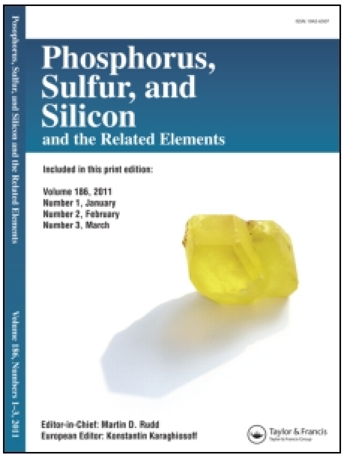

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Thioxocarbon Dianions $C_nS_2^{2-}$ and Other Sulfur-Containing Derivatives of Deltic and Squaric Acid

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THIOXOCARBON DIANIONS $C_nS_n^{2-}$ AND OTHER SULFUR-CONTAINING DERIVATIVES OF DELTIC AND SQUARIC ACID

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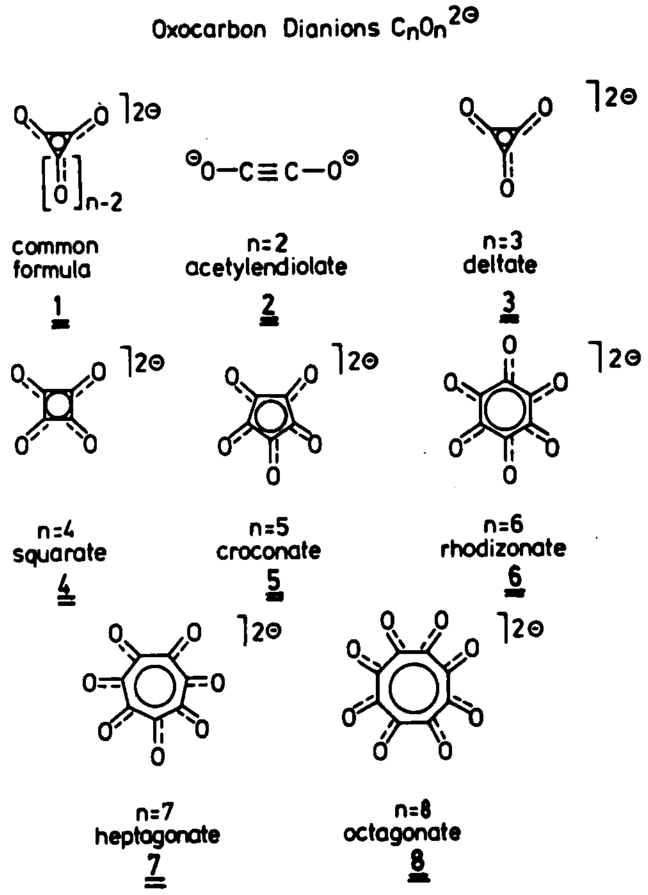
Abstract The earlier and more recent results obtained in the author's laboratory in the field of the C_4 and C_3 thioxocarbon dianions are presented. Several preparative routes, some of the interesting chemical reactions as well as relevant spectroscopic data of the dianion tetrathiosquarate $C_4S_4^{2-}$ are summarized and compared with those of other uniformly substituted C_4 pseudo-oxocarbon dianions. Concerning the C_3 series, syntheses of novel sulfur-bridged three-membered ring compounds such as dication sulfides, thiocarbonyl-ylides and dianion sulfides are described. Finally, the first synthesis of the aromatic dianion trithiodeltate $C_3S_3^{2-}$ is reported, together with some spectroscopic data and an X-ray crystal structure determination.

INTRODUCTION

Recognition that the oxocarbons [1-2] were members of a class of hitherto unknown aromatic substances in the 1960's led to greatly renewed interest in this area. R.West, the University of Wisconsin defined them in the following way [2]:

> **"Oxocarbons are compounds in which all or most of the carbons are linked with each other in the form of carbonyl groups or in the form of hydrated carbonyl groups"**

Scheme 1



Scheme 2

Among the oxocarbons the monocyclic dianions are the most interesting. They represent a new series of polycarbonylated organic species with remarkable structural, chemical and electronic properties. They can be characterized by the common formula $C_nO_n^{2-}$ 1, in which n is any positive integer.[2k] (Scheme 2)

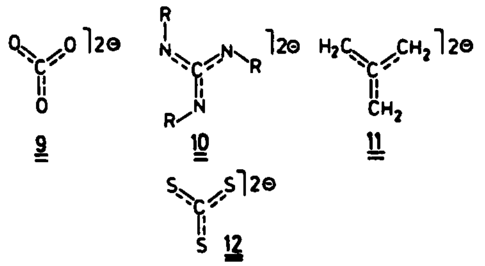
Croconate 5 and rhodizonate 6 are two well-known deeply coloured representatives of the class of oxocarbon dianions first prepared in the early nineteenth century.

Their constitution, however, was elucidated much later.[2k] The analogous three- and four-membered compounds, deltate 3[8] and squarate 4,[9] were synthesized only in recent years, the heptagonate 7 and octagonate 8 are hitherto unknown.[2k]

The oxocarbon dianions are often described as aromatic;[10] however, applying the graph theory of aromaticity, most of the monocyclic oxocarbon dianions were predicted to have very small resonance energies;[11] the planarity and cyclic conjugation of these dianions cannot be viewed as significant evidence of the existance of aromaticity: the deltate alone could be considered to be aromatic and highly diatropic.[11-13]

Nevertheless, the unique electronic structures, a high degree of symmetry and esthetically beautiful geometry of the oxocarbons, generated a fresh impetus to study the effect of replacing the carbonyl oxygen atoms by various other atoms or functional groups, such as nitrogen, sulfur, selenium, phosphorus and dicyanomethylene.[2n]

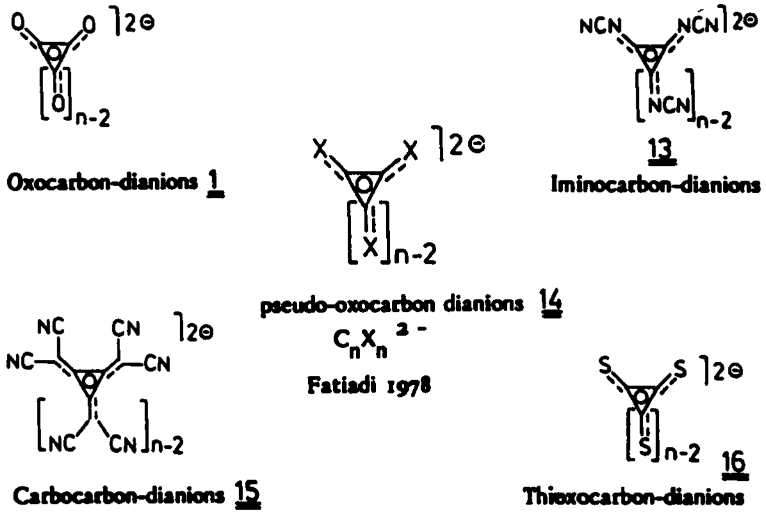
This idea originated from the observation that in the Y-delocalized carbonate dianion 9 the oxygen atoms can be completely replaced by nitrogen, carbon or sulfur to yield more or less stable salts with planar dianions 10-12 exhibiting D_{3h}-symmetry.[14-17] (Scheme 3)



Y-delocalized systems (P.Gund 1972)

Scheme 3

Similar transformations should be possible in the oxocarbon series leading to novel delocalized systems 14, which are called pseudo-oxocarbon dianions, following a suggestion of Fatiady.[18] Typical examples are the iminocarbon dianions 13 with the cyanoimino group,[19] the carbocarbon dianions 15 in which oxygen is replaced by the dicyanomethylene group[20], and the thioxocarbon dianions 16, the sulfur analogues of the oxocarbon dianions 1 (Scheme 4).

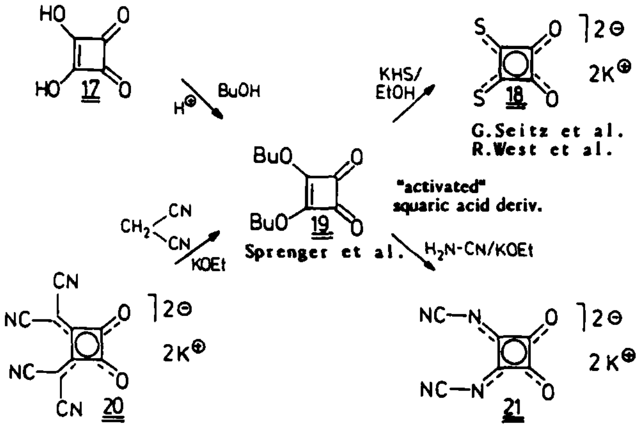


Scheme 4

RESULTS AND DISCUSSION

When planning effective syntheses of novel pseudo-oxocarbon dianions we remembered, that addition-elimination reactions of various nucleophiles proceed smoothly with cyclobutenediones bearing suitable leaving groups on the vinyl carbons.[2c]

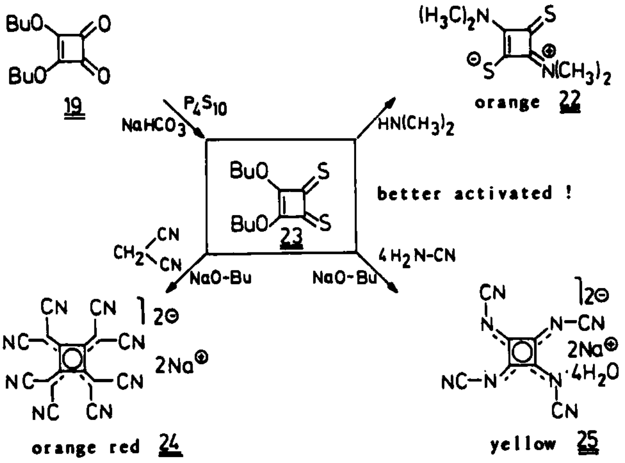
Using this reaction principle, West et al.[21b] and Seitz et al.[21e] reacted squaric acid dibutylester[19] - easily



Scheme 5

prepared by acid catalyzed esterification of squaric acid 17 with n-butanol[2c] - with freshly prepared potassium hydrogen sulfide in ethanol, and obtained the potassium salt 18 of the 1,2-dithiosquarate dianion. The base catalyzed reactions of the squaric acid dibutylester 19 with excess cyanamide and malononitrile, respectively, proceeded in an analogous fashion.[2c] Reaction products are the mixed oxo-iminocarbon dianions 21 and oxo-carbocarbon dianions 20. These non-uniformly substituted pseudo-oxocarbon dianions are easily accessible. However, the synthesis of the uniformly substituted highly symmetric species remained a particular challenge.

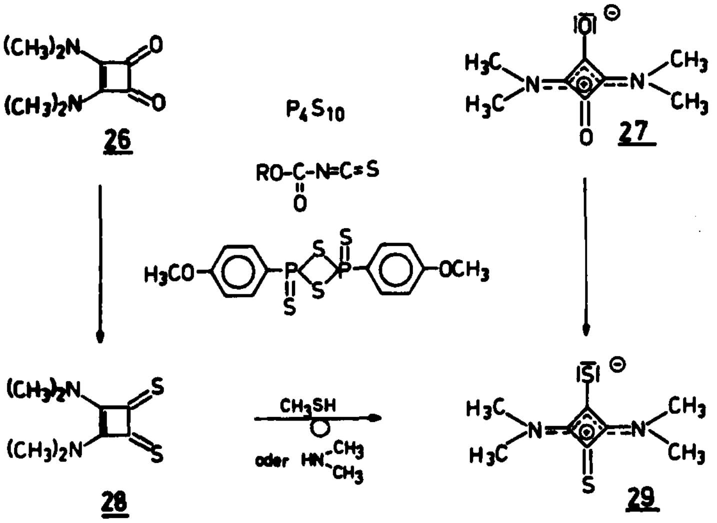
To reach this goal one of our most promising starting materials was the dithio squaric acid dibutylester 23, which can be prepared by reacting squaric acid dibutylester 19 with P_4S_{10}, in the presence of sodium hydrogen carbonate.[20d] This highly reactive squaric acid derivative fulfilled all our expectations (Scheme 6).



Scheme 6

Upon treatment of the dithioester 23 with dimethylamine, the nucleophilic displacement of the butoxy-substituents is accompanied by an unusual rearrangement.

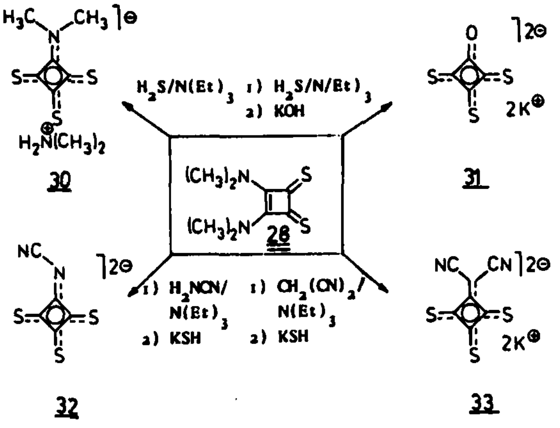
The only reaction product is the interesting bis(dimethylamino)dithiosquaraine 22, an intensely orange coloured compound.[22] Crossover experiments[23] gave evidence of an intermolecular mechanism for the rearrangement of the primarily generated 1,2-dithiosquaric acid diamide into the corresponding squaraine 22. With the anion of malononitrile as nucleophile, the highly activated dithioester 23 permits a complete exchange of substituents in only one step.[20c-d] Thereby the novel carbocarbon dianion 24 of the C_4-series was generated in good yield. Using cyanamide in the presence of an alkali metal alkoxide the first isolable, air-stable salt 25 of an iminocarbon dianion is formed in excellent yield.[19b] A similar reactivity is observed with the corresponding dithiosquaric acid diamides 28 and the diamino-dithiosquaraines 29. The exchange of sulfur for oxygen in squaric acid diamides 26 or bis(amino)squaraines 27 can be accomplished in high yield by the use of convenient sulfur transfer reagents such as P_4S_{10}, ethoxycarbonyl-isothiocyanate or with Lawesson's reagent.[24a-c] The thermodynamically more stable squaraines 29 can also be prepared in excellent yields by reacting the 1,2-dithiosquaric acid diamides 28 with nucleophiles such as dimethyl amine or methylmercaptan.[23] (Scheme 7)



Scheme 7

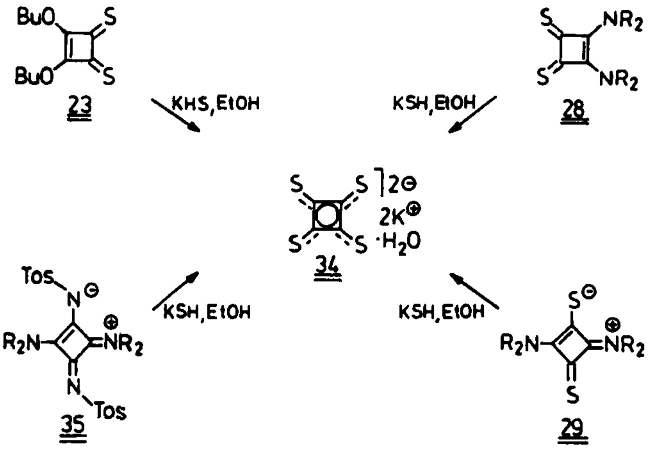
The 1,2-dithio-squaric acid diamide 28 behaves similarly in the reaction with S-, O-, N- or C-nucleophiles as the 1,2-dithioesters 23.

All nucleophiles attack preferentially on the vinylic carbon atoms of the four-membered ring, and successively displace the amino groups via an addition-elimination mechanism. Reaction of the 1,2-dithiosquaric acid diamide 28 with hydrogen sulfide yields an interesting anion 30 with three adjacent sulfur functions, which can be converted to the potassium salt of trithiosquarate dianion 31 by subsequent hydrolysis with potassium hydroxide.[21d] In a similar way high yields of interesting sulfur-containing pseudo-oxocarbon dianions are smoothly obtained in various two-step reactions. The 1,2-dithiosquaric acid diamide 28 can be readily transformed into the mixed pseudooxocarbon dianion 32 by reaction with cyanamide/ triethylamine followed by sulfhydrolysis.[25] In another example the first dimethylamino group is removed by the anion of malononitrile, the second one by hydrogen sulfide (Scheme 8) to yield the sulfur containing dianion 33.[26]



Scheme 8

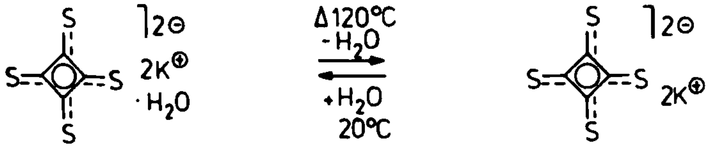
These observations led to several convenient routes for the synthesis of the C_4-thioxocarbon dianion $C_4S_4^{2-}$ 34, the sulfur analogue of the squarate dianion.[21e] As can be seen from Scheme 9, all highly activated squaric acid derivatives can be used as easily available starting materials: the dithioester 23, the dithioamide 28, the diamino dithiosquaraine 29, as well as the tosyl-substituted bis(amidine) of squaric acid 35. Upon treatment with a freshly prepared solution of excess potassium hydrogen sulfide in dry ethanol the relevant substituents are replaced by sulfur to give the C_4 thioxocarbon dianion 34 in almost quantitative yield.



Scheme 9

The $C_4S_4{}^{2-}$-dianion is obtained as the airstable orange-yellow hydrate $K_2[C_4S_4]\cdot H_2O$ 34, which dissolves readily in water and can be recrystallized from aqueous ethanol. By heating in air above 120 °C, the water of crystallization is removed and a dark violet, strongly hygroscopic modification 34a is formed, which readily reconverts to the hydrated salt 34 when exposed to air.[21e] (Scheme 10)

The characteristic orange colour of the tetrathiosquarate dianion 34 is due to an intense UV absorption at 430 nm. The very simple infrared spectrum is dominated by some intense sharp bands around 1240 cm^{-1}, which can be assigned to C⩦C⩦S vibrational frequencies. The ^{13}C-NMR spectrum in D_2O shows one signal at δ ▫ 229.2, indicating that all carbon atoms are equivalent (Scheme 10).



orange-yellow hydrate 34

violett hygroscopic 34a

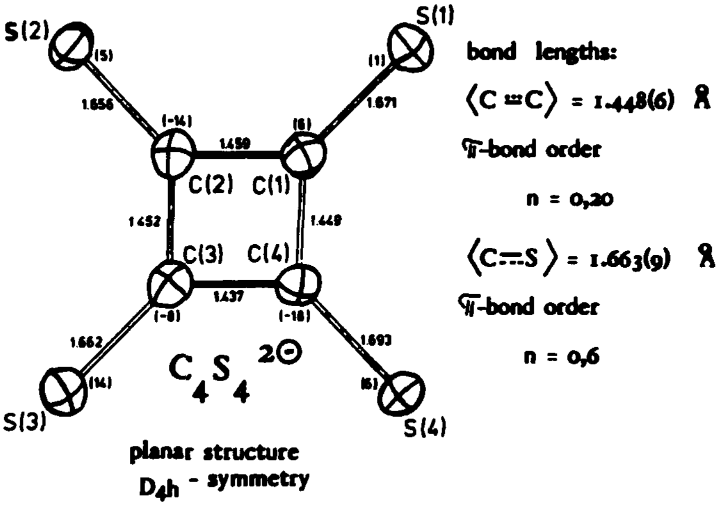
λ_{max} (H_2O) = 430 nm (lgε= 4.39)

IR (KBr): ν = 1240 cm^{-1} ($\nu_{C=C=S}$)

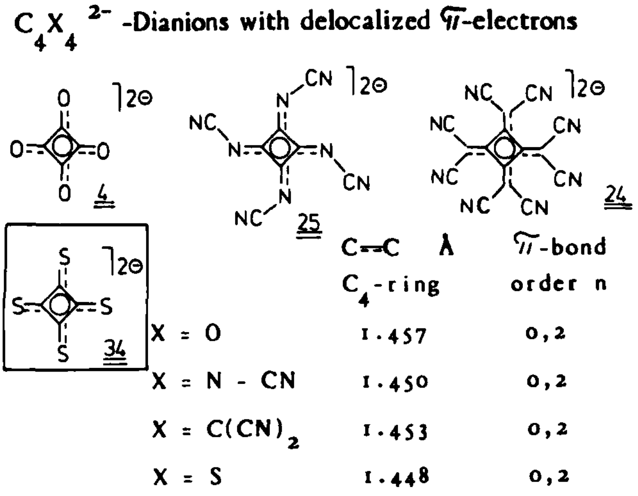
^{13}C-NMR (D_2O): δ = 229,2 ppm

Scheme 10

An X-ray crystal structure determination (Scheme 11) shows that the tetrathiosquarate dianion 34 is planar with near D_{4h} symmetry. The C-C and the C-S bond length are 144.8 and 166.3 pm respectively showing signifikant π-bond orders of n= 0,2 and n = 0.6. This indicates that the C_4 thioxocarbon dianion is a highly symmetric, completely delocalized π-system.[21e]



Scheme 11



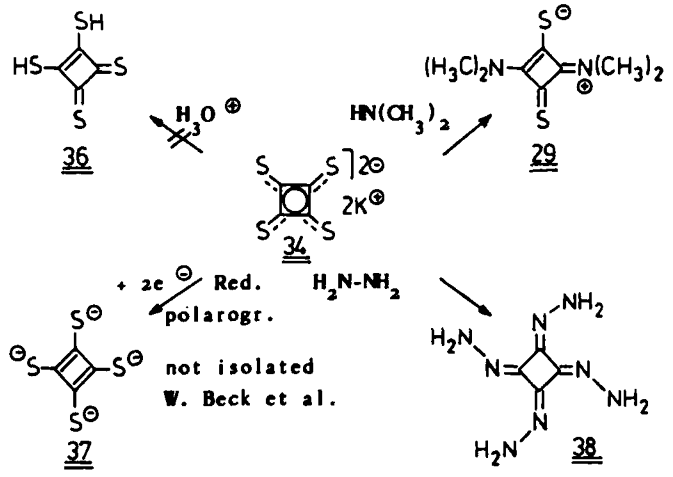
$C_4X_4{}^{2-}$ -Dianions with delocalized π-electrons

X	C–C Å C_4-ring	π-bond order n
X = O	1.457	0,2
X = N - CN	1.450	0,2
X = $C(CN)_2$	1.453	0,2
X = S	1.448	0,2

Scheme 12

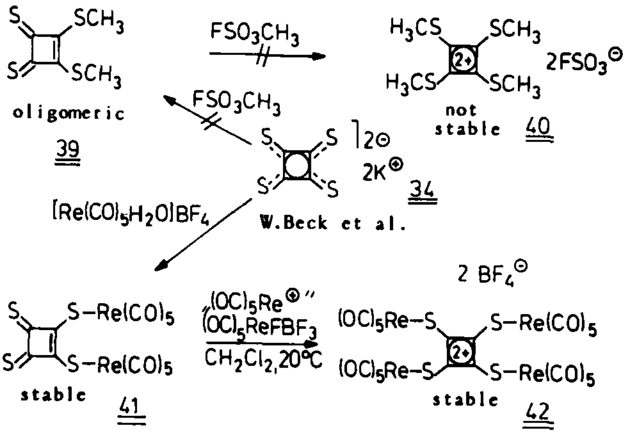
In Scheme 12 the relevant C-C bond length in the four-membered ring of the C_4 pseudo-oxocarbon dianions are compared. The table shows, that the carbon-carbon bonds of all the C_4 dianions hardly differ. They are essentially equal to those in the squarate dianion with C-C bond length close to 1.45 A indicating the same π-bond order of 0.2 for all of them. This demonstrates that all the C_4 pseudo-oxocarbon dianions constitute a series of perfectly delocalized π-systems.

Scheme 13 summarizes some interesting chemical properties of the dianion tetrathiosquarate 34. Free tetrathiosquaric acid 36 cannot be obtained from its dipotassium salt neither with sulfuric acid nor by ion exchange resin.[21e]



Scheme 13

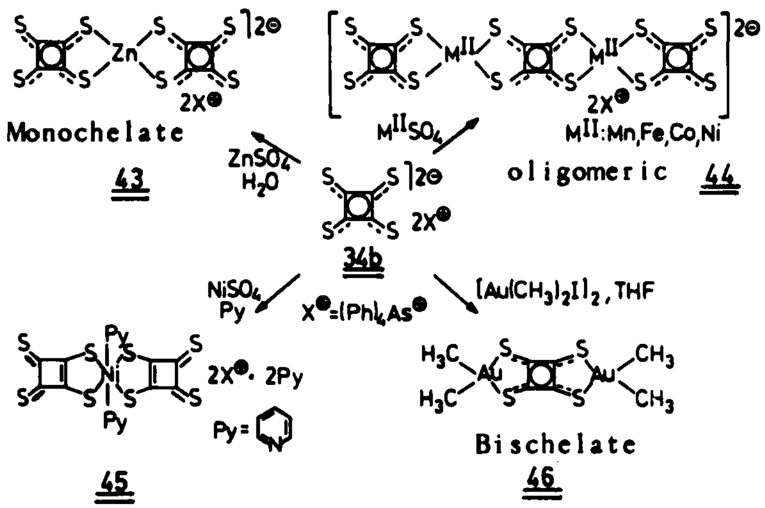
In both cases an insoluble yellow powder is formed, probably a polymer from the free acid. In contrast to the oxygen analogue, the tetrathiosquarate dianion 34 is readily reduced polarographically in two one-electron steps (half-wave potentials -1,53 and -1,79 V) in aqueous solution to the tetraanion $C_4S_4^{4-}$ 37 with an antiaromatic cyclobutadiene structure. Nucleophiles such as dimethyl amine or hydrazine attack the carbon atoms of the four-membered ring. With dimethyl amine two sulfur atoms are replaced by the nucleophile, yielding the bis(dimethylamino)dithiosquaraine 29. With hydrazine as nucleophile substitution of all sulfur atoms is followed by oxidation, yielding the tetrahydrazone 38 of the hitherto unknown cyclobutatetraone.[29]



Scheme 14

Contrary to nucleophiles, electrophiles predominantly attack the sulfur atoms of tetrathiosquarate dianion 34. Thus the reaction with "magic methyl" (FSO_3CH_3) should lead to the interesting tetrathiosquaric ester (dimethyltetrathiosquarate) 39 or the aromatic tetrakis(methylthio)cyclobutenylium dication 40. However, both these species were unstable and could not be isolated.[30] Better results have been obtained by Beck and coworkers;[31] these investigated reactions of tetrathiosquarate 34 with tetrafluoroborato compounds such as $Re(CO)_5H_2O\ BF_4$ or "$(OC)_5Re^+$ ". In both cases the $C_4S_4^{2-}$ 34 reacts as two or fourfold mono-dentate ligand respectively, yielding stable compounds 41 and 42. The fourfold substituted dication 42 is a novel, interesting 4C 2π-"Hückel aromatic" system.

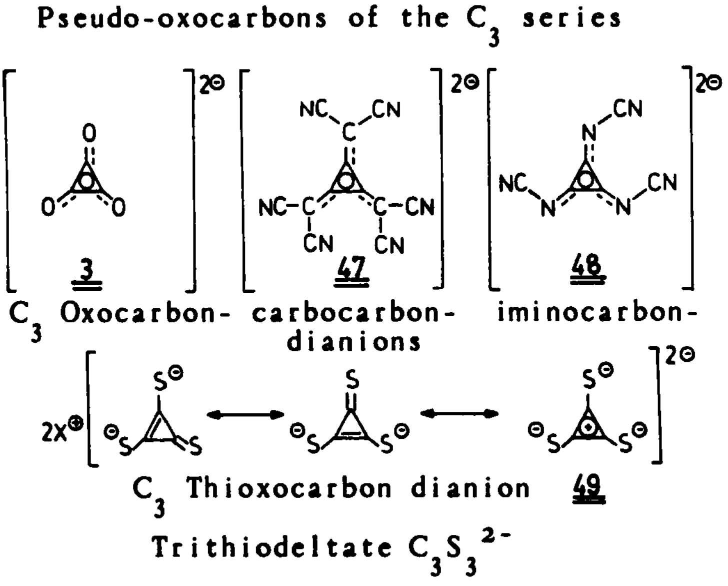
As demonstrated in Scheme 15, the tetrathiosquarate dianion 34 may serve as a versatile ligand in various metal complexes.[28,32]



Scheme 15

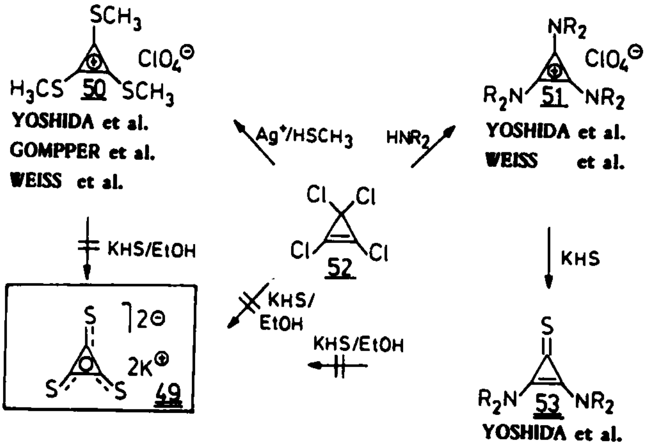
With Zn sulfate in water or with Ni sulfate in the presence of pyridine monochelate complexes 43 and 45 are formed respectively. Well defined oligomeric complexes of type 44 with Mn, Fe, Co and Ni have been obtained from nonaqueous solutions using $(AsPh_4)_2C_4S_4$ 34b. The reaction with $[Au(CH_3)_2I]_2$ gives an example of tetrathiosquarate acting as a bridging bischelate ligand in the complex $Me_2AuC_4S_4AuMe_2$ 46. Furthermore, many polymeric complexes, presumably with chain structure of approximate composition $(M^I{}_2C_4S_4)_n$ (M^I= Cu, Ag, Au) and $(M^{II}C_4S_4)_n$ (M^{II} = Cu, Zn, Cd, Hg, Fe, Co, Ni, Pd, Pt,

Sn, Pb) can be obtained from aqueous solutions of $K_2C_4S_4$ 34 and the corresponding metal salts.
Just as in the C_4 series replacement of the oxygen atoms in the dianion deltate 3 with other functional groups should lead to pseudooxocarbon dianions of the C_3 series (Scheme 16). The well characterized C_3 carbocarbon dianion 47[20a] and the iminocarbon dianion 48[19a], which are easily accessible, exhibited interesting properties as novel aromatic systems. However, many attempts to synthesize the corresponding sulfur analogue, trithiodeltate 49, proved to be unsuccessful.

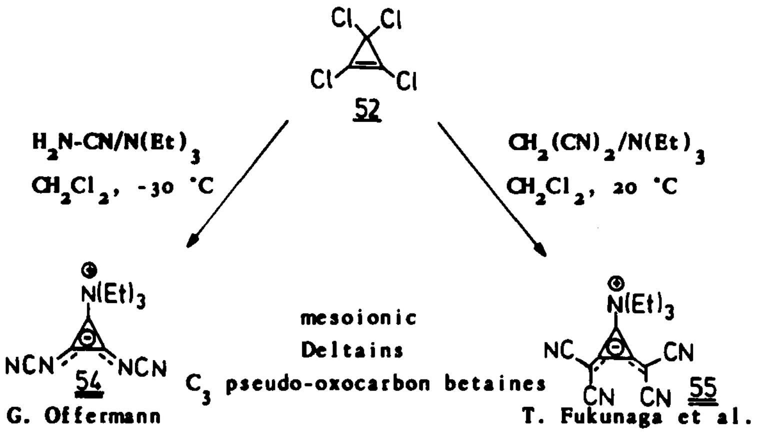


Scheme 16

On the basis of the various routes to the tetrathiosquarate dianion 34[21e] we tried to obtain the trithiodeltate 49 by simple sulfhydrolysis of tetrachlorocyclopropene 52 (Scheme 18); but this obvious way proved to be as unsuccessful as did various other promising routes. The reaction of tetrachlorocyclopropene 52 with secondary aliphatic amines[33] or with dialkyltrimethylsilylamines[34] generates trisaminocyclopropenium cations 51, which can be easily isolated e.g., as perchlorates. They seemed to be particularly suitable for the synthesis of the trithiodeltate 49. However, treating the aromatic cyclopropenium cation 51 with potassium hydrogen sulfide in ethanol leads to the thioamide 53[33] and not to the desired dianion 49. Similar experiments with the easily accessible trisalkylthio cyclopropenium cation 50[35] also proved to be unsuccessful.



Scheme 17

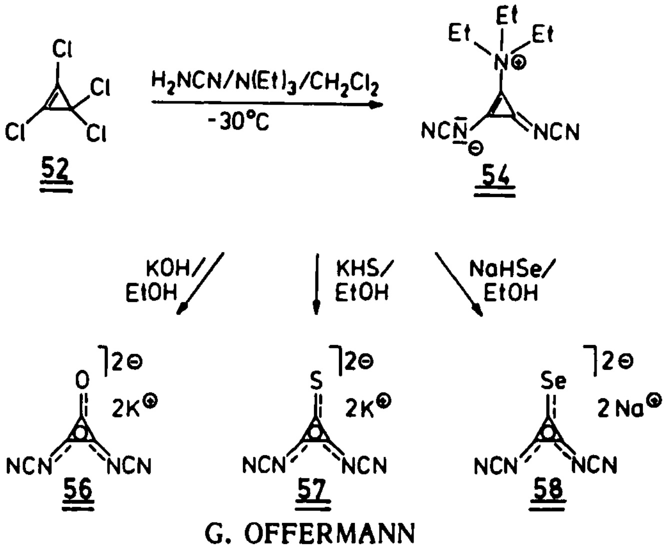


Scheme 18

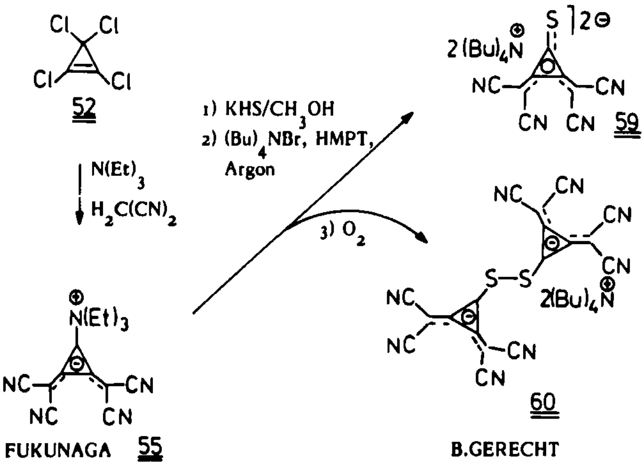
These failures prompted us to choose the novel mesoionic deltains 54[19] and 55[20a] (C_3 pseudo-oxocarbon betaines) which proved to be much more promising starting materials. These deltains are readily accessible from tetrachlorocyclopropene 52 by reaction with cyanamide or malononitrile in the presence of triethyl amine; they are crystalline species. Especially 54 has good leaving groups, which should be easily replaced by sulfur upon treatment with potassium hydrogen sulfide.

In these experiments, however, only the triethylammonium group in the deltain 54 could be replaced by various nucleophiles, resulting in the non-uniformly substituted C_3-pseudo-oxocarbon dianions 56-58[36] with two cyanoimino groups and one oxygen, sulfur or even selenium, respectively (Scheme 19).

Treatment of Fukunaga's deltain 55[20a] (Scheme 20) with potassium hydrogen sulfide in methanol leads to a surprising result,[37] depending on conditions. In the inert atmosphere of Argon the hydrogen sulfide displaces the



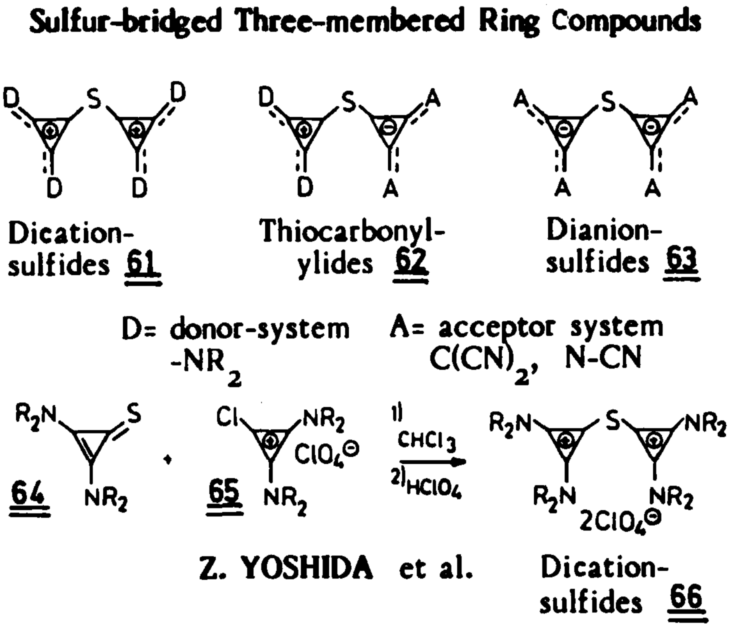
Scheme 19



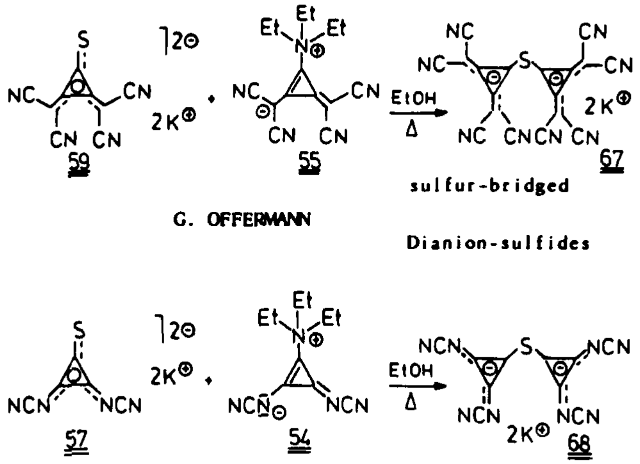
Scheme 20

triethylammonium group to yield the interesting thiodeltate dianion 59. However in the presence of air oxidation takes place and the anions are linked together through a disulfide bridge leading to the salt 60. This interesting finding encouraged us to investigate other sulfur bridged C_3-pseudo-oxocarbons.

As shown in Scheme 21, sulfur-bridged three-membered ring compounds can be devided in dication sulfides 61, thiocarbony-ylides 62[38] and dianion-sulfides 63. Dication sulfides 61[33] are well known and stabilized by donor groups at the cyclopropenylium termini. They are easily obtained when the diaminochlorocyclopropenium ion 64 is allowed to react with diaminocyclopropene thione 65[33].



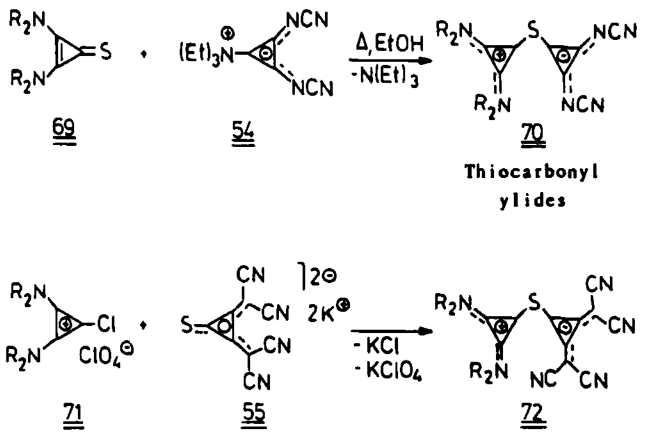
Scheme 21



Scheme 22

Contrary to the dications 66 the sulfur-bridged dianion-sulfides 63 should be stabilized by electron-accepting groups such as the dicyanomethylene or cyanoimino functions. Our experiments[39] have shown, that the thiolate functions in the two thiodeltate dianions 57 and 59 are sufficiently nucleophilic to displace triethylamine from both the deltains 54 and 55, respectively. Triethylamine is completely removed after heating one hour in dry ethanol. The crystalline potassium salts of the dianions precipitate as palebeige airstable crystals and can be recrystallized from methanol. The spectroscopic data confirm the constitutions of these novel sulfur-bridged dianion-sulfides 67 and 68.[39]

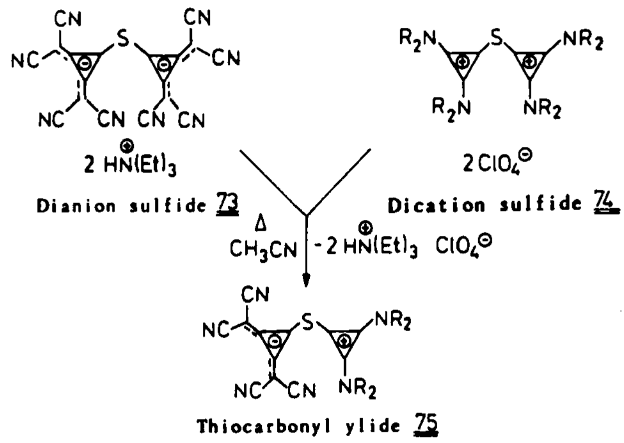
The corresponding thiocarbonyl ylides 62,[38] in which the donor substituted cyclopropenylium cation and the acceptor substituted deltate anion are linked by a sulfur bridge can be synthesized by three different routes.[39]



Scheme 23

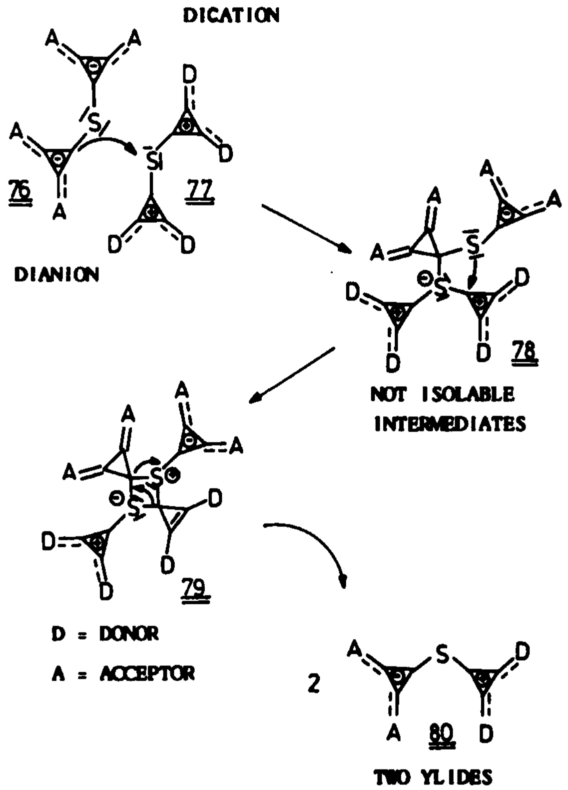
The most convenient way to the thiocarbonyl ylides was found in the reaction of acceptor substituted deltains such as 54 with the diamino-cyclopropene-ethione 69. This route illustrates (Scheme 23) that the thione function in 69 is sufficiently nucleophilic to displace the triethylamino group of 54 to yield the "push-pull" substituted thiocarbonyl ylide 70 as a pale yellow solid. In the second route[39] (Scheme 23), 1,2-bis-diisopropylamino-3-chlorocyclopropenium perchlorate 71 in boiling ethanol solutions is treated with the potassium salt of the thiodeltate 55. The thiocarbonyl ylide 72 separates immediately as a pale yellow solid. Recrystallization from nitromethane gave beige needles in about 90% yield.

The third approach[39] to the crystalline and stable thiocarbonyl ylides is somewhat surprising. According to our observation the sulfur-bridged dianion sulfide 73 and the dication sulfide 74 are thermodynamically unstable compared to the thiocarbonyl ylide 75, the zwitterionic combination of both three-membered ring derivatives: Upon heating the dianion 73 together with the dication sulfide 74 in acetonitrile, the corresponding thiocarbonyl ylide 75 was obtained in about 40% yield together with a hitherto unidentified yellow substance.[39]

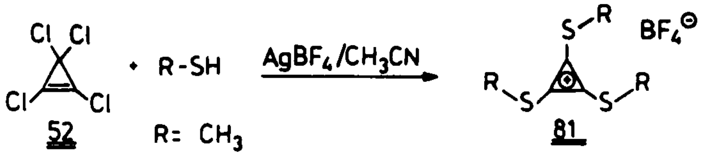


Scheme 24

The mechanism of this unusual generation of a thiocarbonyl ylide could be rationalized by a sequence shown in Scheme 25, whose critical first step requires hypervalent bonding of sulfur via 78 rather than attack at the π-donor substituted carbon atom.[40] After ring closure to the strained four-membered ring 79 in which the positive sulfur is stabilized by an adjacent deltate anion - the negative one by a neighbouring cyclopropenium cation - fragmentation into two molecules of the thermodynamically stable thiocarbonyl ylide 80 is expected to be a fast reaction.[39]



Scheme 25



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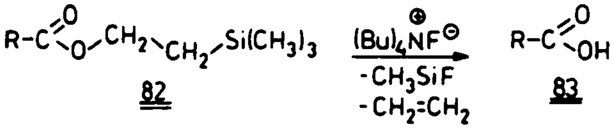
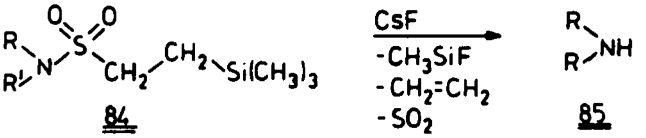


H.Gerlach et al. Helv.Chim. Acta 60, 3039 (1977)

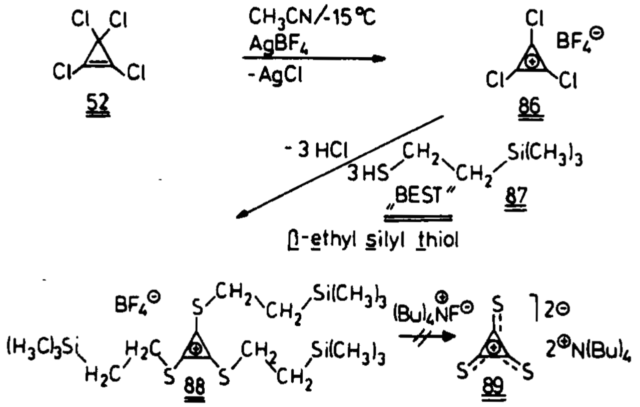


S.M.Weinreb et al. Tetrahedron Lett. 27, 2099 (1986)

Scheme 26

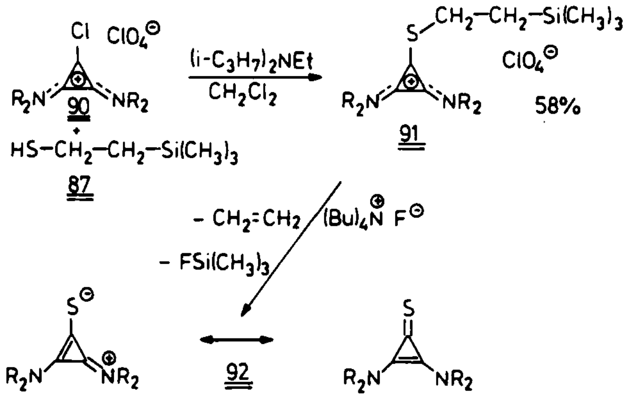
Meanwhile we have continued our efforts to synthesize the dianion trithiodelate 49. As the usual approach - that is the nucleophilic displacement of substituents in suitably activated deltic acid derivatives - failed in this case, we tried to find a totally different route to introduce three sulfhydryl moieties into the deltic acid system.

Firstly, we remembered that the introduction of three sulfur functions into the deltic acid system is well documented:[35a-c] the reaction of tetrachlorocyclopropene 52 with various thiols in the presence of silver ions leads to triply thioalkyl substituted cyclopropenium salts 81 in good yields. Secondly, we knew from the literature that fluoride-mediated cleavage of 2-(trimethylsilyl)ethylesters 82 has been shown to be an efficient reaction.[41] Furthermore, Weinreb recently reported that fluoride treatment of 2-(trimethylsilyl)-ethyl sulfonamides 84 effects fragmentation to the corresponding amino derivatives 85;[42] this example represents the only 2-silyl-substituted sulfur derivative that has been shown to undergo this mode of cleavage.



Scheme 27

Thus we anticipated that threefold thioalkylation of tetrachlorocyclopropene 52 with BEST 87[43-45] [β-ethyl-silyl-thiol, 2-(trimethylsilyl)ethanethiol] should result in the formation of the desired triply thioalkyl- substituted cyclopropenium salt 88; this contains three sulfur functions capable of undergoing elimination reactions to form the dianion trithiodeltate 89.[44] As shown in Scheme 27 BEST in the presence of silver ions reacts with tetrachlorocyclopropene 52 to yield the desired starting material 88 although in rather low yield. Surprisingly the fluoride-mediated cleavage of 89 with Bu_4NF or CsF proved to be unsuccessful.[43c]

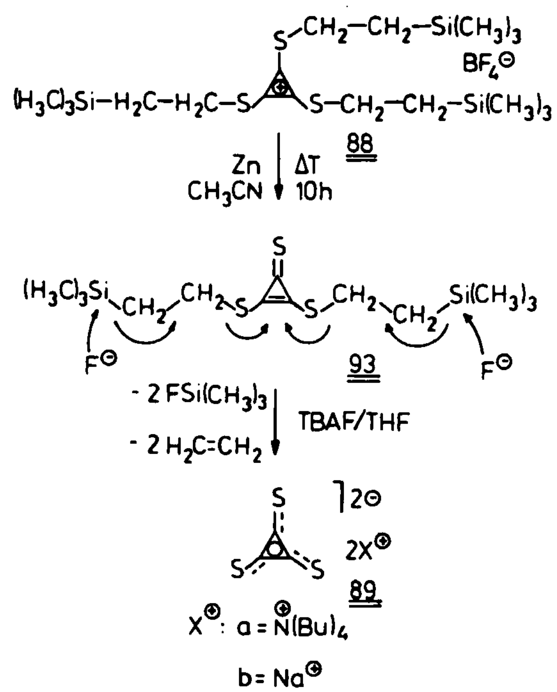


Scheme 28

On the other hand we were able to show (Scheme 28) that the diaminocyclopropenium cation 91 bearing only one BEST-group, smoothly reacts with tetrabutylammonium fluoride to yield the corresponding thione 92 in nearly quantitative yield.[43c]

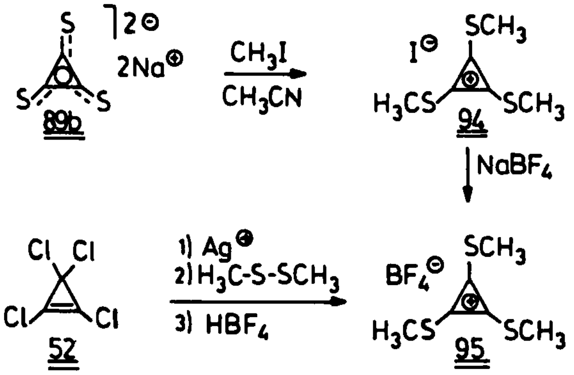
This prompted us, to reduce the threefold BEST-substituted cyclopropenium salt to the corresponding neutral thione, which can be achieved in more than 50% yield with zinc powder in dry acetonitrile.[46] Subsequent fluoride-prompted fragmentation of the thione 93 results in the desired elimination of two molecules of fluorotrimethylsilane and ethylene to give the tetrabutylammonium salt of the trithiodeltate 89a.[44]

This can be converted into the more readily isolated sodium salt 89b by adding sodium perchlorate solution.



Scheme 29

Chemical proof of the structure was easily accomplished by treating the sodium salt 89b of trithiodeltate with methyl iodide in acetonitrile. In this way all three sulfur functions were alkylated. The initially formed tris(methylthio)-cyclopropenium iodide 94 reacts with sodium tetrafluoroborate to give the known salt 95, which is easily accessible by application of the reaction principle of Weiss et al.[35c] (Scheme 30)

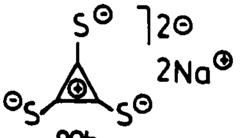


Scheme 30

The spectroscopic data of 89b are in agreement with a planar structure as well as with the expected D_{3h} symmetry. The ^{13}C-NMR spectrum of the sodium salt 89b in D_2O consists of a single signal at $\delta = 176.5$. The electronic absorption spectrum of an aqueous solution of 89b exhibits a long-wave length maximum at 268 nm ($\lg\varepsilon = 4.32$). The Raman and IR-data of the dianion of 89b are similar to those of the isoelectronic cation trichlorocyclopropenylium 96[47] and thus confirm the proposed D_{3h} symmetry.

SPECTROSCOPIC DATA OF THE DIANION TRITHIODELTATE

planar structure, D_{3h} symmetry



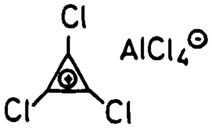
89b

^{13}C-NMR (D_2O) δ = 176.5

IR (KBr): $\nu_{C\doteq C\doteq S}$ = 1219 cm^{-1}
700 cm^{-1}

UV (H_2O): λ_{max} = 268 nm

isoelectronic

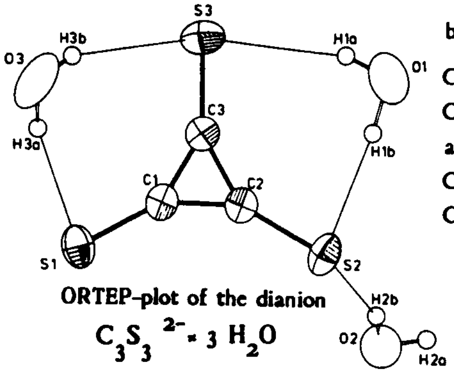


96

trichlorocyclopropenium-cation

Scheme 31

This is also supported by the X-ray crystal structure determination. Scheme 32 shows the ORTEP plot[48] of the molecular structure of the trithiodeltate dianion 89c with surrounding molecules of water. The trithiodeltate dianion exhibits only minor deviations from those expected for D_{3h} symmetry and may be regarded as virtually planar with the following mean distances and angles: C-C 1.405 A, C-S 1.676 A, C-C-C 60,0°, C-C-S 150.0°.



ORTEP-plot of the dianion $C_3S_3{}^{2-} \cdot 3\,H_2O$

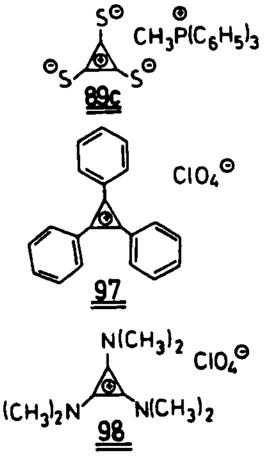
bond lengths:
C - C = 140.5 pm
C - S = 167.6 pm
angles:
C - C - C 60,0°
C - C - S 150,0°

Scheme 32

The C-C distances are equal within experimental error and with 140.5 pm similar to those in triphenylcyclopropenylium perchlorate 97[49] (Scheme 33) or 1,2,3-tris (dimethylamino)cyclopropenylium perchlorate 98[50]. Another point of interest is the C-S bond length of the trithiodeltate dianion 89. As can be seen from Scheme 34, which lists C-S bond length of some other thiocarbonyl compounds, the C-S distance of the trithiodeltate hardly differs from that in the next highest homologue dianion tetrathiosquarate 34.[21e]

However an important difference between the four- and threemembered thioxocarbon dianion has to be considered: as is well known each ring carbon of the cyclopropenium ion system has nonequivalent orbitals[33a] (one sp and two sp^3 orbitals); hence the semicyclic

C-C distances for the cyclopropenium ion (X-ray data)



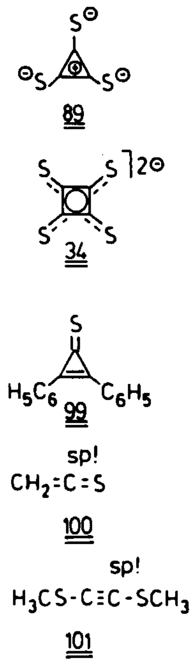
89c 140.5 pm

97 137.3 pm

98 136.3 pm

Scheme 33

C-S - distances in various species



89 167.6 pm[44]

34 166.4 pm[21e]

99 163.0 pm[53]

sp!
$CH_2=C=S$ 100 155.4 pm[51]

sp!
$H_3CS-C\equiv C-SCH_3$ 101 167.1 pm[52]

Scheme 34

bond has essentially C_{sp}—S-character. In order to determine the π-bond order of the C_{sp}—S bond in the dianion trithiodeltate one has to consider the C_{sp}—S-distances of the thioketene 100[51] (π-bond order n = 1.0) and that of the thioalkyl substituted acetylene 101[52] (n = 0).

This comparison makes it evident, that the C-S bond in the dianion trithiodeltate 89 has indeed single bond character. Thus the dianion trithiodeltate can be regarded as a symmetrically trisubstituted cyclopropenium cation and all the sulfur atoms carry a full negative charge. Resonance formulas displaying C=S-character contribute only to a very small extent to the ground state of the trithiodeltate.

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