1981

Radical anions and cations derived from enedithiols, hydroxy-enethiols, and saturated dithiols

Mary Ann Zaleta
Iowa State University

Recommended Citation

Zaleta, Mary Ann, "Radical anions and cations derived from enedithiols, hydroxy-enethiols, and saturated dithiols " (1981). *Retrospective Theses and Dissertations*. 6868.
https://lib.dr.iastate.edu/rtd/6868

8122577

ZALETA, MARY ANN

RADICAL ANIONS AND CATIONS DERIVED FROM ENEDITHIOLS, HYDROXY-ENETHIOLS, AND SATURATED DITHIOLS

Iowa State University PH.D. 1981

University
Microfilms
International 300 N. Zeeb Road, Ann Arbor, MI 48106

Radical anions and cations derived from enedithiols, hydroxy-enethiols, and saturated dithiols

by

Mary Ann Zaleta

A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of the
Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Department: Chemistry
Major: Organic Chemistry

Approved:

In Charge of Major Work

For the Major Department

For the Graduate College

Iowa State University
Ames, Iowa

1981

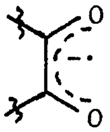
TABLE OF CONTENTS

LIST OF TABLES

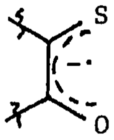
LIST OF FIGURES

NOMENCLATURE AND NUMBERING

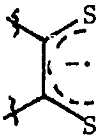
Spin-labels and general compound types will be identified by the names listed below.



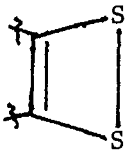
semidione



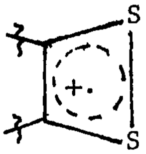
monothiosemidione



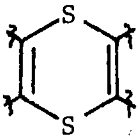
semidithione



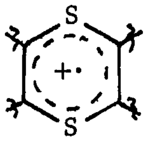
dithiete



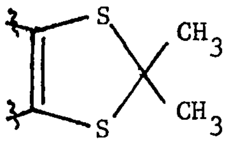
dithiete radical cation



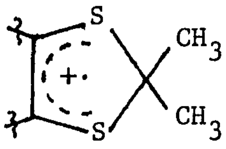
dithiin



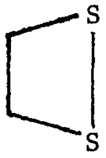
dithiin radical cation



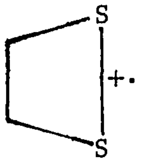
dithiole



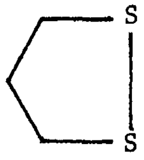
dithiole radical cation



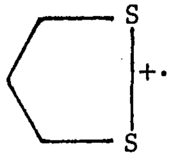
1,2-dithietane



1,2-dithietane radical cation



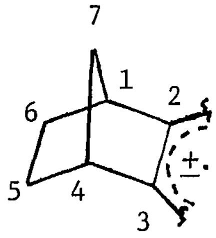
1,2-dithiolane

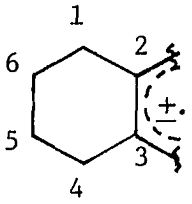


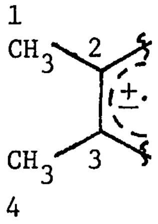
1,2-dithiolane radical cation

Although dithiole itself contains hydrogens instead of the methyl substituents shown in the "dithiole" structure, most of the dithioles which will be mentioned do have the methyl substituents present. Therefore, the term "dithiole" will include the methyl groups unless specific mention is made of some other substitution pattern.

The numbering patterns shown below are not necessarily the patterns normally considered correct, especially where cyclic spin-labels are involved. However, they were chosen so that carbon atoms 2 and 3 of any structure would always correspond to the two carbon atoms shared by the spin-label and the parent structure. These numbering patterns are used only when referring to radical anions and cations, and in naming the precursors to the radicals, normal numbering procedure will be used.

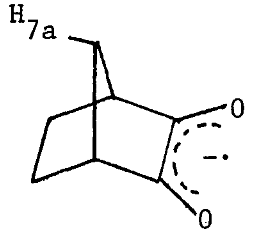




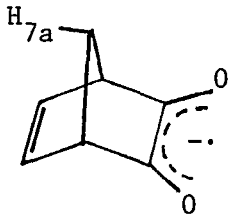


INTRODUCTION

The semidiones of bicyclo[2.2.1]heptane (1) and bicyclo[2.2.1]-hept-5-ene (2) show an unusually large long-range hyperfine splitting



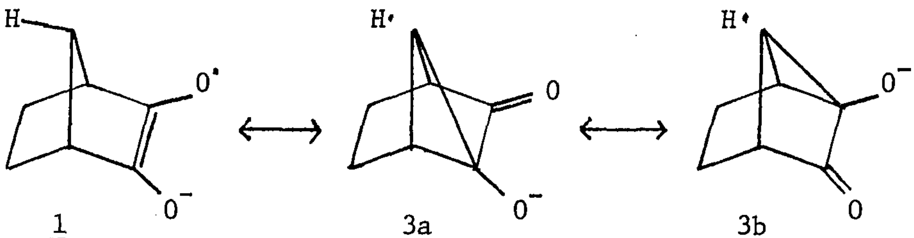
1



2

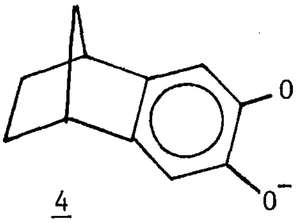
by hydrogen in the 7-anti position (1, 2). A mechanism involving homohyperconjugation can be invoked to explain the large splitting.

Structures 3a and 3b illustrate how spin may be transferred to H_{7a} by homohyperconjugation (2). This mechanism can operate only when



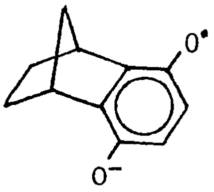
1 3a 3b

the HOMO of the spin-label is symmetric with respect to the plane bisecting the spin-label and containing H_{7a}. Thus, in semidiones 1 and 2 the hyperfine splitting constants are 6.54 G and 8.19 G, respectively, for H_{7a}. Semiquinone 4, which also contains a HOMO symmetric with respect to C_2 and C_3 of the bicyclic system, shows a splitting of 3.10 G for H_{7a} (3), the slightly smaller value being due to lower spin density at C_2 and C_3 in the semiquinone than in the corresponding semidione.

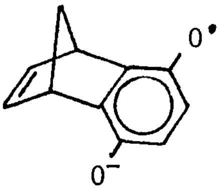


4

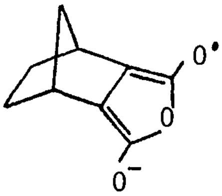
In the semibenzoquinones and semifuraquinones 5 through 8, the HOMO's of the spin-labels are antisymmetric with respect to C_2 and C_3,



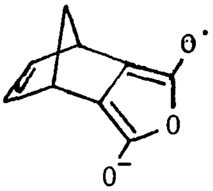
5



6



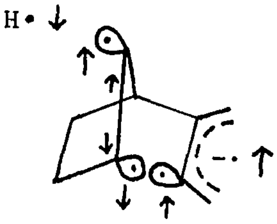
7



8

giving rise to smaller splittings by H_{7a}. The observed values are 0.70 G, 0.80 G, 1.03 G, and 1.41 G, respectively (4-6). Similar results have been observed with the radical anions of nitro- and dinitrobenzonorbornanes (3, 7). These splittings are due to spin polarization, a mechanism which does not depend on the symmetry of the spin-label. A spin-polarized structure such as 9 can account for the small splitting by H_{7a} when spin cannot be transferred via homohyperconjugation (2).

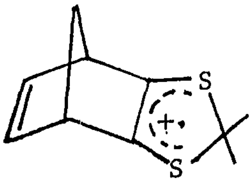
A small splitting by $H_{7\underline{syn}}$ is observed in 1, 2, 6, 7, and 8. The spin polarization mechanism also gives rise to this splitting, the



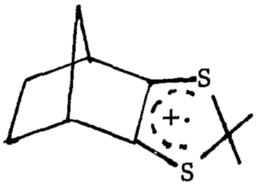
9

magnitude of which is not determined by the symmetry of the HOMO of the spin-label.

The radical cations corresponding to the anions 1, 2, and 4-8 have not been observed. The cations corresponding to 1, 2, and 4 would be expected to have small hyperfine splitting constants for H_{7a} (antisymmetric HOMO's) while those corresponding to 5-8 should have large splittings (symmetric HOMO's). Calculations on the cations of 1, 5, and 7 agree with this prediction (8). It was therefore predicted that the large H_{7a} splitting should be observed in a cationic system such as radical cation 10 or 11.



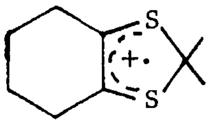
10



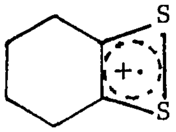
11

Dithiole radical cations have hyperfine splitting constants approximately 10% smaller than those of the corresponding semidiones. They may be generated from α-hydroxyketones or α-diketones in sulfuric acid by addition of acetone and either sodium sulfide, sodium thiosulfate, or sodium dithionite (9). Addition of sulfuric acid to the parent dithiole will also produce the radical cation (10).

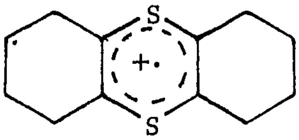
When 1,2-cyclohexanedione, for example, is placed in sulfuric acid and sodium sulfide and acetone are added, the ESR signal for dithiole radical cation 12 is observed. The signals for the dithiete and dithiin radical cations 13 and 14, which would also be observed in the absence of acetone, are present as well. With the bicyclic dithiole radical cations, which would be expected to give more complicated splitting patterns than 12, the presence of additional signals was highly undesirable. It was found, however, that by first dissolving an α-diketone in acetone and then adding sodium sulfide and sulfuric acid to that solution, the dithiole radical cation alone was produced. By this method it was thought that the bicyclic dithiole radical cations could be generated free of interfering signals.



12

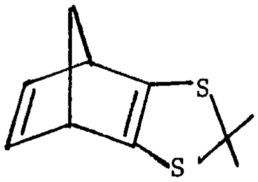


13

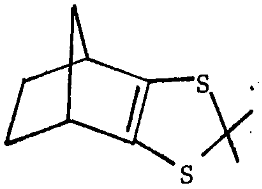


14

Unfortunately, attempts to generate 10 and 11 from the diketones yielded unresolved spectra, and no signal at all was obtained in attempting to form 10 from the corresponding α-hydroxyketone. It was therefore decided that the radical cations would have to be generated from the parent dithioles 15 and 16 themselves.



15



16

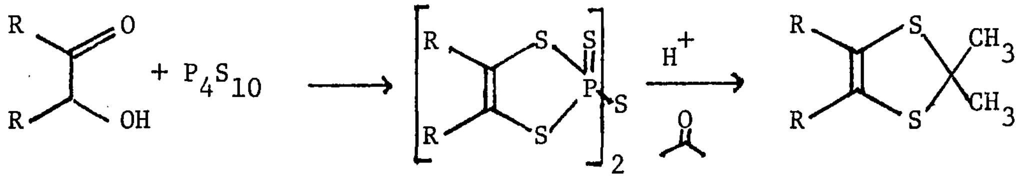
Although all attempts to synthesize 15 or 16 ended in failure, and although neither 10 nor 11 was ever observed, some of the intermediates from the attempted syntheses of 16 did prove useful in generating both anionic and cationic spin-labels. It is these radical anions and cations which will be discussed.

RESULTS

Radical Anions--Semidithiones

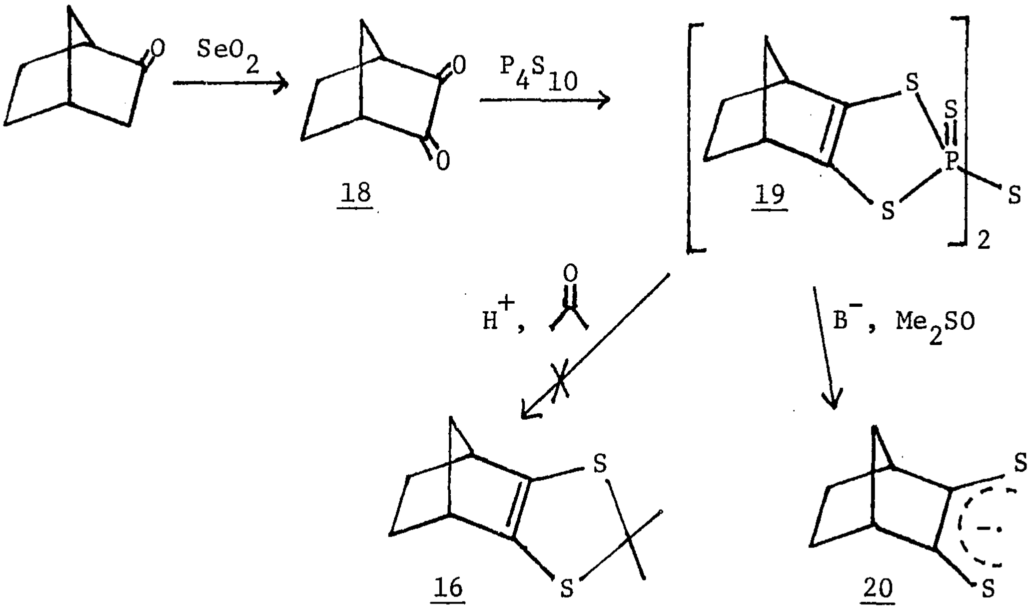
Schrauzer and coworkers (10, 11) have reported the syntheses of two dithioles using the thioesters obtained from the reaction of α-hydroxyketones (or α-diketones or α-haloketones) with phosphorus pentasulfide (Scheme I). It was hoped that a similar scheme could be used to synthesize dithiole 16 starting with the easily-obtained bicyclo[2.2.1]heptane-2,3-dione (18) rather than with the hydroxyketone (Scheme II).

Scheme I



R = CH_3 (17), Ø

Scheme II



No bicyclic dithiole was obtained by this method. However, the ester 19 could be isolated by column chromatography as a brownish resin, and treatment of the resin with potassium *t*-butoxide in dimethyl sulfoxide produced an ESR signal with a g-factor equal to 2.0166 corresponding to semidithione 20.

20 represents the first reported example of the semidithione spin-label. The hyperfine splitting constants observed were $a^H = 4.2$ G (1 H; $H_{7\underline{anti}}$) and 1.3 G (4 H; $H_{1,4,5\underline{exo},6\underline{exo}}$). Although additional splitting by $H_{7\underline{syn}}$ is seen in the bicyclo[2.2.1]heptane-2,3-semidione 1 (1), poorer resolution in the semidithione spectrum made detection of any $H_{7\underline{syn}}$ splitting impossible.

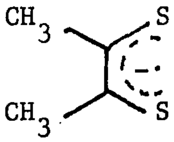
Table I lists the splitting constants and g-factors for semidione 1 and semidithione 20. Note the much larger g-factor for 20 than for 1.

Table I. Splitting constants and g-factors for bicyclo-[2.2.1]heptane-2,3-semidione (1) and bicyclo-[2.2.1]heptane-2,3-semidithione (20)

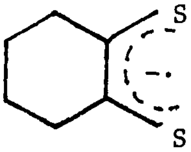
Radical Ion	a^H (In gauss)		g-Factor
	$H_{1,4,5\underline{exo},6\underline{exo}}$	H_{7a}	
semidione 1	2.43	6.54	2.005[a]
semidithione 20	1.3	4.2	2.0166

[a] Estimated, based on g = 2.00505 for *cis*-propane-1,2-semidione (12).

For comparison with bicyclo[2.2.1]heptane-2,3-semidithione (20), semidithiones 21 and 22 were desired. The thiophosphoric ester 17 from

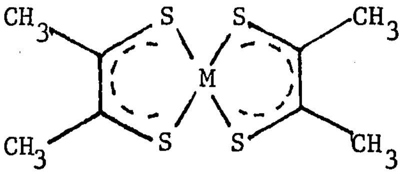


21



22

acetoin and P_4S_{10} is known (10, 13) and has been used in the synthesis of metal complexes of the type illustrated by 23. In synthesizing the

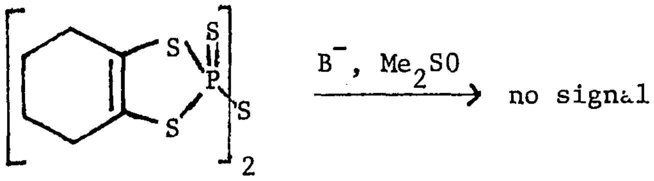


23

metal complexes, however, the thiophosphoric ester is not normally isolated but is used in situ (11, 13). No thiophosphoric ester could be isolated from the reaction of P_4S_{10} with either acetoin, 2,3-butanedione, or 3-chloro-2-butanone, and no ESR signal was observed upon treatment with potassium t-butoxide in Me_2SO of either the solid residue from the reaction or the residue obtained after evaporation of the solvent from the reaction mixture.

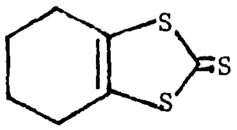
Reaction of P_4S_{10} with 1,2-cyclohexanedione gave a poor yield of an amber resin which was believed to be thiophosphoric ester 24. However, treatment of the resin with potassium t-butoxide in Me_2SO

under both static and flow conditions failed to yield an observable ESR signal.

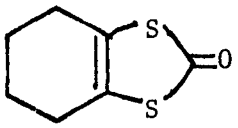


24

A second approach to the formation of semidithione 22 was to generate the radical anion from trithiocarbonate 25 or dithiolcarbonate 26. Treatment of either 25 or 26 with potassium t-butoxide in Me_2SO



25

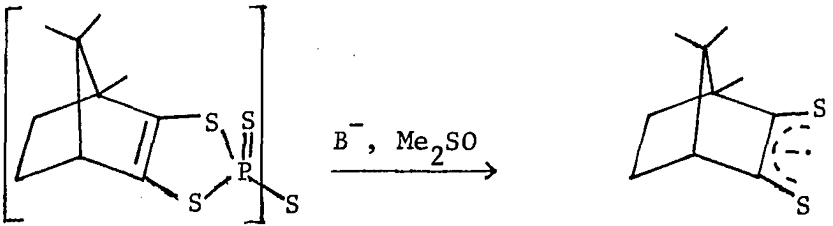


26

produced a color change but no observable ESR signal. When 25 was reacted under flow conditions, no signal was observed, and irradiation of either the static or flow solutions with a UV light did not produce a signal.

Dithiolcarbonates such as 26 may lose carbon monoxide on irradiation to form dithiones (14). Bubbles did appear at the cathode when dithiolcarbonate 26 was irradiated with a UV light while being reduced electrolytically, but no ESR signal for semidithione 22 was observed.

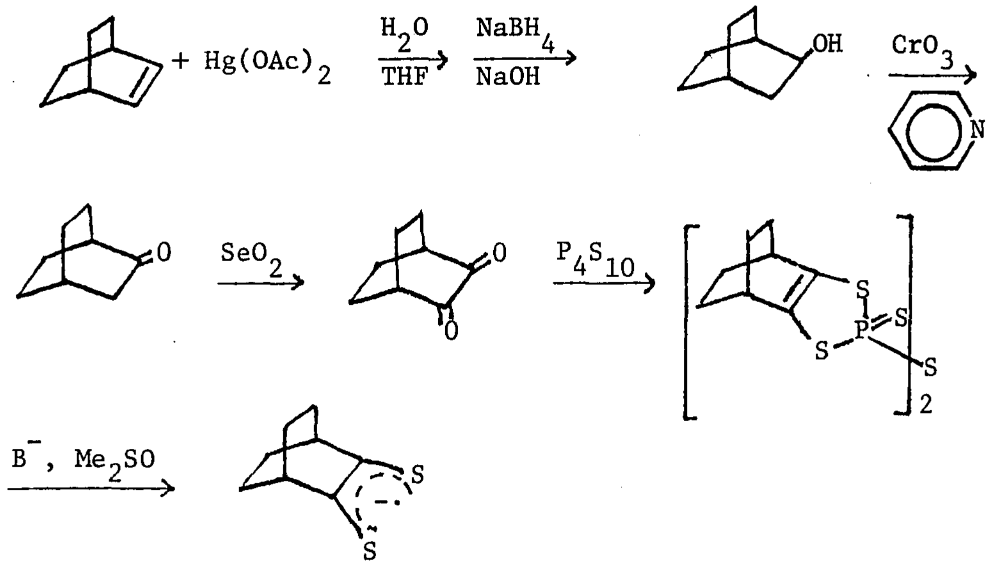
Although neither acyclic nor monocyclic semidithiones were observed, other bicyclic semidithiones were easily prepared. Reaction of camphorquinone with P_4S_{10} gave thiophosphoric ester 27 as a yellow, slightly sticky solid from which semidithione 28 was produced by treatment with potassium *t*-butoxide in Me_2SO. The ESR spectrum of 28 showed a hyperfine splitting of 1.4 G for three hydrogens ($H_{4,5exo,6exo}$). Splitting by hydrogen in the C_{5endo} position and by the methyl hydrogens in the C_1 and C_{7syn} positions could be seen in the corresponding semidione (2), but the spectrum of the semidithione was not sufficiently well-resolved to detect any further splitting.



27 28

Bicyclo[2.2.2]octane-2,3-semidithione (29) was produced according to Scheme III. Its ESR spectrum showed a splitting of 1.2 G by four equivalent hydrogens *anti* to the spin-label at carbons 5, 6, 7, and 8. This assignment is consistent with the observed ESR spectrum of the corresponding semidione (1).

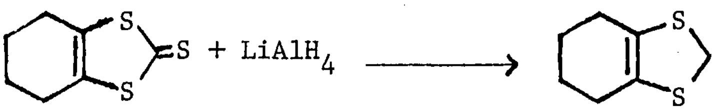
Scheme III



29

Radical Anions--Monothiosemidiones

Grunwell and Willett (15) reported the formation of dithiole 30 by reduction of trithiocarbonate 25 with lithium aluminum hydride.

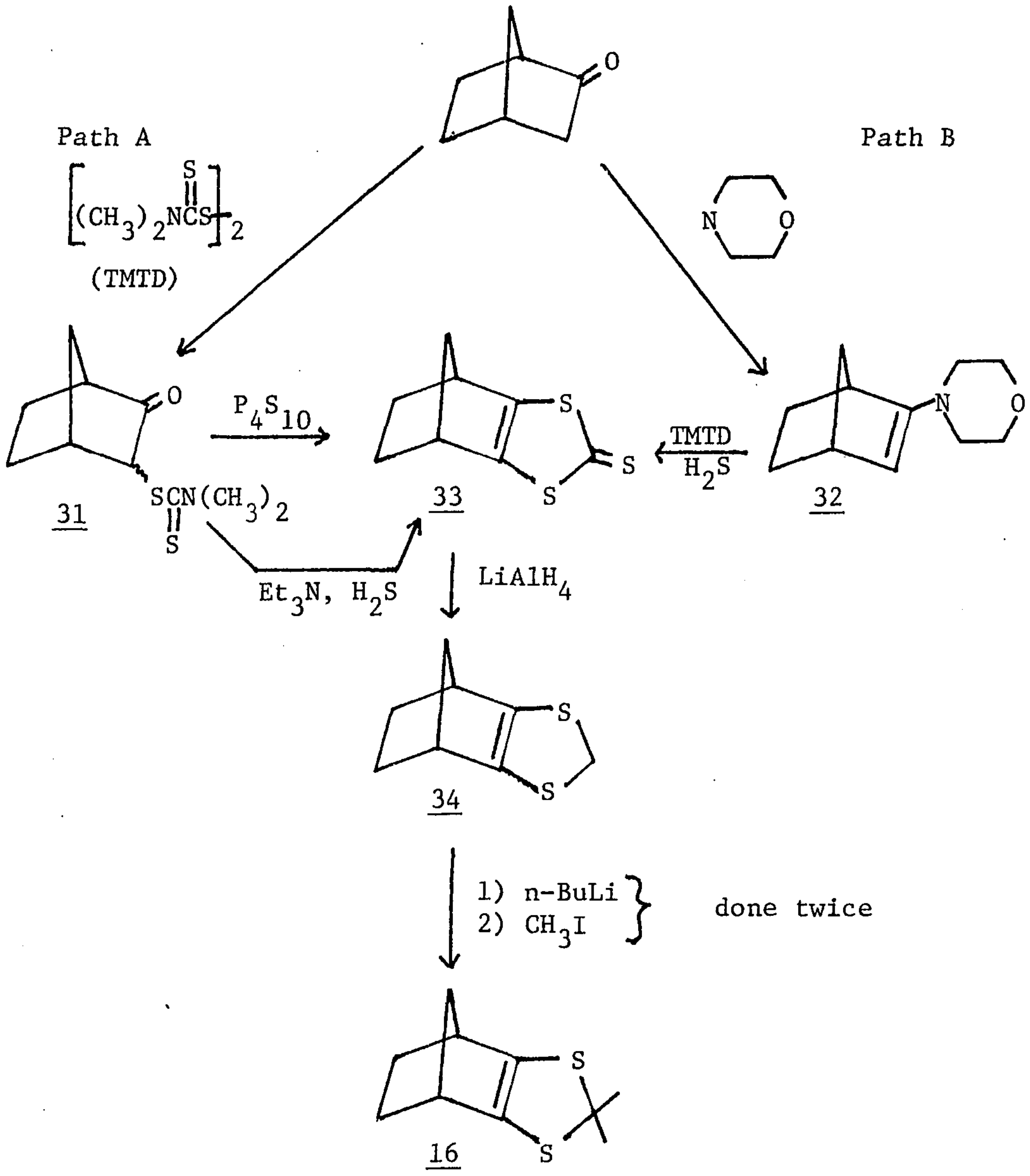


25

30

Trithiocarbonate 25 could be synthesized by several methods (15-17), and using analogous reactions in the bicyclic system, it was thought that bicyclic dithiole 16 could be obtained by one of the paths shown in Scheme IV.

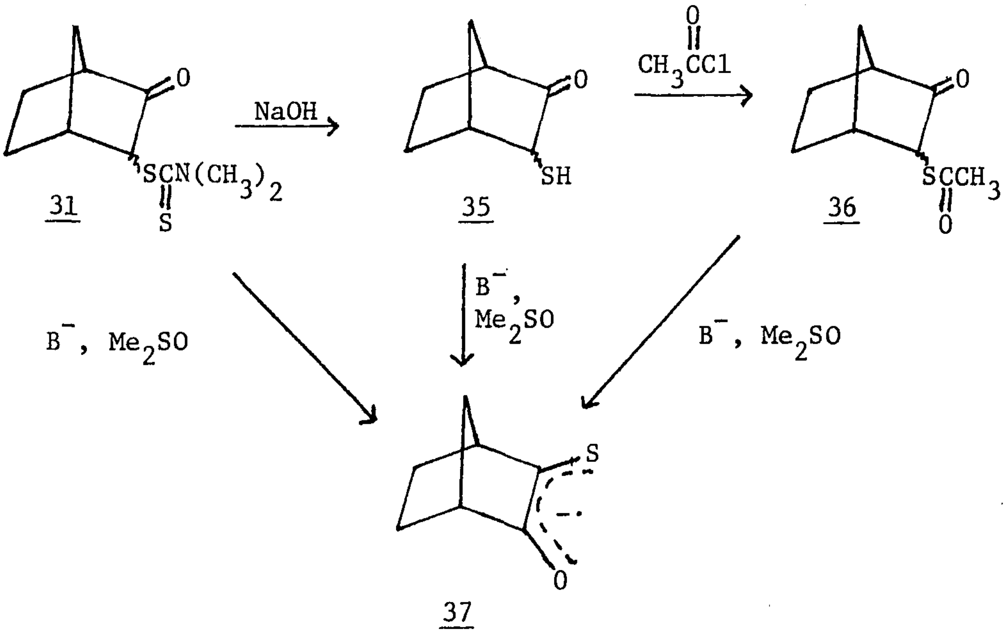
Scheme IV



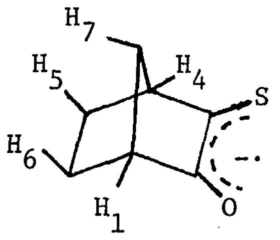
Path A was used on cyclohexanone as well as on norcamphor, shown in Scheme IV, but it proved to be of little synthetic value. The reaction of 2-(N,N-dimethylthiocarbamoylmercapto)cyclohexanone with

P_4S_{10} to form 4,5-tetramethylene-1,3-dithiole-2-thione (25) resulted in only a poor yield of 25, and reaction of 31 with P_4S_{10} was even worse, giving some tar but none of the desired product, bicyclic trithiocarbonate 33. Reaction of 31 with H_2S also failed to yield any trithiocarbonate. Compound 31 itself, however, proved to be useful as a precursor for monothiosemidione 37, which represents the first example of the monothiosemidione spin-label (Scheme V).

Scheme V



Carbamoylmercaptoketone 31, mercaptoketone 35, and acetylmercaptoketone 36 all gave monothiosemidione 37 when treated with potassium t-butoxide in Me_2SO, with 35 and 36 giving stronger ESR signals than 31. The ESR spectrum of 37 showed a signal with a g-factor of 2.0100 and the following hyperfine splitting constants.



37

a^H = 5.2 G (1 H; $H_{7\underline{anti}}$)

2.6 G (2 H; $H_{4,5\underline{exo}}$)

1.3 G (2 H; $H_{1,6\underline{exo}}$)

As in the case of the semidithione, no splitting by $H_{7\underline{syn}}$ could be detected because the spectrum was not sufficiently well-resolved.

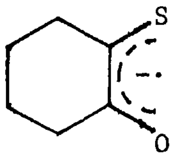
Table II lists the splitting constants and g-factors for semidione 1, monothiosemidione 37, and semidithione 20. Note that the values of both a_{7a}^H and the g-factor for monothiosemidione 37 are between the corresponding values for semidione 1 and semidithione 20.

Table II. Splitting constants and g-factors for bicyclo-[2.2.1]heptane-2,3-semidione (1), -monothiosemidione (37), and -semidithione (20)

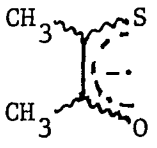
Radical Ion	a^H			g-Factor
	$H_{1,6\underline{exo}}$	$H_{4,5\underline{exo}}$	H_{7a}	
semidione 1	2.43	2.43	6.54	2.005[a]
monothiosemidione 37	1.3	2.6	5.2	2.0100
semidithione 20	1.3	1.3	4.2	2.0166

[a] Estimated.

For comparison, the monothiosemidiones 38 and 39 were desired. 38 was generated by the reaction of potassium *t*-butoxide in Me_2SO with



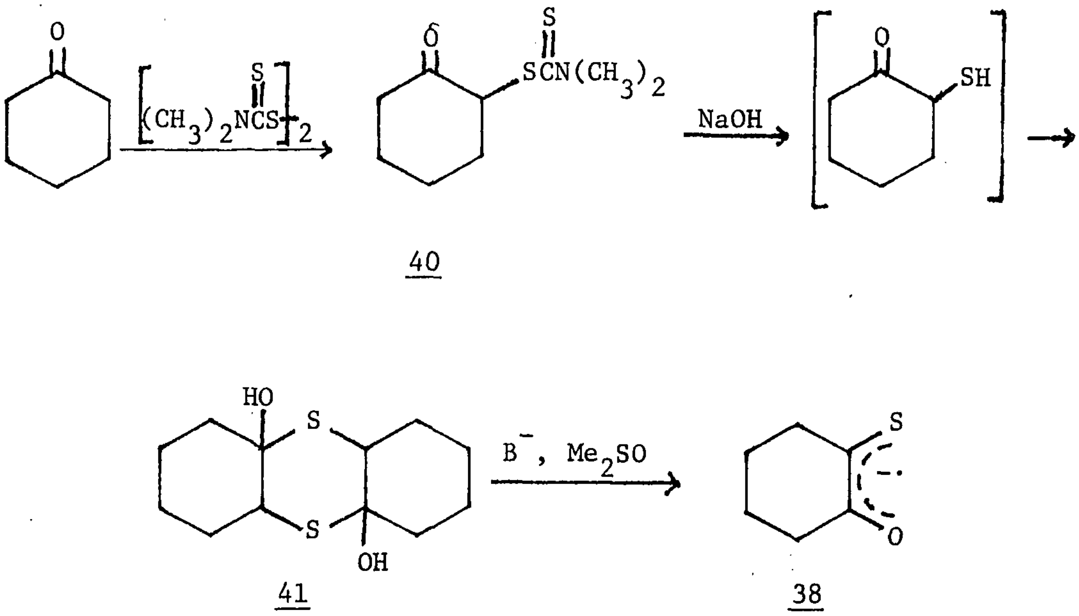
38



39

the dimer of 2-mercaptocyclohexanone (41), which was obtained by hydrolysis of thiocarbamoylmercaptoketone 40 (Scheme VI). (This scheme is probably not the best route for obtaining 41, as the dimer was obtained in very poor yield. However, a supply of ketone 40 had been prepared previously and was therefore used as the precursor of 41).

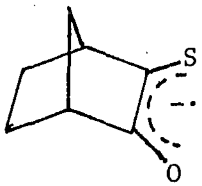
Scheme VI

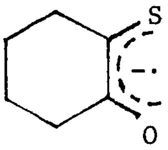


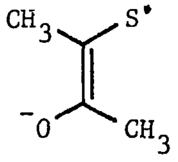
Many α-mercaptoketones exist as dimers but are in equilibrium with their monomers in basic solution (18); the monomer can then be converted to the radical anion. The ESR spectrum of 38 showed splitting by two sets of two equivalent hydrogens: $a^H = 11.45$ G (α-hydrogens on sulfur side) and $a^H = 4.80$ G (α-hydrogens on oxygen side).

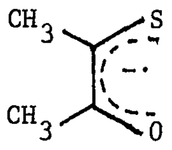
Butane-2,3-monothiosemidione (39) was formed by the reaction of 3-mercapto-2-butanone with potassium t-butoxide in Me_2SO. Hyperfine splitting by two sets of three equivalent hydrogens was observed: $a^H = 7.65$ G (methyl hydrogens on sulfur side) and $a^H = 2.10$ G (methyl hydrogens on oxygen side).

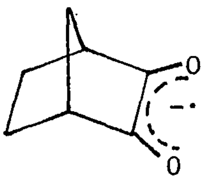
By comparing monothiosemidiones 37, 38, and 39 to the corresponding semidiones 1, 42, and 43, it appears that butane-2,3-monothiosemidione has the *trans* structure 39a rather than the *cis* structure 39b. Table III makes this comparison, where H_a is an α-hydrogen in the semidione, H_b is

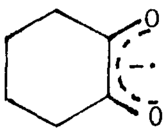

37

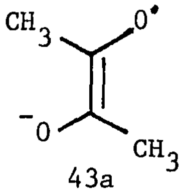

38

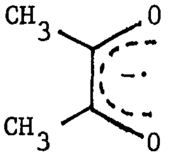

39a


39b


1


42


43a


43b

an α-hydrogen on the sulfur side of the monothiosemidione, and H_c is an α-hydrogen on the oxygen side of the monothiosemidione.

Table III. Comparison of hyperfine splitting constants for semidiones and monothiosemidiones

Anion Pair	a^H	a^{H_b}/a^{H_a}	a^{H_c}/a^{H_a}	a^{H_b}/a^{H_c}
1, 37	H_a 2.43[a]	1.1	0.53	2.0
	H_b 2.6			
	H_c 1.3			
42, 38	H_a 9.82[b]	1.2	0.49	2.4
	H_b 11.45			
	H_c 4.80			
43a, 39	H_a 5.6 [c]	1.4	0.38	3.6
	H_b 7.65			
	H_c 2.10			
43b, 39	H_a 7.0 [c]	1.1	0.30	3.6
	H_b 7.65			
	H_c 2.10			

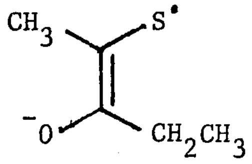
[a] Reference 1.

[b] Reference 19.

[c] Reference 20.

From the ratios given in the table, it can be seen that in going from bicyclic to monocyclic to acyclic monothiosemidione, the spin density on carbon containing the sulfur atom increases relative to the spin density on carbon containing the oxygen atom (therefore, a^{H_b}/a^{H_c} increases). Relative to the semidione, the spin density on carbon next to the sulfur atom increases while the spin density on carbon next to the oxygen atom decreases (therefore, a^{H_b}/a^{H_a} increases while a^{H_c}/a^{H_a} decreases). The trans structure for butane-2,3-monothiosemidione (39a) best fits this trend.

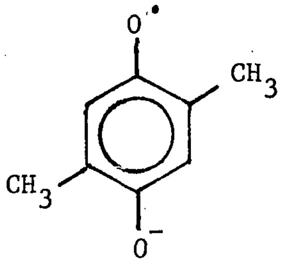
By a similar argument, monothiosemidione 44, generated from 2-mercapto-3-pentanone, probably has the trans structure shown. Hyperfine splitting constants of 7.75 G for three equivalent hydrogens and



44

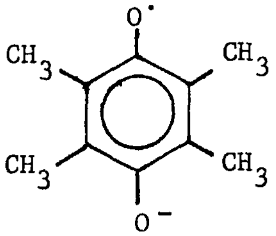
2.25 G for two equivalent hydrogens in 44 confirm the assignment of the larger splitting constants in 37, 38, and 39a to the hydrogens α to the carbon containing the sulfur atom.

When a degassed solution of 39a was opened to the air for a short time, a new ESR signal grew in with the addition of oxygen as the signal for 39a disappeared. The new signal was due to semiquinone 45, with hyperfine splitting constants of 2.15 G (6 H) and 1.96 G (2 H) (21). The semiquinone was a convenient standard relative to which the g-factor of the monothiosemidione, which was determined to be 2.0103, could be measured.



45

Monothiosemidione 44 behaved similarly with addition of traces of oxygen, producing semiquinone 46 (21). The g-factor of 44 was then measured as 2.0109.

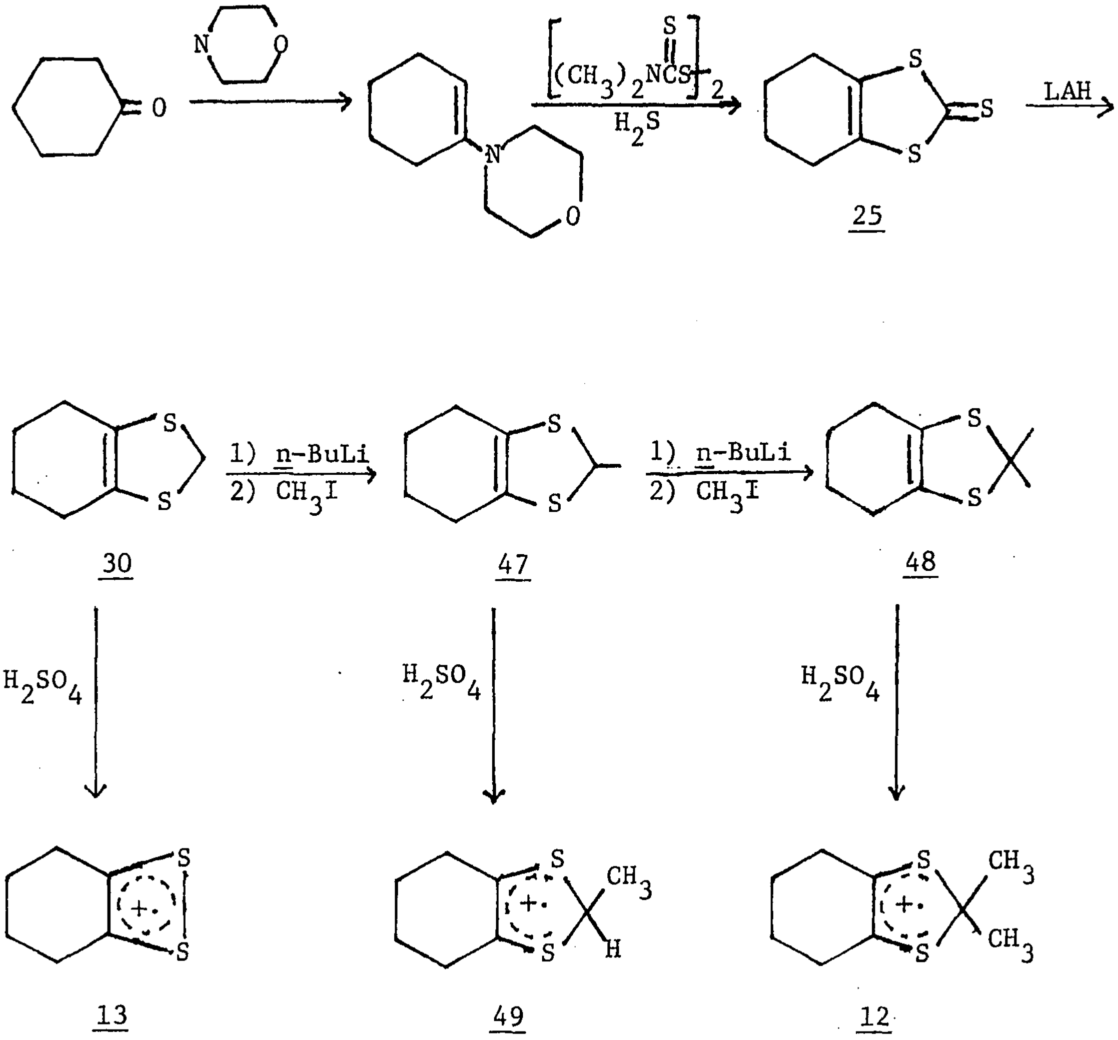


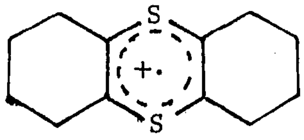
46

Radical Cations--Dithietes, Dithiins, and Dithioles

In an attempt to test the feasibility of synthesizing bicyclic dithiole 16 via Path B of Scheme IV, cyclohexanone was taken through the same reaction scheme (Scheme VII). Trithiocarbonate 25 was obtained in reasonable yield by this method, and reaction of 25 with lithium aluminum hydride produced 4,5-tetramethylene-1,3-dithiole (30). Upon treatment of 30 with sulfuric acid, only a very weak ESR signal was seen for what might have been the radical cation of dithiole 30. Instead, the major ESR signal observed was that of the dithiete radical cation 13: $a^H = 3.04$ G (4 H) (9). A very weak signal probably due to the dithiin radical cation 14 was also present: $a^H = 2.88$ G (8 H).

Scheme VII



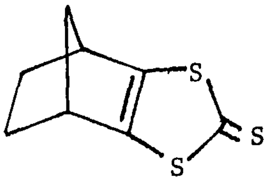


14

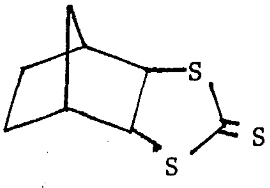
Addition of n-butyllithium and methyl iodide to dithiole 30 converted it to its 2-methyl derivative 47, which gave only the ESR signal for the corresponding radical cation 49 when treated with sulfuric acid. The hyperfine splitting constants observed were $a^H = 24.2$ G (1 H) and 8.5 G (4 H). No splitting by the methyl hydrogens was detected.

Dithiole 30 was methylated twice using n-butyllithium and methyl iodide to give dithiole 48. Treatment of 48 with sulfuric acid gave only the radical cation 12: $a^H = 8.75$ G (4 H). Starting with the parent dithiole, a much stronger signal for the radical cation could be obtained than by generating the cation from the diketone, sodium sulfide, and acetone in H_2SO_4.

After the successful completion of Scheme VII, the same reaction sequence was attempted starting with norcamphor (Scheme IV, Path B). However, treatment of the bicyclic enamine 32 with tetramethylthiuram disulfide and H_2S yielded not the desired trithiocarbonate 33 but an exo-endo mixture of trithiocarbonate 50. 50 was converted to trithiocarbonate 33 by the reaction sequence shown in Scheme VIII. (Where stereochemistry is not indicated, a mixture of exo-endo,cis compound



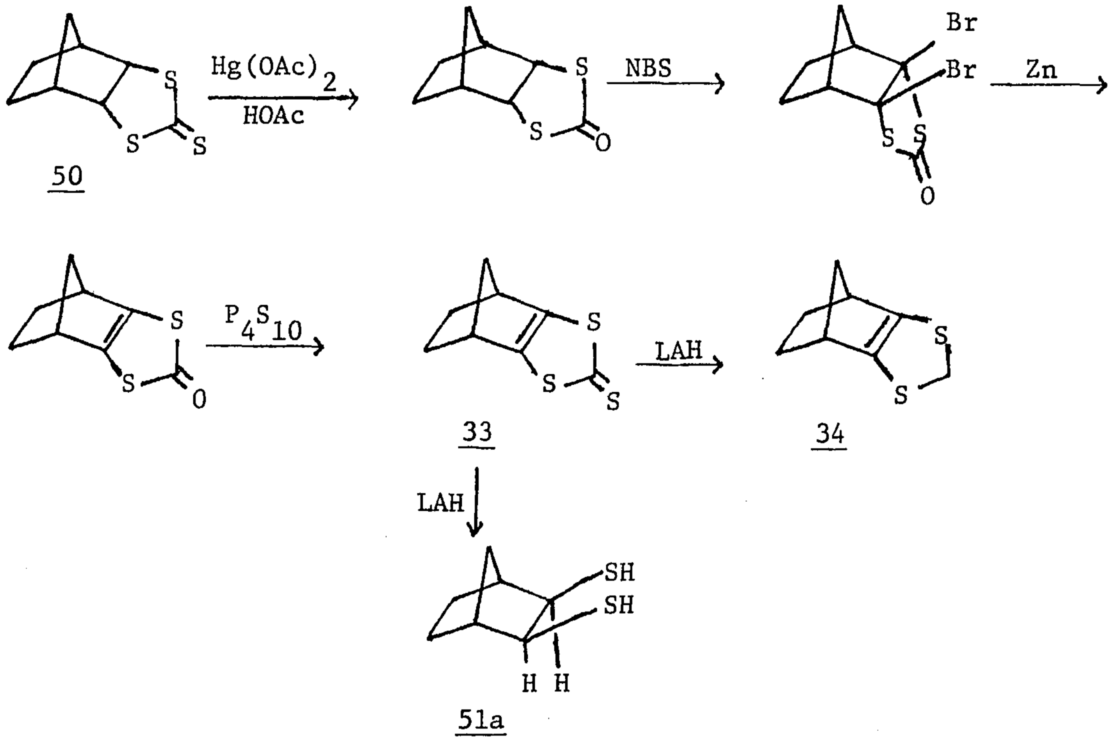
33



50

was present. Where a specific stereoisomer is shown, that stereoisomer was the only one obtained.) When trithiocarbonate 33 was finally obtained and was reacted with lithium aluminum hydride, the resulting product was bicyclo[2.2.1]heptane-2,3-dithiol 51a rather than the hoped-for dithiole 34.

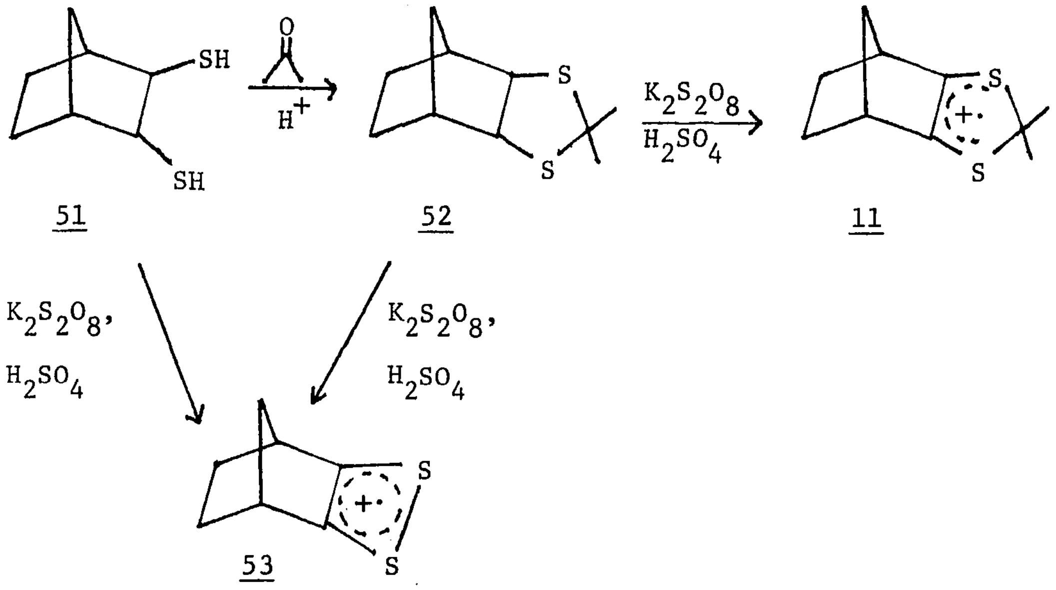
Scheme VIII



Although not the desired product, the dithiol 51a was not a completely unexpected product considering the formation of 1,2-benzenedithiol and 1,2-ethanedithiol, respectively, from benzo-1,3-dithiole-2-thione and 1,3-dithiole-2-thione itself upon treatment with lithium aluminum hydride (22, 23). An *exo-endo* mixture of the dithiol could be obtained much more readily, of course, by hydrolysis of trithiocarbonate 50 with sodium hydroxide, and for subsequent reactions the dithiol was prepared in this manner.

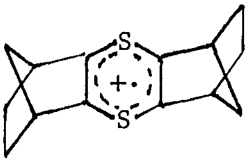
Bicyclo[2.2.1]heptane-2,3-dithiol (*exo-endo* mixture) 51 was reacted with acetone in hopes that the dithiole radical cation 11 could be generated from dithiolane 52 (Scheme IX). Instead, when dithiolane

Scheme IX



52 was dissolved in sulfuric acid and a small amount of solid potassium persulfate was added, an ESR signal with hyperfine splitting constants of $a^H = 2.75$ G (1 H; $H_{7\underline{anti}}$) and $a^H = 0.90$ G (4 H; $H_{1,4,5\underline{exo},6\underline{exo}}$) was observed and was attributed to the bicyclic dithiete radical cation 53. The same signal could be obtained by adding H_2SO_4 and potassium persulfate to the dithiol 51; however, in neither case could the signal for the dithiole radical cation 11 be obtained either by adding acetone to the solution containing the dithiete radical cation or by having acetone present when the sulfuric acid was added to the dithiol or the dithiolane.

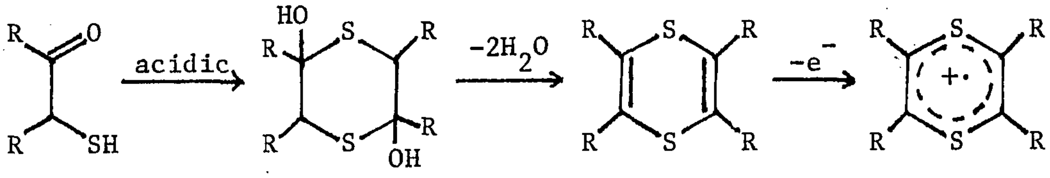
When the solution of dithiete radical cation 53 was allowed to stand overnight, a second signal very slowly grew in and was attributed to the dithiin radical cation 54: $a^H = 2.3$ G (2 H; $H_{7\underline{anti},7'\underline{anti}}$) and $a^H = 0.8$ G (8 H; $H_{1,1',4,4',5\underline{exo},5'\underline{exo},6\underline{exo},6'\underline{exo}}$). The same signal could be observed free of the dithiete radical cation signal by addition



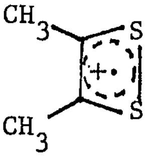
54

of sulfuric acid to 3-mercaptobicyclo[2.2.1]heptane-2-one (35). Since α-mercaptoketones are known to dimerize in acidic solution (18), the dithiin radical cation would be the expected product in sulfuric acid (Scheme X), confirming the identity of the second signal above.

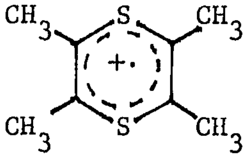
Scheme X



In order to determine whether 1,2-dithiols in general would form dithiete radical cations, 2,3-butanedithiol, 1,2-propanedithiol, and 1,2-ethanedithiol were reacted with sulfuric acid. 2,3-Butanedithiol produced the 3,4-dimethyl-1,2-dithiete radical cation (55) (9): $a^H = 2.19$ G (6 H). (Although $K_2S_2O_8$ was needed as an additional oxidizing agent in the case of the bicyclic dithiol, it was not necessary with the acyclic dithiols.) An unidentified impurity in the dithiol produced a second signal which obscured the region in which the signal for tetramethyl-1,4-dithiin radical cation (56) would have appeared if it had been present. Therefore, the dithiin radical cation was not observed in this solution.

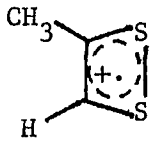


55



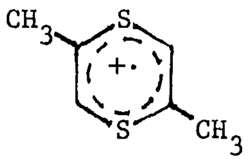
56

Addition of sulfuric acid to 1,2-propanedithiol produced the 3-methyl-1,2-dithiete radical cation (57) (9), with $a^H = 3.3$ G (1 H)

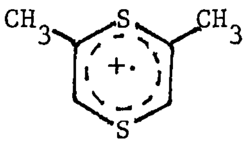


57

and $a^H = 1.8$ G (3 H), plus a second complex signal which grew in rather rapidly. The complex signal was actually made up of two signals with identical g-factors, one showing eleven equally spaced lines with hyperfine splitting constants of 3.50 G for two equivalent hydrogens and 1.75 G for six equivalent hydrogens and the other, a triplet of septets, with $a^H = 2.85$ G for two equivalent hydrogens and $a^H = 2.45$ G for six equivalent hydrogens. The two signals were attributed to the two possible dithiin radical cations that could form, 58 and 59; however,



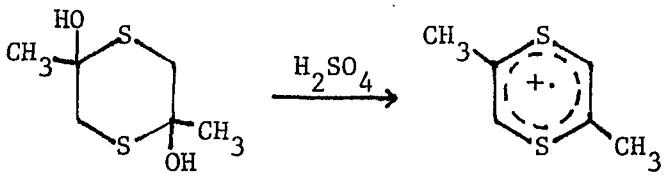
58



59

it was not obvious which set of splitting constants corresponded to each cation.

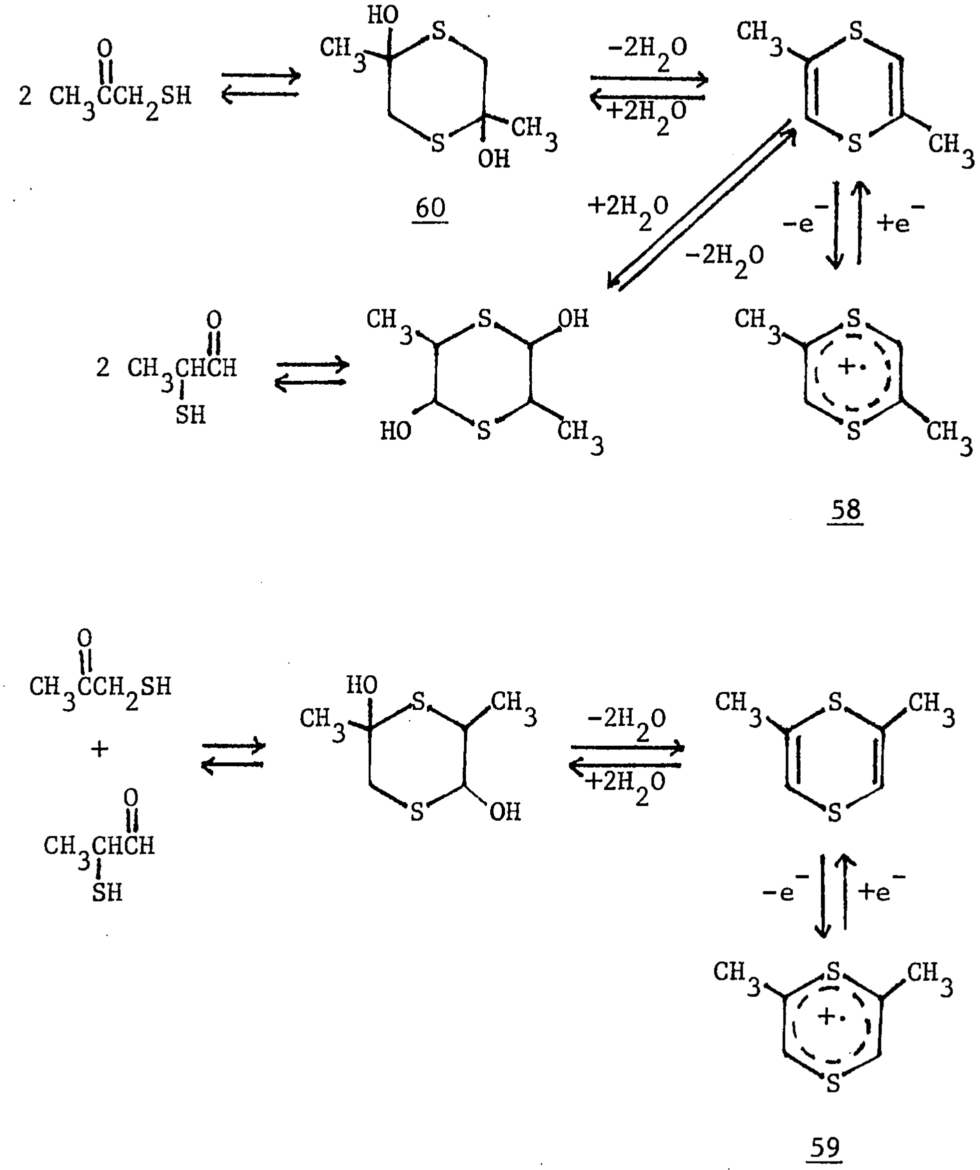
It was thought that radical cation 58 could be identified by adding sulfuric acid to the dimer of α-mercaptoacetone (60), which was expected to give only 58. Upon treating the dimer with H_2SO_4 and waiting until the ESR signal had stopped growing, a mixture of both 58 and 59 was again observed. An equilibrium mixture of the two cations was obviously forming almost as quickly as radical cation 58 was being formed (Scheme XI); therefore, by the time the growth of the signals had slowed down enough (after twenty to thirty minutes) so that an ESR spectrum could be taken, the same mixture of the two radical cations was always present.



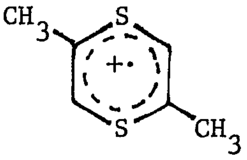
60 58

A scan of the ESR spectrum within a few minutes after addition of H_2SO_4 to the dimer 60 showed mainly the eleven-line signal present at first with both signals growing during the time the spectrum was being scanned. Repeated scans showed the triplet of septets growing relative to the eleven-line signal until the usual equilibrium mixture was reached after about thirty minutes. The signal which

Scheme XI

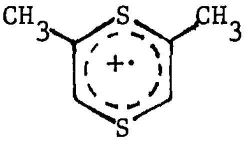


appeared first was assigned to dithiin radical cation 58, while the triplet of septets was assigned to 59.



58

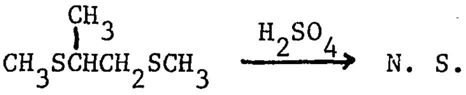
a^H = 3.50 G (2 H)
1.75 G (6 H)



59

a^H = 2.85 G (2 H)
2.45 G (6 H)

As the bicyclic dithiolane 52 did, 2,2,4-trimethyl-1,3-dithiolane in sulfuric acid produced the same ESR signals as the corresponding 1,2-propanedithiol. However, 3-methyl-2,5-dithiahexane (61) failed to give an ESR signal in sulfuric acid.



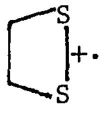
$$CH_3S\overset{CH_3}{\overset{|}{C}}HCH_2SCH_3 \xrightarrow{H_2SO_4} N.\ S.$$

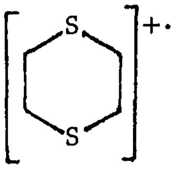
61

1,2-Ethanedithiol and 2,2-dimethyl-1,3-dithiolane in sulfuric acid both gave the same ESR spectrum, but it was not the spectrum of the dithiete radical cation. This case will be discussed separately below.

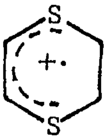
Radical Cations--Cyclic Disulfides

Addition of sulfuric acid to 1,2-ethanedithiol produced a radical cation with a hyperfine splitting constant of a^H = 3.7 G for four equivalent hydrogens, which was believed to be the 1,2-dithietane radical cation (62). A second signal grew in very rapidly and had a hyperfine splitting constant of $a^H = 2.40$ G (8 H). It was originally believed to be that of the 1,4-dithiane radical cation (63), which is observed when 1,4-dithiane is oxidized by hydroxyl radical (24, 25). However, 1,4-dithiane itself in sulfuric acid failed to give an ESR signal.

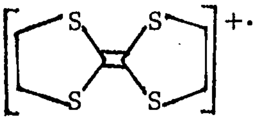

62


63

An attempt was then made to generate radical cation 64 to see what the magnitude of the hyperfine splitting constant for the methylene

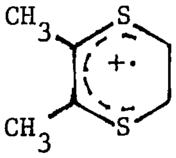

64

hydrogens would be in comparison to the hfsc for the dithietane radical cation (62). When sulfuric acid was added to the parent 2,3-dihydro-1,4-dithiin, the ESR signal for 64 was not seen. Instead, the signal with $a^H = 2.40$ G (8 H) grew in fairly rapidly. This signal was eventually identified as that of the $\Delta^{2,2'}$-bi-1,3-dithiolane radical cation 65 (26).



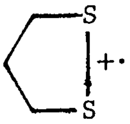
65

An example of a 2,3-dihydro-1,4-dithiin radical cation was still desired as a comparison to cations 62 and 65. Addition of sulfuric acid to 5,6-dimethyl-2,3-dihydro-1,4-dithiin produced radical cation 66, with hyperfine splitting constants a^H = 5.65 G (6 H) and a^H = 3.50 G (4 H).



66

1,3-Propanedithiol also formed a cyclic disulfide radical cation when treated with sulfuric acid. The 1,2-dithiolane radical cation (67) had a hyperfine splitting constant of a^H = 10.00 G for four equivalent hydrogens. No other signal was observed.



67

1,4-Butanedithiol (68) failed to give an observable ESR signal when treated with sulfuric acid. Also failing to give an ESR signal with H_2SO_4 was 2,5-dithiahexane (69).

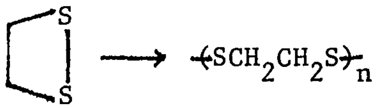
$$HSCH_2CH_2CH_2CH_2SH \xrightarrow{H_2SO_4} N.\ S.$$

68

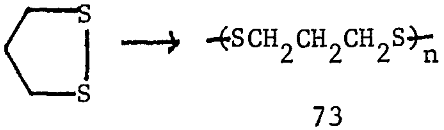
$$CH_3SCH_2CH_2SCH_3 \xrightarrow{H_2SO_4} N.\ S.$$

69

To help confirm the presence of the 1,2-dithietane radical cation (62) and 1,2-dithiolane radical cation (67), an attempt was made to synthesize the parent compounds 70 and 72. Small cyclic disulfides polmerize easily (27), and in the attempted synthesis of 70, only the polymeric disulfide 71 was obtained. 1,2-Dithiolane is known to polymerize more slowly when in solution than when isolated; therefore, 72 was left in a benzene solution after it was made and the solution was mixed with sulfuric acid. Taking the acid layer only, the signal with hfsc a^H = 10.00 G (4 H) was again observed.



70 71

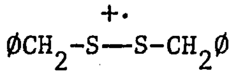


72 73

The 1,2-dithiolane (72) was isolated and given time to polymerize, and the polymeric disulfide 73 was treated with sulfuric acid. It gave the same signal as did 1,3-propanedithiol and 1,2-dithiolane (72).

Polymer 71, when treated with sulfuric acid, gave only the signal for the 1,2-dithietane radical cation (62). No signal for radical cation 65 was observed.

To see if monothiols would form disulfide radical cations, 1-butanethiol, sodium methanethiolate, and benzyl mercaptan were treated with sulfuric acid. Only benzyl mercaptan gave an observable ESR signal, $a^H = 1.4$ G (4 H), with a g-factor close to that of the 1,3-dithiolane radical cation (67). Benzyl disulfide, the only disulfide to yield an observable signal, gave the same signal as the mercaptan did, probably radical cation 74. Isopropyl disulfide, methyl disulfide, and isopropyl methyl disulfide did not give ESR signals when treated with sulfuric acid.



$$\phi CH_2\text{-}\overset{+\cdot}{S\text{—}S}\text{-}CH_2\phi$$

74

Tabulation of ESR Results

Table IV lists the splitting constants and g-factors of observed radical anions and cations mentioned earlier. Entries in the table are arranged so that radical ions of the same type appear consecutively, with the different types appearing in the following order: semidithiones, monothiosemidiones, semiquinones, dithiete radical cations, dithiin radical cations, dithiole radical cations, disulfide radical cations, and other radical cations.

(It has been stated that the signal for tetramethyl-1,4-dithiin radical cation (56) was not observed in solution with 3,4-dimethyl-1,2-dithiete radical cation (55). However, 56 was generated from 3-mercapto-2-butanone in the process of determining the g-factor for 55, and it is therefore included in Table IV.)

ESR Spectra

Figures 1-13 show the ESR spectra of some of the radical anions and cations mentioned earlier which had not been observed previously.

Table IV. Splitting constants and g-factors of observed radical anions and cations

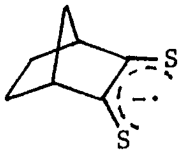
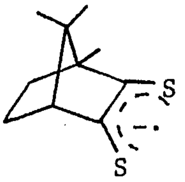
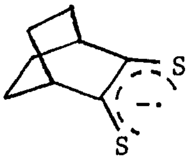
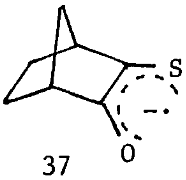
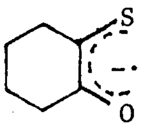
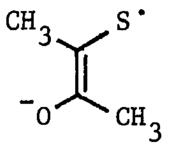
Radical Ion	a^H	g-Factor	Reference
 20	4.2 (1) 1.3 (4)	2.0166	28
 28	1.4 (3)		
 29	1.2 (4)		
 37	5.2 (1) 2.6 (2) 1.3 (2)	2.0100	28
 38	11.45 (2) 4.80 (2)		
 39a	7.65 (3) 2.10 (3)	2.0103	

Table IV (continued)

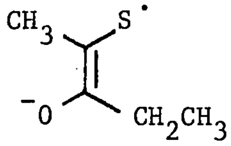
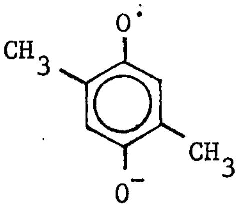
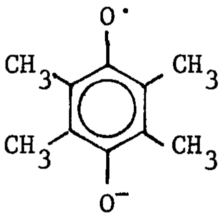
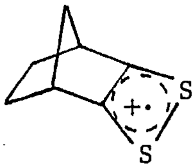
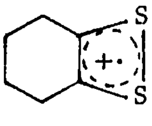
Radical Ion	a^H	g-Factor	Reference
 44	7.75 (3) 2.25 (2)	2.0109	
 45	2.15 (6) 1.96 (2)	2.0050	28 21
 46	1.95 (12)	2.0055	21
 53	2.75 (1) 0.90 (4)	2.0144	
 13	3.04 (4)	2.0155	9

Table IV (continued)

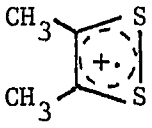
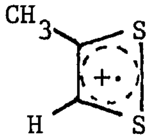
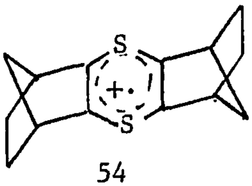
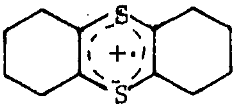
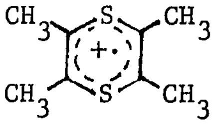
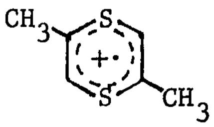
Radical Ion	a^H	g-Factor	Reference
 55	2.19 (6)	2.0156	9
 57	3.3 (1) 1.8 (3)	2.0159	9
 54	2.3 (2) 0.8 (8)	2.0084	
 14	2.88 (8)	2.0092	9
 56	2.10 (12)	2.0092	9
 58	3.50 (2) 1.75 (6)	2.0094	

Table IV (continued)

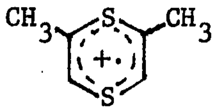
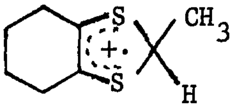
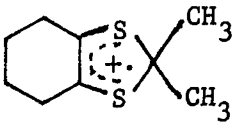
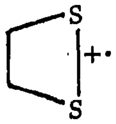
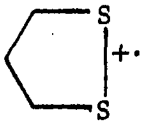
Radical Ion	a^H	g-Factor	Reference
 59	2.85 (2) 2.45 (6)	2.0094	
 49	24.2 (1) 8.5 (4)		
 12	8.75 (4)	2.0103	
 62	3.7 (4)	2.0193	
 67	10.00 (4)	2.0182	

Table IV (continued)

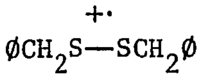
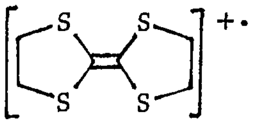
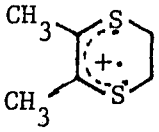
Radical Ion	a^H	g-Factor	Reference
 $\phi CH_2\overset{+\cdot}{S-S}CH_2\phi$ 74	1.4 (4)		
 65	2.40 (8)	2.0089	26
 66	5.65 (6) 3.50 (4)		

Figure 1. First derivative ESR spectrum of 2,2-dimethyl-4,5-tetramethylene-1,3-dithiole radical cation (12)

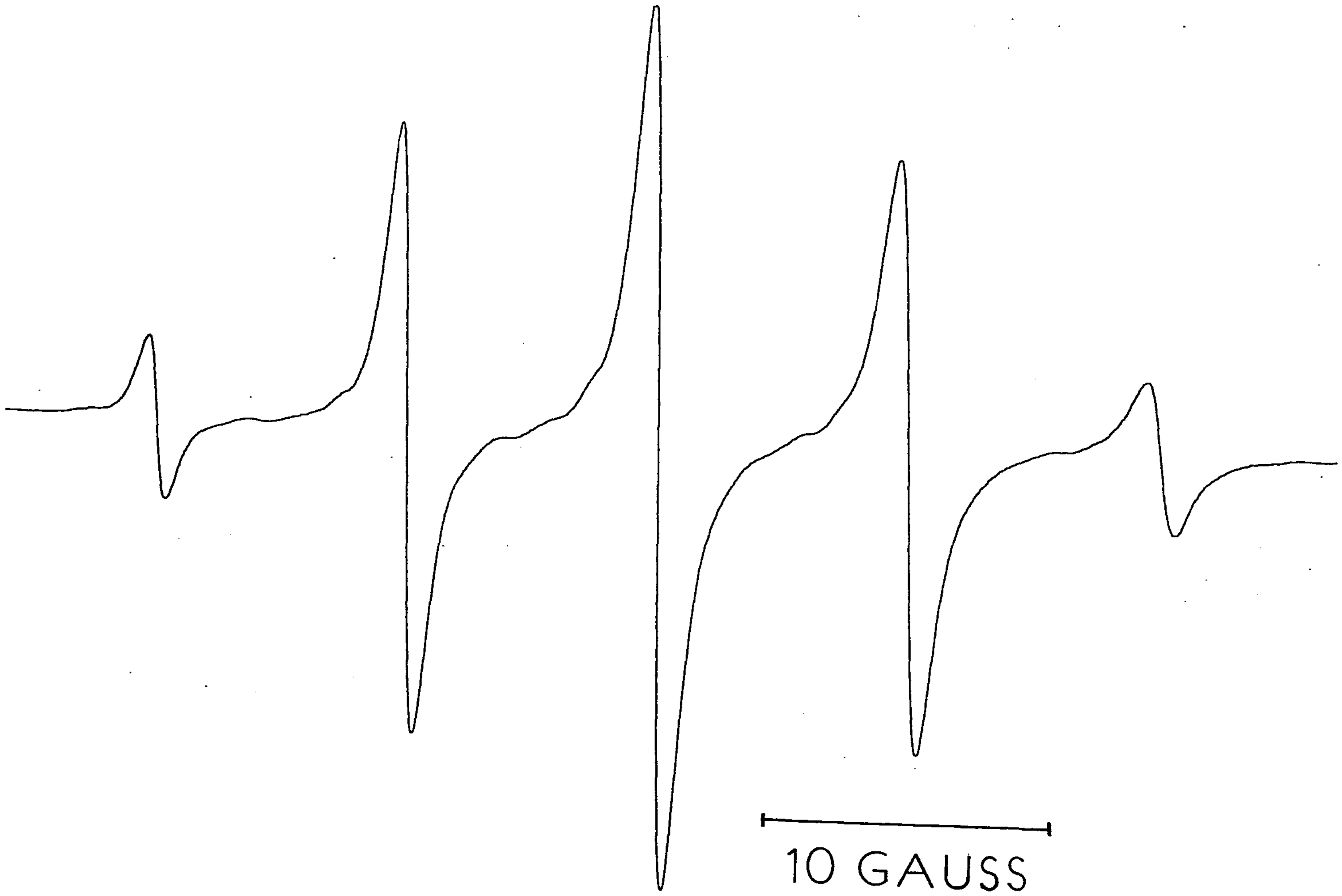

10 GAUSS

Figure 2. First derivative ESR spectrum of bicyclo-[2.2.1]heptane-2,3-semidithione (20)

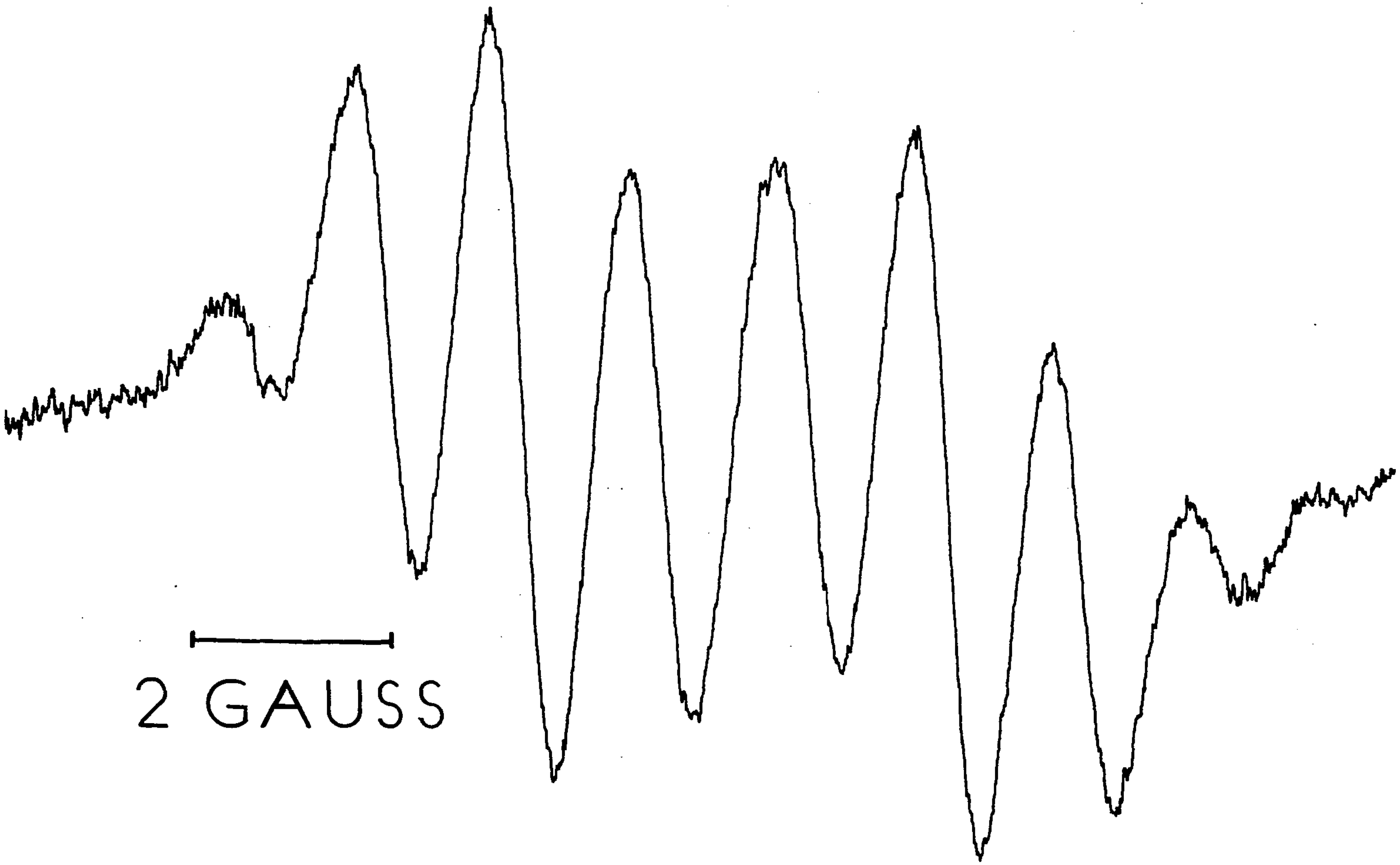

2 GAUSS

Figure 3. First derivative ESR spectrum of bicyclo[2.2.1]heptane-2,3-monothiosemidione (37)

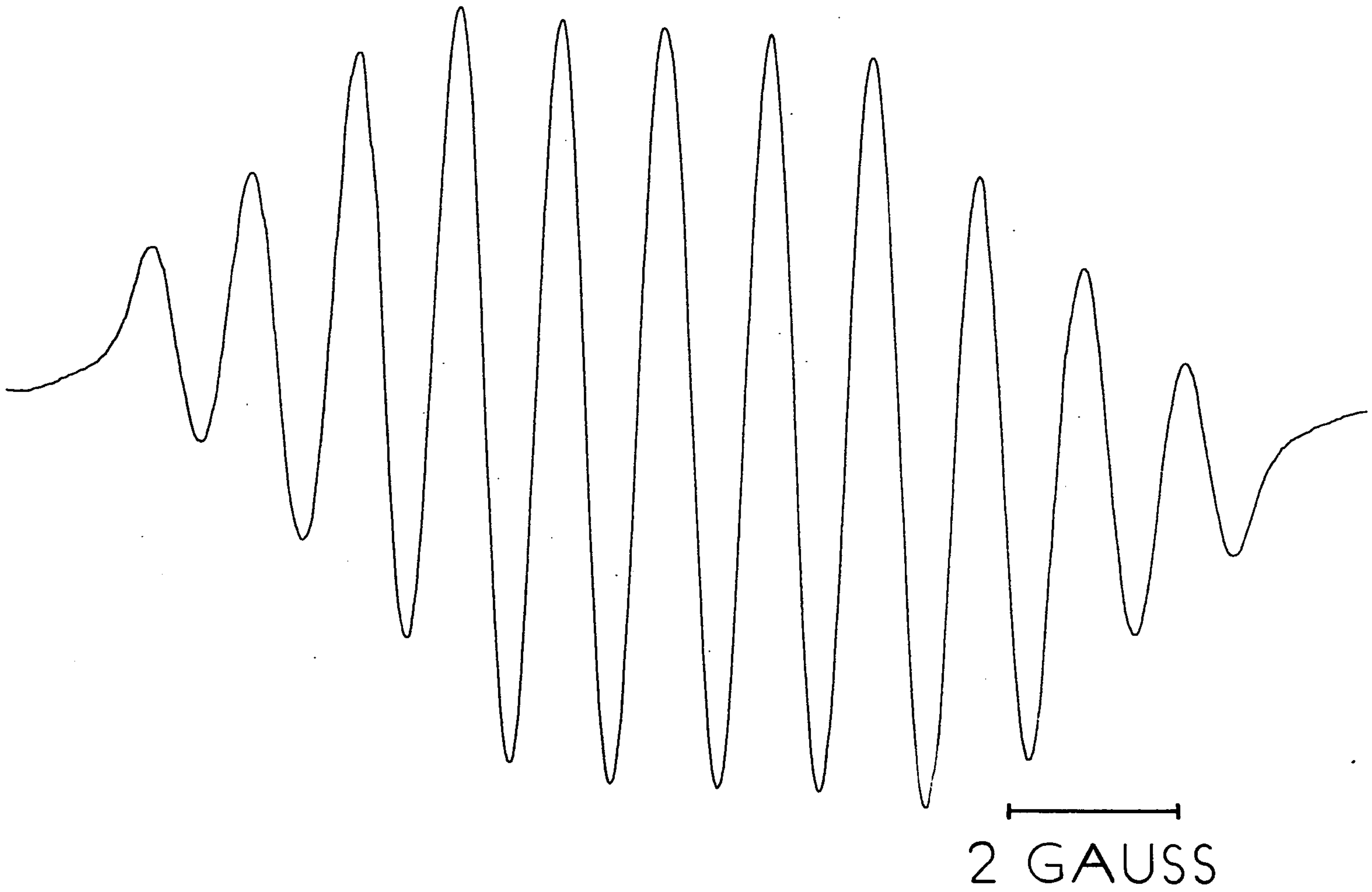

2 GAUSS

Figure 4. First derivative ESR spectrum of cyclohexane-1,2-monothiosemidione (38)

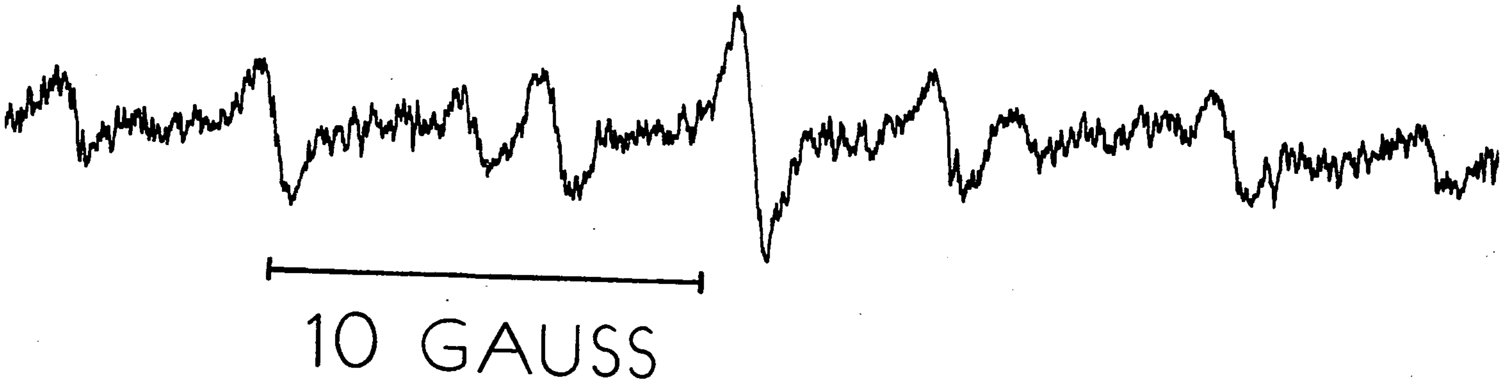

10 GAUSS

Figure 5. First derivative ESR spectrum of butane-2,3-monothiosemidione (39a)


5 GAUSS

Figure 6. First derivative ESR spectrum of pentane-2-thio-2,3-semidione (44)

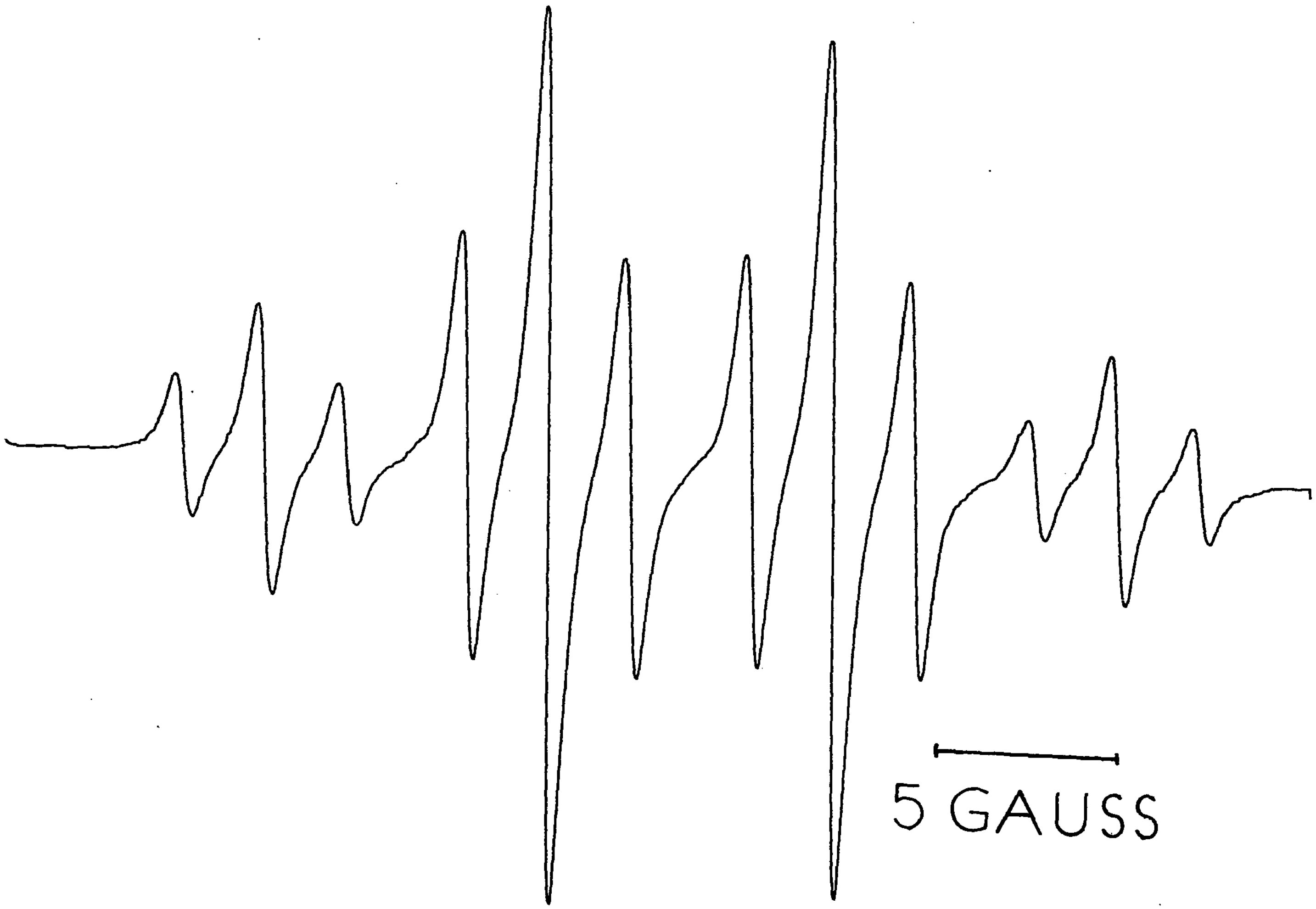

5 GAUSS

Figure 7. First derivative ESR spectrum of the bicyclic dithiete radical cation (53) obtained from bicyclo[2.2.1]heptane-2,3-dithiol in sulfuric acid

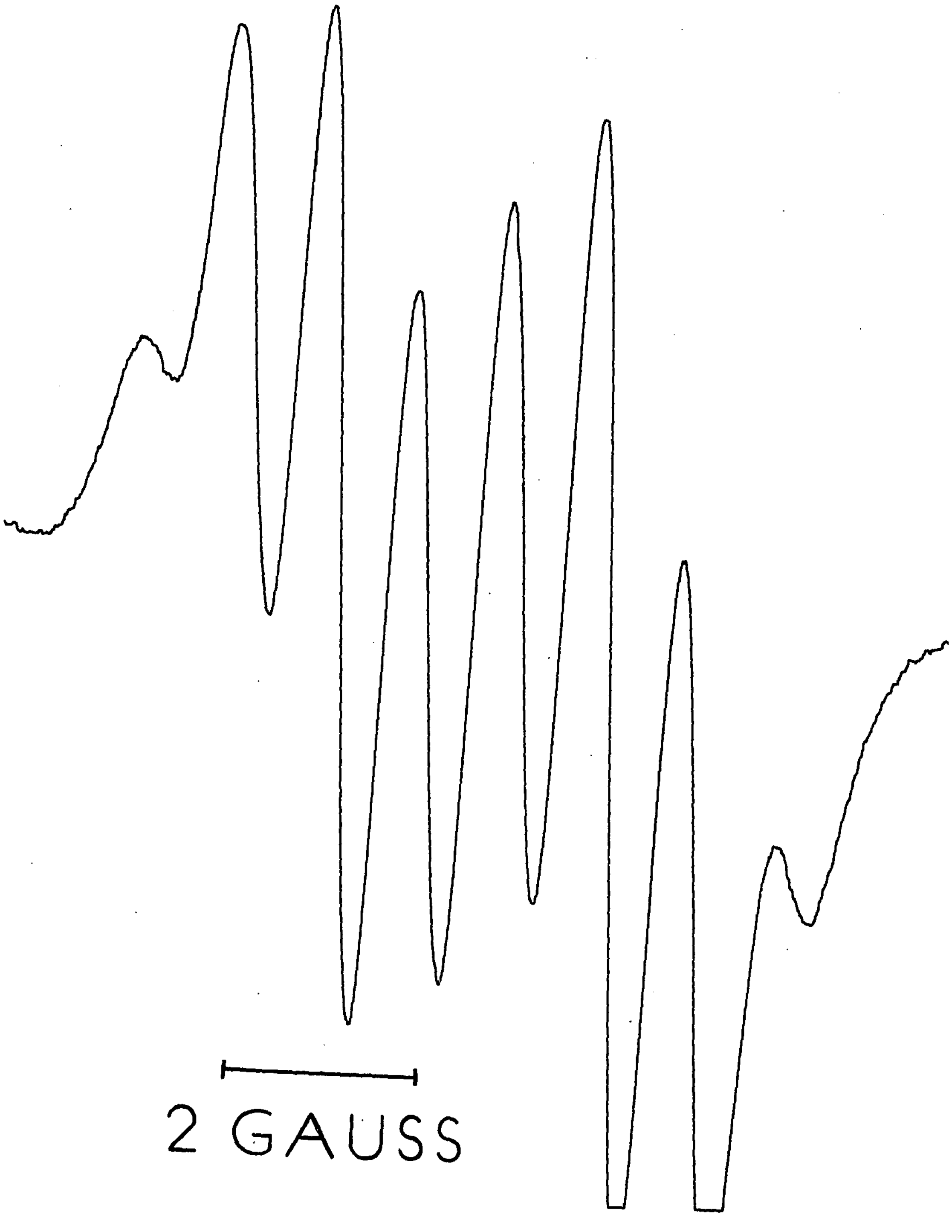

2 GAUSS

Figure 8. First derivative ESR spectrum of the bicyclic dithiin radical cation (54) obtained from 3-mercaptobicyclo[2.2.1]heptan-2-one in sulfuric acid

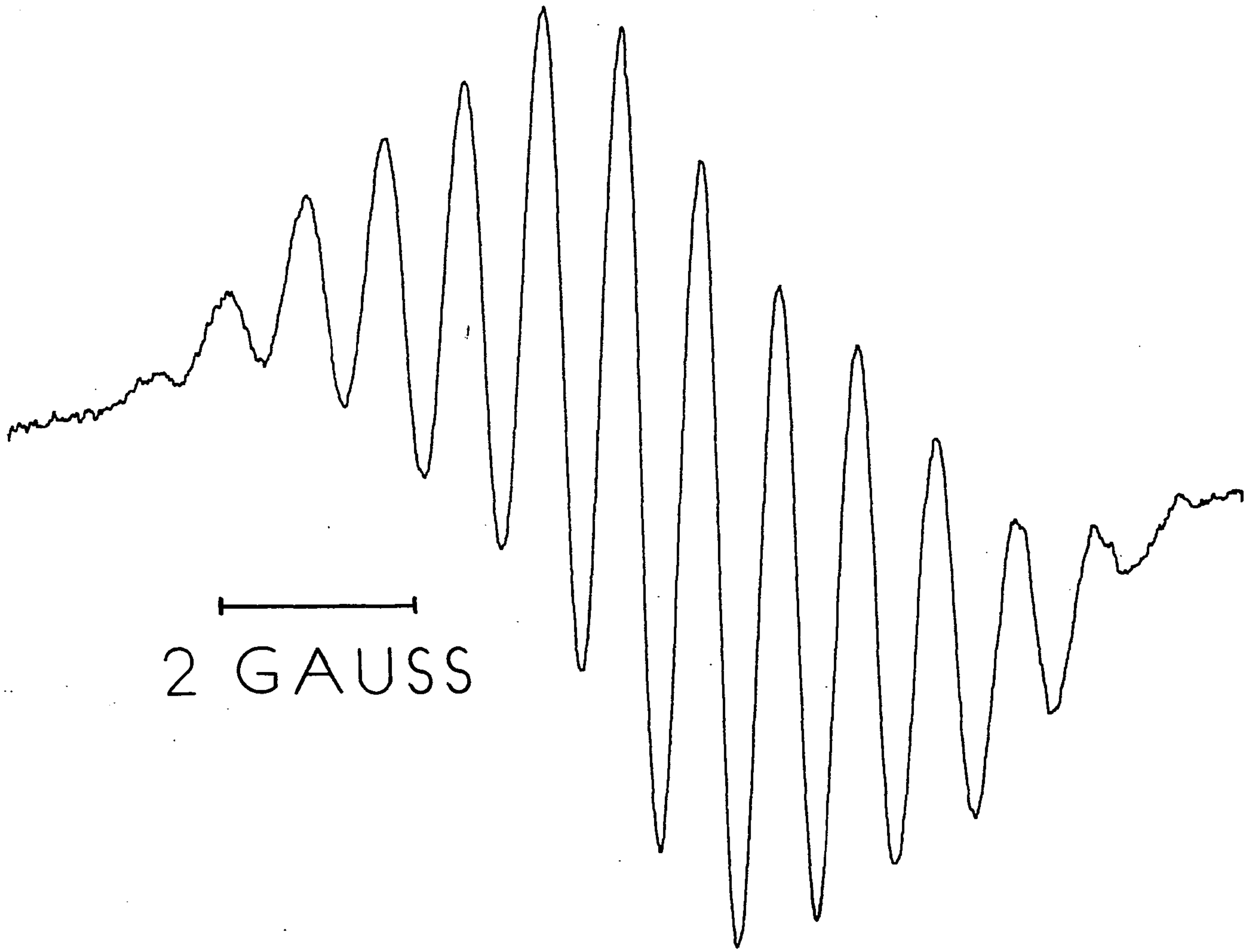

2 GAUSS

Figure 9. First derivative ESR spectrum of 1,2-dithietane radical cation (<u>62</u>)

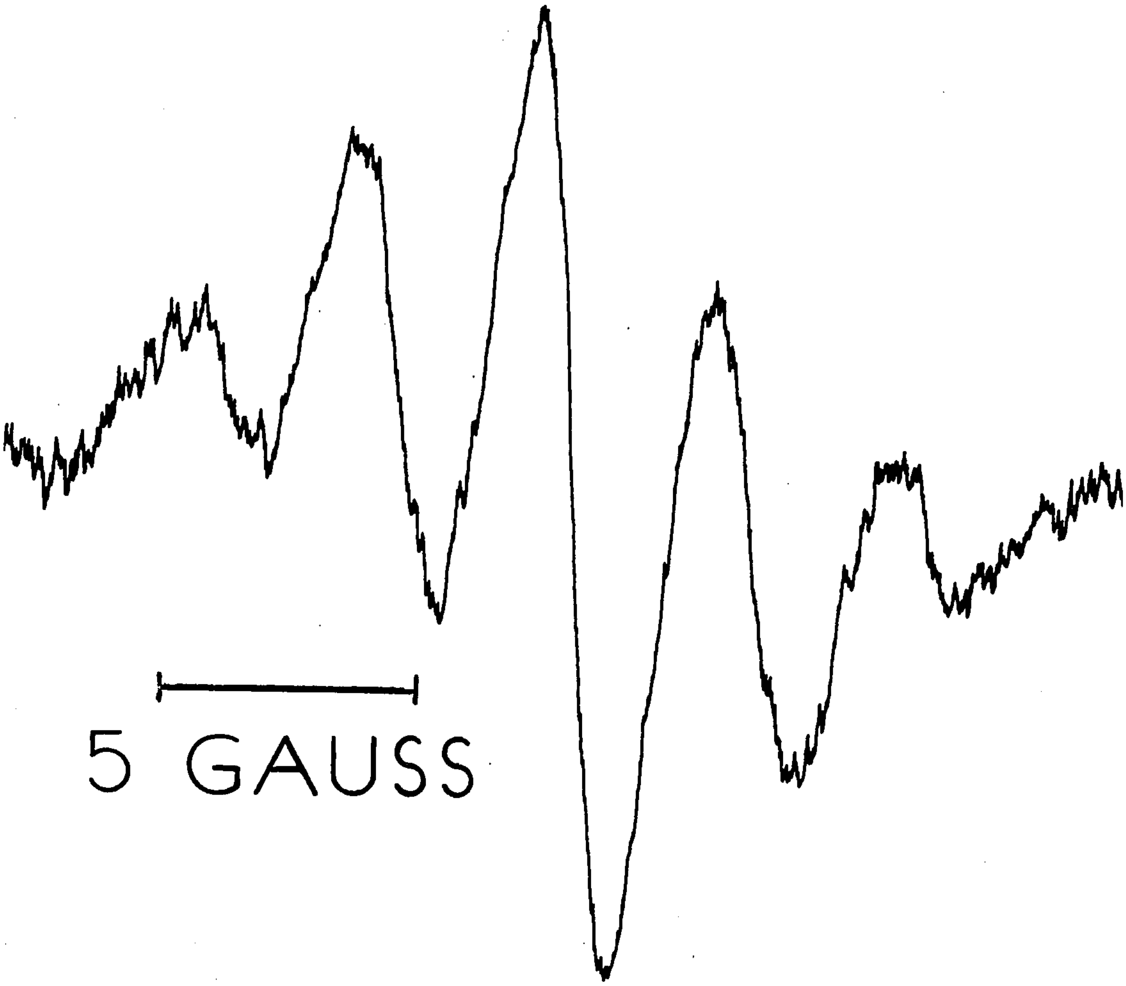

5 GAUSS

Figure 10. First derivative ESR spectrum of $\Delta^{2,2'}$-bi-1,3-dithiolane radical cation (65)

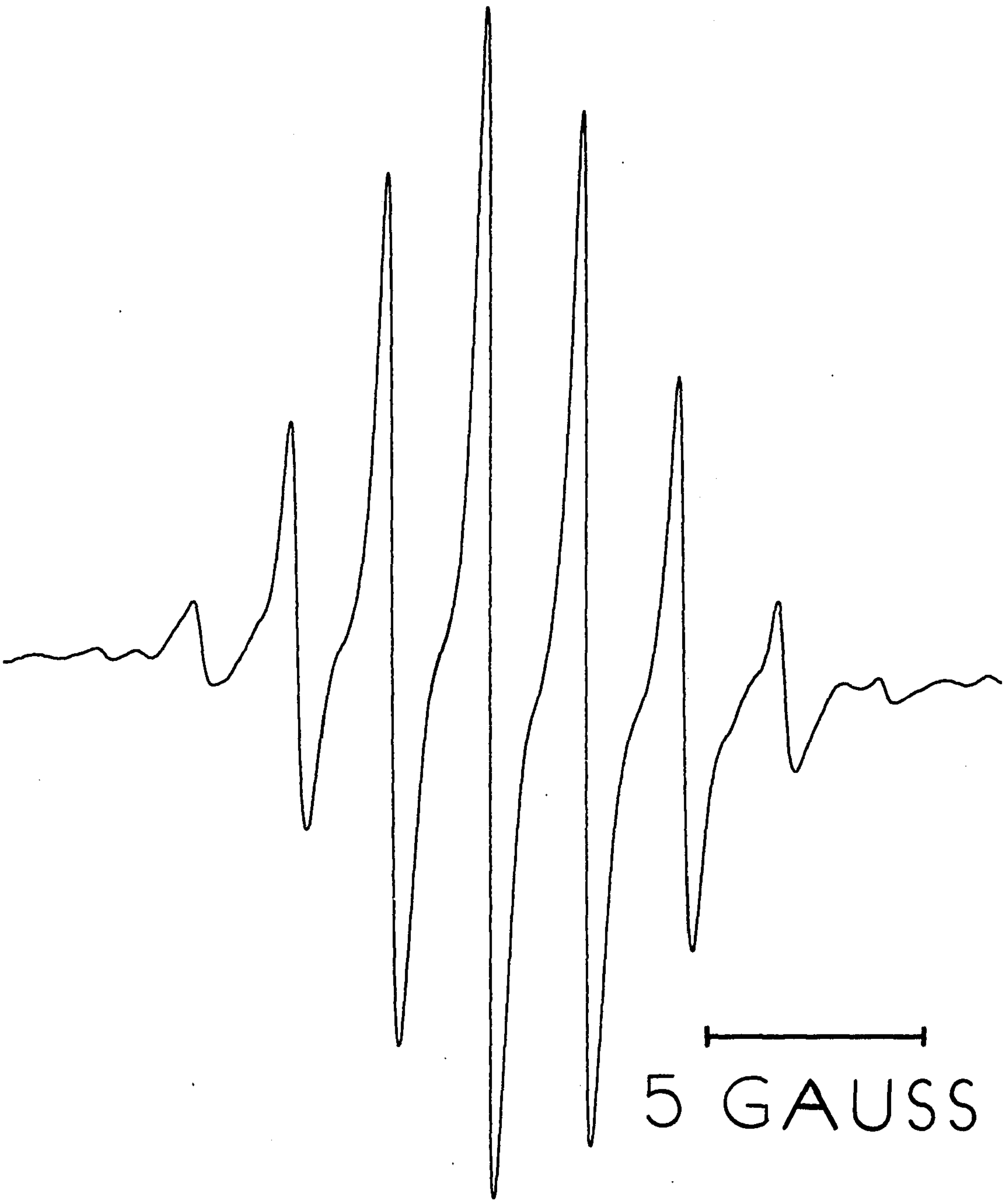

5 GAUSS

Figure 11. First derivative ESR spectrum of 5,6-dimethyl-2,3-dihydro-1,4-dithiin radical cation (66)

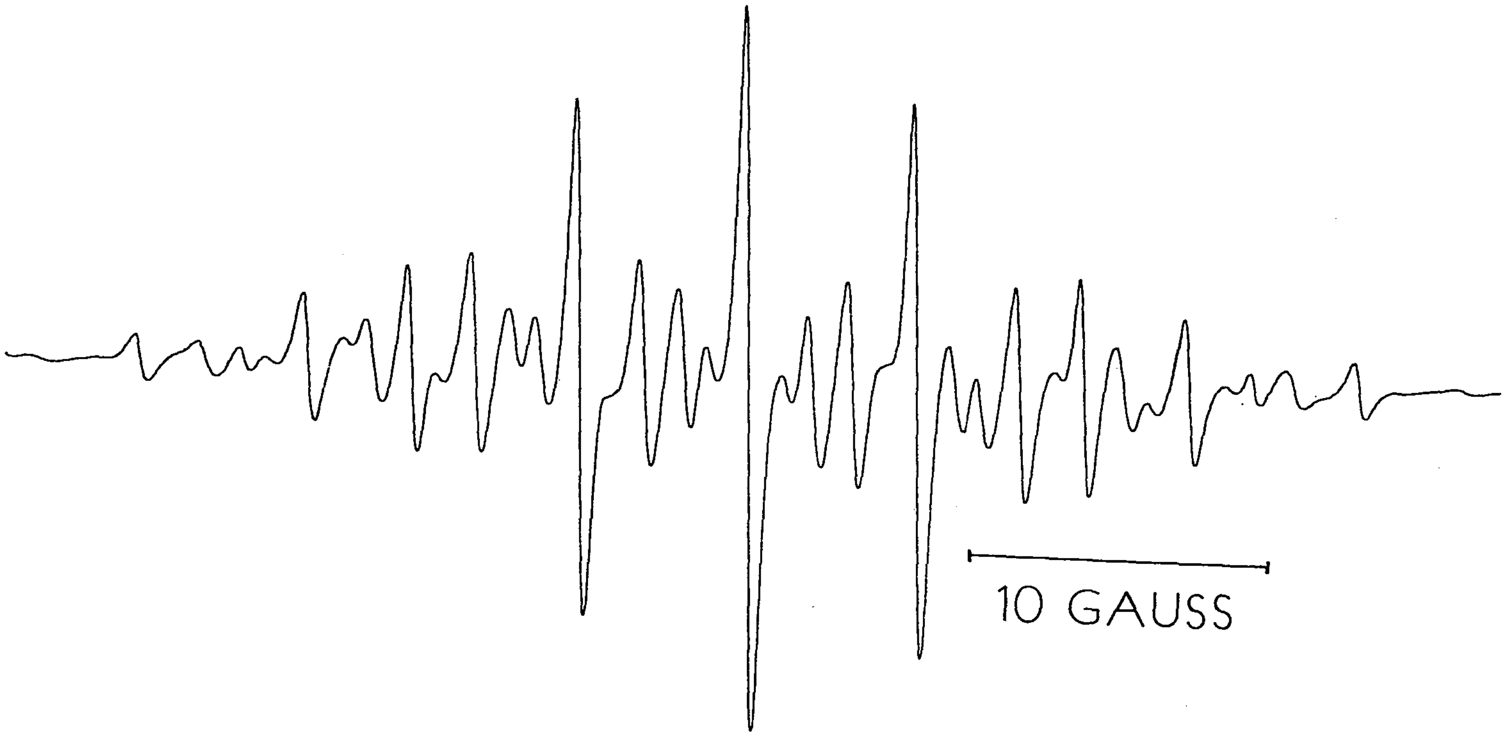

10 GAUSS

Figure 12. First derivative ESR spectrum of 1,2-dithiolane radical cation (67)

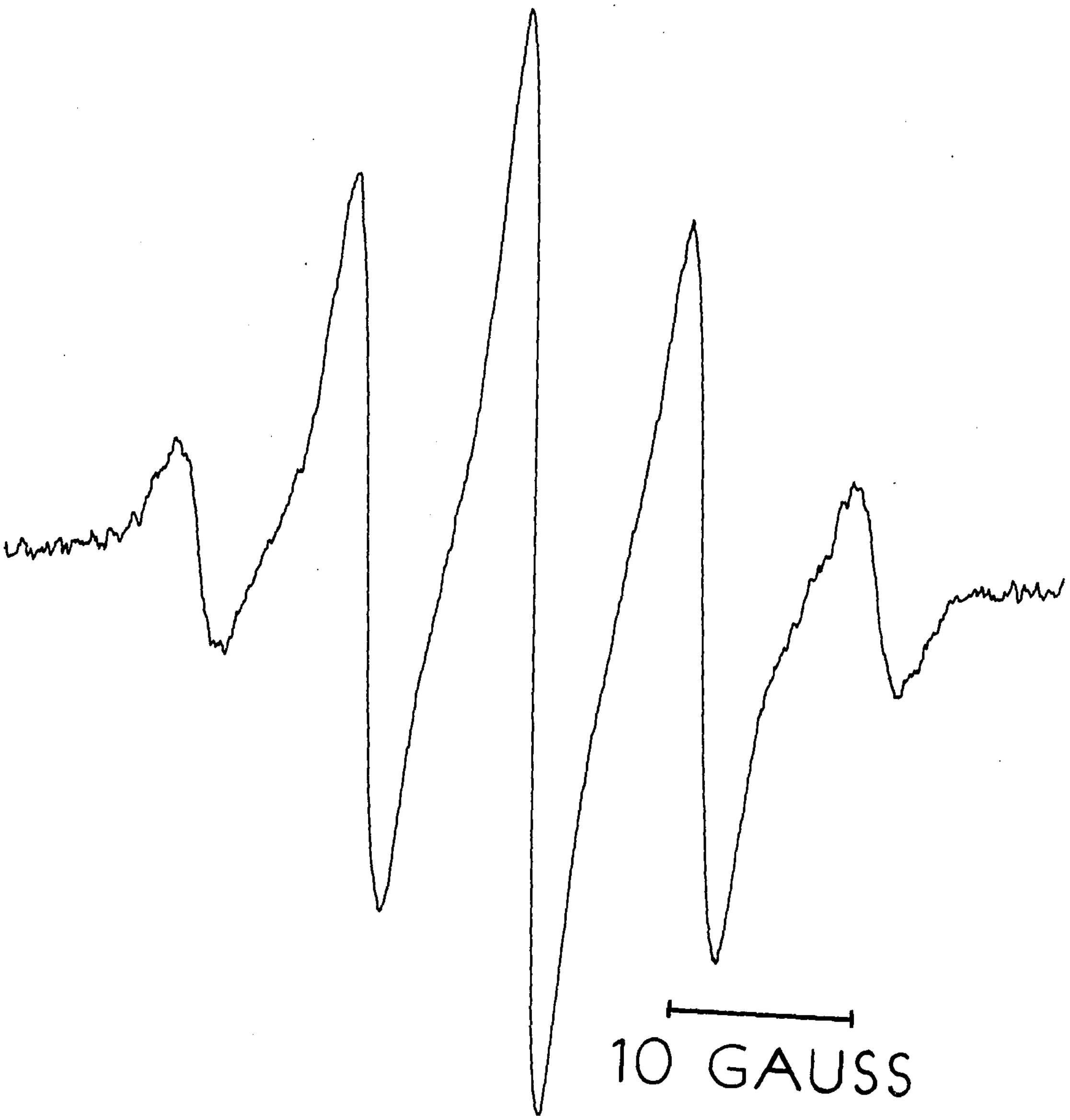
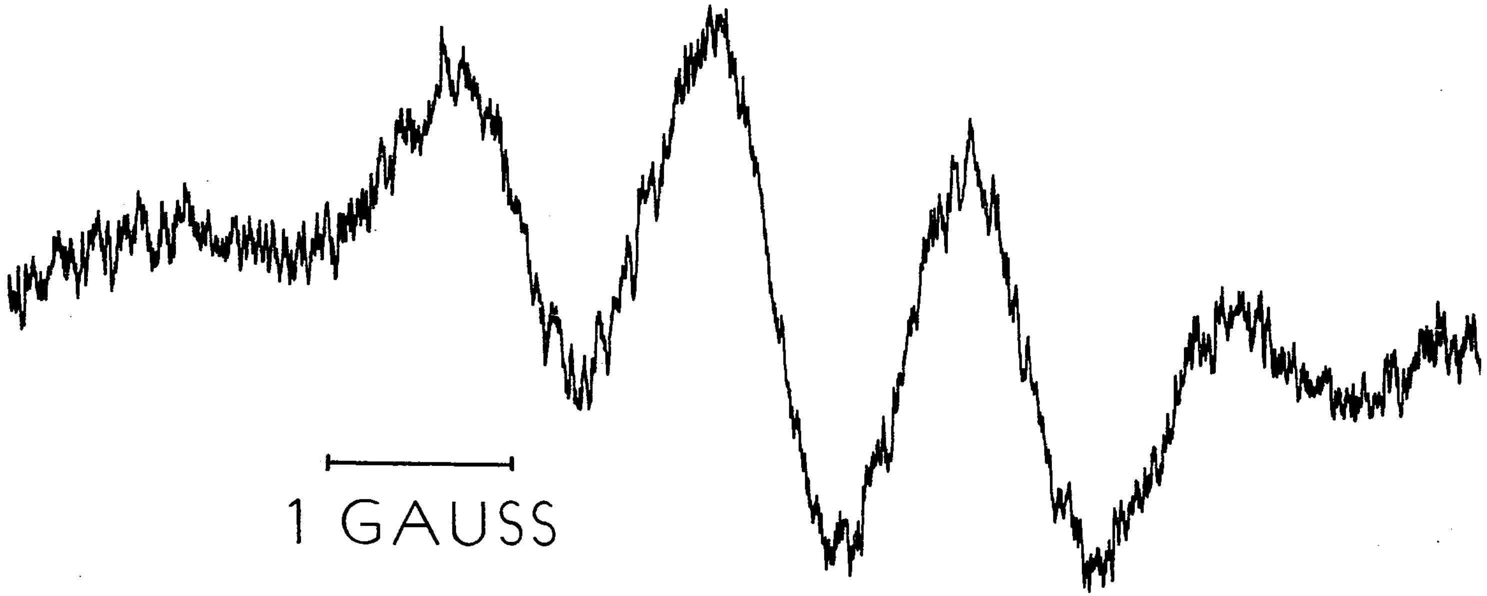
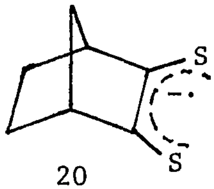

10 GAUSS

Figure 13. First derivative ESR spectrum of benzyl disulfide radical cation (74)

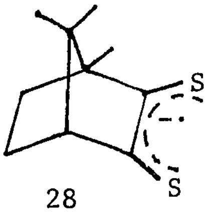

1 GAUSS

DISCUSSION

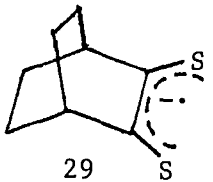
The semidithiones 20, 28, and 29 proved to be much like semidiones 1, 75, and 76, but with greater spin density at the sulfur atoms than on the oxygen atoms (and, therefore, less spin density at carbons 2 and 3). The shift in spin density is reflected in the smaller hyperfine splitting constants observed for the semidithiones than for the semidiones. The ratio a^H(semidithione)/a^H(semidione) remains constant, within the accuracy of the a^H measurements, with a^H(20)/a^H(1) = 0.53, a^H(28)/a^H(75) = 0.55, and a^H(29)/a^H(76) = 0.57 (1). [For 75, a doublet of triplets could be seen in a well-resolved spectrum but a quartet was observed at lower resolution. Because the poorly-resolved spectrum of 28 showed a quartet, the doublet and triplet values of 75 were averaged in figuring a^H(28)/a^H(75).] The a^H values used in calculating the ratios are those for the bridgehead and exo hydrogens. (In 29,



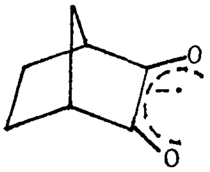
20



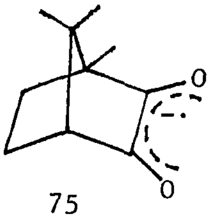
28



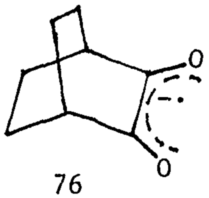
29



1



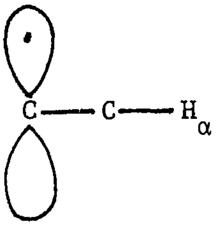
75



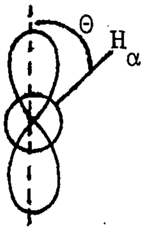
76

where $a^H = 0$ for the bridgehead hydrogens, only the value for the *exo* hydrogens was used.)

The splitting constants of hydrogen atoms α to a carbon atom containing an unpaired electron in a p orbital (77, 78) can be related



77



78

to the spin density at that carbon atom using Equation 1. a_α^H is the hfsc for the α-hydrogen (the bridgehead hydrogens in 20 and 1), B is a

$$a_\alpha^H = B\rho\langle\cos^2 \Theta\rangle \qquad \text{(Eqn. 1)}$$

constant, ρ is the spin density at carbon (C_2 or C_3 in 20 and 1), and Θ is the angle between the p orbital containing the unpaired electron and the C-H bond (29). Assuming that Θ (and, consequently, $\langle\cos^2 \Theta\rangle$) remains constant in going from 1 to 20, $a_\alpha^H(20)/a_\alpha^H(1) = \rho(20)/\rho(1)$, and the smaller value of a^H for the bridgehead hydrogens in the semidithione must be due to lower spin density at carbons 2 and 3.

The *exo* hydrogens at carbons 5 and 6 (β-hydrogens) show the same decrease in a^H in going from 1 to 20. Since $a_\beta^H(20)/a_\beta^H(1) = a_\alpha^H(20)/a_\alpha^H(1) = \rho(20)/\rho(1)$, the magnitude of a_β^H must also be some linear function of ρ. The equivalence of the ratios $a_\beta^H(20)/a_\beta^H(1)$ and $a_\beta^H(29)/a_\beta^H(76)$ indicates that the shift of spin density away from carbon (more toward sulfur) in going from semidione to semidithione is of like magnitude in both the bicyclo[2.2.1]heptane and bicyclo[2.2.2]-octane systems.

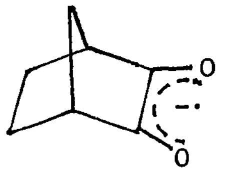
In both 1 and 20, the bridgehead hydrogens and exo hydrogens happen to be equivalent. This equivalence is lost in 75 due to changes in geometry of the system caused by the presence of the methyl groups. Under high resolution, hyperfine splitting constants of $a^H = 3.01$ G and $a^H = 2.08$ G are observed for the exo hydrogens and the one bridgehead hydrogen, respectively. Had the ESR spectrum for semidithione 28 been more highly resolved, observed splitting constants of $a^H = (3.01 \text{ G})(0.55) = 1.7$ G and $a^H = (2.08 \text{ G})(0.55) = 1.1$ G would have been expected for the exo and bridgehead hydrogens, respectively.

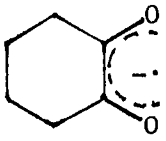
The ratio $a^H(\underline{20})/a^H(\underline{1})$ is larger for $H_{7\underline{anti}}$ than for the exo and bridgehead hydrogens. $a_{7a}{}^H$ is a function of $[(\rho_{C_2})^{1/2} \pm (\rho_{C_3})^{1/2}]^2$, where the sum is used when, for the HOMO, the coefficients of the atomic orbitals at C_2 and C_3 are of like sign and the difference is used when the coefficients are of opposite sign (2). Because this relationship is not a linear one with respect to ρ, different a^H ratios are observed for H_{7a} and $H_{\underline{exo}}$ or $H_{\text{bridgehead}}$.

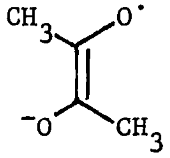
The important feature of $a_{7a}{}^H$ is that it is large, which is the result expected because of the symmetry of the semidithione spin-label with respect to C_2 and C_3. The observation of the large H_{7a} hfsc serves as a reassurance that the large splitting effect may be seen in radical anions other than those with oxygen-containing spin-labels.

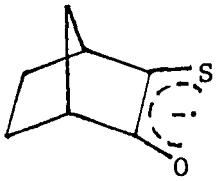
Although the monothiosemidione spin-label is symmetric with respect to C_2 and C_3 in relation to its HOMO, it is not symmetric in relation to atoms. This property gives rise to a trend which cannot be observed with symmetric (in relation to atoms) spin-labels.

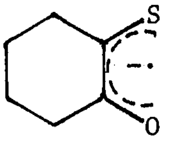
Table V lists the spin densities calculated for carbons 2 and 3 in the semidiones and monothiosemidiones listed below. The values were calculated using Equation 1, with B = 40 gauss (29), $\Theta = 68°$ for the bicyclic systems, $\Theta = 30°$ for the monocyclic systems, and $\Theta = 45°$ for the acyclic systems. a_O^H and a_S^H refer to the splitting constants of the hydrogens α to the carbon on the oxygen side and on the sulfur side, respectively, and ρ_{CO} and ρ_{CS} refer to the spin densities at carbon next to oxygen and carbon next to sulfur, respectively. ρ_{tot} is the total spin density on carbons 2 and 3 and is equal to 2 X ρ_{CO} for semidiones and equal to $\rho_{CO} + \rho_{CS}$ for monothiosemidiones.


1


42


43a


37


38

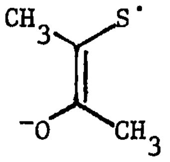
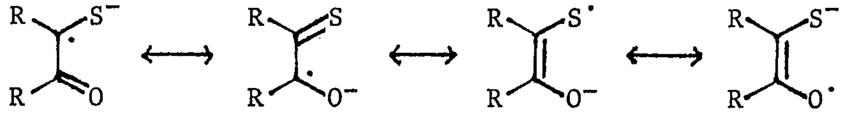

39a

Table V. Calculated spin densities at carbons 2 and 3 in semidiones and monothiosemidiones

Anion	a_O^H	a_S^H	ρ_{CO}	ρ_{CS}	ρ_{tot}
1	2.43		0.43		0.86
42	9.82		0.33		0.66
43a	5.6		0.28		0.56
37	1.3	2.6	0.23	0.46	0.69
38	4.80	11.45	0.16	0.38	0.54
39a	2.10	7.65	0.11	0.38	0.49

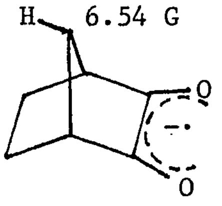
In going from bicyclic to monocyclic to acyclic semidione, the spin density at carbons 2 and 3 decreases. The same decrease in total spin density is observed in the monothiosemidiones. However, a shift of spin density toward the sulfur side of the spin-label is also observed, indicating that reasonance structure 79a becomes more important relative to 79b, but 79a and 79b together become less important relative to 79c and 79d together.



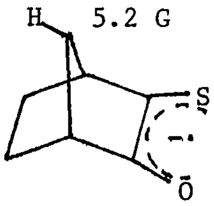
79a 79b 79c 79d

Looking at the decrease in ρ_{tot} for both the semidiones and monothiosemidiones is another way of viewing the problem of whether the observed butane-2,3-monothiosemidione (39) has the *cis* or *trans* structure. The *cis* semidione (43b) has a calculated ρ_{tot} slightly greater than that of cyclohexanesemidione (42), and if the *cis*-butane-2,3-monothiosemidione (39b) were seen, it would probably have ρ_{tot} greater than ρ_{tot} for cyclohexanemonothiosemidione (38). Thus, the *trans* structure (39a) is again indicated.

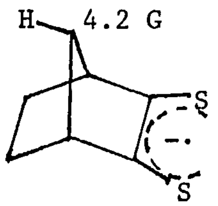
Bicyclo[2.2.1]heptane-2,3-monothiosemidione (37) shows the expected large hyperfine splitting constant for H_{7a}. Its value is between the values of the hfsc for H_{7a} in the corresponding semidione 1 and semidithione 20, which is the logical result if 37 is considered a "cross" between 1 and 20.



1

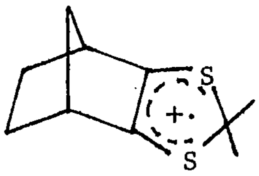


37

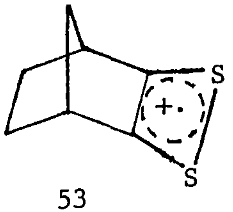


20

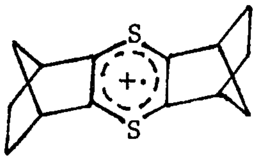
Semidithiones and monothiosemidiones, while providing additional examples of radical anions which show a large hfsc for H_{7anti}, were not the systems initially desired for study. Although the original target radical cation 11 was never observed, radical cations 53 and 54 do fulfill the original requirement of showing a large hyperfine splitting constant for H_{7a} in a cationic system having the unpaired



11



53

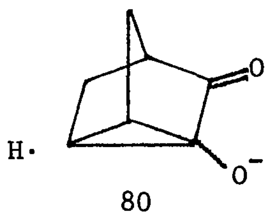


54

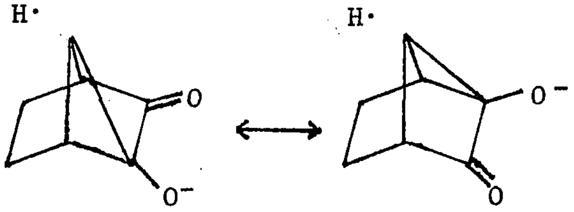
electron in a molecular orbital symmetric with respect to a plane bisecting the C_2-C_3 bond and the methano bridge.

It is true that the values of the hfsc for H_{7a} (a^H = 2.75 G in 53 and a^H = 2.3 G in 54) are quite a bit smaller than the corresponding value in semidione 1 (a^H = 6.54 G), but the difference is due to much lower spin density at carbons 2 and 3 in the cations. The usual signs of a HOMO symmetric with respect to C_2 and C_3 are present in both cationic systems. The bridgehead and exo hydrogens have equal splitting constants (a^H = 0.90 G in 53 and a^H = 0.8 G in 54), the values of which are about one third the values of the respective H_{7a} splitting constants. The H_{7a} splitting constants, then, are defined as "large" in comparison to the bridgehead and exo values and not "large" in terms of absolute values.

Comparison to the exo value seems especially appropriate, since both the $H_{\underline{exo}}$ splitting and H_{7a} splitting arise via homohyperconjugation (structures 80 and 3). The variable spin polarization contribution to the H_{7a} splitting and the difference in how $a_{\underline{exo}}^H$ and a_{7a}^H depend on spin density at C_2 and C_3 make the ratio $a_{7a}^H/a_{\underline{exo}}^H$ vary slightly, but its value is always close to 3.



80



3a 3b

Huckel molecular orbital calculations predict that both the dithiete and dithiin radical cations 53 and 54 should have HOMO's symmetric with respect to C_2 and C_3, as should the elusive 11. Using values of $\alpha_S = \alpha_C + 1.0\beta_{CC}$ and $\beta_{CS} = 0.6\beta_{CC}$ for the dithiin and dithiole radical cations (30), the calculated spin density at carbons 2 and 3 is $\rho = 0.125$ for the dithiin and $\rho = 0.25$ for the dithiole. For the dithiete, values of $\alpha_S = \alpha_C + 0.2\beta_{CC}$, $\beta_{CS} = 0.6\beta_{CC}$, and $\beta_{SS} = 0.3\beta_{CC}$ were employed (31, 32), resulting in a value of $\rho = 0.15$ at C_2 and C_3. (In agreement with the numbering system described previously, carbons 2 and 3 are the carbon atoms shared by the spin-label and the parent system and do not necessarily correspond to the carbons normally given those designations in numbering the spin-label itself.)

Table VI lists the calculated molecular orbital coefficients for the dithiete system. A symmetric HOMO, Ψ_3, for the dithiete radical cation results only if β_{SS} is very low. This low β_{SS} value essentially gives more butadiene-like character to the dithiete system and reduces its cyclobutadiene-like character. Although β_{SS} may well be only about 30% of β_{CC}, another reason may exist for the symmetry which has been assigned to the molecular orbital containing the unpaired electron on the basis of experimental evidence.

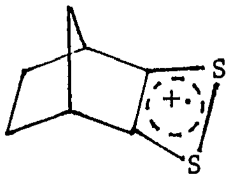
Table VI. Molecular orbital coefficients for dithiete

MO	c_1	c_2	c_3	c_4	Symmetry
Ψ_1	0.39	0.59	0.59	0.39	S
Ψ_2	-0.63	-0.32	0.32	0.63	A
Ψ_3	0.59	-0.39	-0.39	0.59	S
Ψ_4	0.32	-0.63	0.63	-0.32	A

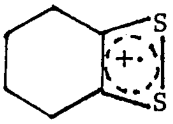
One alternative explanation is that the dithiete radical cation is a σ-species rather than a π-species. The unpaired electron might reside in the σ-S,S bond, a symmetric molecular orbital. A σ-radical cation such as this should not display a $<\cos^2 \Theta>$ relationship for hyperfine splitting by hydrogens α to the dithiete system. However, there is no evidence that the hyperfine splitting constants of α-hydrogens in dithiete radical cations do not exhibit a $<\cos^2 \Theta>$ dependence.

In the bicyclo[2.2.1]heptane-2,3-semidione (1), for example, the ratio a_{7a}^H/a_α^H, where H_α is a bridgehead hydrogen, is equal to 6.5/2.4 = 2.7. In 54 the ratio is 2.3/0.8 = 2.9, and in 53 it is 2.75/0.90 = 3.1. One cannot avoid the conclusion that the unpaired electrons in the semidione, dithiin radical cation, and dithiete radical cation are all in molecular orbitals of similar symmetry and nature; that is, all are π-systems.

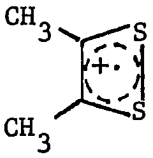
Table VII lists the values of spin density at C_2 and C_3, calculated using Equation 1, for the radical cations shown below. A value of B = 80 gauss was used (29), and, as in the calculations for the corresponding semidiones and monothiosemidiones, Θ = 68° in the bicyclic systems, Θ = 30° in the cyclohexane systems, Θ = 45° in the dimethyl systems, a_S^H = the hfsc for the hydrogen α to the carbon to which sulfur is attached, and ρ_{CS} = the spin density at the carbon to which sulfur is attached.



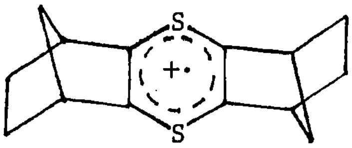
53



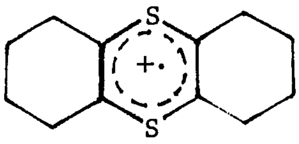
13



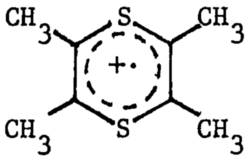
55



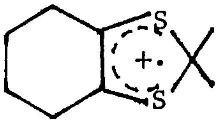
54



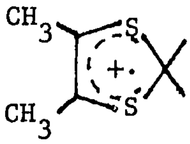
14



56



12



81

It can be seen that the values for ρ calculated by the molecular orbital method are higher than those given in Table VII, but they agree

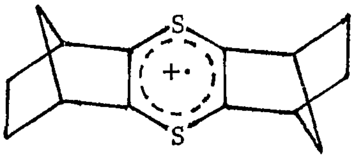
Table VII. Calculated spin densities at carbons 2 and 3 in radical cations

Cation	a_S^H	ρ_{CS}
53	0.90	0.080
13	3.04	0.051
55	2.19	0.055
54	0.8	0.07
14	2.88	0.048
56	2.10	0.053
12	8.75	0.15
81	6.15[a]	0.15

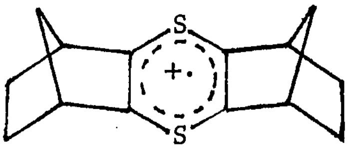
[a] Reference 9.

well as far as predicting that spin density at C_2 and C_3 in the dithiete should be slightly higher than in the dithiin and quite a bit lower than in the dithiole.

One more comment should be made on the bicyclic dithiin radical cation. It has been drawn as structure 54, but 82 is also a possible

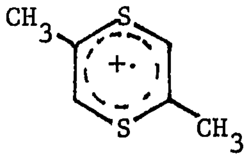


54

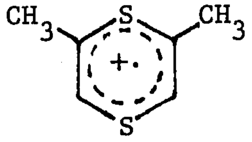


82

structure. 54 and 82 would probably have identical g-factors, as do 58 and 59, and equal (or certainly very nearly equal) hyperfine splitting constants. Therefore, it cannot be determined whether the signal seen for the bicyclic dithiin radical cation is due to 54, 82, or a mixture of both. The cation is represented as 54 strictly for the sake of convenience.

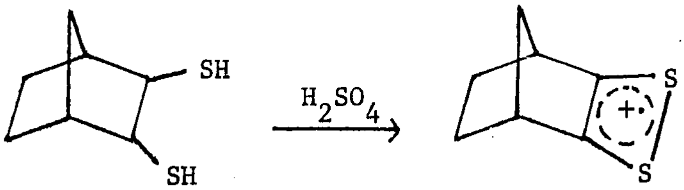


58

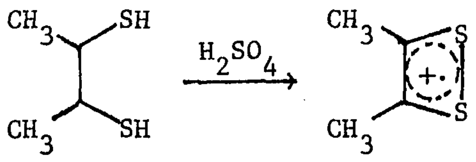


59

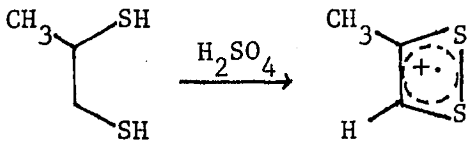
The fact that dithiete radical cations could be formed from 1,2-dithiols in sulfuric acid was a welcome discovery because the bicyclic dithiete radical cation 53 could not be generated by the method previously used for other dithiete radical cations (α-diketone or α-hydroxyketone plus Na_2S in H_2SO_4). 2,3-Butanedithiol and 1,2-propanedithiol gave dithiete radical cations 55 and 57, respectively, in sulfuric acid, indicating that the dithiol to dithiete radical cation reaction is a general one, but 1,2-ethanedithiol did not follow the pattern, giving the 1,2-dithietane radical cation (62).



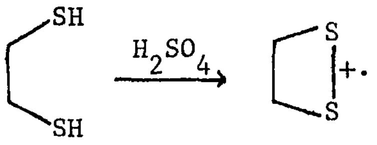
53



55



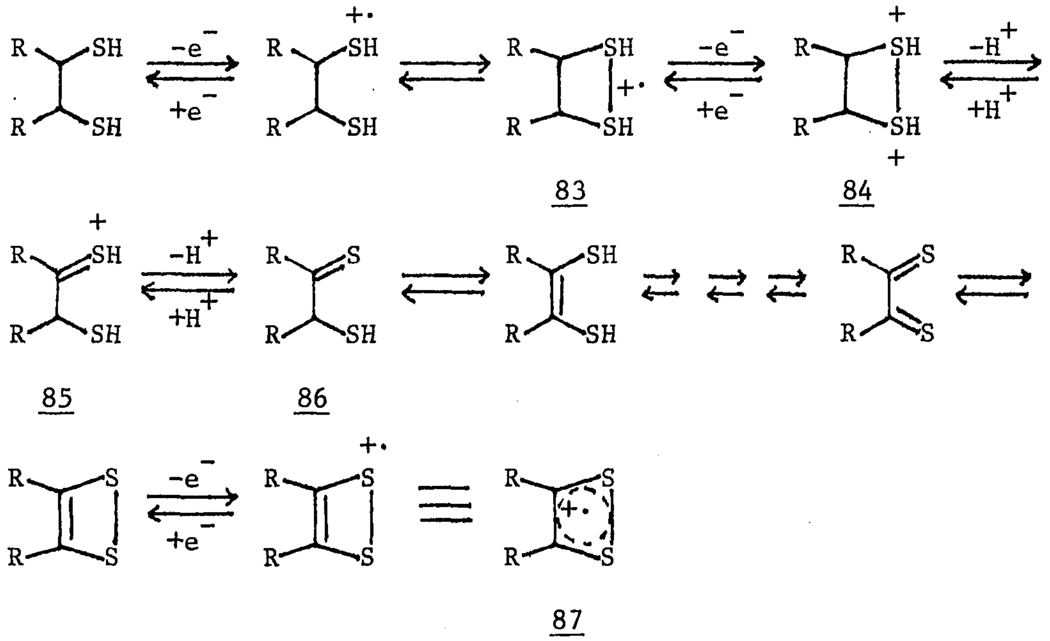
57



62

A possible mechanism for formation of a dithiete radical cation (87) from a 1,2-dithiol is shown in Scheme XII. Acyclic radical cations

Scheme XII



83

84

85

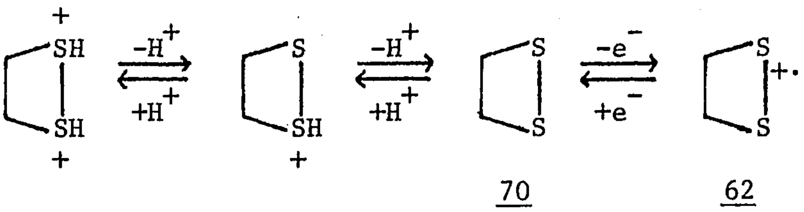
86

87

similar to 83 have been observed by irradiation of thiols at low temperature (33) and by oxidation of disulfides in a flow system (34), and both cyclic and bicyclic analogs have also been observed (24, 25, 35). With excess oxidant, dications such as 84 have been formed and are believed to decompose by the route shown in step 84 ⟶ 85 (36).

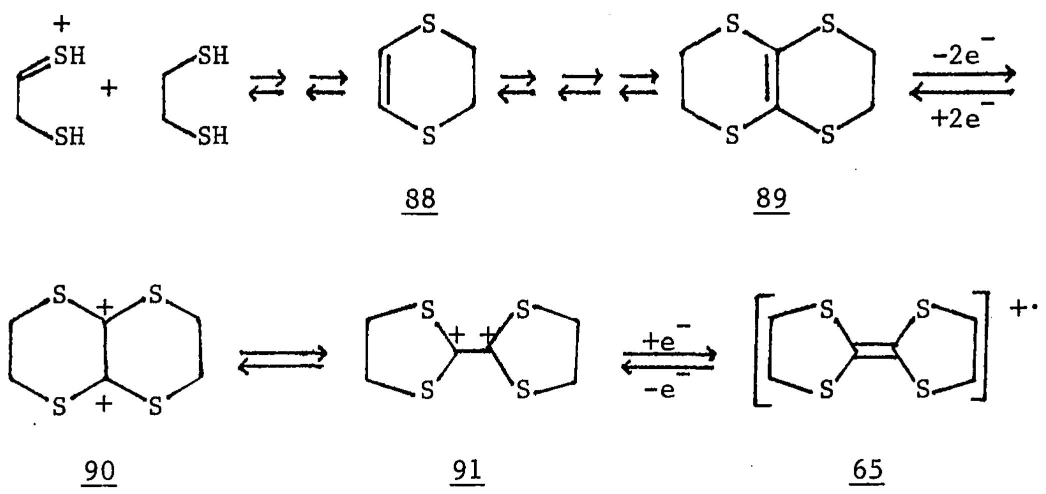
One explanation for the failure of 1,2-ethanedithiol to form dithiete radical cation is that step 84 ⟶ 85 does not occur when R = hydrogen. With R = H, a sulfur atom rather than a carbon atom loses a proton, and subsequently the other sulfur atom is deprotonated. The dithietane (70) formed is then oxidized to its radical cation 62 (Scheme XIII).

Scheme XIII



A second possibility is that 85 does form when R = H but it reacts rapidly with 1,2-ethanedithiol producing 2,3-dihydro-1,4-dithiin (88). 88 could react further with 1,2-ethanedithiol, eventually producing the $\Delta^{2,2'}$-bi-1,3-dithiolane radical cation 65 (Scheme XIV). 88 itself in sulfuric acid gives rise to 65, making it a likely intermediate in the formation of 65 from 1,2-ethanedithiol. The sequence 89 ⟶ 90 ⟶ 91 ⟶ 65 has been observed when 89 is electrolytically oxidized (37) and could also be part of the pathway leading to radical cation 65.

Scheme XIV

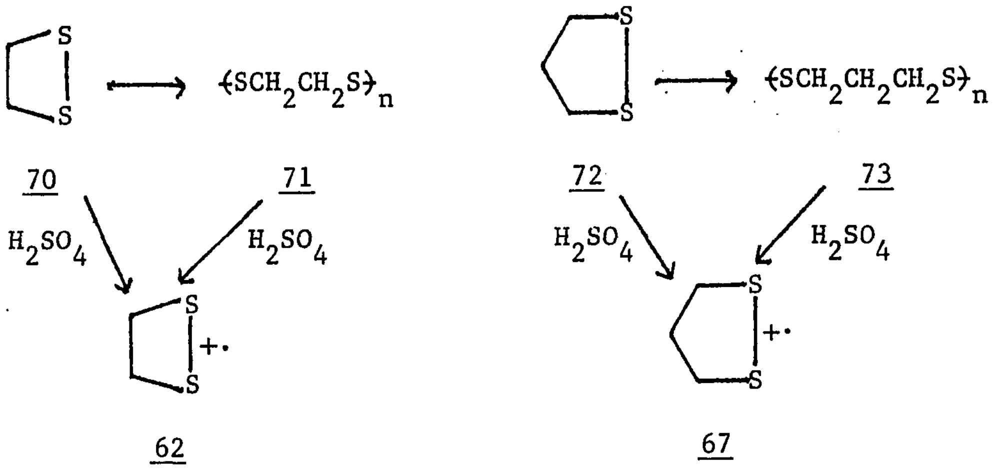


A cation corresponding to 65 could not form when R ≠ H, making this a "dead end" pathway for other dithiols.

The dithiolanes made from 1,2-dithiols and acetone produce the same signals in sulfuric acid as do the dithiols themselves, indicating that in acid the dithiolanes are hydrolyzed back to the dithiols. The bis(methyl sulfide) analogs of dithiols, however, fail to give ESR signals in H_2SO_4. The failure is probably due to step 85 ⟶ 86, which would not occur if the thiocarbonyl group of 85 were methylated rather than protonated.

The formation of 1,2-dithietane radical cation (62) is interesting in that 1,2-dithietane itself is not stable but rapidly polymerizes, as does 1,2-dithiolane (72), which also forms a stable radical cation (67) (Scheme XV). A consideration of molecular orbitals in 72 indicates that 67 should form readily (38).

Scheme XV



Disulfides may be viewed as having one lone pair of electrons on each sulfur atom occupying a p orbital while the other lone pair occupies the 3s orbital. Repulsion is least when the angle ϕ between the two p orbitals is 90°; therefore, most disulfides R_1-S-S-R_2 exist in a shape in which the dihedral angle between the R_1-S-S plane and the S-S-R_2 plane is about 90°. In 1,2-dithiolane (72), the angle ϕ is close to 0°, resulting in maximum repulsion. By forming a linear polymer (73), the preferred disulfide conformation may be assumed.

However, in the radical cation the most stable conformation is the one in which $\phi = 0°$ (39). The cyclic radical cation should be preferred over the polymeric form, and, indeed, radical cation 67 is formed from polymer 73 in sulfuric acid.

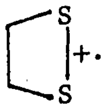
1,2-Dithietane (70) is planar with $\phi = 0°$ and thus polymerizes, but its radical cation is also expected to be preferred over an acyclic radical cation, and the 1,2-dithietane radical cation (62) does form from the polymer 71 in sulfuric acid.

Benzyl mercaptan was the only monothiol which formed a disulfide radical cation. The signal was very weak and could possibly have been due to the initial presence of benzyl disulfide rather than to the formation of disulfide radical cation from mercaptan. In either case, the failure to see more disulfide radical cations was not surprising, considering the fact that disulfide radical cations are usually observed at low temperature and decompose if the temperature is raised (40-48). Thiophenol, *p*-thiocresol, and diphenyl disulfide, which do give ESR signals in sulfuric acid at room temperature, do not appear to form disulfide radical cations (49-52).

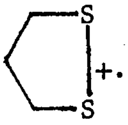
The splitting constants for the disulfide radical cations do not appear to follow the $\rho<\cos^2\Theta>$ relationship of Equation 1. Chambers and coworkers have made the same observation for the $\Delta^{2,2'}$-bi-1,3-dithiolane radical cation (65) in relation to other sulfur-containing radical cations (26).

Table VIII lists the calculated (using Equation 1) B values for the radical cations shown below. The wide range of B values indicates that there is no simple relationship between a_α^H and $\rho<\cos^2\Theta>$ for hydrogens which are α to a sulfur atom containing an unpaired electron in a p orbital.

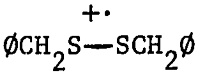
Geske and Merritt (53) have claimed that various substituted tetrathioethylenes such as 94 do follow a $\rho<\cos^2\Theta>$ relationship at low



62

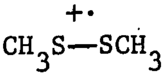


67



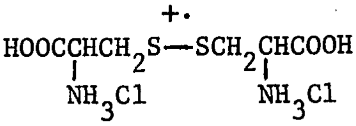
$\emptyset CH_2\overset{+\cdot}{S{-}S}CH_2\emptyset$

74



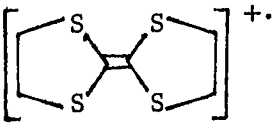
$CH_3\overset{+\cdot}{S{-}S}CH_3$

92

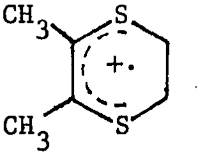


$HOOC\underset{NH_3Cl}{\underset{|}{C}}HCH_2\overset{+\cdot}{S{-}S}CH_2\underset{NH_3Cl}{\underset{|}{C}}HCOOH$

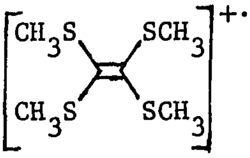
93



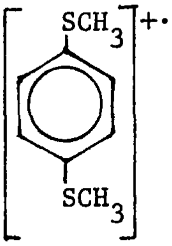
65



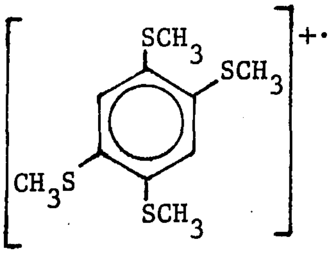
66



94



95



96

Table VIII. Calculated B values for some radical cations

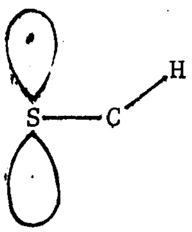
Cation	a^H	ρ_S	$\langle\cos^2 \Theta\rangle$	B	Reference
62	3.7	0.50	0.75	9.9	
67	10.00	0.50	0.75	27	
74	1.4	0.50	0.50[a] 0.75 0.25	5.6 3.7 11	
92	7.7	0.50	0.50	31	48
93	6.57[b] 2.85	0.50 0.50	0.40 0.17	33 34	47
65	2.40	0.19	0.75	17	26
66	3.50	0.36[c]	0.75	13	
94	2.69	0.19	0.50	28	53
95	5.42	0.30	0.50	36	54
96	2.57	0.13	0.50	40	55

[a] $\langle\cos^2 \Theta\rangle = 0.50$ for a freely rotating $-CH_2\phi$ group. $\langle\cos^2 \Theta\rangle = 0.75$ and 0.25 are the two extremes if $-CH_2\phi$ has a conformational preference.

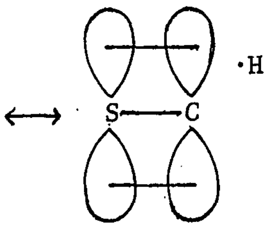
[b] Two sets of two equivalent hydrogens were observed.

[c] Calculated using $\rho_S = (1.0 - \rho_C)/2$, where ρ_C was determined using Equation 1, with $a^H = 5.65$ G for the methyl groups.

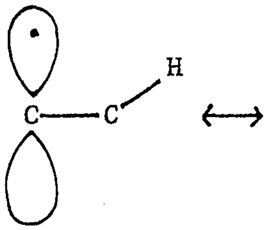
temperature, and Zweig and Hodgson (55) have made the same claim for 95 and 96. By grouping 65 and 66 together and 95 and 96 together (or 94-96), an argument could be made for a $\rho<\cos^2 \Theta>$ relationship being followed among very similar compounds. The lower B values, compared to the value of 80 gauss used for hydrogens α to carbon containing the unpaired electron, could then be explained in terms of poorer π overlap in 97 than in 98.



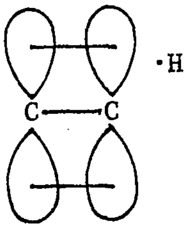
97a



97b



98a

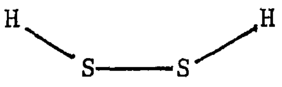


98b

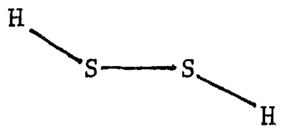
However, a closer look at the groups (65, 66) and (94-96) reveals why the B values calculated within each group are of approximately the same magnitude. Within each group, $<\cos^2 \Theta>$ remains constant, and the results indicate only that a^H does depend linearly on ρ. When only ρ is varied and $<\cos^2 \Theta>$ remains constant, no valid conclusion on the dependence of a^H upon $<\cos^2 \Theta>$ can be drawn. Consideration of both groups (65, 66) and (94-96) clearly indicates that whatever the dependence of a^H on Θ, it is not a $<\cos^2 \Theta>$ dependence.

For the disulfide radical cations, as well, no linear dependence on $<\cos^2 \Theta>$ is indicated. 62 and 67 would be expected to exhibit hyperfine splitting constants of about equal magnitude, and even taking the extreme values of $<\cos^2 \Theta>$ for 74, the calculated B value is much smaller than that for 92 or 93.

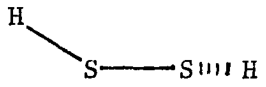
The disulfide radical cations have been pictured as having the unpaired electron in a p orbital on sulfur. Perhaps the assumption that the unpaired electron occupies a pure sulfur 3p orbital is not a valid one. Calculations on hydrogen persulfide (HSSH) indicate that as rotation about the S-S bond occurs to go from the *cis* to the *trans* form (99 → 100), the p orbitals are hybridized by mixing with the 3s orbitals (39).



99



100



101

The preferred conformation for disulfides is that corresponding to 101, but if rotation about the S-S bond occurred in the radical cations, the α hydrogens in 74 and 92, for example, would feel an averaged effect of the changes in hybridization of the orbital containing the unpaired electron. If rotation occurred more readily in 74 than in 92, the α hydrogens in each might not "see" the same averaged picture. Rotation about the S-S bond could also occur more easily in the five-membered ring of 67 than in the four-membered ring of 62; consequently, the α hydrogens in these radical cations would not "see" the same averaged hybridization of the sulfur orbital.

Disulfide radical cations 92 and 93 were observed as single crystals at low temperature, and very little rotation about the S-S bond should occur in these species. Assuming that they both exist in the same conformation in the crystalline state (and, therefore, sulfur orbital hybridization is the same in both), the nearly equal B values for 92 and 93 do appear to indicate a $<\cos^2 \Theta>$ dependence for a^H. It is not certain, however, whether this dependence would also be observed for radical cations in solution, even if two or more species did exhibit the same average hybridization.

The unpredictability of the values of hyperfine splitting constants for disulfide radical cations, then, is due to two factors. One is the changing hybridization of the orbital containing the unpaired electron on sulfur. The other is the possible lack of a $<\cos^2 \Theta>$ dependence for a^H, as in the case of 65, 66, and 94-96, even when the sulfur orbital hybridization does remain unchanged.

SUMMARY

In the bicyclo[2.2.1]heptane system, the following radical ions were prepared: semidithione, monothiosemidione, dithiete radical cation, and dithiin radical cation. All exhibited a large hyperfine splitting by hydrogen in the 7-anti position. The large splitting was expected in all cases due to the symmetry of the HOMO of each spin-label with respect to a plane bisecting the C_2-C_3 bond in the bicyclic system. The differences in values of splitting constants in the various radical ions could be related to differences in spin density at carbons 2 and 3.

Monothiosemidiones, dithiete radical cations, and dithiin radical cations were also prepared in the cyclohexane and butane systems. The differences in spin density at C_2 and C_3 in these systems were the same as those noted for the bicyclic radical ions.

Bicyclo[2.2.1]heptane-2,3-dithiol, 2,3-butanedithiol, and 1,2-propanedithiol produced dithiete radical cations in sulfuric acid, while 1,2-ethanedithiol and 1,3-propanedithiol gave cyclic disulfide radical cations. Benzyl disulfide radical cation was obtained from benzyl mercaptan. The splitting constants for the disulfide radical cations and several other sulfur-containing radical cations did not fit the $a^H \propto \rho\langle\cos^2 \Theta\rangle$ relationship observed for hfsc of hydrogens α to a carbon atom containing an unpaired electron. For the disulfides, the inconsistency was believed to be due in part to changes in hybridization of the orbital on sulfur occupied by the unpaired electron.

EXPERIMENTAL

Instrumentation

ESR spectra were recorded on a Varian E-3 spectrometer. NMR spectra were recorded on a Varian A60 spectrometer. Melting points were determined using a Thomas-Hoover melting point apparatus.

Generation of Radical Cations and Anions

Radical cations were generated by addition of concentrated sulfuric acid to the precursor to give 0.05 - 1.0 M solutions. When acetone or sodium sulfide was needed, it was mixed with the precursor before addition of the acid.

Radical anions were generated by mixing bubble-deoxygenated solutions (0.1 - 1.0 M) of the precursor in dimethyl sulfoxide (distilled from CaH_2 at reduced pressure and stored over molecular sieves) and potassium *t*-butoxide (purified by sublimation at reduced pressure) in dimethyl sulfoxide as described by Holland (56).

Flow experiments were performed as described by Schmitt (57). Electrolytic experiments were carried out in fused silica flat cells with platinum electrodes using dimethyl formamide (distilled from CaH_2 and stored over molecular sieves) as solvent and tetrabutylammonium perchlorate (0.1 M) as supporting electrolyte. Electrolytic solutions were deoxygenated by nitrogen or argon bubbling for 20 - 30 minutes.

Determination of g-Factors

g-Factors were determined by measuring the difference in gauss between the centers of the signals of a radical ion of known g-factor and of the radical ion whose g-factor was to be determined. The relationship $g_2 = g_1H_1/(H_1 + \Delta H)$ was used, where g_1 is the known g-factor and H_1 is the field, in gauss, corresponding to the center of the known signal. H values corresponded to the field setting on the ESR spectrometer. The radical ion of known g-factor was always present in solution with the radical ion of unknown g-factor.

Butane-2,3-monothiosemidione (39a) and 2,5-dimethyl-1,4-semibenzoquinone (45) could be detected simultaneously, as could pentane-2-thio-2,3-semidione (44) and tetramethyl-1,4-semibenzoquinone (46).

The ultimate standard for the determination of all radical cation g-factors was the $\Delta^{2,2'}$-bi-1,3-dithiolane radical cation (65), generated from 2,3-dihydro-1,4-dithiin (88) in sulfuric acid. A solution of the 1,2-dithiolane radical cation (67) was mixed with a solution of 65 in order to find its g-factor, and the 1,2-dithiolane radical cation (67) could subsequently be used as a standard itself. 67 was useful in determining the g-factors of dithiin radical cations, which were conveniently generated free of the corresponding dithiete radical cations from α-mercaptoketones. Dithiete radical cation g-factors could then be measured using the corresponding dithiin radical cations as knowns after generating the dithiete and dithiin radical cations together.

g-Factors taken as previously known values (values determined by someone other than this author) were those of bicyclo[2.2.1]heptane-2,3-semidithione (20), bicyclo[2.2.1]heptane-2,3-monothiosemidione (37), 2,5-dimethyl-1,4-semibenzoquinone (45) (28), tetramethyl-1,4-semibenzoquinone (46) (21), and $\Delta^{2,2'}$-bi-1,3-dithiolane radical cation (65) (26).

Preparation of Compounds

General procedure for synthesis of thiophosphoric esters

A 0.2 M solution of diketone in xylene was refluxed with 2 to 3 mole equivalents of P_4S_{10} for 2 1/2 hours, cooled, and filtered (11). After the solvent was removed *in vacuo*, the residue was chromatographed on silica gel (2 g/mmol of starting diketone), using first CCl_4, then benzene as eluent. The yellowish fraction was saved and evaporated, giving a resinous product.

Tetrachloroethylene carbonate

Tetrachloroethylene carbonate was prepared by Holland's method (56). Ethylene carbonate (100.0 g, 1.14 mol) and benzoyl peroxide (1.1 g) were dissolved in 500 ml of CCl_4 in a photolysis cell equipped with magnetic stirring bar, cold finger, and gas inlet tube. Chlorine was bubbled through the stirred solution while it was irradiated with a sun lamp. Reaction was continued until the solution showed no NMR signal. The solution was dried over anhydrous $MgSO_4$, CCl_4 was removed *in vacuo*, and the residue was distilled, giving a colorless liquid, bp 64-66°/15 torr, weighing 214.30 g (83%). [Lit. bp 52°/7 torr (58)]

Dichlorovinylene carbonate

70.2 g (0.310 mol) of tetrachloroethylene carbonate was stirred with zinc-copper couple (prepared by stirring 45 g of zinc with 1.5 g of copper(II) acetate) in 150 ml of refluxing ether containing 5 ml of DMF for 18 hours. The solution was filtered, washed with 25 ml of H_2O, and dried over $MgSO_4$. The ether was removed and the residue distilled to give a colorless liquid, bp 54-58°/15 torr, which separated into two layers. The bottom layer was dichlorovinylene carbonate, weighing 31.2 g (65%). [Lit. bp 39-40°/10 torr (59)]

exo,*cis*-2,3-Dichlorobicyclo[2.2.1]hept-5-ene-*endo*,*cis*-2,3-diol carbonate

This compound was prepared according to the procedure of Scharf and Küsters (60). Freshly distilled cyclopentadiene (9.78 g, 148 mmol) was reacted with 7.63 g (49.2 mmol) of dichlorovinylene carbonate in portions. The carbonate and one third of the cyclopentadiene were heated in 15 ml of xylene at reflux for one hour. The solution was cooled and the addition and refluxing were repeated two more times. Vacuum distillation gave one fraction, bp 26-40°/0.15 torr, which contained starting material and solvent, and a second fraction, bp 68-115°/0.15 torr, which solidified upon cooling. The solid was recrystallized from CH_2Cl_2-pentane to give 4.24 g (39%) of the bicyclic dichlorocarbonate, mp 143.5-144°. [Lit. mp 148° (60)]

Bicyclo[2.2.1]hept-5-ene-2,3-dione

3.00 g (13.6 mmol) of exo,cis-2,3-dichlorobicyclo[2.2.1]hept-5-ene-endo,cis-2,3-diol carbonate in 30 ml of ether was stirred overnight with a solution of 3.0 g of KOH in water. Continuous ether extraction of the mixture followed by removal of the ether left an orange oil which was vacuum distilled, bp 65-80°/0.1 torr. The resulting oil was chromatographed on 100 g of silica gel, with elution first by CH_2Cl_2, then by 20:80 (v:v) ether:CH_2Cl_2, and the product was sublimed at 58°/0.1 torr to give 0.58 g (35%) of the dione as an orange solid, mp 31-33°. [Lit. mp 43° (60)]

Dibromoethylene carbonate

To a stirred, refluxing mixture of vinylene carbonate (31.9 g, 0.370 mol) in 150 ml of CCl_4 was added 59 g (0.37 mol) of bromine in 20 ml of CCl_4. Addition took four hours, and refluxing was continued for four more hours. The CCl_4 was distilled off and the residue vacuum distilled to give 85.3 g (94%) of a colorless liquid, bp 56-64°/0.2 torr [lit. bp 93-102°/12 torr (61)], which crystallized to a colorless solid, mp 26.5-28.5°.

Bromovinylene carbonate

Triethylamine (34.5 g, 0.341 mol) in 100 ml of absolute ether was added over 3 hours to a refluxing mixture of dibromoethylene carbonate (84.0 g, 0.341 mol) in 300 ml of absolute ether. Refluxing was continued for 22 hours, the amine hydrobromide was filtered off, the ether was removed by distillation, and the residue was distilled to give 10.4 g of colorless liquid, bp 68-77°/19 torr [lit. bp 60-65°/11 torr (62)], which froze in the condenser. The product contained about 86% bromovinylene carbonate. (Yield = 16%)

2-Bromobicyclo[2.2.1]hept-5-ene-*endo*,*cis*-2,3-diol carbonate

4.7 g (28 mmol) of bromovinylene carbonate and 2.0 g (30 mmol) of freshly-distilled cyclopentadiene were dissolved in 10 ml of diethylene glycol diethyl ether, and the solution was refluxed for 45 minutes, then cooled. Another 2.0 g of cyclopentadiene was added, the solution was refluxed for 45 minutes, and a third 2.0-g portion of cyclopentadiene was added. The solution was refluxed for 1.5 hours and vacuum distilled to give a greenish liquid, bp 60-98°/0.15 torr, which crystallized on cooling. The solid was recrystallized from CH_2Cl_2-hexane to give 2.4 g (35%) of the adduct, mp 72.5-75.0° [lit. mp 76.5° (63)].

endo-3-Hydroxybicyclo[2.2.1]hept-5-en-2-one

2-Bromobicyclo[2.2.1]hept-5-ene-*endo*,*cis*-2,3-diol carbonate (2.4 g, 10 mmol) in 25 ml of ether and potassium hydroxide (2.5 g, 45 mmol) in 25 ml of water were rapidly stirred together at room temperature for 2 hours. The layers were separated and the aqueous layer was washed five times with CH_2Cl_2. The combined organic layers were dried over $MgSO_4$, the solvent was removed, and the residue was recrystallized from CH_2Cl_2-hexane to give a white, flaky solid, mp 97-100° [lit. mp 101-103° (64)].

Bicyclo[2.2.1]heptane-2,3-dione (18)

10.8 g (98 mmol) of norcamphor and 11.1 g (100 mmol) of selenium dioxide were stirred in 40 ml of refluxing xylene for 4 hours. The selenium formed was filtered off, the xylene was removed by distillation, and the residue was vacuum distilled, giving an orangish liquid, bp 140-150°/0.2 torr, which subsequently solidified. After two sublimations the still impure solid was chromatographed on 100 g of silica gel, with chloroform as eluent. A yellow liquid (18), which solidified after several weeks, was obtained in 14% yield (1.67 g). In agreement with the results of Chang (65), the solid did not have the well-defined melting point reported by Alder, *et al*. (66).

Thiophosphoric ester of bicyclo[2.2.1]hept-2-ene-2,3-dithiol (19)

Bicyclo[2.2.1]heptane-2,3-dione (0.86 g, 6.9 mmol) reacted by the general method gave a 20% yield of the resinous thioester.

Thiophosphoric ester of cyclohexene-1,2-dithiol (24)

Cyclohexane-1,2-dione (1.5 g, 12 mmol) reacted by the general method gave 0.16 g (6%) of the thioester as an amber resin.

1-(*N*-Morpholino)cyclohexene

46.8 g (0.537 mol) of morpholine and 52.8 g (0.538 mol) of cyclohexanone were stirred for 20 1/2 hours in refluxing benzene while the water formed was collected in a Dean-Stark trap. The solution was filtered and dried over $MgSO_4$ and the benzene was evaporated, leaving an orangish oil which was distilled to give 55.9 g (62%) of the enamine as a colorless liquid, bp 75-83°/0.1 torr. [Lit. bp 117-20°/10 torr (67)]

4,5-Tetramethylene-1,3-dithiole-2-thione (25)

The procedure of Grunwell and Willett was used (15). 25.5 g (0.150 mol) of 1-(N-morpholino)cyclohexene was added to a solution of 40 ml of dioxane and 40 ml of triethylamine under N_2, the solution was stirred for 10 minutes, and 37.3 g (0.150 mol) of tetramethylthiuram disulfide was added. The mixture was stirred for 4.5 hours, after which time all of the tetramethylthiuram disulfide had dissolved. As hydrogen sulfide was bubbled through the solution, a precipitate formed and it became necessary to add more dioxane to the mixture. The addition of H_2S was continued for 4 hours, after which time the precipitate was filtered and washed with benzene until white. The solvent was removed from the filtrate and the resulting solid was chromatographed on 175 g of neutral Woelm alumina, with benzene as the eluent. The yellow solid obtained was recrystallized from CH_2Cl_2-hexane to give 7.0 g (25%) of 25, mp 80-82°. [Lit. mp 83° (17)]

4,5-Tetramethylene-1,3-dithiole-2-one (26)

The procedure of Kardouche and Owen (68) was used. Trithiocarbonate 25 (3.6 g, 18 mmol) and 14.5 g (46 mmol) of mercuric acetate were stirred in 180 ml of acetic acid at 60° for 4.5 hours. Chloroform (360 ml) was added, the mixture was filtered, and the filtrate was washed twice with water and then with 5% $NaHCO_3$. The basic layer was washed with $CHCl_3$, the combined $CHCl_3$ layers were dried over $MgSO_4$, and the solvent was removed *in vacuo*. Recrystallization of the residue from CH_2Cl_2-hexane gave 1.84 g (56%) of white needles, mp 31.0-31.8°. [Lit. mp 33° (69)]

Thiophosphoric ester of 1,7,7-trimethylbicyclo[2.2.1]hept-2-ene-2,3-dithiol (27)

Camphorquinone (2.0 g, 12 mmol) reacted by the general method gave a 22% yield of orange resin which eventually solidified but did not have a definite melting point.

Bicyclo[2.2.2]octan-2-ol

The procedure used was that of Brown, *et al*. (70). Mercuric acetate (14.8 g, 46.4 mmol) was stirred in 46 ml of water until dissolved, and 46 ml of THF was added to produce a yellow precipitate. Bicyclo[2.2.2]oct-2-ene (5.00 g, 46.2 mmol) was added as a solid, the flask was stoppered, and the solution was stirred for 25 minutes. Sodium hydroxide (46 ml, 3 M soln) was added followed by 46 ml of 0.50 M $NaBH_4$ in 3 M NaOH, and the mixture was stirred for one hour until the mercury had coagulated. The solution was decanted and extracted twice with benzene, and the combined benzene layers were washed with sat. NaCl, dried over $MgSO_4$, and evaporated. Recrystallization of the resulting solid gave 4.1 g (70%) of a white powder which sublimed rapidly at 195°. [Lit. mp 216-217° (71)]

Bicyclo[2.2.2]octanone

To 41 g (0.52 mol) of pyridine in 300 ml of dry CH_2Cl_2 was added 26 g (0.26 mol) of chromium trioxide, and the solution was stirred for 20 minutes. Bicyclo[2.2.2]octan-2-ol (4.1 g, 0.032 mol) was added and the solution was stirred for an additional 20 minutes, filtered, washed with 5% $NaHCO_3$, twice with 5% HCl, with 5% $NaHCO_3$, and with water, and dried over $MgSO_4$. The solvent was removed and the residue chromatographed on 50 g of silica gel, with elution first by CCl_4, then by $CHCl_3$. The chloroform fraction gave a white solid which was recrystallized from CH_2Cl_2-hexane to give 1.94 g (49%) of white powder, mp 169-172°. [Lit. mp 178-179° (72)]

Bicyclo[2.2.2]octane-2,3-dione

1.94 g (15.6 mmol) of bicyclo[2.2.2]octanone and 1.73 g (15.6 mmol) of selenium dioxide were stirred in 10 ml of refluxing xylene for 3.5 hours. The solution was filtered, dried over $MgSO_4$, and evaporated, leaving a solid which was chromatographed on 50 g of silica gel, with first benzene, then $CHCl_3$ as eluent. Evaporation of the liquid from the yellow fraction gave a solid which was sublimed under reduced pressure. Some unreacted monoketone sublimed along with the diketone, resulting in a product which did not have a sharp melting point [lit. mp 168° (73)]. (Yield = 24%)

Thiophosphoric ester of bicyclo[2.2.2]oct-2-ene-2,3-dithiol

Bicyclo[2.2.2]octane-2,3-dione was reacted by the general method to give a 30% yield of the ester as a yellow oil which hardened on standing.

4,5-Tetramethylene-1,2-dithiole (30)

To 1.8 g (47 mmol) of lithium aluminum hydride stirred at 0° in 25 ml of dry ether under nitrogen was added 7.0 g (37 mmol) of 25 in 300 ml of ether. Addition took 20 minutes. The mixture was stirred overnight at 0°, poured into sat. NH_4Cl solution, acidified with 10% H_2SO_4, and separated. The ether layer was washed with water, dried over $MgSO_4$, and evaporated, leaving an oil which was distilled at 90-100°/0.6 torr using a Hickman still. 2.7 g (46%) of yellowish liquid (30) was obtained. [Lit. bp 55°/0.1 torr (15)]

3-(N,N-Dimethylthiocarbamoylmercapto)bicyclo[2.2.1]heptan-2-one, exo-endo mixture (31)

17.2 g (0.15 mol) of norcamphor in 75 ml of benzene was added dropwise over 35 minutes to 37.6 g (0.15 mol) of tetramethylthiuram disulfide in 150 ml of refluxing benzene. The solution was refluxed for 20 hours, cooled, filtered, washed twice with water, and dried over $MgSO_4$. Removal of the solvent left an oil which was chromatographed about 4 g at a time on 100 g of silica gel, with elution by 50:50 (v:v) CCl_4:benzene, then by benzene. The desired product was the second fraction obtained and had to be eluted slowly in order to separate it from tetramethylthiourea, which was eluted third. Total yield was about 30% of dark yellow oil (31).

NMR($CDCl_3$) δ 4.88 (d, J = 4 Hz, C_3 exo H), 4.23 (d, J = 4 Hz, C_3 endo H), 3.5 (m, 6, CH_3), 2.6, 2.75, and 3.0 (m's, 2, C_1 H and C_4 H), and 1.5-1.9 (m's, 6, C_5 H, C_6 H, and C_7 H).

2-(*N*-Morpholino)bicyclo[2.2.1]hept-2-ene (**32**)

The synthesis of **32** was repeated several times. In a typical run, 0.10 mol of norcamphor and 0.15 mol of morpholine were refluxed under N_2 in 100 ml of toluene while the water formed was collected in a Dean-Stark trap. After one week, the toluene was distilled off and the residue was vacuum distilled to give a first fraction containing unreacted norcamphor and a second fraction, bp 64-73°/0.1 torr, containing the desired enamine in 50-60% yield. [Lit. bp 70-72°/0.5 torr (74)]

3-Mercaptobicyclo[2.2.1]heptan-2-one, *exo-endo* mixture (**35**)

10.1 g (44 mmol) of **31** and 7.0 g (180 mmol) of NaOH were stirred in 220 ml of methanol and 44 ml of water at reflux for 20 hours. The solution was acidified with 10% HCl to pH ≈ 8, methylene chloride and water were added, and the layers were separated. The aqueous layer was washed again with CH_2Cl_2 and the combined CH_2Cl_2 layers were washed with water, dried over $MgSO_4$, and evaporated to give 5.3 g (85%) of a brownish oil which was used without purification.

3-(Acetylmercapto)bicyclo[2.2.1]heptan-2-one, *exo-endo* mixture (**36**)

Mercaptoketone **35** (5.3 g, 37 mmol) was stirred in pyridine (15 g, 190 mmol) and acetyl chloride (2.9 g, 37 mmol) was added dropwise. The solution was refluxed for 2.5 hours and excess 5% HCl was added. The solution was extracted twice with chloroform and the combined $CHCl_3$ layers were washed with 5% HCl, water, 5% $NaHCO_3$, and water and dried over $MgSO_4$. Evaporation of the solvent left an oil which was chromatographed on 100 g of silica gel. Elution with benzene gave 2.0 g (29%) of the thiolacetate.

NMR($CDCl_3$) δ 4.07 (d, J = 4.5 Hz, C_3 exo H), 3.62 (d, J = 3.5 Hz, C_3 endo H), 2.6 and 2.7 (m's, 2, C_1 H and C_4 H), 2.37 (s, 3, CH_3), and 1.5-1.9 (m's, 6, C_5 H, C_6 H, and C_7 H).

2-(N,N-Dimethylthiocarbamoylmercapto)cyclohexanone (40)

Cyclohexanone (9.86 g, 100 mmol) in 10 ml of benzene was added dropwise over 2 hours to 24.8 g (100 mmol) of tetramethylthiuram disulfide and 10 drops of acetic acid in 50 ml of refluxing benzene. Refluxing was continued for 1.5 hours after addition was complete, the solution was cooled, and the solid which formed was filtered off. Removal of the solvent and addition of ether gave, on cooling, a solid which was recrystallized from CH_2Cl_2-hexane to yield 4.06 g of 40 as a pale yellow powder, mp 104.5-108.5° [lit. mp 112-113° (75)], and a second crop of 1.93 g. (Total yield = 28%)

Dimer of 2-mercaptocyclohexanone (41)

Thiocarbamoylmercaptoketone 40 (0.31 g, 1.4 mmol) and sodium hydroxide (0.23 g, 5.8 mmol) were stirred in 7 ml of methanol and 1.4 ml of water at reflux for 20 hours. The solution was brought to pH 8-9 by addition of 10% H_2SO_4 and extracted twice with methylene chloride, and the combined CH_2Cl_2 layers were washed twice with water and dried over $MgSO_4$. Evaporation of the solvent and recrystallization of the resulting solid from $CHCl_3$ gave 0.02 g (10%) of a white powder, mp 133-138°. [Lit. mp 145-146° (76)]

3-Mercapto-2-butanone

The procedure of McIntosh and Masse was used (77). 3-Chloro-2-butanone (10.7 g, 0.100 mol) in 13 ml of ethanol was added dropwise to a solution of 15 g (0.27 mol) of KOH in 60 ml of water saturated with H_2S at 0°. The solution was allowed to warm to room temperature, stirred for an additional two hours, and extracted twice with ether. The combined ether layers were washed with water, dried over $MgSO_4$, and evaporated, leaving an oil which was distilled to give 3.5 g (34%) of the mercaptoketone as a colorless liquid, bp 39-40°/10 torr. [Lit. bp 39°/8 torr (78)]

2-Bromo-3-pentanone

The procedure of Bauer and Macomber (79) was used. 3-Pentanone (10.0 g, 0.116 mol) was stirred in 200 ml of chloroform (50%)-ethyl acetate (50%) at 70-80° and cupric bromide (51.8 g, 0.232 mol) was added in portions over three hours. The mixture was stirred overnight and filtered. The solvent was removed *in vacuo*, leaving a light brown oil. The oil was dissolved in ether and the solution was washed twice with water and twice with 5% $NaHCO_3$ and dried over $MgSO_4$. Evaporation of the solvent gave 13 g (68%) of an oil which was used without purification.

2-Mercapto-3-pentanone

Potassium hydroxide (13 g, 0.23 mol), H_2S, and 2-bromo-3-pentanone (13 g, 0.079 mol) were reacted by the method used for preparation of 3-mercapto-2-butanone. After work-up the resulting liquid was distilled to give 1.1 g (12%) of the mercaptoketone, bp 47-49°/10 torr [lit. bp 51-53°/12 torr (80)], and a second fraction, bp 130-155°/10 torr, containing the corresponding disulfide.

2-Methyl-4,5-tetramethylene-1,3-dithiole (47)

The procedure of Corey and Seebach was used (81). 15 ml of dry THF was added via syringe to 0.84 g (5.3 mmol) of dithiole 30 under nitrogen in a 25 ml, 3-necked flask equipped with condenser, rubber septum, and nitrogen inlet tube. The solution was cooled to -30°, 2.6 ml of 2.2 M *n*-butyllithium in hexane (5.4 mmol) was added by syringe, and the solution was stirred for 1.5 hours. After cooling the solution to -70°, 0.76 g (5.4 mmol) of methyl iodide and 1 ml of THF were added, and the mixture was kept below 0° while being stirred overnight.

The reaction mixture was poured into 60 ml of H_2O and extracted four times with $CHCl_3$, and the combined $CHCl_3$ layers were washed twice with H_2O, twice with 7% KOH, and twice with water and dried over K_2CO_3. The $CHCl_3$ was removed *in vacuo* and the residue distilled using a Hickman still at 85-110°/0.15 torr to give 0.5 g of a pale yellow liquid which was 80% 47 and 20% 30. (Yield = 44%)

NMR($CDCl_3$) δ 4.72 (quar, 1, J = 6.5 Hz, C_2 H), 2.2 (m, 4), 1.7 (m, 4), and 1.58 (d, 3, J = 6.5 Hz, CH_3).

2,2-Dimethyl-4,5-tetramethylene-1,3-dithiole (48)

The procedure was the same as that used for the preparation of 47, but after stirring the solution overnight, a second equivalent of n-butyllithium was added, followed by a second equivalent of CH_3I. The solution was stirred at -10-0° for 65 hours and worked up as before. Distillation using a Hickman still resulted in a 49% yield of light yellow liquid (48).

NMR($CDCl_3$) δ 2.2 (m, 4), 1.83 (s, 6, CH_3), and 1.7 (m, 4).

Bicyclo[2.2.1]heptane-cis-2,3-dithiol thionocarbonate, exo-endo mixture (50)

Enamine 32 was reacted by the procedure used for preparing 25, but instead of chromatographing on alumina, silica gel was used with CCl_4 as eluent. Recrystallization of the resulting solid gave a 30-40% yield (the preparation was repeated several times) of a mixture of exo and endo trithiocarbonates, with endo predominating. The NMR spectrum of the mixture agreed well with that reported by Petermann and Pleininger for the exo trithiocarbonate (82).

NMR($CDCl_3$) δ 4.8 (m, C_2 exo H and C_3 exo H), 4.40 (d, J = 2 Hz, C_2 endo H and C_3 endo H), 2.5 (m, 2, C_1 H and C_4 H), and 1.4-2.15 (m's, 6, C_5 H, C_6 H, and C_7 H).

Bicyclo[2.2.1]heptane-cis-2,3-dithiol carbonate, exo-endo mixture

5.6 g (28 mmol) of trithiocarbonate 50 and 22 g (69 mmol) of mercuric acetate were stirred in 250 ml of acetic acid at 50° for 2 3/4 hours. Chloroform (500 ml) was added and the solution was filtered, washed with water, and washed with 5% $NaHCO_3$ until the acid was removed. The aqueous layer was washed again with $CHCl_3$, and the combined $CHCl_3$ layers were dried over $MgSO_4$. The chloroform was removed and the residue was recrystallized from CH_2Cl_2-hexane to give 4.04 g (78%) of dithiolcarbonate as white needles.

NMR(CCl_4) δ 4.2 (m, C_2 exo H and C_3 exo H), 4.03 (d, J = 2 Hz, C_2 endo H and C_3 endo H), 2.38 and 2.53 (m's, 2, C_1 H and C_4 H), and 1.3-2.2 (m's, 6, C_5 H, C_6 H, and C_7 H).

exo,cis-2,3-Dibromobicyclo[2.2.1]heptane-endo,cis-2,3-dithiol carbonate

Bicyclo[2.2.1]heptane-cis-2,3-dithiol carbonate (4.04 g, 21.7 mmol) and N-bromosuccinimide (12.1 g, 68.0 mmol) were stirred in 100 ml of CCl_4 for 3 3/4 hours while the solution was irradiated with a sunlamp. The mixture was filtered, the solvent evaporated, and the residue chromatographed on 110 g of silica gel, with elution by CCl_4. The first fraction gave a solid which was recrystallized from CH_2Cl_2-hexane to yield 2.29 g (31%) of the dibromo derivative as a white solid, mp 114-116°.

NMR(CCl_4) δ 3.2 (m, 2, C_1 H and C_4 H), 2.7 (d of m's, J = 12 Hz (d), C_7 syn H), and 1.6-2.1 (m's, 5, C_5 H, C_6 H, and C_7 anti H).

Bicyclo[2.2.1]hept-2-ene-2,3-dithiol carbonate

2.29 g (6.66 mmol) of exo,cis-2,3-dibromobicyclo[2.2.1]heptane-endo,cis-2,3-dithiol carbonate was stirred with 0.89 g (14 mmol) of zinc dust in 20 ml of refluxing ether for 64 hours. The solution was evaporated, leaving a colorless oil which was used without purification.

NMR(CCl_4) δ 3.42 (m, 2, C_1 H and C_4 H) and 1.0-1.8 (m's, 6, C_5 H, C_6 H, and C_7 H).

Bicyclo[2.2.1]hept-2-ene-2,3-dithiol thionocarbonate (33)

The crude dithiol carbonate (described above) was stirred with 0.95 g (4.3 mmol) of P_4S_{10} in 30 ml of refluxing xylene for 5.5 hours. The mixture was left overnight, filtered, and distilled to remove xylene. The residue was chromatographed on 25 g of silica gel, with elution by CCl_4, and the yellow fraction gave, after recrystallization from CH_2Cl_2-hexane, 0.55 g (41% based on dibromodithiol carbonate) of 33, mp 135-138°.

NMR($CDCl_3$) δ 3.43 (m, 2, C_1 H and C_4 H) and 1.2-2.0 (m's, 6, C_5 H, C_6 H, and C_7 H).

Bicyclo[2.2.1]heptane-2,3-dithiol, *exo-endo,cis* mixture (51)

Trithiocarbonate 50 (0.86 g, 4.3 mmol) and sodium hydroxide (0.74 g, 19 mmol) were stirred in 13 ml of methanol and 2.6 ml of water at reflux for 20 hours, the solution was acidified with 10% HCl, water was added, and the mixture was extracted with methylene chloride. The CH_2Cl_2 layer was washed with water, dried over $MgSO_4$, and evaporated, and the residue was chromatographed on 20 g of silica gel, with elution by 2:1 (v:v) CCl_4:benzene, to give 51 as a colorless oil. The NMR spectrum agreed well with that reported by Shields and Kurtz for the *exo* dithiol (83).

NMR(CCl_4) δ 3.5 (m, C_2 *exo* H and C_3 *exo* H), 3.15 (m, C_2 *endo* H and C_3 *endo* H), 1.68 and 1.72 (d's, 2, J = 4 Hz, SH), and 1.2-2.0 (m's, 6, C_5 H, C_6 H, and C_7 H).

4,4-Dimethyl-3,5-dithiatricyclo[5.2.1.$0^{2,6}$]decane (52)

Trithiocarbonate 50 (1.5 g, 7.5 mmol) was stirred with 1.3 g (32 mmol) of NaOH in 22 ml of methanol and 4.4 ml of water at reflux for 5 hours. The solution was acidified and washed twice with CH_2Cl_2, the combined CH_2Cl_2 layers were washed with water and dried over $MgSO_4$, and the solvent was removed. The residual oil was dissolved in 30 ml of acetone to which 6 drops of conc HCl had been added, and the solution was refluxed for 2 hours. Methylene chloride was added, and the solution was washed twice with water, dried over $MgSO_4$, and concentrated to give an oil which was chromatographed on 30 g of silica gel, with elution by 2:1 (v:v) CCl_4:benzene. A pale yellow oil (0.9 g, 60%) was obtained upon removal of the solvent.

NMR(CCl_4) δ 4.17 (m, C_2 exo H and C_6 exo H), 3.72 (m, C_2 endo H and C_6 endo H), 2.3 (m, 2, C_1 H and C_7 H), 1.78 (s, 6, CH_3), and 1.2-2.0 (m's, 6, C_8 H, C_9 H, and C_{10} H).

4,5-Dimethyl-1,3-dithiolane-2-thione

Sodium sulfide nonahydrate (33 g, 0.14 mol) and carbon disulfide (20 g, 0.26 mol) were stirred in 100 ml of refluxing 50% ethanol for 2 hours. Meso-2,3-dibromobutane (23 g, 0.11 mol) in 20 ml of ethanol was added dropwise over 1 hour. The solution was refluxed for 2 days, water was added, and the solution was extracted twice with CH_2Cl_2. The combined organic layers were washed twice with water, dried over $MgSO_4$, and evaporated, leaving an oil which was chromatographed on 100 g of silica gel, with CCl_4 as eluent. The yellow fraction yielded 1.7 g

(8%) of a solid, which partially melted at 33-36°, then melted completely at 37-39°. [Lit. mp for trans 40-41° (84)]

2,3-Butanedithiol

To a stirred mixture of 0.20 g (5.0 mmol) of lithium aluminum hydride in 7 ml of ether, 4,5-dimethyl-1,3-dithiolane-2-thione (0.92 g, 6.0 mmol) in 10 ml of ether was added at a rate such that the yellow color was continuously discharged. After the solution was cooled to 0°, water and more ether were added and the mixture was acidified with 10% HCl. The organic layer was separated, washed with 5% $NaHCO_3$ and water, dried over $MgSO_4$, and evaporated, leaving a yellow liquid. In attempting to distill the liquid at aspirator pressure using a Hickman still, only a few drops of colorless liquid were collected at 45° before the yellow liquid began condensing on the cold finger; therefore, very little of the colorless dithiol was obtained. [Lit. bp 86-87°/50 torr (85)]

2,5-Dihydroxy-2,5-dimethyl-1,4-dithiane (60)

Chloroacetone (9.3 g, 0.10 mol) in 20 ml of ethanol was added dropwise over 25 minutes to a cooled solution of sodium hydrosulfide (40 g) in 100 ml of water. The solution was stirred overnight and extracted twice with chloroform, the combined $CHCl_3$ layers were washed with water and dried over $MgSO_4$, and the $CHCl_3$ was evaporated. The resulting oil was chromatographed on 100 g of silica gel, with elution by $CHCl_3$, giving, as a first fraction, a colorless oil from which a very small amount of white solid eventually crystallized. The solid was 60, mp 106-109° [lit. mp 109-111° (86)]. The yield was 0.5 g (6%).

2,2,4-Trimethyl-1,3-dithiolane

1,2-Propanedithiol (11 g, 0.10 mol) was stirred overnight in refluxing acetone (100 ml) to which 0.5 ml of conc HCl had been added. The acetone was evaporated, the residue was taken up in methylene chloride, and the solution was washed with water, 5% $NaHCO_3$, and water and dried over $MgSO_4$. Distillation gave 10.4 g (70%) of colorless liquid, bp 61-66°/10 torr. [Lit. bp 43-45°/3.8 torr (87)]

3-Methyl-2,5-dithiahexane (61)

1,2-Propanedithiol (11 g, 0.10 mol) in 10 ml of ethanol was added dropwise to a stirred, cooled solution of sodium hydroxide (16 g, 0.40 mol) in 170 ml of 50% ethanol. The mixture was stirred for an additional 45 minutes, and dimethyl sulfate (25 g, 0.20 mol) in 20 ml of ethanol was added over one hour. The solution was allowed to warm to room temperature and stirred overnight. Methylene chloride was added and the solution was washed three times with water, dried over $MgSO_4$, and evaporated. Distillation of the residue gave a colorless liquid, bp 73-75°/15 torr (8.9 g, 65%). [Lit. bp 75-76°/18 torr (88)]

2,2-Dimethyl-1,3-dithiolane

A solution of 1,2-ethanedithiol (2.0 g, 21 mmol) in 20 ml of acetone to which 0.1 ml of conc HCl had been added was refluxed for 17.5 hours. Benzene was added and the mixture was washed with water, 10% NaOH, and water and the organic layer was dried over $MgSO_4$. Evaporation of the solvent and distillation of the product at 70-80°/ 10 torr using a Hickman still gave 1.92 g (68%) of the dithiolane as a colorless liquid. [Lit. bp 89°/14 torr (89)]

2,3-Dihydro-1,4-dithiin (88)

Chloroacetaldehyde diethyl acetal (10.9 g, 71 mmol) and 1,2-ethanedithiol (6.8 g, 72 mmol) were stirred with a small amount of *p*-toluenesulfonic acid in 50 ml of refluxing benzene for 23 hours. The benzene was evaporated and the residue chromatographed on 200 g of silica gel, with elution by CCl_4. The product was distilled at 80-100°/10 torr [lit. bp 101°/29 torr (90)] to give 1.56 g (19%) of the dihydrodithiin as a colorless liquid.

5,6-Dimethyl-2,3-dihydro-1,4-dithiin

3-Chloro-2-butanone (5.2 g, 49 mmol) and 1,2-ethanedithiol (4.6 g, 49 mmol) were stirred with a small amount of *p*-toluenesulfonic acid in 30 ml of refluxing benzene for 26 hours while the water produced was collected in a Dean-Stark trap. The benzene was removed *in vacuo* and the residue was chromatographed on 60 g of silica gel, with elution by CCl_4. The resulting product was distilled to give the dihydrodithiin as a colorless liquid, bp 50°/0.2 torr [lit. bp 113-114°/25 torr (91)], in 24% yield.

2,5-Dithiahexane (69)

1,2-Ethanedithiol (10.6 g, 0.113 mol), sodium hydroxide (16 g, 0.40 mol), and dimethyl sulfate (27.7 g, 0.220 mol) were reacted by the procedure used for preparation of 61. Distillation of the product gave 11 g (82%) of a pale yellow liquid, bp 71-73°/10 torr. [Lit. bp 80.1°/20.5 torr (92)]

Poly(dithio-1,2-ethanediyl) (71)

The procedure of Cragg and Weston (93) was used. To a stirred suspension of 3.41 g (10.5 mmol) of lead(II) acetate in 50 ml of water was added 1.01 g (10.7 mmol) of 1,2-ethanedithiol. The mixture was stirred for five minutes and the solid that formed was filtered off and stirred in 100 ml of benzene with 0.33 g (10 mmol) of sulfur for 30 minutes. The solution was filtered and dried over $MgSO_4$ and the benzene was evaporated, leaving only a small amount of polymer. (Being only slightly soluble in benzene, most of the polymer was probably removed in the last filtration. However, because it was originally hoped that 1,2-dithietane (70) rather than the polymer (71) would be the final product, the polymer which was filtered off was not saved.)

1,2-Dithiolane (72)

1,3-Propanedithiol (2.22 g, 20.5 mmol) was added to a stirred suspension of lead(II) acetate (6.64 g, 20.4 mmol) in 150 ml of water. The mixture was stirred for 10 minutes and the yellow solid that formed was filtered off and placed in 200 ml of benzene. Sulfur was added, the mixture was stirred for 30 minutes, PbS was filtered off, and the solution was dried over $MgSO_4$. The product was kept in solution to prevent polymerization (27).

REFERENCES

1. Russell, G. A.; Chang, K.-Y. J. Am. Chem. Soc. 1965, 87, 4381.
2. Russell, G. A.; Holland, G. W.; Chang, K.-Y.; Keske, R. G.; Mattox, J.; Chung, C. S. C.; Stanley, K.; Schmitt, K.; Blankespoor, R.; Kosugi, Y. J. Am. Chem. Soc. 1974, 96, 7237.
3. Terabe, S.; Konaka, R. J. Am. Chem. Soc. 1971, 93, 6323.
4. Kosman, D.; Stock, L. M. J. Am. Chem. Soc. 1969, 91, 2011.
5. Kosman, D.; Stock, L. M. J. Am. Chem. Soc. 1966, 88, 843.
6. Nelsen, S. F.; Seppanen, E. D. J. Am. Chem. Soc. 1967, 89, 5740.
7. Terabe, S.; Konaka, R. J. Am. Chem. Soc. 1973, 95, 4976.
8. King, F. W. J. Magn. Reson. 1975, 17, 362.
9. Russell, G. A.; Tanikaga, R.; Talaty, E. R. J. Am. Chem. Soc. 1972, 94, 6125.
10. Schrauzer, G. N.; Rabinowitz, H. N. J. Am. Chem. Soc. 1970, 92, 5769.
11. Schrauzer, G. N.; Mayweg, V. P.; Heinrich, W. Inorg. Chem. 1965, 4, 1615.
12. Russell, G. A.; Lawson, D. F. J. Am. Chem. Soc. 1972, 94, 1699.
13. Schrauzer, G. N.; Mayweg, V. P. J. Am. Chem. Soc. 1965, 87, 1483.
14. Jacobsen, N.; de Mayo, P.; Weedon, A. C. Nouv. J. Chim. 1978, 2, 331.

15. Grunwell, J. R.; Willett, J. D. *Int. J. Sulfur Chem., Part A* 1971, 1, 60.

16. Leaver, D.; Robinson, W. A. H.; McKinnon, D. M. *J. Chem. Soc.* 1962, 5104.

17. Fanghänel, E. *Z. Chem.* 1964, 4, 70.

18. McIntosh, J. M.; Goodbrand, H. B.; Masse, G. M. *J. Org. Chem.* 1974, 39, 202.

19. Russell, G. A.; Strom, E. T. *J. Am. Chem. Soc.* 1964, 86, 744.

20. Russell, G. A.; Stevens, R. D. *J. Phys. Chem.* 1966, 70, 1320.

21. Fischer, H. In "Landolt-Börnstein, Numerical Data and Functional Relationships in Science and Technology"; Hellwege, K.-H., Ed.; Springer-Verlag: Berlin, 1965; Vol. I, Chapter 2.

22. Huisgen, R.; Weberndorfer, V. *Experientia* 1961, 17, 566.

23. Challenger, F.; Mason, E. A.; Holdsworth, E. C.; Emmott, R. *J. Chem. Soc.* 1953, 292.

24. Asmus, K.-D. *Colloq. Int. C. N. R. S.* 1977, 278, 305; *Chem. Abstr.* 1979, 91, 210 573u.

25. Asmus, K.-D.; Bahnemann, D.; Fischer, Ch.-H.; Veltwisch, D. *J. Am. Chem. Soc.* 1979, 101, 5322.

26. Chambers, J. Q.; Canfield, N. D.; Williams, D. R.; Coffen, D. L. *Mol. Phys.* 1970, 19, 581.

27. Affleck, J. G.; Dougherty, G. *J. Org. Chem.* 1950, 15, 865.

28. g-Factor was determined by Chris Osuch, Department of Chemistry, Iowa State University.

29. Russell, G. A.; Strom, E. T.; Talaty, E. A.; Weiner, S. A. *J. Am. Chem. Soc.* 1966, 88, 1998.

30. Lucken, E. A. C. *Theoret. Chim. Acta* 1963, 1, 397.

31. Simmons, H. E.; Blomstrom, D. C.; Vest, R. D. *J. Am. Chem. Soc.* 1962, 84, 4756.

32. Simmons, H. E.; Blomstrom, D. C.; Vest, R. D. J. Am. Chem. Soc. 1962, 84, 4782.

33. Nelson, D. J.; Petersen, R. L.; Symons, M. C. R. J. Chem. Soc., Perkin Trans. 2 1977, 2005.

34. Gilbert, B. C.; Hodgeman, D. K. C.; Norman, R. O. C. J. Chem. Soc., Perkin Trans. 2 1973, 1748.

35. Musker, W. K.; Wolford, T. L. J. Am. Chem. Soc. 1976, 98, 3055.

36. Musker, W. K.; Wolford, T. L.; Roush, P. B. J. Am. Chem. Soc. 1978, 100, 6416.

37. Harnden, R. M.; Moses, P. R.; Chambers, J. Q. J. Chem. Soc., Chem. Commun. 1977, 11.

38. Bergson, G. Arkiv. Kemi 1958, 12, 233.

39. Snyder, J. P.; Carlsen, L. J. Am. Chem. Soc. 1977, 99, 2931.

40. Truby, F. K. J. Chem. Phys. 1964, 40, 2768.

41. Akasaka, K.; Ohnishi, S.-I.; Suita, T.; Nitta, I. J. Chem. Phys. 1964, 40, 3110.

42. Box, H. C.; Freund, H. G. J. Chem. Phys. 1964, 41, 2571.

43. Box, H. C.; Freund, H. G.; Frank, G. W. J. Chem. Phys. 1968, 48, 3825.

44. Box, H. C.; Freund, H. G.; Lilga, K. T.; Budzinski, E. E. J. Phys. Chem. 1970, 74, 40.

45. Akasaka, K.; Kominami, S.; Hatano, H. J. Phys. Chem. 1971, 75, 3746.

46. Gillbro, T. Chem. Phys. 1974, 4, 476.

47. Naito, A.; Akasaka, K.; Hatano, H. J. Magn. Reson. 1976, 24, 53.

48. Petersen, R. L.; Nelson, D. J.; Symons, M. C. R. J. Chem. Soc., Perkin Trans. 2 1978, 225.

49. Hirshon, J. M.; Gardner, D. M.; Fraenkel, G. K. J. Am. Chem. Soc. 1953, 75, 4115.

50. Wertz, J. E.; Vivo, J. L. J. Chem. Phys. 1955, 23, 2193.

51. Yokozawa, Y.; Miyashita, I. J. Phys. Soc. Japan 1957, 12, 107.

52. Yokozawa, Y. J. Phys. Soc. Japan 1958, 13, 727.

53. Geske, D. H.; Merritt, M. V. J. Am. Chem. Soc. 1969, 91, 6921.

54. Forbes, W. F.; Sullivan, P. D. Can. J. Chem. 1968, 46, 317.

55. Zweig, A.; Hodgson, W. G. Proc. Chem. Soc. 1964, 417.

56. Holland, G. Ph.D. Dissertation, Iowa State University, Ames, Iowa, 1969.

57. Schmitt, K. D. Ph.D. Dissertation, Iowa State University, Ames, Iowa, 1973.

58. Ellingboe, E. K. U.S. Patent 2 816 287, 1957; Chem. Abstr. 1958, 52, 12 899g.

59. Scharf, H.-D.; Droste, W.; Liebig, R. Angew. Chem. Int. Ed. Engl. 1968, 7, 215.

60. Scharf, H.-D.; Küsters, W. Chem. Ber. 1972, 105, 564.

61. Newman, M. S.; Addor, R. W. J. Am. Chem. Soc. 1955, 77, 3789.

62. Scharf, H.-D.; Busse, W.-D.; Pinske, W. Chem. Ber. 1970, 103, 3949.

63. Scharf, H.-D. Angew. Chem. Int. Ed. Engl. 1974, 13, 520.

64. Scharf, H.-D., Institut für Organische Chemie der RWTH Aachen, West Germany, Private communication.

65. Chang, K.-Y. Ph.D. Dissertation, Iowa State University, Ames, Iowa, 1965.

66. Alder, K.; Schäfer, H. K.; Esser, H.; Krieger, H.; Reubke, R. Justus Liebigs Ann. Chem. 1955, 593, 23.

67. Hünig, S.; Benzing, E.; Lücke, E. Chem. Ber. 1957, 90, 2833.

68. Kardouche, N. G.; Owen, L. N. J. Chem. Soc., Perkin Trans. 1 1975, 754.

69. Bhattacharya, A. K.; Hortmann, A. G. J. Org. Chem. 1974, 39, 95.

70. Brown, H. C.; Lynch, G. J.; Hammar, W. J.; Liu, L. C. J. Org. Chem. 1979, 44, 1910.

71. Komppa, G. Chem. Ber. 1935, 68B, 1267.

72. Diels, von O.; Alder, K. Justus Liebigs Ann. Chem. 1930, 478, 137.

73. Alder, K.; Reubke, R. Chem. Ber. 1958, 91, 1525.

74. Stephen, J. F.; Marcus, E. J. Org. Chem. 1969, 34, 2535.

75. Usui, Y. Yakugaku Zasshi 1968, 88, 1535; Chem. Abstr. 1969, 71, 49 830a.

76. Asinger, von F.; Thiel, M.; Kaltwasser, H. Justus Liebigs Ann. Chem. 1957, 606, 67.

77. McIntosh, J. M.; Masse, G. M. J. Org. Chem. 1975, 40, 1294.

78. Hromatka, O.; Haberl, R. Monatsh. Chem. 1954, 85, 830.

79. Bauer, D. P.: Macomber, R. S. J. Org. Chem. 1975, 40, 1990.

80. Asinger, von F.; Thiel, M.; Pallas, E. Justus Liebigs Ann. Chem. 1957, 602, 37.

81. Corey, E. J.; Seebach, D. Angew. Chem. Int. Ed. Engl. 1975, 4, 1075.

82. Petermann, J.; Pleininger, H. Tetrahedron 1975, 31, 1209.

83. Shields, T. C.; Kurtz, A. N. J. Am. Chem. Soc. 1969, 91, 5145.

84. Iqbal, S. M.; Owen, L. N. J. Chem. Soc. 1960, 1030.

85. Lazier, W. A.; Signaigo, F. K.; Werntz, J. H. U.S. Patent 2 402 643, 1946; Chem. Abstr. 1946, 40, 5765.

86. Hromatka, O.; Engel, E. Justus Liebigs Ann. Chem. 1948, 78, 29.

87. Roberts, R. M.; Cheng, C.-C. J. Org. Chem. 1958, 23, 983.

88. Fitt, P. S.; Owen, L. N. J. Chem. Soc. 1957, 2250.

89. Fuhrer, von H.; Günthard, Hs. H. Helv. Chim. Acta 1962, 45, 2036.

90. Parham, W. E.; Heberling, J.; Wynberg, H. *J. Am. Chem. Soc.* 1955, 77, 1169.

91. Massingill, J. L., Jr.; Reinecke, M. G.; Hodgkins, J. E. *J. Org. Chem.* 1970, 35, 823.

92. Mathias, S. *Univ. Sao Paulo, Fac. Filos. Cienc. Let. Bol. Quim.* 1942, 14, 75; *Chem. Abstr.* 1946, 40, 2792.

93. Cragg, R. H.; Weston, A. F. *Tetrahedron Lett.* 1973, 655.