyclopentene-1,2,3-trione (147) derives its trivial name from the yellow (Greek, *krokos*)



color of the acid and its salts. In spite of their early discovery, croconates (and also rhodizonates, the next higher homologues; see following section) have been investigated and synthesized to a much lesser degree than deltates and squarates. This is probably mainly due to the fact that croconic acid is difficult to obtain in large quantities. The oxidative ring concentration of rhodizonate 149a, obtained from the cyclotrimerization of glyoxal and oxidation of the intermediate, tetrahydroxy-*p*-benzoquinone 148, still remains the recommended procedure<sup>115</sup> for the preparation of croconate (Scheme 50).

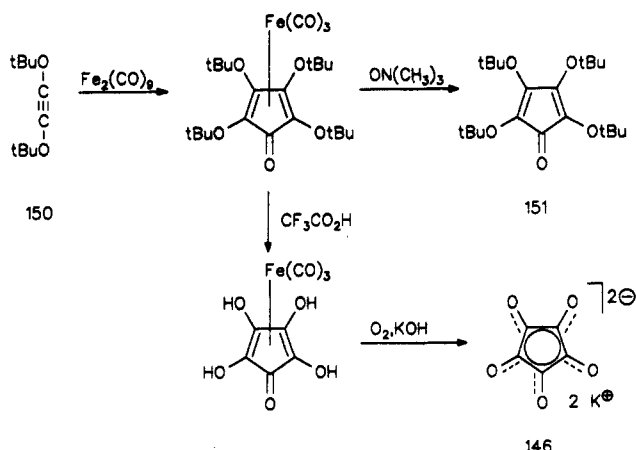
Scheme 50



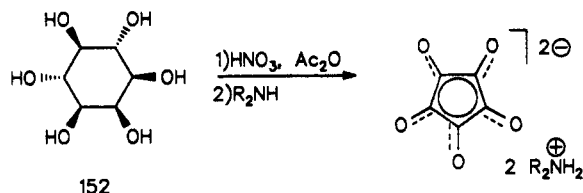
Newer syntheses did not have much impact on this situation, although the procedure of Scheme 50 suffers from very low yield in the first step. Serratos and co-workers published<sup>116</sup> a synthesis (Scheme 51) of croconate 146 from di-*tert*-butoxyethyne 150, but this preparation needs somewhat more expensive chemicals than the older one. They also disclosed a synthetic path to the tetra-*tert*-butyl ester 151. Croconates were also formed by nitration of myoinositol 152 with fuming nitric acid in acetic anhydride, followed by treatment of the hexanitrate with a secondary amine (Scheme 52).<sup>117a</sup> Unfortunately, the authors do not give much experimental detail and no yield. In 1942, other workers<sup>117b</sup> obtained tetrahydroxyquinone and rhodizonic acid from the oxidation of myoinositol with nitric acid.

As was the case with deltate and squarate (see previous sections), there was also a report on the formation of croconate from the oligomerization of carbon monoxide, mimicking the historical preparation. In this study,<sup>118</sup> adsorption of carbon monoxide onto thermally activated magnesium oxide or calcium oxide

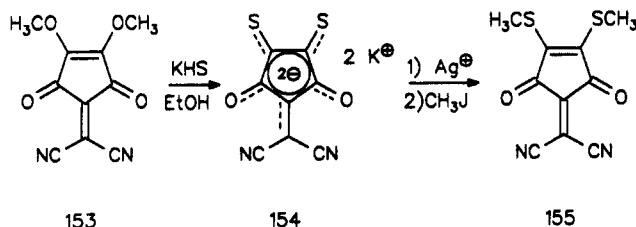
## Scheme 51



## Scheme 52



## Scheme 53



leads to the formation of a variety of adsorbed anionic species, among them rhodizonate and croconate. The latter one is favored when lower temperatures (400–500 °C) are used. This preparation, of course, has mechanistic but no synthetic value.

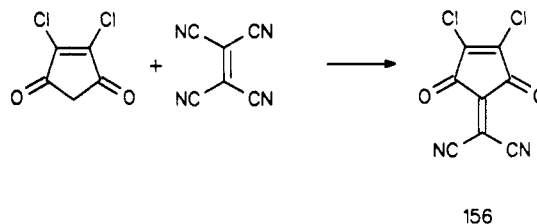
B. C<sub>5</sub> Pseudooxocarbons

What is true for croconic acid itself also applies for its heterosubstituted analogues: a lot remains to be done. Fatiadi<sup>119a</sup> and one of us (G.S.)<sup>119b</sup> reported on earlier results in this field. After that, a few publications appeared, mainly dealing with sulfur- and dicyanomethylene-substituted derivatives. A study from our group<sup>30</sup> reported the synthesis of 4-(dicyanomethylene)-3,5-dioxo-1-cyclopentene-1,2-dithiolate (154), as depicted in Scheme 53.

The pseudooxocarbon 154, which is violet in solution, was converted to the bis(methylthio)cyclopentenedione (155) by the alkylation of its silver salt with methyl iodide. 153 and 155 may be addressed as the dimethyl and bis(methylthio) esters of 4-(dicyanomethylene)-croconic acid. The dichloride 156 of this acid was prepared as shown in Scheme 54.

Such as mesoionic derivatives of squaric acid ("squaraines") proved to be useful educts in the squarate field (see section III.A.2.a–c), so similar zwitterions were prepared and reacted in the croconate field. Scheme 55 outlines the preparation and interconversion of some of them (157–159).<sup>121</sup>

## Scheme 54



On reaction with malononitrile or cyanamide, the zwitterion 158 was converted to the known<sup>122</sup> carbocarbon 161 and the new iminocarbon 162 (Scheme 55).<sup>123</sup> The corresponding 1,2-disubstituted iminocarbon 160, on the other hand, was directly obtained from the croconic acid bis(dimethylamide) 157.<sup>123a</sup>

In the same paper, we reported the preparation of the croconate 164 with only one cyanoimino substituent (Scheme 55).<sup>123a</sup>

The tris(dicyanomethylene)-substituted croconate 165b was called "croconate blue" by Fatiadi, who first synthesized it from malononitrile and croconic acid 147 itself in very good yield.<sup>124</sup> From the reaction of the previously mentioned (cf. Scheme 55) croconic acid bis(dimethylamide) 157 with malononitrile in two steps, a substance was obtained<sup>125</sup> in our laboratories that was identical with Fatiadi's product as for analytical data, but by X-ray crystallography of its tetraphenylphosphonium salt we could prove that its structure was not 165b, as proposed by Fatiadi,<sup>124</sup> but the substituents are located in 1, 2, and 4 positions (164a; Scheme 56).<sup>125</sup>

The interesting dicationic derivative 168 of croconic acid was prepared by chemical or electrochemical oxidation of tetrakis(diethylamino)cyclopentadienone-iron tricarbonyl (167), as depicted in Scheme 57.<sup>126</sup>

168, whose X-ray structure analysis and behavior in cyclic voltammetry were also reported, was hydrolyzed to the croconic acid diamide 169 and the ring-contracted cyclobutenedione 170, depending on the amount of water present.

A heterosubstituted radialene of the C<sub>5</sub>-series, 172, was prepared by the same methodology as an analogous tetraazaradialene (see section III.A.3). Scheme 58 depicts the synthesis.<sup>75</sup>

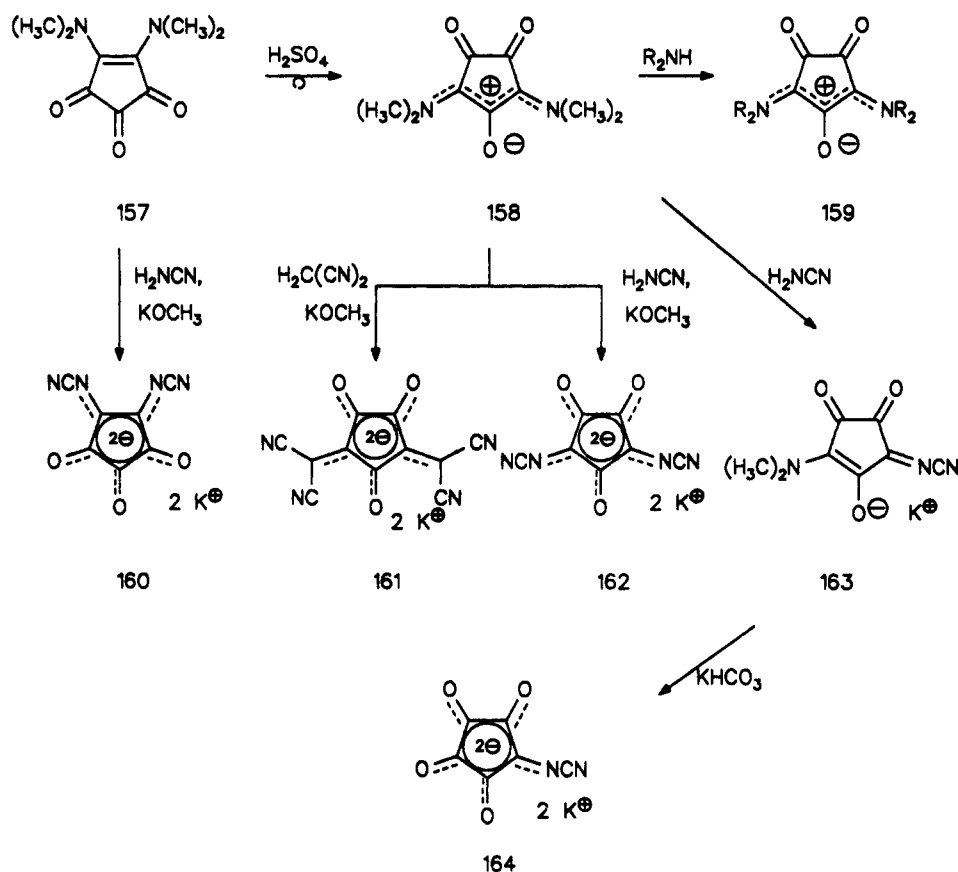
As far as we know, this is all that has been published in the croconate field—so, as we said in the introduction to this chapter—a lot remains to be done.

Not an easy lot for those who take it up, we're afraid.

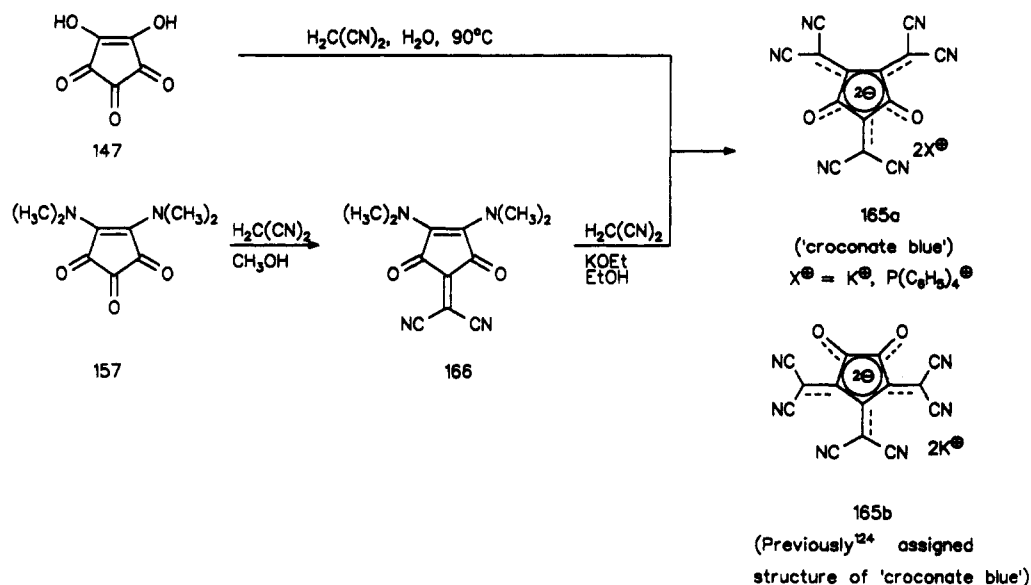
V. C<sub>6</sub> Derivatives of Rhodizonic Acid

During the time under review (and before), the chemistry of rhodizonic acid 149b and its derivatives has been worked on even less than on that of croconates. Rhodizonate 149a was found together with croconate among the products of the reduction of potassium carbonate with charcoal in 1837.<sup>127</sup> Actually, croconate is formed from rhodizonate by ring contraction and loss of carbon monoxide. This was the basis of a standard synthesis<sup>115</sup> of croconic acid we presented in the previous section. The reader is referred to that, also for the formation of rhodizonate, together with croconate, by adsorption of carbon monoxide onto thermally activated magnesium and calcium oxides.<sup>118</sup> Rhodizonate was also detected in the hydroxide ion

Scheme 55



Scheme 56



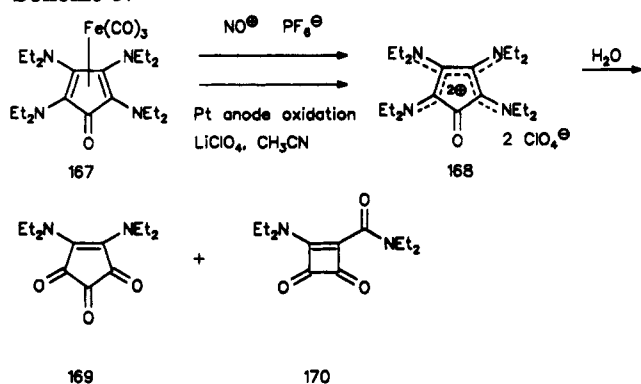
induced oxygenation of *p*-benzoquinone.<sup>128</sup> The authors found that a solution of tetramethylammonium hydroxide in acetonitrile readily reduced *p*-benzoquinone 173 to the semiquinone radical anion 174, but they could not find oxidized products of the hydroxide ion or the solvent. A detailed scrutiny of the stoichiometry revealed that some of the quinone was oxidized to rhodizonate 149a; this is summed up by the equation in Scheme 59.

There were no reports on cationic, zwitterionic, or anionic pseudooxo derivatives of rhodizonic acid, but some have appeared on substituted radialenes. The

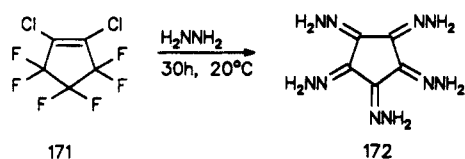
annulated hexakisiminocarbons 176 were obtained from tetraamino-*p*-benzoquinone 175 in two steps (Scheme 60).<sup>129a</sup> Related radialenes, e.g. 177, had been obtained earlier by Eistert and co-workers<sup>129b</sup> from rhodizonic acid and diaminobenzenes.

Scheme 60 also depicts the preparation of a tetracyanoquinodimethane 178.<sup>129c</sup> This compound, which in our terminology may be regarded as a pseudooxoradialene, formed highly conductive complexes with various types of donors.<sup>129d</sup> In the crystal, it showed stacks of two dimensionally expanded sheetlike net-

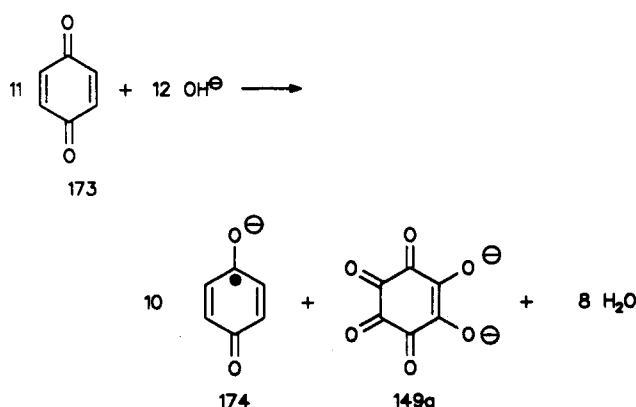
## Scheme 57



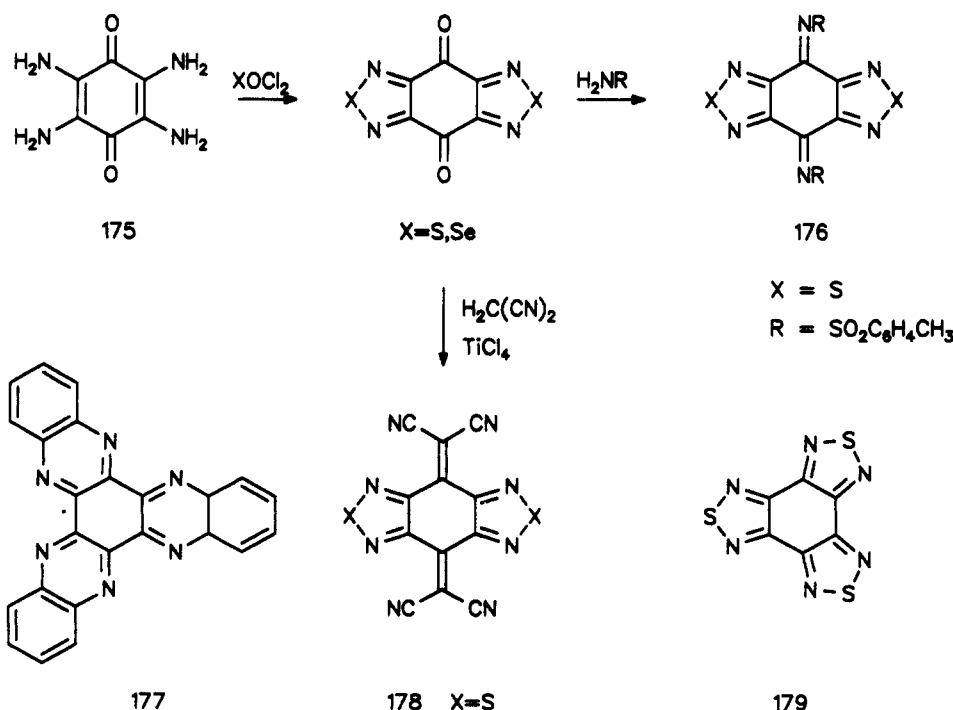
## Scheme 58



## Scheme 59



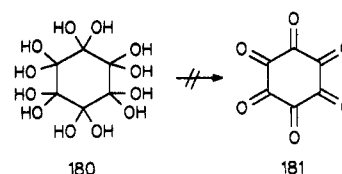
## Scheme 60



works in which the molecules are connected to one another by short S-NC contacts.<sup>129e</sup>

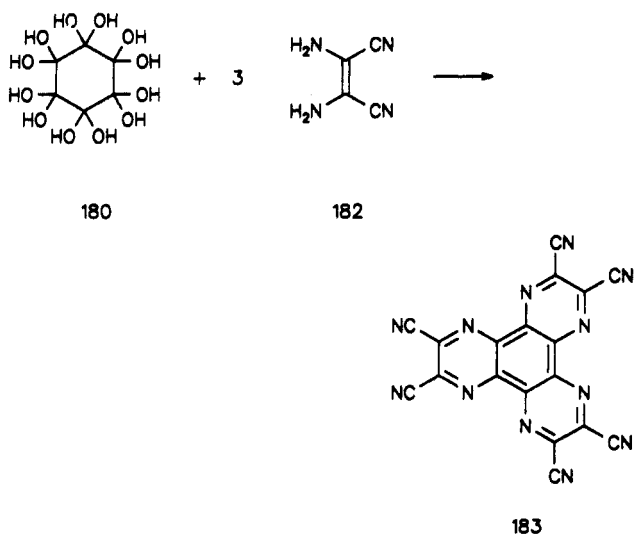
A Japanese group reported the low-yield preparation of the hexakisiminocarbon 179 from tetrasulfur tetranitride and brominated phenols.<sup>129f</sup>

As was mentioned before (section III.A.3), the oxocarbons C<sub>n</sub>O<sub>n</sub>, e.g. cyclohexanehexaone 181, are not known, in spite of synthetic efforts,<sup>73,74</sup> but only their hydrated derivatives, e.g. dodecahydroxycyclohexane 180,<sup>115</sup> are known.



This was reacted with the diamine 182, yielding hexaazatriphenylenehexacarbonitrile (183), a hydrogen-free heterocycle with *D*<sub>3h</sub> symmetry (Scheme 61).<sup>130</sup> The hexathio analogue 185a of the oxocarbon 181 was detected during a neutralization-reionization mass spectrometric investigation of the fragmentation of benzo[1,2-*d*:3,4-*d'*:5,6-*d''*]tris[1,3]dithiole-2,5,8-trione (184) (Scheme 62).<sup>131</sup> The authors suggested the valence isomeric structures 185a or 185b for C<sub>6</sub>S<sub>6</sub>, but did not have any evidence in favor of the one or the other. Frenking<sup>132a</sup> calculated the geometries and energies of the two, of the quinoid structure 185c, and of the chain conformation 185d. Several semiempirical and ab initio computations point to the quinoid structure 185c as being energetically most favored and the planar hexathioketone 185a to have a higher energy content than the chair form 185b. In contrast to that, he calculated<sup>132</sup> that for C<sub>6</sub>O<sub>6</sub>, the hexaketo structure 181 should definitely have the lowest energy. He calculated the strength of a C-C bond in 181 to be 4.6 kcal mol<sup>-1</sup>. This implies that it will not be easy to detect

## Scheme 61

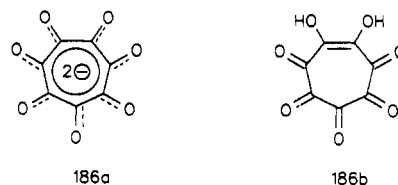
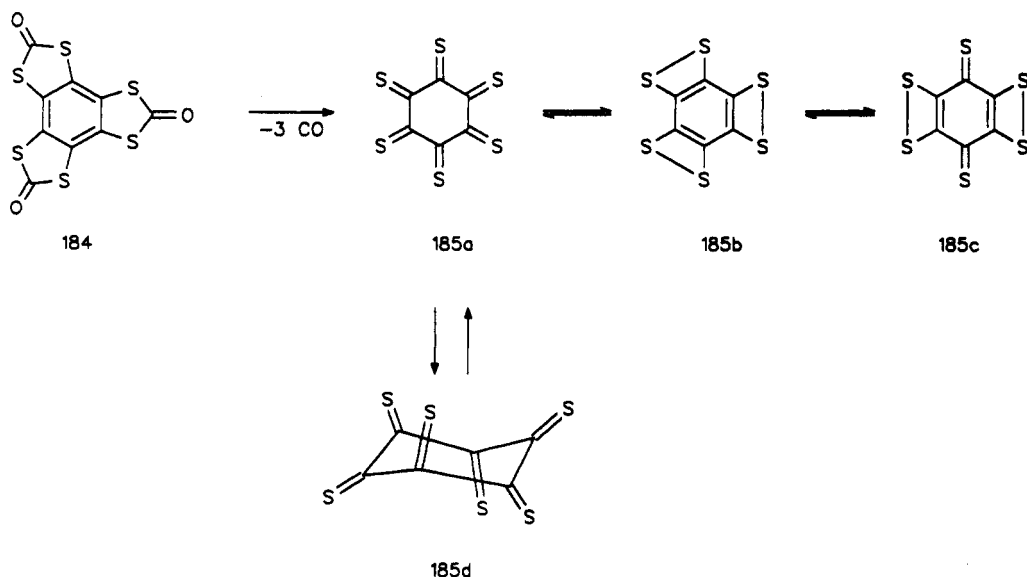


181, but in a footnote he referred to a private communication by Sülzle (who also detected  $\text{C}_6\text{S}_6$ <sup>131</sup>) who claimed to have generated  $\text{C}_6\text{O}_6$  from esters of ethene tetracarboxylic acid in the gas phase. A yellow  $\text{C}_6\text{S}_6$  isomer, which can be interconverted photochemically into a colorless second  $\text{C}_6\text{S}_6$  isomer, was obtained upon matrix photolysis and flash pyrolysis of the precursor molecule 184. The structures of these isomers are most likely 185c and 185b, as shown by comparison of their experimental with the calculated infrared spectra of the possible cyclic isomers of  $\text{C}_6\text{S}_6$ .<sup>132b</sup>

### VI. C<sub>7</sub>. Will There Be "Heptagonic Acid" Derivatives?

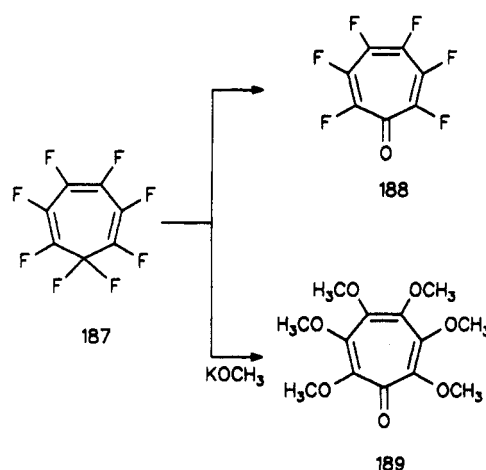
There is almost nothing to report but a challenge that remains to be met. Despite several efforts, heptagonate 186a, heptagonic acid 186b, and hetero-derivatives of them have escaped preparation until now.

## Scheme 62



West<sup>133</sup> tried to get them from the reaction of tetrahydroxy- or tetraalkoxyquinones with carbenoids; we<sup>134</sup> chose perchlorinated cycloheptatrienes as possible educts. Probably Tatlow and co-workers came nearest to it when they converted perfluorocycloheptatriene 187 to hexafluorotropone 188 and to hexamethoxytropone 189 (Scheme 63).<sup>135</sup> Perfluorinated cyclo-

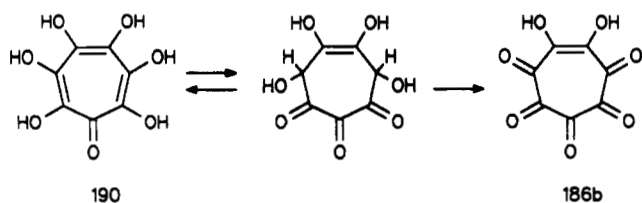
## Scheme 63



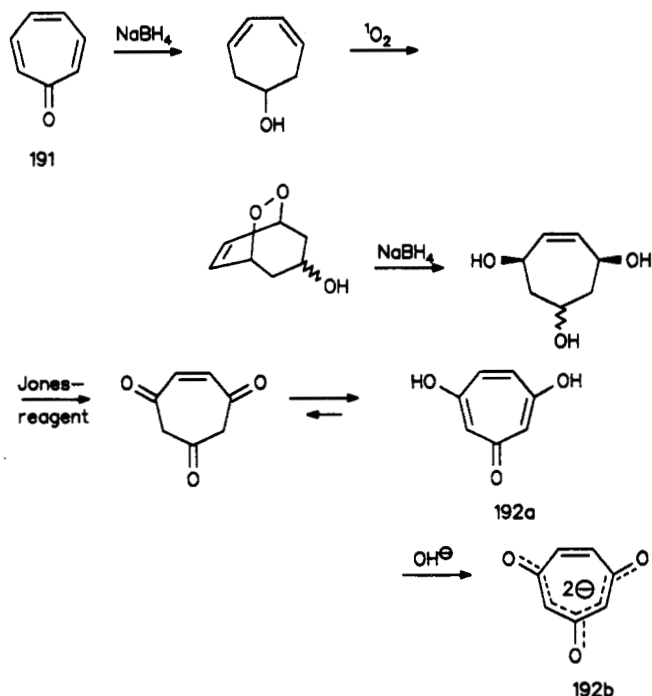
heptatrienes have the advantage that they undergo ring contraction of benzoic acid derivatives less easily than other tropones. Perhaps one day somebody will prepare hexahydroxytropone 190 (or an anion of it) and oxidize it to heptagonic acid 186b (Scheme 64)?

From our efforts in this field, at least we reaped a vinylogous deltate, viz. 3,5-dihydroxytropone 192a and its dianion 192b whose four-step synthesis from tropone 191 is depicted in Scheme 65.<sup>136</sup>

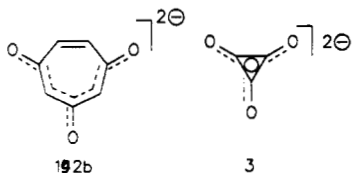
## Scheme 64



## Scheme 65

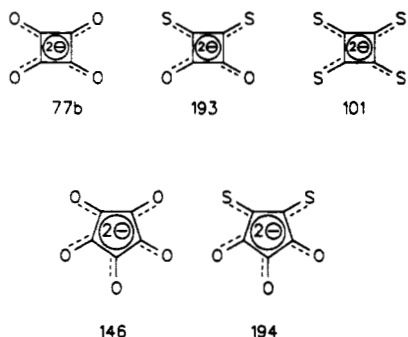


We propose that 192b is another example of a Y-delocalized aromatic system.<sup>1</sup> As such, it is an analogue of deltate 3 and may be regarded as the first C<sub>7</sub> oxocarbon. Which one will be next?



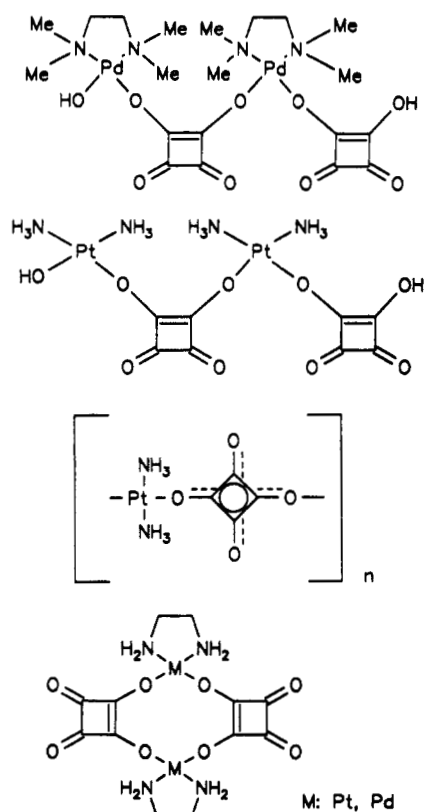
## VII. Complexes with Oxocarbon Ligands

Squarate 77b, dithiosquarate 193, tetrathiosquarate 101, croconate 146, and dithiocroconate 194 were reported to form complexes with various metals.



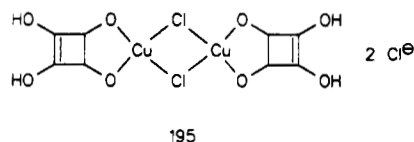
Squarate served as a bridging ligand in complexes of (diamido)palladium(II) and -platinum(II). They were

## Scheme 66



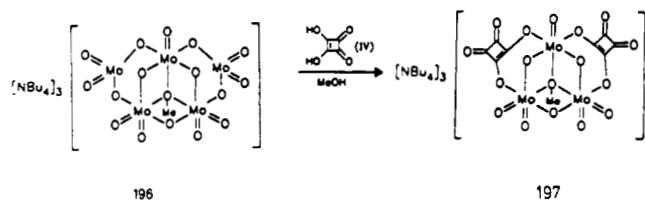
prepared<sup>137</sup> in 73–88% yield from the corresponding *cis*- or *trans*-(diamido)diaquanitrates and dipotassium squarates. Their structures are given in Scheme 66.

Much simpler, squaric acid reacted with cupric chloride to give the chloro-bridged complex 195.<sup>138</sup>



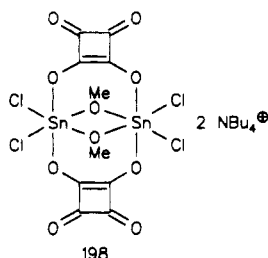
Squarate was also shown to be able to replace MoO<sub>4</sub><sup>2-</sup> units from the molybdenum(VI) complex 196 to give the derivative 197 without concomitant structural rearrangement (Scheme 67).<sup>139</sup> This reflects the anal-

## Scheme 67

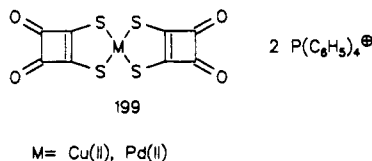


ogous electronic and structural features of molybdate (MoO<sub>4</sub><sup>2-</sup>) and squarate (C<sub>4</sub>O<sub>4</sub><sup>2-</sup>): both are capable of bidentate bridging or monodentate ligation modes, and the ligand "bite" distances are nearly identical at 310 pm.

The binuclear tin(IV) species 198 was prepared<sup>140</sup> from squaric acid and stannic chloride in methanol and subsequent treatment with tetrabutylammonium chloride in ether. It again shows the bridging capacity of squarate as a ligand.



Dithiosquarate **193**, in contrast to squarate, has good chelating properties, as was recently again proved by the isolation of the copper<sup>141,142</sup> and palladium<sup>142</sup> complexes **199**.

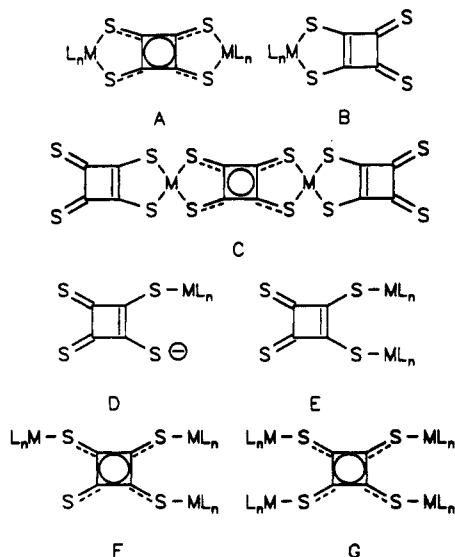


One of these studies<sup>142</sup> was concerned with the structural properties of **199**. An X-ray and ESR analysis showed that the voluminous cation precluded inter-stack interactions. Tetrathiosquarate **101** forms a lot of monochelating, bridging bis(chelating), and mono- to four-fold monodentate complexes. Its coordination chemistry, which was intensively studied by W. Beck's group,<sup>143-145</sup> resembles very much that of dithiolates, tetrathiooxalate, and tetrathiomolybdate.

Scheme 68 lists all the possible coordination modes A-G for **101**. For all of them, examples have been prepared.<sup>143-145</sup>

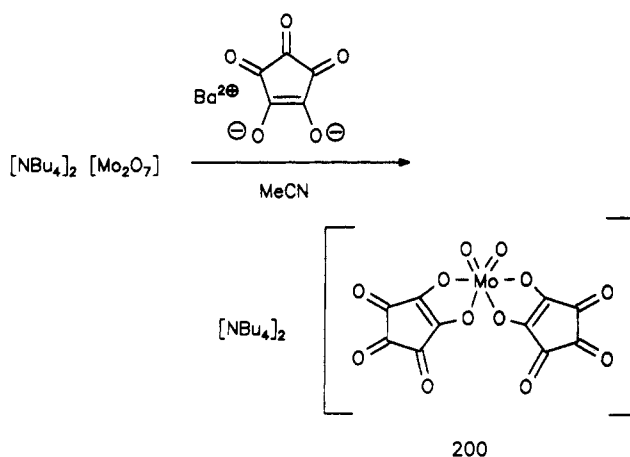
Some of these complexes have been found to be of interest because of their electrical conductivity properties. In that, they are comparable to "metal dithiolenes".<sup>146,143</sup> This is why there was also a report<sup>147</sup> on the LAXS and EXAFS investigation of (among others) the poly(nickel tetrathiosquarate),  $[\text{Ni}(\text{C}_4\text{S}_4)\text{K}_{0.15}]_n$ .<sup>143</sup> In this complex, tetrathiosquarate indeed acts as a bis-

Scheme 68

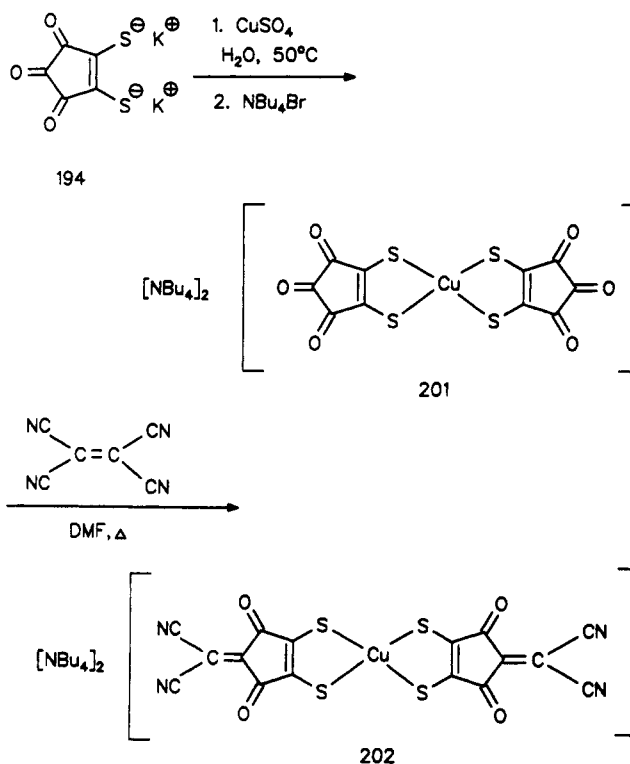


$\text{ML}_n = (\text{e.g.}) \text{Mn}(\text{CO})_4, \text{Rh}(\text{CO})_2, \text{Ir}(\text{COD}), \text{W}(\text{CO})_3(\text{C}_5\text{H}_5),$   
 $\text{Ni}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2), \text{Ni}(\text{C}_5\text{H}_5\text{N})_2, \text{Zn}(\text{II}), \text{GePh}_3, \dots$

Scheme 69



Scheme 70



chelating ligand on two metal atoms. The resulting coplanar parallel polymer chains are located in parallel planes.

In contrast to squarate, croconate formed a bischelating complex **200** with molybdate(VI). Scheme 69 gives the recent preparation of **200**.<sup>148</sup>

Dithiocroconate **194**, like dithiosquarate, reacted with cupric sulfate to give the 2:1 chelate complex **201** that was further transformed—in what is a piece of true pseudooxocarbon chemistry—to the dicyanomethylene analogue **202** (Scheme 70).<sup>149</sup>

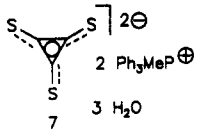
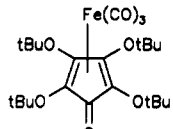
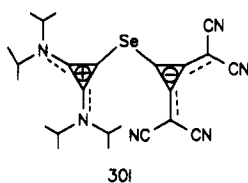
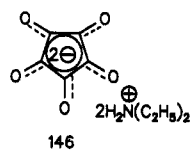
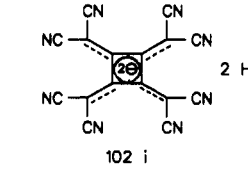
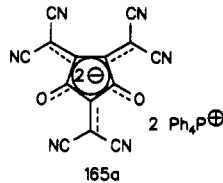
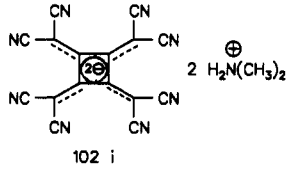
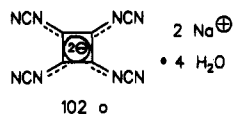
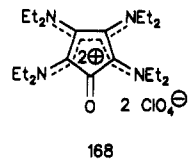
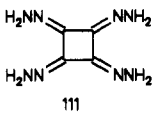
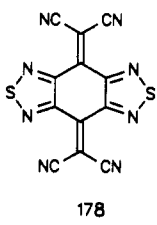
## VIII. Physicochemical Studies

### A. X-ray Diffraction

Since in many cases oxocarbons are symmetrical and possess few or no hydrogen substituents attached to their core, X-ray diffraction was an indispensable means for establishing structures because otherwise there

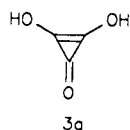


Table 4. Oxocarbons for Which X-ray Diffractions Were Reported (Treated in Previous Sections)

	ref, section of this review		ref, section of this review
	23, II.A.2		116, IV.A
	20, II.A.2		117a, IV.A
	65, III.A.2c		125, IV.B
			
	66, III.A.2c		126, IV.B
	75, III.A.3		129c, V

would have been negative proof only from the lacking of certain structural elements in spectroscopy. For matters of convenience, several X-ray studies were already mentioned in the preceding chapters, together with the synthesis of the respective compound. Therefore we will now give a list (Table 4) of the derivatives for which an X-ray diffraction was published and refer the reader to the pertinent chapter of this review for further detail. This will be followed by a short discussion of some structural studies not mentioned before.

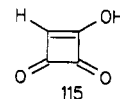
A structural determination of deltic acid 3a was published in 1987.<sup>150</sup> For a long time after the first synthesis of this compound in 1976, because of stability and crystallization problems there had been vibrational analyses only (see below). In the crystal, the molecules



of 3a have  $C_{2v}$  symmetry and are tied together in strings in a "dimeric" fashion resembling the well-known dimeric carboxylic acid units, but with each carbonyl group accepting two equivalent, strong hydrogen bonds which are almost linear. Although the molecular geometry clearly is that of 2,3-dihydroxycyclopropen-

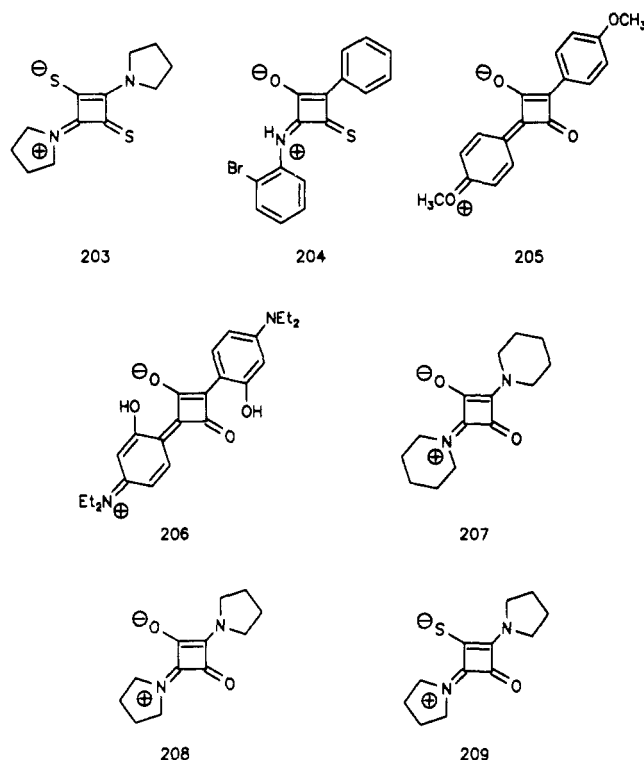
1-one, the covalent bond lengths in deltic acid show a remarkable degree of conjugation: compared with squaric acid, both the C—O (130.1 pm) and C=O (126.5 pm) bonds have been enlarged and the difference in bond lengths between the C—C and C=C bonds is rather small (2.4 nm). From this and from a comparison with data of cyclopropenes,<sup>151</sup> the authors conclude that there may be significant contributions from dipolar and cyclopropylum resonance forms to the deltic acid structure in the solid state.

The same authors (who before had also investigated the structure of squaric acid<sup>152</sup>) undertook an X-ray structure analysis of semisquaric acid (moniliformin, 115).<sup>153</sup> In the crystal, hydrogen bonding between the molecules occurs between the two groups arranged oppositely along a diagonal of the molecule.

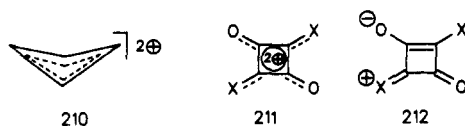


Its length has an average value of 254.3 pm, comparable to that found in squaric acid (254.9 pm),<sup>152</sup> but definitely shorter than the standard value (264 pm) for carboxylic acids. The conjugation in the molecules seems to be concentrated in the alternating bond system linking the hydrogen-bond donor and acceptor groups.

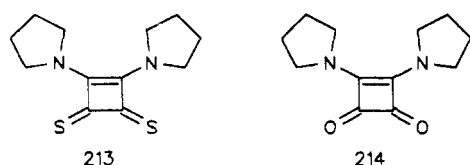
The structures of the squaraines **203**,<sup>154</sup> **204**,<sup>155</sup> **205**,<sup>156</sup> **206**,<sup>157</sup> **207**,<sup>158</sup> **208**,<sup>159</sup> and **209**<sup>159</sup> were reported. These



compounds all have a planar skeleton and do not exhibit the ring puckering expected<sup>160</sup> for a cyclobutadiene dication **210**. This is again evidence that squaraines should be represented by a mesoionic, e.g. **212**, rather than a dicationic structure, e.g. **211**.



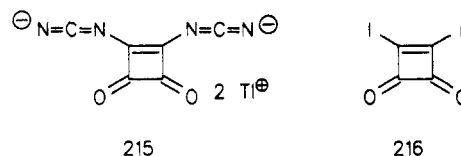
Both experimental and theoretical evidence indicated the presence of considerable C-X  $\pi$ -bonding but only a small amount of C-C  $\pi$ -bonding in the squaraine system.<sup>158,159</sup> The length of the C-C bonds is hardly influenced by the nature and charge of the substituents, as was substantiated by the diffraction analyses of the squaric amides **213**<sup>154</sup> and **214**,<sup>159</sup> isomers of the squaraines **203** and **208**.



In contrast to squaraines, in these amides the exchange of sulfur for oxygen causes a marked alteration of the structural parameters so that for **214** the representation as a cyclobutenedione was considered best, whereas in **213** a bis(thiolate) structure seems to participate considerably in the ground state.<sup>159</sup>

Another study determined the crystal structure of the dithallium salt of 1,2-bis(cyanimino)cyclobutenedione (**215**) and of 1,2-diiodocyclobutenedione (**216**).<sup>161</sup>

The representation given in formula **215** seemed to be the most important because it accounted for the principal geometric features. The uncharged species **216** exhibits less pronounced delocalization but more deformation of the C<sub>4</sub> ring into a trapezium because of  $\sigma$ -bond strain.



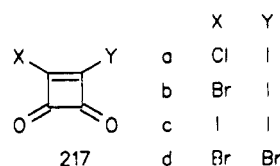
## B. Vibrational Analyses

Since up to 1987 there was no X-ray diffraction of deltic acid or of a deltate (still not!), several vibrational analyses and force field calculations were concerned with the structure and bonding of this oxocarbon. Vibrational investigations on oxocarbon dianions done before 1980 were reviewed in Chapter 7 of the monograph on oxocarbons.<sup>2</sup>

West and co-workers<sup>162</sup> recorded and analyzed the infrared and Raman spectra of dilithium and dipotassium deltate. The results confirmed  $D_{3h}$  symmetry for **3a**. Normal coordinate analyses in both modified valence force field and Urey-Bradley models gave C-C and C-O stretching force constants which are consistent with increased C-C and decreased C-O bond orders compared to those in larger ring oxocarbon anions. This finding is inconsistent with theoretical considerations—presented in the following section—that of the oxocarbon dianions, only deltate should be considerably “aromatic”.

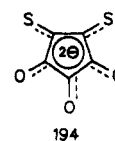
Two other papers<sup>163,164</sup> reported the vibrational spectra and valence force field calculations of deltic acid **3a** itself and of its dideuterated derivative. Essentially, their results were confirmed by the X-ray analysis of **3a** (see previous section).

A vibrational analysis of the 1,2-dihalocyclobutenediones (**217**) was aimed at the assessment of the force field of the cyclobutene-3,4-dione fragment.<sup>165</sup> From



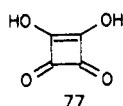
the infrared spectra in solution and as isooriented polycrystalline films in polarized radiation, a planar force field for all dihalocyclobutenediones not containing fluorine was proposed. The electron diffraction data<sup>166</sup> of gaseous 1,2-dibromo-cyclobutenedione (**217d**) also complied with a planar molecule of  $C_{2v}$  point group symmetry.

The degree of delocalization in oxocarbon anions has always been a point of great interest. The delocalized nature of the chromophore of dithiocroconate **194** was indicated by the fact that in a resonance Raman



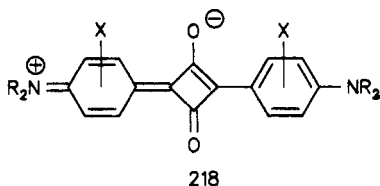
experiment, excitation at 465 nm caused the enhancement of virtually all the observed modes.<sup>167</sup> Still, as was to be expected, a comparison of the Raman frequency values for croconate and dithiocroconate revealed that for the latter, electron delocalization is not as symmetrical as in the former.<sup>167</sup>

Lastly, a recent Raman and IR study<sup>168</sup> of squaric acid **77** (with various contents of deuterium) should be mentioned. The authors monitored the vibrational spectra in a pressure range between 0 and 44 kbar, looked for symmetry changes and dielectric phase transitions, and determined the temperature dependence of the dielectric constant. Earlier work on the phase transition and dielectric properties of squaric acid was reviewed in Chapter 8 of the monograph on oxocarbons.<sup>2</sup>



### C. Electronic Spectra

Squaraines, e.g. **218**, exhibit a panchromatic (400–1000 nm) intense absorption in the solid state, but very sharp visible absorption in solution.<sup>169</sup> These features have made them very attractive for various optical applications in industry, as will be reviewed in the last chapter.



The ground-state and the excited-state electronic structures of **218** were studied using MNDO and CNDO semiempirical approximations.<sup>170</sup> The authors showed that the electronic distribution of **218** is highly polarized, with the anilino moiety being an electron donor (D), and the central C<sub>4</sub>O<sub>2</sub> unit being an electron acceptor (A). The localized charges at the nitrogen, the oxygen, and the central C<sub>4</sub>O<sub>2</sub> unit in the ground state are approximately −0.4 e, −0.35 e, and +0.37 e, respectively. They further showed that there is a charge transfer (CT) during the S<sub>0</sub> → S<sub>1</sub> transition, but that the CT is primarily confined in the C<sub>4</sub>O<sub>2</sub> unit. MO calculations suggest that both S<sub>0</sub> and S<sub>1</sub> states of the squaraines **218** are intramolecular D-A-D CT states.

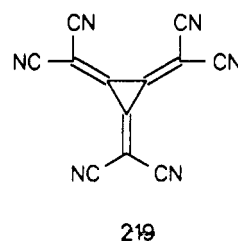
The effect of this symmetric D-A-D arrangement on the general spectroscopic properties of intramolecular CT states is an interesting subject, and another investigation reported and discussed the absorption and the fluorescence emission spectra of a number of squaraines **218**.<sup>171</sup> Small bathochromic shifts of the

sharp and intense absorption in the red in dichloromethane solution primarily originated from the minor involvement in the electronic transition of the D moiety in a solute-solvent complex. In the fluorescence spectra, multiple emission was observed. This is due to the formation of excited states of free squaraines, of solute-squaraine complexes, and of a twisted relaxed excited state.

### D. Electrochemical Behavior

Oxocarbons may be anionic, cationic, or neutral (radialenes). Scheme 71 outlines the possible equilibria.

The accessibility of any of these forms of course depends on the nature of the substituent X, viz. its electron-donating and -accepting ability. In the sections of this review dealing with synthesis, quite a number of dianions (examples of state E), some dications (A), but only a few radialenes (C) were introduced. For electron-withdrawing substituents X (e.g. O, NCN, C(CN)<sub>2</sub>), the respective radialenes are expected to be strong Lewis acids. This behavior was indeed proved for the tris(dicyanomethylene)cyclopropane (**219**) because it served as the acceptor component of charge-transfer complexes.<sup>172</sup> **219** was first spectroscopically characterized, but not isolated by Fukunaga in 1976.<sup>14</sup> Its redox behavior was determined by himself, by Breslow,<sup>172b</sup> and in our laboratories.<sup>173</sup>



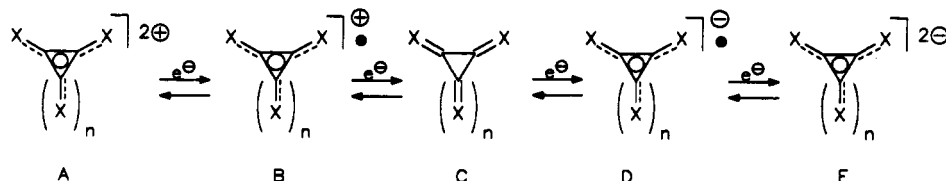
Of the three pertinent oxidation states C, D, and E (X = C(CN)<sub>2</sub>, n = 1), Fukunaga isolated salts of the anions D and E and observed incompletely reversible redox behavior. In our group,<sup>173</sup> we essentially confirmed his findings, but not his potentials. We instead confirmed the ones Breslow<sup>172b</sup> published.

With substituents X that are equally capable of donating or accepting electrons, all five oxidation states (A–E) were observed, for example the case of the cyclic tetrahydrazone **220** of squaric acid.<sup>174</sup> Scheme 72 depicts the redox equilibria. The potentials were determined by dc, ac, and cyclic voltammetry. K<sub>SEM</sub>, the formation constant of the semiquinone form, was defined by the fraction, [SEM]<sup>2</sup>·[RED]<sup>−1</sup>·[OX]<sup>−1</sup>.

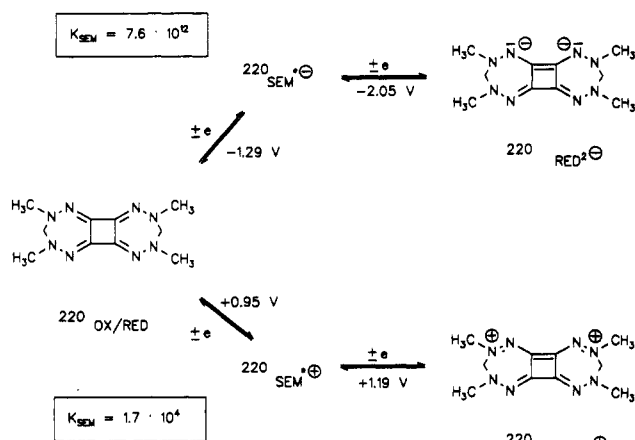
In contrast to **220**, which reacted as a four-step redox system, the tetraaza[4]radialenes **221** and **114** could only be reduced in two steps (Scheme 73).<sup>174</sup>

The aforementioned study<sup>173</sup> from our group remains to be the broadest investigation of the redox behavior

Scheme 71



Scheme 72



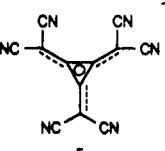
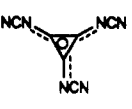
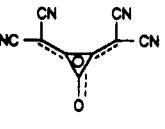
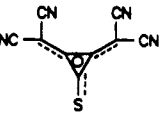
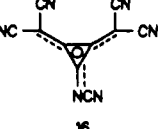
of oxocarbons. For about 20 cyanoimino- and dicyanomethylene-substituted pseudooxocarbon dianions, cyclic voltammograms were recorded in dry, oxygen-free acetonitrile. The conducting salt was tetrabutylammonium perchlorate; in most cases, the dianions were employed as their tetraphenylarsonium or -phosphonium salts. The measurements were performed using a glass-carbon working electrode, a platinum counter electrode, and a standard calomel reference electrode. Table 5 lists the standard potentials  $E^\circ$  (arithmetic means of the cathodic and anodic potentials), formation constants  $K_{SEM}$  of the semiquinone form, and the ratio of peak currents  $i_a/i_c$  ( $a$  = anodic,  $c$  = cathodic) of  $C_3$  pseudooxocarbons investigated.

All the compounds could be oxidized in two electrochemically reversible steps. The potentials increase in the order  $S < O < C(CN)_2 < NCN$ . The sulfur-substituted derivative 15 did not exhibit chemical reversibility which is probably due to the oxidative formation of the corresponding disulfide, which was also prepared chemically and isolated<sup>18</sup> (see section II.A.2). Only the tris(dicyanomethylene) derivative 5 (see above) and the mixed substituted iminocarbon 16 showed chemical reversibility for both steps.

Table 6 lists the results obtained for  $C_4$  pseudooxocarbon dianions.

It deserves special mention that West and Blinka<sup>175</sup> also investigated the derivatives 102f and 102i, but

Table 5. Cyclic Voltammetry of  $C_3$  Pseudooxocarbons

compd	$E^\circ_1$ (mV)	$E^\circ_2$ (mV)	log $K_{SEM}$	$i_a/i_c$ (1st step)	$i_a/i_c$ (2nd step)
	385	1175	13.4	1.00	1.19
	505	1380	15.6	1.51	not ana- lyzable
	205	1020	13.6	0.90	1.87
	200	950	12.7	1.61	not ana- lyzable
	480	1270	14.6	1.01	0.97

published potentials quite different from ours. They did not observe, e.g., the second step of the oxidation of 102i, which in our opinion is a very surprising finding. For every derivative listed in Table 6, we found two oxidation steps with electrochemical reversibility, but we did not find complete chemical reversibility for any of them. The monosubstituted compounds 102e and 102i also showed a third anodic peak at potentials 1260 and 1584 mV. Both in the dicyanomethylene and the cyanoimino series there is a linear correlation between the degree of substitution and the potentials of the first and of the second oxidation step. The formation constants of the semiquinones (radical anions) decrease

Scheme 73

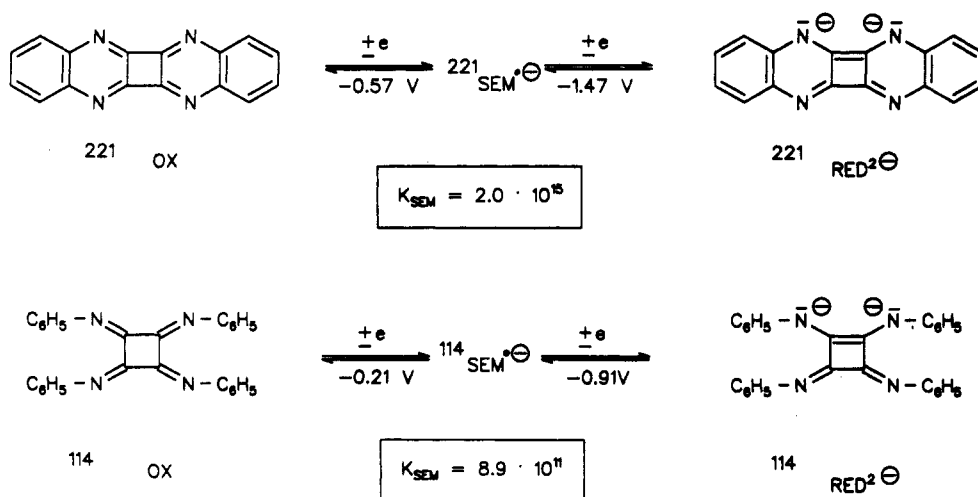
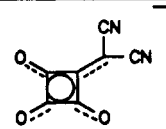
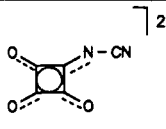
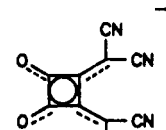
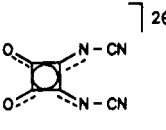
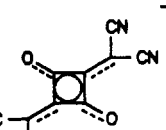
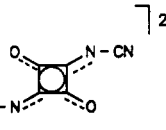
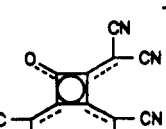
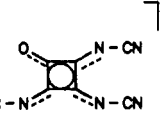
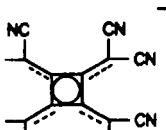
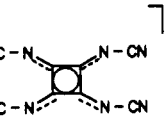


Table 6. Cyclic Voltammetry of C<sub>4</sub> Pseudooxocarbons

compd	$E^{\circ}_1$ (mV)	$E^{\circ}_2$ (mV)	$\log K_{SEM}$	$i_a/i_c$ (1st step)	$i_a/i_c$ (2nd step)	compd	$E^{\circ}_1$ (mV)	$E^{\circ}_2$ (mV)	$\log K_{SEM}$	$i_a/i_c$ (1st step)	$i_a/i_c$ (2nd step)
	91	977	15.0	1.11	1.97		167	1025	14.5	1.10	2.35
102e						102l					
	255	1047	13.4	1.00	1.50		375	1204	14.1	1.12	1.40
102f						222					
	251	1103	14.4	1.33	1.29		370	1233	14.6	1.00	1.34
102g						102m					
	370	1110	12.3	0.99	1.01		544	1351	13.7	1.21	1.39
102h						102n					
	415	1035	10.5	0.95	1.13		696	1470	13.1	1.00	1.18
102i						102o					

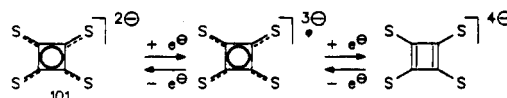
with increasing substitution of oxygen for C(CN)<sub>2</sub> or NCN, more pronouncedly in the latter case. Indeed, the radical anion of **102f** was isolated previously.<sup>176</sup>

From the cyclic voltammograms of the C<sub>4</sub> pseudooxocarbons of Table 6 we conclude that the eventual isolation of a C<sub>4</sub> radialene of these is doubtful; the voltammograms indicated that some secondary reaction occurred after reaching the radialene form.

The general trend of our results is in accordance with the values Doane and Fatiadi<sup>177</sup> found for dicyanomethylene-substituted croconates. Table 7 lists the potentials of the waves they determined by cyclic voltammetry. (It should be kept in mind that Fatiadi assumed that in **165a** the dicyanomethylene groups were adjacent to each other, but we later proved **165a** to be the correct structure, see section IV.B.)

In their papers,<sup>177a,b</sup> they also found two electrochemically reversible one-electron transfers. The disproportionation constants were quite small for all the croconate radical anions investigated. Like us, they noticed that the second oxidation process was accompanied by secondary reactions.

For the sake of completeness we would like to mention that Beck and co-workers<sup>143</sup> noted the polarographic reduction of tetrathiosquarate **101** to its tetraanion in two steps ( $E_1 = -1.53$  V,  $E_2 = -1.79$  V in aqueous solution). This was not possible for squarate.<sup>178</sup>



In conclusion we would like to point out that all the electrochemical investigations reviewed were of an analytical nature. They did not lead to the isolation of the oxidation or reduction products, but only to the spectroscopic characterization of a few of them. Synthetic work in this field remains to be done.

## E. ESR Investigations

In connection with the synthesis and electrochemistry (see the previous section) of C<sub>4</sub> and C<sub>5</sub> pseudooxocarbons substituted with dicyanomethylene, West and co-worker<sup>175</sup> and Fatiadi and Doane<sup>177a</sup> carried out ESR measurements.

The ESR spectrum<sup>175</sup> of **223** exhibited the 17-line pattern expected for eight equivalent nitrogens ( $\alpha(^{14}\text{N})$ )

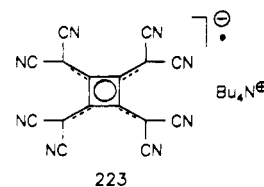
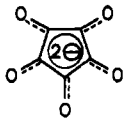
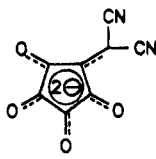
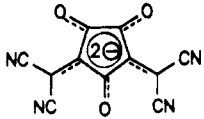
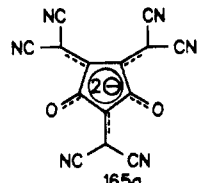
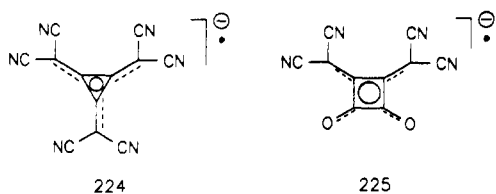


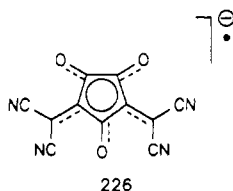
Table 7. Cyclic Voltammetry of  $C_5$  (Pseudo)oxocarbons

compd	$E^\circ_1$ (mV)	$E^\circ_2$ (mV)
	230	470
146		
	330	690
164		
	440	860
162		
	540	970
165a		

= 1.06 G), and one set of  $^{13}\text{C}$  sidebands ( $a(^{13}\text{C}) = 22.5$  G), with  $g = 2.00398$ . The  $^{14}\text{N}$  coupling of **223** is comparable to that found in the related compounds **224** and **225**. From spin density calculations it was concluded that about 80% of the odd electron density is exo to the ring. The radical anion **226** was generated



by electrochemical oxidation. Its ESR spectrum<sup>177a</sup> exhibited a nine-line pattern ( $a(^{14}\text{N}) = 5.2$  G), expected for coupling with four equivalent nitrogens. Its half-life was about 100 min.



### IX. Theoretical Studies

In 1960, West and co-workers expressed their view that monocyclic oxocarbon dianions of general formula  $C_nO_n^{2-}$  might represent a new class of aromatic substances.<sup>179</sup> This has been the subject of much discussion, and several theoretical studies were concerned with the question of whether the oxocarbon dianions are really aromatic. According to West,<sup>2,3c,179</sup> evidence supporting the aromaticity was provided by a study of their vibrational spectra which show that they have

Table 8. Resonance Energies of Oxocarbons (from Ref 181)

Resonance Energies of the Neutral Oxocarbons			
species	resonance energy, <sup>a</sup> $\beta$		
	$h = 1.0,$ $k = 0.8$	$h = 0.2,$ $k = 1.6$	$h = 0.22,$ $k = 0.99$
$C_3O_3$	0.197 (0.066)	0.015 (0.005)	0.050 (0.017)
$C_4O_4$	-0.016 (-0.004)	-0.023 (-0.006)	-0.070 (-0.017)
$C_5O_5$	-0.035 (-0.007)	-0.001 (-0.000)	-0.009 (-0.002)
$C_6O_6$	-0.008 (-0.001)	0.001 (0.000)	0.008 (0.001)
$C_7O_7$	0.003 (0.000)	0.000 (0.000)	0.002 (0.000)
$C_8O_8$	0.002 (0.000)	-0.000 (-0.000)	-0.001 (-0.000)
Resonance Energies of the Oxocarbon Dianions			
species	resonance energy, <sup>a</sup> $\beta$		
	$h = 1.0,$ $k = 0.8$	$h = 0.2,$ $k = 1.6$	$h = 0.22,$ $k = 0.99$
$C_3O_3^{2-}$	0.338 (0.113)	0.159 (0.053)	0.147 (0.049)
$C_4O_4^{2-}$	0.060 (0.015)	0.057 (0.014)	-0.017 (-0.004)
$C_5O_5^{2-}$	0.013 (0.003)	0.050 (0.010)	0.025 (0.005)
$C_6O_6^{2-}$	0.025 (0.004)	0.037 (0.006)	0.031 (0.005)
$C_7O_7^{2-}$	0.027 (0.004)	0.026 (0.004)	0.019 (0.003)
$C_8O_8^{2-}$	0.021 (0.003)	0.020 (0.002)	0.012 (0.001)

<sup>a</sup> Values in parentheses are resonance energies per unit structure.

symmetric  $D_{nh}$  structures and large delocalization energies.<sup>162</sup> However, others<sup>180</sup> pointed out that this alone cannot be used as a measure of aromatic stabilization, but the aromaticity index of a cyclic conjugated system must be related to some thermodynamic stability estimated relative to an appropriate olefinic reference structure.<sup>181</sup>

A graph-theoretical approach to aromaticity has been advanced.

Trinajstić and co-workers<sup>182</sup> have defined a topological resonance energy. Aihara<sup>181</sup> extended this method to oxocarbons. He calculated resonance energies of the neutral oxocarbons  $C_nO_n$  and the oxocarbon dianions  $C_nO_n^{2-}$  (Table 8; for comparison, his resonance energies for benzene are  $0.273 \beta$  and for fulvene,  $0.020 \beta$ ). His values predict the deltate ion alone to be aromatic. He also calculated diamagnetic susceptibilities of these systems, again reaching the conclusion that only the deltate ion is diatropic and aromatic.

In his bond order approach to ring current and aromaticity, Jug,<sup>183</sup> although he is generally in doubt about Aihara's approach, for the oxocarbon dianions also states that no aromaticity is expected for rings with six or more atoms, and that the aromaticity decreases rapidly with increasing ring size. He defined the minimal bond order in a ring system in its equilibrium as an index of aromaticity based on ring current. He calculated the ring current index to be 1.501 for deltate, 1.390 for squarate, and 1.332 for croconate, so that in his model, these three should be considered "moderately aromatic".

However, West's original proposal that oxocarbon dianions are aromatic not only rests on the symmetry shown from vibrational spectra, but also on the great stability of the anions, shown from the large dissociation constants for the corresponding acids (ref 2, Chapter 3). The acid dissociation constants are markedly greater than expected for diketone diols without cyclic delocalization. Moreover, the moderately large diamagnetic anisotropy of the croconate dianion provides evidence

for a ring current in this anion (ref 2, Chapter 1). Finally, the excited states of oxocarbon dianions were studied (ref 2, Chapter 5). The observed absorption and MCD (magnetic circular dichroism) spectral patterns were found to be in accordance with expectations from a classic perimeter model, again indicating that the oxocarbon dianions should be regarded as aromatic according to several viewpoints.

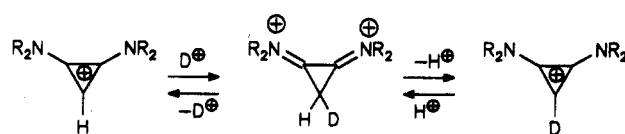
Ha and Puebla published two papers on the quantum chemical study of the cyclic oxocarbon dianions, one of them concerned with ground states,<sup>184a</sup> the other one with electronically excited states.<sup>184b</sup> They were also interested in the question of aromaticity in the oxocarbon family. From their systematic study of the ground state by the semiempirical MNDO and *ab initio* methods, they conclude that this question cannot be answered in a definitive form. They compared the C-C and C-O bonds in the oxocarbon dianions, calculated the vibrational frequencies and force constants employing optimized geometries, and studied molecular electronic structures in terms of LMO and PMO analysis. The two electrons of the double charge were shown to be delocalized. The interaction between the oxygen and carbon atoms increases strongly in going from deltate to squarate, but more smoothly as the ring size continues to increase. The C-C bonds have double bond character in all members of the series. All this agrees with the suggestion of the existence of resonance structures, and so does their calculation of the ring current anisotropy. They further calculated the quadrupole moment and the electric field gradient for oxygen.

The electronic spectra they studied<sup>184b</sup> by the *ab initio* SCF-CI and CNDO/S methods. The excited energies for the singlet-singlet transitions compared well with the available experimental values; the energies for the singlet-triplet transitions for the deltate and squarate dianions also compared well.

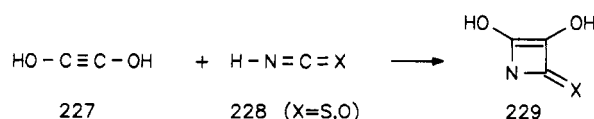
The same authors carried out a similar study for deltate and squaric acids in which they started with optimizing their geometries using a split-valence 4-31G basis set.<sup>184c</sup> Contrary to previous STO-3G calculations,<sup>185</sup> the (*Z,Z*) rotamer of squaric acid was predicted to be the most stable, likewise—in accordance to the previous publication<sup>185</sup>—for deltate acid. They further determined IR frequencies from the *ab initio* harmonic force field and calculated the dipole moment, quadrupole moment, and electric field gradient for oxygen. The crystal structure of deltate acid, published later<sup>150</sup> (see section VIII.A), corresponds better with the model proposed by Lautie and co-workers<sup>163,164</sup> (see section VIII.B) than with Puebla and Ha's predictions.

Leaving the subject of the structure and aromaticity of the oxocarbons, we mention two theoretical studies concerned with reactions involving them. Clark and Weiss<sup>186</sup> showed by *ab initio* molecular orbital theory that electrophilic attack by a proton on the cyclopropenium ion involves a planar tetracoordinate carbon atom. The process is, however, strongly endothermic, and the protonated cyclopropenium ion ring opens without activation energy. In the case of a diamino-substituted cyclopropenium ion, the protonated ion is highly stabilized by charge delocalization to nitrogen, so the calculations predict direct C protonation to occur preferentially (Scheme 74). (See also Scheme 16,

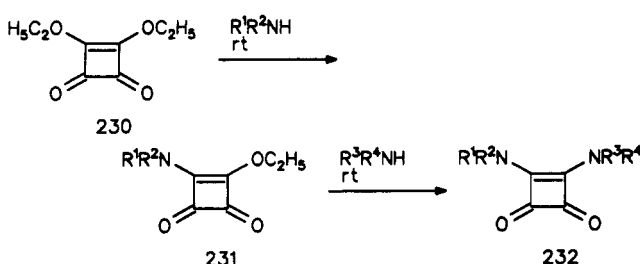
Scheme 74



Scheme 75



Scheme 76



section II.A.3, for the related reaction of a pseudosemi-deltate.<sup>36,186</sup>)

A model theoretical study was concerned with an unknown [2 + 2]-cycloaddition leading to the unknown aza analogues 229 of squaric acid (Scheme 75).<sup>187</sup>

The reaction of dihydroxyethyne (227), as a model of its stable di-*tert*-butyl ester, with the heterocumulenes 228 to give the four-membered rings 229 was investigated by the MNDO method.

Lastly, a paper on dimerization and stacking in transition-metal bis-dithiolenes and -tetrathiolates reports a band structure calculated for a nickel-tetrathio-squarate ribbon.<sup>188</sup> The d bands are full, and the conduction bands were shown to be formed by the *e* ( $\pi$ ) orbitals of the ligand, split due to their interaction with the metal d orbitals.

A theoretical study concerned with the geometries of the cyclo[*n*]carbons C<sub>6</sub>O<sub>6</sub> 181 and C<sub>6</sub>S<sub>6</sub> 185 was already discussed in section V.

## X. Applications

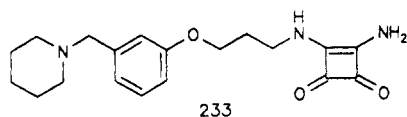
Of the various oxocarbons, only squaric acid derivatives have found application during the time of review, viz. squaric acid diethyl ester as a coupling reagent for biopolymer conjugates, squaric diamides as constituents of H<sub>2</sub> antihistaminic and antibiotic drugs, squaric dibutyl ester as a contact allergen, and squaraines because of their photoconductive properties.

The recent use of diethyl squarate in biochemical research shall be considered first. There is a great need for the development of new mild coupling procedures to immobilize enzymes or to bind pharmacologically active molecules to polymer carriers. Tietze and co-workers<sup>189</sup> developed a mild coupling procedure of diethyl squarate 230 with two amines, resulting in the sequential formation of the ester amides 231 and the diamides 232 (Scheme 76).

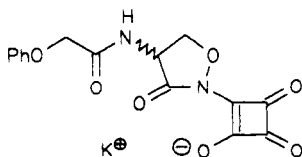
This is another example (cf. section III.B) of the fact that the two similar groups of squaric acid derivatives may be distinguished: the substitution of just one ester group was carried out selectively. The reaction could

also be performed in a buffered aqueous solution (pH 7). Tietze aims for the construction of selective anti-cancer agents,<sup>190</sup> using acid labile acetal glycosides. If these are immobilized onto a carrier to give a neoglycoprotein, the carbohydrate moieties of the carrier will help in directing these compounds to certain types of organs and hopefully also to the tumor. With diethyl squarate as the coupling reagent, Tietze, Gabius, and co-workers<sup>191</sup> prepared a conjugate of the disaccharide *p*-(aminophenyl)-2-acetamido-2-deoxy-3-*O*- $\beta$ -D-galactopyranosyl- $\beta$ -D-galactopyranoside (reacting with the *p*-aminophenyl group) and bovine serum albumin (reaction with a lysyl  $\epsilon$ -amino group). The obtained neoglycoprotein with T-antigen structure was used for glyco cytological and glyco histochemical studies with tumor cells.<sup>191</sup> Its efficiency was similar to a probe delivered by conventional methods. In another paper,<sup>192</sup> this neoglycoprotein and several others were biotinylated and used for the histochemical determination of the expression of sugar receptors (lectins) in primary and secondary lesions of colorectal adenocarcinoma cells. The squaric bisamide conjugate differed only quantitatively from the other conjugates in its capacity to detect specific binding on the cells; thus squaric acid diethyl ester proved to be a useful coupling reagent in these investigations that are aimed at the unraveling of recognition processes within the metastatic cascade.<sup>193</sup>

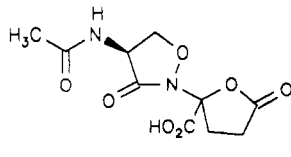
Scientists of Bristol-Myers Co. found that several squaric diamides inhibit H<sub>2</sub> receptors.<sup>194,195</sup> A compound **233** called BMY 25368 showed the strongest effect. The preparation of constituent cyclobutenedione (alkyl)amides was patented by Smith, Kline and French Laboratories.<sup>196</sup>



Another recent contribution from medicinal chemistry (Bristol-Myers Squibb Co.) reported that the enantiomeric (phenoxyacetyl)-L-cycloserines (**234**), activated by a cyclobutenedione moiety, have antibacterial activity.<sup>197</sup> They are analogues of the new lactam antibiotic, lactivicin (**235**). The squarate residue may be regarded as an expanded carboxylate moiety. Unfortunately, they proved to be hydrolytically unstable, just like lactivicin itself.



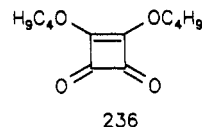
234



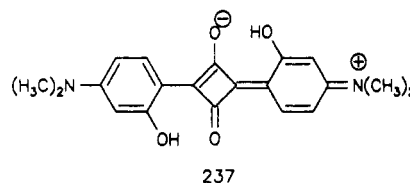
235

Squaric acid dibutyl ester (**236**) was found not to be mutagenic; so due to its potency as a contact allergen, it was tested with some success against alopecia areata.<sup>198</sup>

The photoconductivity of squaraines such as **237** has been known for some time.<sup>199</sup> These cyanine-like dyes are useful for xerographic diode laser (780 nm) printers.<sup>200</sup>

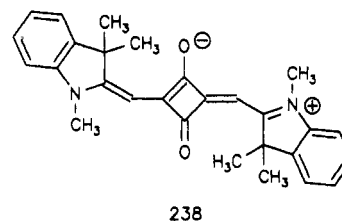


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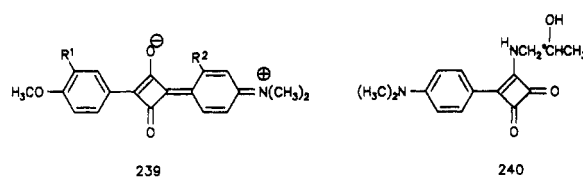
237

Owing to the continuing interest in materials for photovoltaic devices, research in this field has been fruitful. There were reports on the crystal structure analysis<sup>201</sup> of the indolinyl squaraine **238** and on high-pressure syntheses of related dyes.<sup>202</sup>



238

Scientists of the Xerox Corporation also showed unsymmetrical squaraines of type **239** to be sensitive in the near-IR region (564–592 nm,  $\lambda_{\text{max}} = 5.1\text{--}5.4 \text{ cm}^{-1} \text{ dm}^3 \text{ mol}^{-1}$ ) and published ways to synthesize them.<sup>203</sup> Another recent contribution<sup>204</sup> proved properly substituted cyclobutenediones, e.g. **240**, to be excellent electron acceptors for nonlinear optical materials.



239

240

Due to its chiral side chain, **240** crystallized non-centrosymmetrically, showed a high second harmonic generation intensity (64 times that of urea), and was proposed to be a suitable material for a highly efficient frequency doubler optical device.<sup>204</sup>

**Acknowledgments.** Our work on pseudooxocarbons was generously supported by grants from the Deutsche Forschungsgemeinschaft and from Fonds der Chemischen Industrie. G.S. heartily thanks his co-workers whose names appear in the references for their experimental and intellectual contributions. The authors thank Frau C. Cloos for outstanding secretarial assistance.

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