changes can be counterbalanced by favorable interactions of the liberated crown oxygens with excess sodium cations in solution, even if this results in a loss of activation entropy ($\Delta S^\ddagger = -32$ J mol^{-1} K^{-1}). The negative value of $\Delta S^\ddagger$ is in agreement with a bimolecular process and is indicative of the fact that the associating species are not desolvated to a large extent. This transition state can lead, by further cation desolvation and crown wrapping, to the 1:1 complex, which provides a mechanism for cation exchange inside the wrapped crown or can lead by further solvent and/or counteranion reorganization to the 2:1 complex or higher aggregates. At any stage of the aggregation, the slow step for the process remains the opening of the wrapped 1:1 complex. So, formation of aggregated species does not provide any "fast" way for cation exchange inside the 1:1 complex. Moreover, since the concentration of these species is minor (<2%), their exchange contribution to the observed transverse relaxation rate is negligible. This is what we observe (Figure 2) where the kinetic treatment is applicable for a two-site case. The unimolecular decomplexation mechanism becomes competitive only at low concentrations (<10^{-3} M). $\Delta G^\ddagger_{uni}$ can be estimated: 65 kJ mol^{-1} at 300 K. The barrier for the unimolecular decomplexation should originate in the same kind of conformational changes of the 1:1 complex than for the associative process. However the extra stabilization afforded by interaction of exposed crown oxygens with the (poorly) solvated sodium, operative in the associative process, is absent in the unimolecular decomplexation process.

In conclusion, we have shown the efficiency of an associative cation interchange mechanism for the complexation–decomplexation reactions of crown ethers. This process is operative for DB24C8 and sodium concentrations higher than 10^{-3} M at 295

K. At lower concentrations, the "classical" unimolecular decomplexation mechanism is operative. We are now pursuing our investigations to define the roles of solvent and counteranion.

Experimental Section

(24) Truter, M. R., cited as a private communication in ref 10.
(25) Deming, S. N.; Morgan, S. S. *Anal. Chem.* **1973**, *45A*, 278–282.
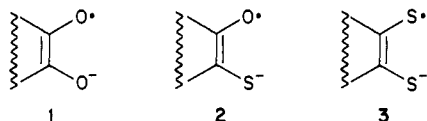
Spin Probes Derived from Dithiols[1]

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Abstract: Mono- and dithio-1,2-semidiones have been prepared. The dithiosemidiones have lower a_α^H and higher g values than the semidiones. The dithiete, 1,4-dithiin, and 2,3-dihydro-1,4-dithiin radical cations derived from bicyclo[2.2.1]hept-2-ene-2,3-dithiol have been prepared and demonstrated to possess a strong W-plan interaction with the 7_{anti}- and $5,6_{exo}$-hydrogen atoms as expected for a symmetric SOMO. The radical cation of 2,3-dithiabicyclo[2.2.1]heptane has an antisymmetric SOMO, and the long-range interaction with the 7_{anti}-hydrogen atom is not observed. 2,5-Dithiabicyclo[4.2.1]non-3-ene radical cation possesses a symmetric SOMO, and long-range splitting is observed at the anti position of the methylene bridge. 1,2-Dithietane and 1,2-dithiolane radical cations have been prepared, and the surprising values of a_α^H of 3.7 and 10 G, respectively, discussed in terms of an antisymmetric SOMO. 2,3-Dihydro-1,4-dithiin radical cations exist in a half-chair conformation with nonequivalent quasi-equatorial and quasi-axial hydrogen atoms. For the 5,6-dimethyl derivative $\Delta H^\ddagger = 2.3$ kcal/mol and $\Delta S^\ddagger = -20$ eu were measured in H$_2$SO$_4$ with a coalescence temperature of 70 °C.

Radical Anions. We have investigated the effect on spin distribution and ESR parameters (a^H, g value) of replacing 1,2-semidione oxygen atoms by sulfur atoms ($1 \rightarrow 2 \rightarrow 3$). Mo-

nothiosemidiones were synthesized from the α-mercapto ketones

4 or their cyclic dimers 5, by treatment with Me$_3$CO$^-$K$^+$ in Me$_2$SO (Scheme I).
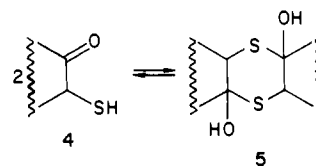
In certain cases, dithiosemidiones 3 could be prepared by treatment of thiophoshoric esters of enedithiols 7 with Me$_3$CO$^-$K$^+$ in Me$_2$SO (reaction 1). This procedure worked for the thiophosphoric esters derived from bicyclo[2.2.1]heptane-2,3-dione, camphorquinone, or bicyclo[2.2.2]octane-2,3-dione but failed for

$$RC(=O)C(=O)R \text{ or } RC(=O)CH(OH)R \xrightarrow{P_4S_{10}}$$

7
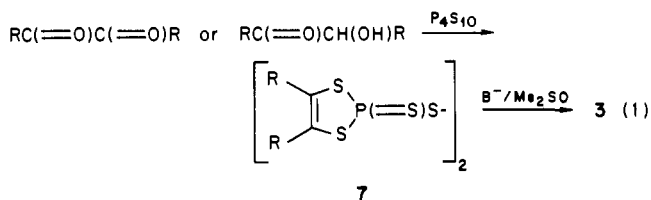
cyclohexane-1,2-dione or biacetyl. Treatment of the dithiocarbonate **8a** or trithiocarbonate **8b** of cyclohexene-1,2-dithiol with $Me_3CO^-K^+$ in Me_2SO with and without UV irradiation, and in static or flow systems, failed to produce cyclohexane-1,2-semidithione. Electrolytic reductions with and without UV irradiation

8a. X = O
b. X = S

of **8a** also failed to produce an ESR signal even though with UV irradiation the explusion of CO (bubbles at the cathode) appeared to occur.
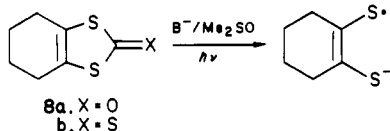
Table I lists the values of a^H and g for the examples of **2** and **3** that have been prepared as well as the previously reported values for **1**.[2] The g values increase from **1** to **2** to **3**, while at the same time a_α^H decreases nearly 50% between **1** and **3**. Since the g values of oxygen- and sulfur-centered radicals are approximately equal (e.g., O^-· vs. S^-·, HO· vs. HS·, CH_3O· vs. CH_3S·)[3] but greater than the g values of carbon-centered radicals (CH_3CH_2·, $g = 2.0026$; CH_3O·, $g = 2.0143$; CH_3S·, $g = 2.0137$),[3] the increase in g values and decrease in a_α^H must be connected with spin distribution. The resonance structure **9b** must be favored over **9a,c** when X is


9a　　　　　　**9b**　　　　　　**9c**
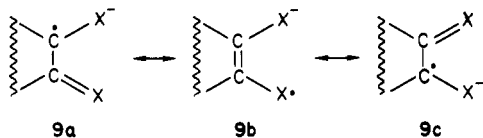
changed from oxygen to sulfur. In the monothiosemidiones, the values of a_α^H adjacent to the C=O group show a large decrease, whereas a_α^H adjacent to the C=S group is slightly larger than in the semidione. For the bicyclo[2.2.1] system, the same effect is observed for a_β^H. Resonance structure **9c′** must be greatly preferred to **9a′** in agreement with a greater π-bond energy for C=O than for C=S.

9a′　　　　　　**9b′**　　　　　　**9c′**
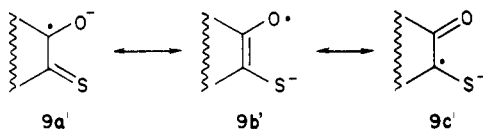
For the acyclic monothiosemidione ($CH_3C(O^-)=C(S$·$)CH_3$ or $CH_3CH_2C(O$·$)=C(S^-)CH_3$), only a single isomer could be detected. This is probably the trans isomer, and if so, it indicates, as would be expected, that ion pairing with K^+ in Me_2SO is less important for **2** and **3** than for **1**. For $CH_3C(O$·$)=C(O^-)CH_3$ in Me_2SO at 25 °C, $K_{eq} = trans/cis$ is 725 for the free ions but only 2 for the ion pairs with K^+.[2a]
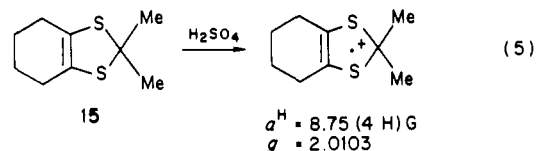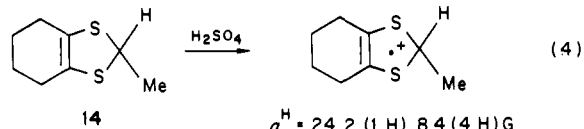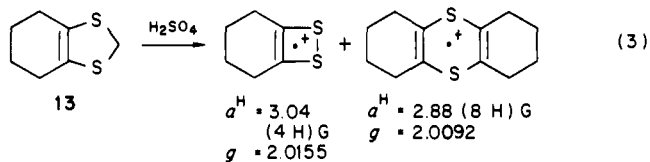
Radical Cations. We have previously reported radical cations of the dithiete (**10**), 1,3-dithiole (**11**), and 1,4-dithiin (**12**) types.[4] However, our previous synthesis of **10–12** (Scheme II) failed when


10　　　　　　**11**　　　　　　**12**
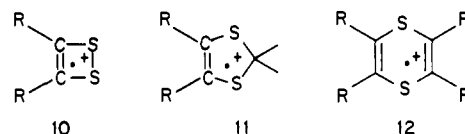
applied to the bicyclo[2.2.1]heptane system. We, therefore, have investigated alternate routes to these radical cations. The trithiocarbonates (e.g., **8b**) seemed to be reasonable precursors, particularly since these substances are readily formed from cyclic ketones (reaction 2). Reduction of **8b** with $LiAlH_4$[5] followed by

8b. $n = 4$
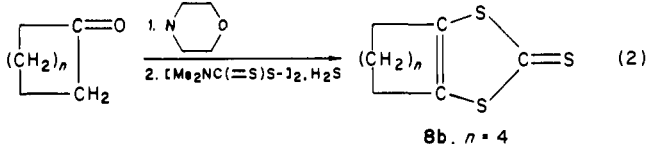
stepwise alkylation with BuLi and MeI formed **13–15**. Treatment of **13** with concentrated H_2SO_4 did not yield the 1,3-dithiole radical cation. Instead, the methylene group was expelled to yield the dithiete and 1,4-dithiin radical cations (reaction 3). However,

13

$a^H = 3.04$ (4 H) G
$g = 2.0155$

$a^H = 2.88$ (8 H) G
$g = 2.0092$

14

$a^H = 24.2$ (1 H), 8.4 (4 H) G

15

$a^H = 8.75$ (4 H) G
$g = 2.0103$

14 and **15** yielded the expected 1,3-thiole radical cations (reactions 4 and 5).[6,7] Treatment of **13** with $AlCl_3$ in CH_2Cl_2 yielded **13**+·

13+·
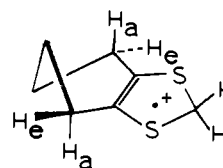
$a^H(-30$ °C, $CH_2Cl_2) = 26.6$ (2 H), 8.20 (4 H) G
$g = 2.0101$
$a^H(-90$ °C, $CH_2Cl_2) = 26.6$ (2 H), 11.0 (2 H), 5.5 (2 H) G

which was stable for several hours at −30 °C. At −90 °C, **13**+·

(2) (a) Russell, G. A.; Osuch, C. E. *J. Am. Chem. Soc.* **1982**, *104*, 3353. (b) Russell G. A.; Lawson, D. F.; Malkus, H. L.; Stephens, R. D.; Underwood, G. R.; Takano, T.; Malatesta, V. *J. Am. Chem. Soc.* **1974**, *76*, 5830. (c) Russell, G. A.; Osuch, C. E. *J. Am. Chem. Soc.* **1978**, *100*, 5979; *J. Org. Chem.* **1980**, *45*, 1242. (d) 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. (e) Russell, G. A.; Holland, G. W.; Chang, K.-Y. *J. Am. Chem. Soc.* **1967**, *89*, 6629. (f) Russell, G. A.; Underwood, G. R.; Lini, D. C. *J. Am. Chem. Soc.* **1967**, *67*, 6636.

(3) Landolt-Börnstein "New Series, Group II"; Fischer, H., Hellwege, K.-H., Eds.; Springer-Verlag: Berlin, 1979; Vol. 9, part c2.

(4) Russell, G. A.; Tanikaga, R.; Talaty, E. R. *J. Am. Chem. Soc.* **1972**, *94*, 6125.

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

(6) The observation that a^H for the methylene and methine hydrogen atoms of **13**+· and **14**+· are 26.2 and 24.2 G conclusively demonstrates that hyperfine splitting by hydrogen atoms α to a sulfur atom possessing unpaired spin density is not determined solely or mainly by a spin polarization effect independent of dihedral angle or symmetry of the SOMO, even though a number of systems have been reasonably well correlated by $a_\alpha^H = |17\rho_S|$.[7] Using this equation, **13**+· and **14**+· have impossibly large values of $\rho_S = 0.7–0.8$. The dramatic increase in a_α^H from **26** and **30** ($a_{CH_2}^H \approx 3.6, 4.5$ G) to **13**+· and **14**+· is understandable from a hyperconjugation model with a constant value of $\rho_S = (c_S)^2$ since for **26** and **30** a_α^H is a function of $(c_S)^2$ but for **13**+· and **14**+· a_α^H is a function of $(2c_S)^2$. Dependence of a_α^H upon the dihedral angle is clearly demonstrated by the temperature dependence of hfsc observed for **29** and **30**.

(7) Hyperfine splitting by methyl or methylene hydrogen atoms α to a sulfur atom with unpaired spin density have been interpreted as arising mainly from an angle-independent spin polarization effect in tetrathioethylene radical cations: Chambers, J. Q.; Canfield, N. D.; Williams, D. R.; Coffen, D. L. *Mol. Phys.* **1970**, *19*, 581. Bock, H.; Brähler, G.; Henkel, U.; Schlecker, R.; Seebach, D. *Chem. Ber.* **1980**, *113*, 289.

Spin Probes Derived from Dithiols

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Table I. Values of a^H and g for $R_1C(X_1\cdot)=C(X_2^-)R_2$ at 25 °C in Me$_2$SO

R_1, R_2	X_1, X_2	g	a_α^H, G	other a^H, G	ref
cis-CH$_3$, CH$_3$	O, O (free ion)	2.005 11	6.75 (6 H)		2a
cis-CH$_3$, CH$_3$	O, O (K$^+$, ion pair)	2.004 91	7.26 (6 H)		2a
trans-CH$_3$, CH$_3$	O, O (free ion)	2.005 08	5.67 (6 H)		2a
trans-CH$_3$, CH$_3$	O, O (K$^+$, ion pair)	2.004 88	6.23 (6 H)		2a
trans-CH$_3$, CH$_3$	O, S	2.010 3	2.10 (3 H), 7.65 (3 H)		
cis-CH$_3$, C$_2$H$_5$	O, O		6.10 (2 H), 7.05 (3 H)		2b
trans-CH$_3$, C$_2$C$_5$	O, O		4.85 (2 H), 5.75 (3 H)		2b
trans-CH$_3$, C$_2$H$_5$	S, O	2.010 9	2.25 (2 H), 7.75 (3 H)		
–(CH$_2$)$_4$–	O, O (free ion)	2.005 10	9.50 (4 H)^{a,b}		2c
–(CH$_2$)$_4$–	O, O (K$^+$, ion pair)	2.004 90	10.04 (4 H)^a		2c
–(CH$_2$)$_4$–	O, S		4.80 (2 H), 11.45 (2 H)^a		
	O, O	2.005 01	2.49 (2 H)	2.5 (5,6$_{exo}$), (5,6$_{exo}$), 6.48 (7$_{anti}$), 0.36 (7$_{syn}$)	2d
	O, S	2.010 0	2.6 (1 H), 1.3 (1 H)	1.3 (1 H), 2.6 (1 H), 5.2 (7$_{anti}$)	
	S, S	2.016 6	1.3 (2 H)	1.3 (5,6$_{exo}$), 4.2 (7$_{anti}$)	
	O, O		2.08 (1 H)	3.01 (5,6$_{exo}$), 0.55 (syn 7-Me), 0.18 (Li-Me)	2d
	S, S		1.4 (1 H)	1.4 (5, 6$_{exo}$)	
	O, O		<0.1	2.09 (5–8$_{anti}$, 4 H)	2e
	S, S		<0.3	1.2 (5–8$_{anti}$, 4 H)	

^{a}Conformationally time averaged values. $^b a_a^H = 13.0$, $a_e^H = 6.5$, coalescence temperature $= -42$ °C, Cs$^+$ in DMF.^{2f}

Scheme I

Scheme II

$$RC(=O)C(=O)R \text{ or } RC(=O)CH(OH)R \xrightarrow{H_2S, H_2SO_4} 10 \rightleftharpoons 12$$
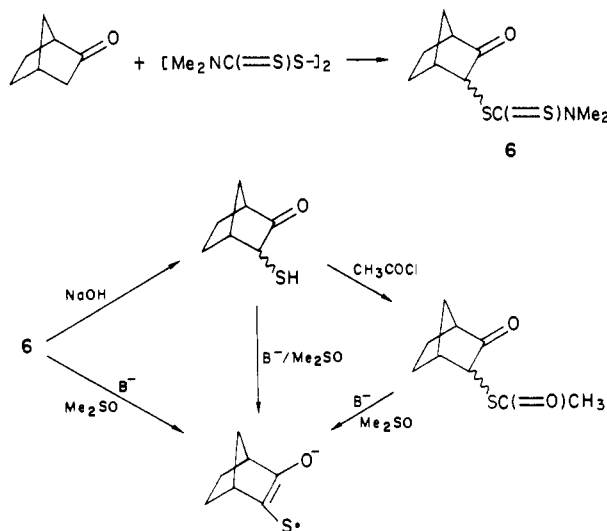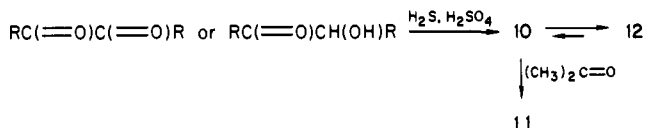
gave a hfs pattern of t × t × t with selective line broadening in the slow exchange mode. At –30 to –40 °C, the spectrum was a triplet of pentets, and at intermediate temperatures, selective line broadening was observed from the ring flip of the half-chair cyclohexene ring which interconverts the quasi-equatorial and equasi-axial hydrogen atoms. From the selective line broadening, a value of $\Delta H^* = 6.2$ kcal/mol and $\Delta S^* = 5.6$ eu was calculated for **13$^+$·** with a coalescence temperature of ~ -80 °C.

When applied to bicyclo[2.2.1]heptan-2-one, the expected trithiocarbonate of the enedithiol was not produced in reaction 2, but instead the saturated trithocarbonate **16** (mixture of exo and endo isomers) was formed. However, by the sequence of Scheme III, **16** could be converted to the desired trithiocarbonate **20**. Reduction of **20** by LiAlH$_4$ failed to form the thiole but instead formed cis-bicyclo[2.2.1]heptane-2,3-dithiol (**21**)^{8,9} as a

mixture of exo and endo isomers. It has been previously observed that benzo-1,3-dithiole-2-thione or 1,3-dithiole-2-thione are reduced to the corresponding dithiols by LiAlH$_4$.^{10,11} Treatment of **21** or the 1,3-dithiolane **22** with H$_2$SO$_4$/K$_2$S$_2$O$_8$ led to the formation of the dithete radical cation **23** with no indication of the formation of the dithiole or dithietane radical cations (Scheme IV). Upon standing, the dithete radical cation slowly gave rise to the corresponding 1,4-dithiin system. The dithiete radical cation **23** is also formed slowly (2 days) by treatment of norbornene with S$_2$Cl$_2$ in H$_2$SO$_4$ or by treatment of exo-3,4,5-trithiatricyclo-[5.2.1.0^{2,6}]decane with H$_2$SO$_4$. The synthesis of **24** free from the ESR signal of **23** was achieved by the action of H$_2$SO$_4$ on 3-mercaptobicyclo[2.2.1]heptan-2-one. Presumably, the intermediate 2,5-dihydroxy-2,3,4,5-tetrasubstituted 1,4-dithiane **5** underwent dehydration to the 1,4-dithiin which was oxidized by H$_2$SO$_4$ to **24**.

2,3-Dihydro-1,4-dithiin radical cations were also prepared in the bicyclo[2.2.1]heptane system (Scheme V). The spectrum observed for **26+·** in H$_2$SO$_4$ changed with temperature below 70 °C but was independent of temperature from 70 to 120 °C. The 2,3-dihydro-1,4-dithiin radical cation is not a planar system and involves a conformational equilibrium which time-averages the hydrogen atoms of the methylene groups. The parent 2,3-dihydro-1,4-dithiin radical cation (**29**) was not observed in H$_2$SO$_4$
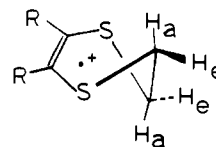
29, R = H; 30, R = CH$_3$

a_{29} ^{H}(CH$_2$Cl$_2$, –80 °C) = 8.15 (2 H), 3.4 (2 H), 2.7 (2 H) G; g = 2.0092
a_{30} ^{H}(CH$_2$Cl$_2$, –80 °C) = 5.7 (6 H), 6.9 (2 H), 2.1 (2 H) G; g = 2.0080
a_{30} ^{H}(H$_2$SO$_4$, –10 °C) = 5.59 (6 H), 6.99 (2 H), 2.09 (2 H) G; g = 2.0080

but could be formed by treatment of the dihydrodithiin with AlCl$_3$ in CH$_2$Cl$_2$ at –60 °C. 5,6-Dimethyl-2,3-dihydro-1,4-dithiin^{12} gave the radical cation **30** in H$_2$SO$_4$ at –10 to 70 °C or at –60 °C with AlCl$_3$/CH$_2$Cl$_2$ or SbCl$_3$/CH$_2$Cl$_2$. Both **29** and **30** in the

(8) Shields, T. C.; Kurtz, A. N. *J. Am. Chem. Soc.* **1969**, *91*, 5415.

(9) Conveniently prepared by treatment of **16** with aqueous NaOH or by reduction of exo-3,4,5-trithiatricyclo[5.2.1.0^{2,6}]decane.^{8}
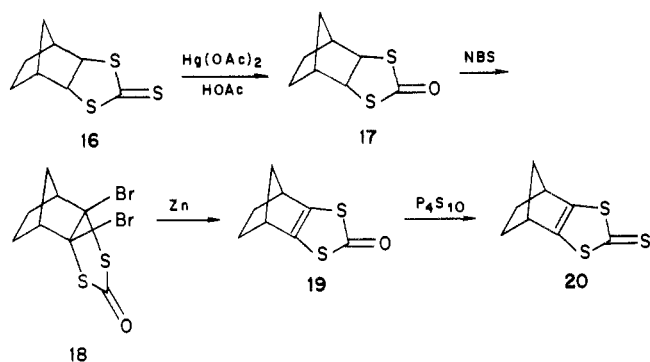
(10) Huisgen, R.; Webendorfer, V. *Experientia* **1961**, *17*, 566.

(11) Challenger, F.; Mason, E. A.; Holdsworth, E. C.; Emmott, R. *J. Chem. Soc.* **1953**, 292.
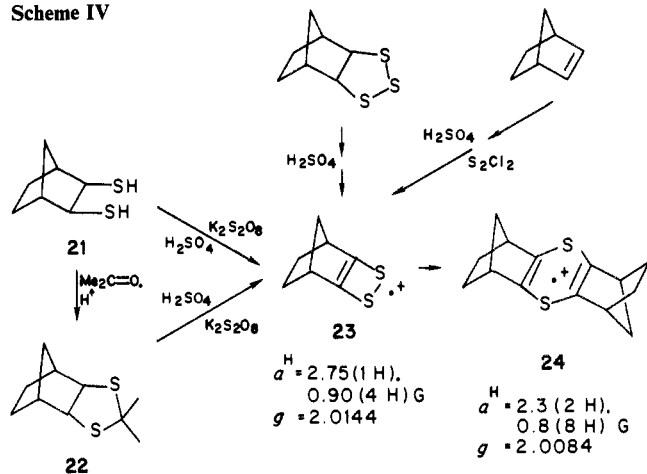
(12) Massingill, J. L.; Reinecke, M. G.; Hodgkins, J. E. *J. Org. Chem.* **1970**, *35*, 823.

Scheme III

Scheme IV

$$a^H = 2.75(1\ H).$$
$$0.90\ (4\ H)\ G$$
$$g = 2.0144$$

$$a^H = 2.3\ (2\ H).$$
$$0.8\ (8\ H)\ G$$
$$g = 2.0084$$

Scheme V

25 or 26 $\xrightarrow{\text{H}_2\text{SO}_4}$ 26$^+$· ($a^H = 5.0$ (1 H). 3.6 (4 H).1.55 (4 H) G:
$g = 2.0075$)

27 or 28 $\xrightarrow{\text{H}_2\text{SO}_4}$ 28 ($a^H = 7.7$ (4 H). 4.8(2 H). 0.8 (1 H) G;
$g = 2.0077$)
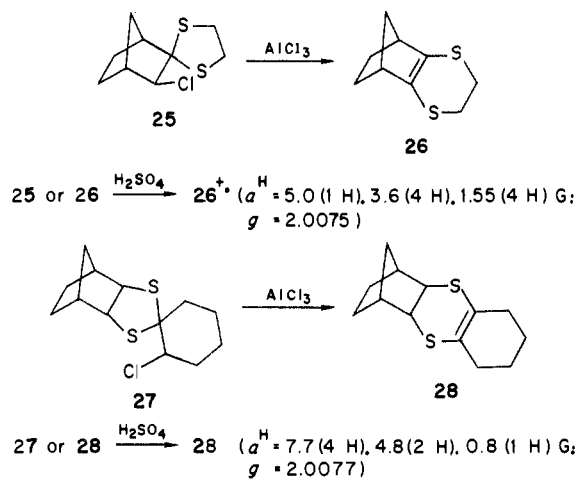
AlCl$_3$/CH$_2$Cl$_2$ system gave well-resolved spectra with non-equivalent quasi-axial and equatorial hydrogen atoms which for 30 coalesced in H$_2$SO$_4$ at ~70 °C (Figure 1). In H$_2$SO$_4$, the values of a^H (apparent) for the quasi-equatorial and quasi-axial hydrogen atoms of 30 were measured in the slow exchange mode, and the ring flip was calculated to have $\Delta H^\ddagger$ = 2.3 kcal/mol and $\Delta S^\ddagger$ = -20 eu with $\Delta G^\ddagger$ = 9.2 kcal/mol at the coalescence temperature of ~70 °C. The methylene hydrogen atoms in 29 are assigned as 8.15 (axial) and 2.7 (equatorial), and the time-averaged methylene hydrogens of 26+· assigned as 3.6 G.[7]

The spectra of 23, 24, 26$^+$·, and 28$^+$· provide examples of radical cations, wherein the unpaired spin is in an MO that is symmetric relative to a plane bisecting the bicyclo[2.2.1] ring system. This leads to large values for $a^H_{7\text{-anti}}$ and to high ratios for $a^H_{7\text{-anti}}/a^H_{7\text{-syn}}$.[2d] In Table II are collected other examples of the hfsc
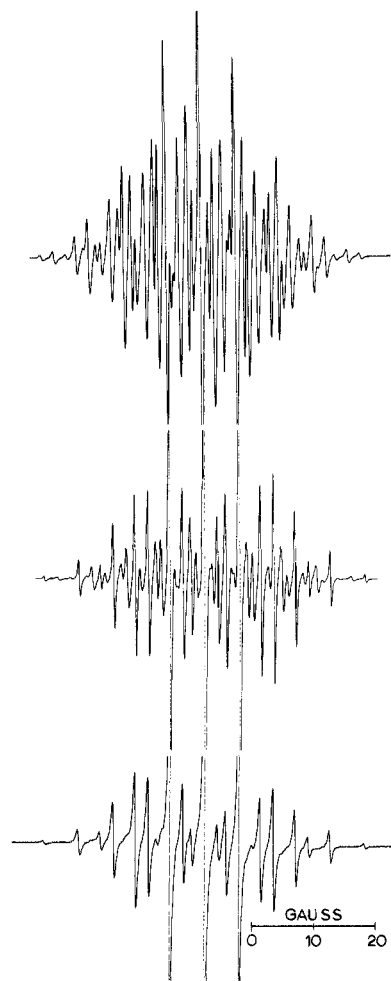
Figure 1. ESR spectra of 5,6-dimethyl-2,3-dihydro-1,4-*p*-dithiin radical cation (30): top, AlCl$_3$/CH$_2$Cl$_2$, -60 °C; middle, H$_2$SO$_4$, 20 °C; bottom, H$_2$SO$_4$, 70 °C at ca. coalescence temperature, second and fourth peaks of pentet splitting are not observed because of line broadening.

observed for bicyclo[2.2.1] systems with a variety of spin labels (31) having different spin densities at atoms 2 and 3 in the bi-

cyclo[2.2.1] system.[13] If the values of $a^H_{5,6\text{-exo}}$ are taken as measures of the spin density, we note that for the symmetric spin labels the value of $a^H_{7\text{-anti}}/a^H_{5,6\text{-exo}}$ is ~3 for the first eight spin labels in Table II but much less for the three antisymmetric labels where the bridging methylene group lies in the nodal plane of the spin label. The value of 1 for the *p*-benzosemiquinone seems a bit puzzling but is more in line with an antisymmetric SOMO.
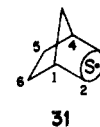
The observed hyperfine splitting constants summarized in Table II define the symmetries of the SOMO 10-12 as well as the 2,3-dihydro-1,4-dithiin radical cation as symmetric relative to the plane of symmetry of the molecules. This is a bit surprising for the dithete radical cation 10 which as a cyclobutadiene analogue might have been expected to have degenerate orbitals Ψ_{sa} and Ψ_{as}. The experimental result is consistent with $\beta_{CS} > \frac{1}{2}(\beta_{CC} + \beta_{SS})$. Another contributing factor may be the higher electronegativity of sulfur. With $\alpha_S > \alpha_C$ and $\beta_{CC} > \beta_{SS}$, the splitting between the C=C and S—S π-orbitals (leading to Ψ_{ss} and ψ_{sa}) would be greater than the splitting between the corresponding π^* orbitals

(13) (a) Nelsen, S. F.; Seppanen, E. D. *J. Am. Chem. Soc.* 1967, *84*, 5740. Nelsen, S. F.; Travecedo, E. F.; Seppanen, E. D. *J. Am. Chem. Soc.* 1971, *93*, 2913. (b) Kosman, D.; Stock, L. M. *J. Am. Chem. Soc.* 1969, *91*, 2011. (c) Nelsen, S. F.; Weisman, G. R.; Hintz, P. J.; Olp, D.; Fahey, M. R. *J. Am. Chem. Soc.* 1974, *96*, 2916.

ψ_{sa} ψ_{as}
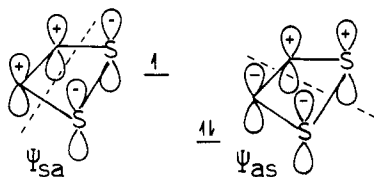
(leading to ψ_{as} and ψ_{aa}) resulting in ψ_{sa} having a higher energy than ψ_{as}.

Having observed that the 1,2-dithiol **21** is oxidized by H_2SO_4 to the dithiete and 1,4-dithiin radical cations, we examined the oxidation of other 1,2-dithiols. 2,3-Butanedithiol produced the known[4] 3,4-dimethyl-1,2-dithiete radical cation (reaction 6) in

$$CH_3CH(SH)CH(SH)CH_3 \xrightarrow{H_2SO_4} \quad (6)$$

$a^H = 2.19$ (6 H) G
$g = 2.0155$
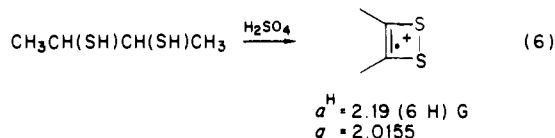
H_2SO_4 in the absence of $K_2S_2O_8$. 1,2-Propanedithiol gave first the 3-methyl-1,2-dithiete radical cation (reaction 7) which slowly

$$CH_3CH(SH)CH_2SH \xrightarrow{H_2SO_4} \quad (7)$$

$a^H = 3.3$ (1 H), 1.8 (3 H) G
$g = 2.0159$

gave rise to a mixture of the two *p*-dithiin radical cations, **32** and **33**. 2,2,4-Trimethyl-1,3-dithiolane[14] in H_2SO_4 produced the same

32   **33**

$a^H = 2.85$ (2 H), 2.45 (6 H) G $a^H = 3.50$ (2 H), 1.75 (6 H) G
$g = 2.0094$ $g = 2.0094$

ESR signals as 1,2-propanedithiol.[15] The assignment of splitting constants to **32** and **33** was possible since the dimer of mercaptoacetone (2,5-dihydroxy-2,5-dimethyl-1,4-dithiane) upon t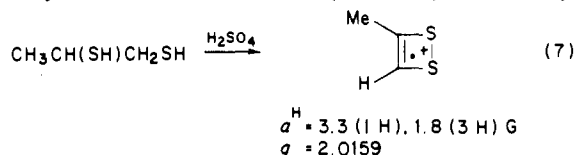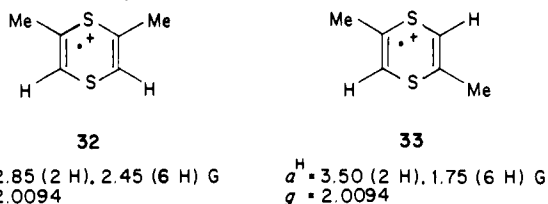reatment with H_2SO_4 formed initially **33** which equilibrated within a few minutes to the same mixture of **32** and **33** formed from 1,2-propanedithiol or 2,2,4-trimethyl-1,3-dithiolane.

Ethane-1,2-dithiol or 2,3-dihydro-1,4-dithiin gave rise to an ESR signal of 2.40 (8 H) G with $g = 2.0089$ which was identified as the previously reported $\Delta^{2,2'}$-bi-1,3-dithiolanylidene radical cation **34** (reaction 8).[16] Starting from ethane-1,2-dithiol, an initial ESR

$$HSCH_2CH_2SH \text{ or } \xrightarrow{H_2SO_4} \quad (8)$$

34
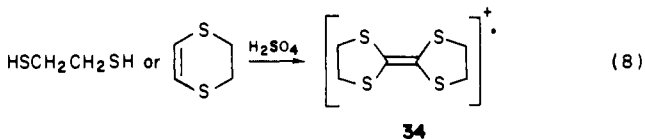
signal of $a^H = 3.7$ (4 H) G, $g = 2.0193$, was observed which slowly decayed to **34**. Since the 1,4-dithiin radical cation **35** is known[4] and can be excluded, it appears that the species with $g = 2.0193$ is the 1,2-dithietane radical cation **36**. Radical cations of di-

35   **36**

$a^H = 2.84$ (4 H) G $a^H = 3.7$ (4 H) G
$g = 2.0089$ $g = 2.0193$
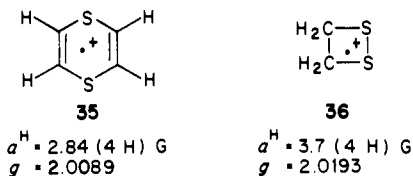
sulfides have g values in the solid state or in solution in the range 2.018–2.019 (*n*-C_5H_{11}SS·$^+C_5H_{11}$-*n*, glass, $g = 2.019$;[17]
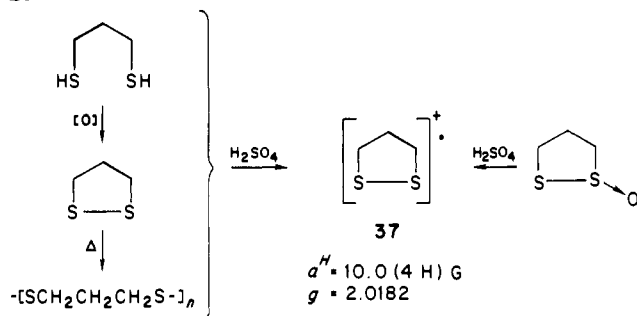
(14) Roberts, R. M.; Cheng, C.-C. *J. Org. Chem.* **1958**, *23*, 983.
(15) In H_2SO_4, $MeSCH(CH_3)CH_2SCH_3$ failed to give an ESR signal.
(16) Chambers, J. Q.; Canfield, N. D.; Williams, D. R.; Coffen, D. L. *Mol. Phys.* **1970**, *19*, 581.
(17) Truby, F. K. *J. Chem. Phys.* **1964**, *40*, 2768.

Scheme VI

37

$a^H = 10.0$ (4 H) G
$g = 2.0182$

$HO_2CCH_2SS·^+CH_2CO_2H$, $g = 2.018$;[18] cystine$^+$·, crystalline, $g = 2.012$–2.028;[19] 1,2-dithiolane$^+$·, 1,2-dithiane$^+$·, 1,2-dithiepane$^+$·, α-lipoic acid$^+$·, CH_2Cl_2, $g = 2.0183$).[20] In fact, oxidation of 1,3-propanedithiol, 1,2-dithiolane,[21] the polymer of 1,2-dithiolane,[21] or the monosulfoxide of 1,2-dithiolane[22] with H_2SO_4 produced the 1,2-dithiolane radical cation **37**, Scheme VI.[23]

Poly(dithio-1,2-ethanediyl),[24] when treated with H_2SO_4, produced only the species with $a^H = 3.7$ (4 H) G. If this species is the 1,2-dithietane radical cation **36**, one is faced with a problem explaining the magnitude of a_α^H since in **37** a_α^H is 10.0 G in H_2SO_4 (9.5 G in CH_2Cl_2) and the corresponding six- and seven-membered ring cyclic 1,2-disulfides also have values of a_α^H of 9.5 G (C-H_2Cl_2).[20] We believe the solution to this difference lies in the symmetry of the disulfide radical cation spin probe. With a spin probe having a symmetric SOMO, the value of a_α^H is significantly greater in the four-membered ring than in the five- or six-membered ring, e.g., in the semidiones **38a–c**.[2e] In cyclic systems,
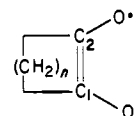
38a. $n = 2$, $a_\alpha^H = 13.85$ G
    b. $n = 3$, $a_\alpha^H = 12.93$ G
    c. $n = 4$, $a_\alpha^H = 9.50$ G

the value of a_α^H will be determined by the values of the MO coefficients at C-1 and C-2. The observed value of a_α^H can be considered to be the composite of a 1,2-hyperconjugative interaction ($a_{1,2}$) depending on the value of c_1^2 and a 1,3-homohyperconjugative interaction ($a_{1,3}$) depending on the value of c_2^2.[25,26] When c_1 and c_2 have the same sign, the interactions will reinforce each other and be additive, whereas when c_1 and c_2 are opposite in sign (antisymmetric SOMO), the two delocalization mechanisms will partially cancel each other ($a_H = a_{1,2} - a_{1,3}$).[26] The

(18) Box, H. C.; Freund, H. G.; Frank, G. W. *J. Chem. Phys.* **1968**, *48*, 3825.
(19) Landolt-Börnstein "New Series, Group II"; Fischer, H., Hellwege, K.-H., Eds.; Springer-Verlag: Berlin, 1979, Vol. 9, part c2, p 300.
(20) Bock, H.; Stein, U. *Angew. Chem.* **1980**, *92*, 863; *Angew Chem., Int. Ed. Engl.* **1980**, *19*, 834. Bock, H.; Stein, U.; Semkow, A. *Chem. Ber.* **1980**, *113*, 3208.
(21) Affleck, J. G.; Dougherty, G. *J. Org. Chem.* **1950**, *15*, 865.
(22) Cristau, H.-J. Chabaud, B.; Labaudiniere, R.; Christol, H. *Syn. Commun.* **1981**, *11*, 423.
(23) Treatment of 1,5-dithiacyclooctane with H_2SO_4 yields a species with $a^H = 9.9$ (4 H) G: Musker, W. K.; Wolford, T. L.; Roush, P. B. *J. Am. Chem. Soc.* **1978**, *100*, 6416. Brown, T. G.; Hirschon, A. S.; Musker, W. K. *J. Phys. Chem.* **1981**, *85*, 3767. We have repeated this experiment and find $g = 2.018$ instead of the 2.012 reported previously. Apparently, degradation has occurred to form the 1,2-dithiolane radical cation **37**.
(24) Prepared by the method of: Cragg, R. H.; Weston, A. F. *Tetrahedron Lett.* **1973**, 655.
(25) Bauld, N. L.; Farr, F. R. *J. Am. Chem. Soc.* **1974**, *96*, 5633. Bauld, N. L.; Farr, F. R.; Hudson, C. E. *J. Am. Chem. Soc.* **1974**, *96*, 5635.
(26) Actually these interactions should be formulated as $a_\alpha^H = f(c_1 + Fc_2)^2$ where F is a scaling factor relating the magnitude of the hyperconjugative and homohyperconjugative interactions. Both interactions have a geometry dependence which must be considered. Quantitatively the net interaction is predicted quite well by use of extended Hückel or INDO calculations (which include spin polarization effects). Thus, with standard geometries, INDO calculations for **39** and **40** yielded the following:[2d] **39**, $a^H_{bridgehead} = 1.8$, $a^H_{5,6-exo} = 1.8$, $a^H_{5,6-endo} = -0.2$, $a^H_{7-syn} = -0.8$, $a^H_{7-anti} = 5.9$ G. **40**, $a^H_{bridgehead} = -0.3$, $a^H_{5,6-exo} = 1.8$, $a^H_{5,6-endo} = 0.22$, $a^H_{7-syn} = -0.5$, $a^H_{7-anti} = -2.0$ G.

Table II. Hyperfine Splitting Constants for 31

spin label (S)	symmetry of SOMO	$a^H_{7\text{-anti}}$	$a^H_{7\text{-syn}}$	$a^H_{1,4}$	$a^H_{5,6\text{-exo}}$	$a^H_{5,6\text{-endo}}$	ref
	S	6.5	0.4	2.5	2.5	<0.2	2d
	S	4.2	<0.5	1.3	1.3	<0.5	
	S	2.75	<0.3	0.9	0.9	<0.3	
	S	2.3	<0.3	0.8	0.8	<0.3	
	S	3.6	<0.5	1.15	1.15	<0.5^a	
	S	4.95	<0.3	1.55	1.55	<0.3^b	
	S	1.80	0.51	5.10	0.51	<0.1^c	
	S	3.45	<0.5	1.05	1.05	<0.5^d	
	A	1.0	0.5	0.4	2.0	0.3	13a
	A	1.7	0.8		4.8		13c
	A	<0.3	<0.3	<0.3	6.3	<0.3	
		0.7	<0.2	<0.2	0.7	<0.2	13b

^{a} a^H_{Ar} = 1.15 (2 H) G. ^{b} $a^H_{CH_2}$ = 3.55 (4 H) G. ^{c} a^H_{vinyl} = 2.85 (2 H) G. ^{d} a^H_{vinyl} = 2.1 (2 H) G.

magnitude of the 1,3-interaction should decrease rapidly with ring size (i.e., with the ∠CSS), whereas the 1,2-interaction will vary with the $\cos^2 \theta$ of the dihedral angle between the $C_\alpha$–H bond and the p orbital at the adjacent atom. We conclude that $a_{1,3}$ is much more significant in the four-membered cyclic disulfide radical cation then in the five- or six-membered rings. A somewhat similar situation exists when cyclic semidiones and semifuranquinones are considered. Thus, the bridgehead hfsc decrease from 2.5 G in **39** (symmetric SOMO)^{2e} to 0.4 G in **40** (antisymmetric

(2.5) H —[structure] 2.5 G   **39**

(2.0) H —[structure] 0.4 G   **40**
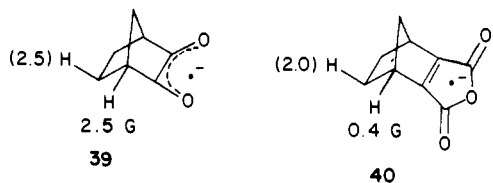
SOMO)^{13a} even though the spin densities at C-1,2 in **39** and **40** are nearly equivalent ($a^H_{5,6\text{-exo}}$ = 2.5 G for **39**, 2.0 G for **40**).^{2e}

Another example of the consequence of the unpaired electron being in an antisymmetric MO for RSSR$^+$· is the ESR spectrum observed for **42**. The triplet hfs is assigned to the exo hydrogens

[structure] **41** $\xrightarrow{H_2SO_4}$ [structure] **42**

(9)

a^H = 6.3 (2H) G
g = 2.018
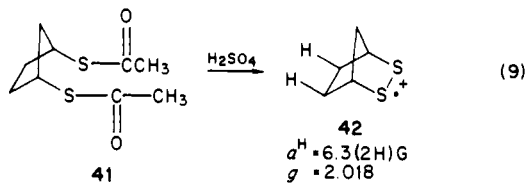
at C-5,6. The antisymmetry of the spin probe reduces the

magnitude of the bridgehead hfs and doublet splittings are not observed for the methylene hydrogen atoms at C-7 which lie in the nodal plane of the spin probe.

Reaction of **41** with base followed by *cis*-1,2-dichloroethylene formed **43** which reacted with H_2SO_4 to form **35** but with $AlCl_3$

[structure] **43** $\xrightarrow{AlCl_3/CH_2Cl_2}$ [structure] **43$^+$·**

(10)

a^H = 5.10 (2 H), 2.85 (2 H), 1.80 (1 H),
0.51 (3 H) G
g = 2.0099
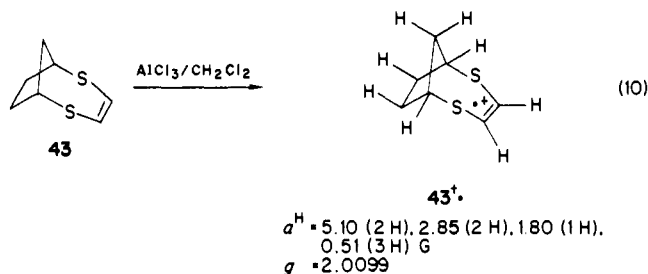
in CH_2Cl_2 to form the radical cation. The anti hydrogen at C-9 is assigned the 1.8-G doublet splitting and the syn hydrogen as 0.51 G. The vinyl hydrogens are assigned as the 2.85 G triplet splitting and the bridgehead hydrogens as 5.10 G by comparison with **29** and **30**. This leaves 0.51 g (2 H) for the exo hydrogen atoms at C-7,8 and a ratio of a^H_{anti}/a^H_{exo} of 3.5.

Reaction of **21** with *cis*-1,2-dichloroethylene formed the 2-methylene-1,3-dithiolane **44** (Scheme VII) which with $AlCl_3/CH_2Cl_2$ at –60 °C formed the rearranged radical cation **45$^+$·**. The hfsc for this symmetric spin label can be assigned as a^H_{vinyl} = 2.10, a^H_{anti} = 3.45, $a^H_{bridgehead}$ = 1.05, and a^H_{exo} = 1.05 G with a^H_{anti}/a^H_{exo} = 3.3. The structure of **45$^+$·** was established by the oxidation of **26** with DDQ to yield **45** which with $AlCl_3/CH_2Cl_2$ (–60 °C) yielded **45$^+$·**.

Spin Probes Derived from Dithiols

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Scheme VII

a^H = 3.45(1 H), 2.10(2 H), 1.05(4 H) G
g = 2.0082
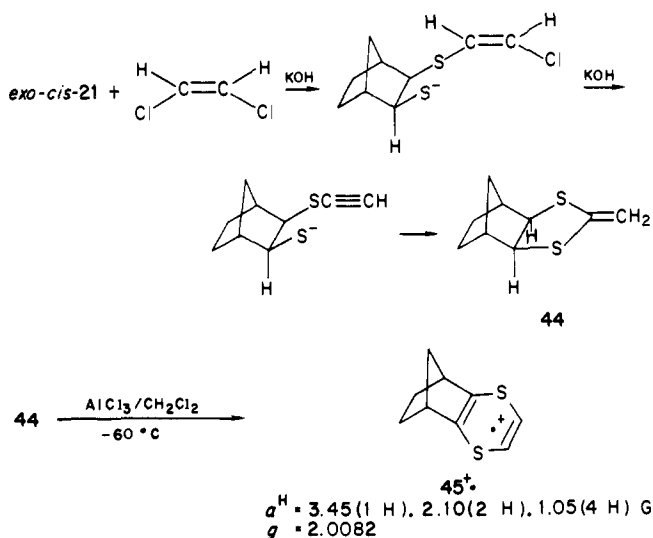
Experimental Section

ESR Spectra. Radical anions were generated by mixing solutions deoxygeneated by N_2 bubbling of the precursor and sublimed *t*-BuOK in Me_2SO that had been distilled at reduced pressure from CaH_2 and stored over molecular sieves. An inverted U-type mixing chamber and flat fused silical cells was used.[2] Radical cations were generated by mixing the precursor with H_2SO_4 in the U-type mixing chamber in the presence of air.[4] *g* values were obtained by observing the desired radical ion in a solution containing a radical of known *g* value. 2,5-Dimethyl-1,4-benzosemiquinone or tetramethyl-1,4-benzosemiquinone were used for radical anions. For radical cations, the $\Delta^{2,2'}$-bi-1,3-dithiolanylidene (34)[16] was used as standard. Mixing of a solution of 34 and 37 allowed the *g* value of 37 to be defined, and 37 was then used in determining the *g* values of dithiin radical cations prepared from the α-mercapto ketone dimers. The *g* values for dithiete radical cations could then be obtained by comparison with the dithiin species.

α-**Mercapto Ketones.** 3-Chloro-2-butanone was converted to the mercapto ketone by reaction with aqueous KOH saturated with H_2S,[27] bp 39–40 °C (10 torr), lit.[28] bp 39 °C (8 torr). 2-Bromo-3-pentanone[29] was converted to 2-mercapto-3-pentanone, bp 47–49 °C (10 torr), lit.[30] bp 51–53 °C (12 torr). Cyclohexanone was converted to 2-[(dimethyl-thiocarbamoyl)thio]cyclohexanone[31] which was hydrolyzed to the dimer of 2-mercaptocyclohexanone, mp 133–138 °C (from CHCl₃), lit.[32] mp 145–146 °C. Norcamphor was converted to an exo–endo mixture of 3-[(dimethylthiocarbamoyl)thio]bicyclo[2.2.1]heptan-2-one (6) by reaction with tetramethylthiuram disulfide in refluxing C_6H_6 for 20 h. Removal of the solvent under vacuum left an oil which was chromatographed on silica gel by elution with CCl_4/C_6H_6 (1:1) and then with C_6H_6 to give a 30% yield of a dark yellow oil: ¹H NMR (CDCl₃) δ 4.88 (d, *J* = 4 Hz, *exo*-H at C-3), 4.23 (d, *J* = 4 Hz, *endo*-H at C-3), 3.5 (m, 6 H, CH₃), 2.6–3.0 (m, 2 H, bridgehead), 1.5–1.9 (m, 6 H). Reaction of 10 g of 6 with 7 g of NaOH in 220 mL of MeOH and 44 mL of H_2O at reflux for 20 h gave, after acidification and extraction by CH_2Cl_2, 5.3 g of 2-mercaptobicyclo[2.2.1]heptan-2-one as a brownish oil that was used without purification. Reaction of this oil with AcCl in pyridine at reflux for 2.5 h gave, after acidification and extraction with CHCl₃, 3-(acetylthio)bicyclo[2.2.1]heptan-3-one (29%) as a mixture of exo and endo isomers; ¹H NMR (CDCl₃) δ 4.07 (d, *J* = 4.5 Hz, *exo*-H at C-3), 3.62 (d, *J* = 3.5 Hz, *endo*-H at C-3), 2.6–2.7 (m, 2 H, bridgehead), 2.37 (s, 3 H), 1.5–1.9 (m, 6 H).

Thiophosphoric Esters (7). A solution of the α-diketone in xylene was refluxed with 3 equiv of P_4S_{10} for 2.5 h, cooled, and filtered.[33] After evaporation of the solvent under vacuum, the residue was chromatographed on silica gel (2 g/g of starting diketone) eluting first with CCl_4

and then with C_6H_6 to give a yellow resinous product after evaporation of the C_6H_6. Bicyclo[2.2.1]heptane-2,3-dione gave a 20% yield of the thiophosphate ester and cyclohexane-1,2-dione gave a 6% yield, while camphorquinone gave a 22% yield of a orange resin which eventually solidified. Bicyclo[2.2.2]octane-2,3-dione gave a 30% yield of a yellow oil which hardened upon standing. We were unable to isolate the thiophosphate ester of biacetyl although it has been prepared in situ.[34] The thiophosphate esters were used to generate dithiosemidiones without further purification.

1,3-Dithioles, 1,3-Dithole-2-thiones, and 1,3-Dithiole-2-ones. 4,5-Tetramethylene-1,3-dithiole-2-thione (8b) was prepared from 1-morpholinocyclohexane and tetramethylthiuram disulfide,[5] mp 80–82 °C, lit.[35] mp 83 °C. The trithiocarbonate was reacted with Hg(OAc)₂ in HOAc[36] to give 4,5-tetramethylene-1,3-dithiole-2-one (8a), mp 31–32 °C, lit.[37] mp 33 °C. Reduction of 7 g of 8b with 1.8 g of LiAlH₄ in Et₂O gave 2.7 g (46%) of 4,5-tetramethylene-1,3-dithiole (13), bp 90–100 °C (0.6 torr), lit.[5] bp 55 °C (0.1 torr). The 1,3-dithiole (13) was treated with 1 equiv of *n*-BuLi at –30 °C in THF for 1.5 h, cooled to –70 °C, and reacted with 1 equiv of MeI. The mixture, after being kept below 0 °c while being stirred overnight, was hydrolyzed, extracted with CHCl₃, and distilled at 85–110 °C (0.15 torr) to give a 44% yield of 2-methyl-4,5-tetramethylene-1,3-dithiole (14): ¹H NMR (CDCl₃) δ 4.72 (q, 1 H, *J* = 6.5 Hz), 2.2 (m, 4 H), 1.7 (m, 4 H), 1.58 (d, 3 H, *J* = 6.5 Hz). Repetition of the methylation starting from 14 yielded 2,2-dimethyl-4,5-tetramethylene-1,3-dithiole (15) as a yellow oil (49%): ¹H NMR (CDCl₃) δ 2.2 (m, 4 H), 1.83 (s, 6 H), 1.7 (m, 4 H).

2-Morpholinobicyclo[2.2.1]hept-2-ene, bp 64–73 °C (0.1 torr), lit.[38] bp 70–72 °C (0.5 torr), was reacted with tetramethylthiuram disulfide in dioxane in the presence of Et₃N.[5] Chromatography on silica gel with CCl_4 as the eluent gave 30–40% yield of a mixture of exo (minor) and endo (major) isomers of bicyclo[2.2.1]heptane-*cis*-2,3-dithiol thiono-carbonates (16):[39] ¹H NMR (CDCl₃) δ 4.8 (m, *exo*-H at C-2,3), 4.40 (d, *J* = 2 Hz, *endo*-H at C-2,3), 2.5 (m, 2 H, bridgehead), 1.40–2.15 (m, 6 H). Bromination of 17 with 3 equiv of NBS in CCl_4 with sunlamp irradiation gave *exo-cis*-2,3-dibromobicyclo[2.2.1]heptane-*endo-cis*-2,3-dithiol carbonate (18) in 31% yield isolated by chromatography on silica gel with CCl_4 as the eluent, mp 114–116 °C: ¹H NMR (CCl₄) δ 3.2 (m, 2 H, bridgehead), 2.7 (d of multiplets, 1 H, *J*. = 12 Hz, *syn*-H at C-7), 1.6–2.1 (m, 5 H). Treatment of 18 with Zn dust in refluxing Et₂O for 64 h gave bicyclo[2.2.1]hept-2-ene-2,3-dithiol carbonate (19) as a colorless oil: ¹H NMR (CCl₄) δ 3.42 (m, 2 H, bridgehead), 1.0–1.8 (m, 6 H). Crude 19 from 2.3 g of 18 was stirred with 1 g of P_4S_{10} in 30 mL of refluxing xylene for 5.5 h and filtered and the xylene removed by distillation. The residue was chromatographed on silica gel with CCl_4 eluent to yield 41% of bicyclo[2.2.1]hept-2-ene-2,3-dithiol thiono-carbonate (20), mp 135–138 °C: ¹H NMR (CDCl₃) δ 3.43 (m, 2 H, bridgehead), 1.2–2.0 (m, 6 H).

1,3-Dithiolanes and 1,2-Dithiols. Compound 16 was hydrolyzed with NaOH in CH₃OH/H₂O (reflux, 20 h) to give, after acidification, extraction with CH_2Cl_2, and chromatography on silica gel with CCl_4/C_6H_6 (2:1) elution, an exo/endo mixture of *cis*-bicyclo[2.2.1]heptane-2,3-dithiol (21) as a colorless oil:[8] ¹H NMR (CCl₄) δ 3.5 (m, *exo*-H at C-2,3), 3.15 (m, *endo*-H at C-2,3), 1.68 and 1.72 (d, 2 H, *J* = 4 Hz, SH), 1.2–2.0 (m, 6 H). Reaction of 21 from 1.5 g of 20 with excess acetone (30 mL) containing 6 drops of concentrated HCl gave, after reflux for 2 h followed by CH_2Cl_2 extraction, a 60% yield of 4,4-dimethyl-3,5-di-thiatricyclo[5.2.1.0²,⁶]decane (22) as a mixture of exo and endo isomers after chromatography on silica gel with CCl_4/C_6H_6 (2:1) eluent: ¹H NMR (CCl₄) δ 4.17 (m, *exo*-H at C-2,6) 3.72 (m, *endo*-H at C-2,6), 2.3 (m, 2 H, bridgehead), 1.78 (s, 6 H), 1.2–2.0 (m, 6 H).

meso-2,3-Dibromobutane was converted to 4,5-dimethyl-1,3-di-thiolane-2-thione by reaction with CS₂ and Na₂S.[40] Reduction with LiAlH₄ in Et₂O gave 2,3-butanedithiol, bp 86–87 °C (50 torr).[41] 1,2-Propanedithiol was stirred overnight in 100 mL of refluxing acetone to which 0.5 mL of concentrated HCl had been added. Evaporation of the acetone, extraction with CH_2Cl_2, and distillation gave 70% of 2,2,4-tri-methyl-1,3-dithiolane, bp 61–66 °C (10 torr), lit.[42] bp 43–45 °C (3.8 torr).

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4-Methylene-3,5-dithia-*exo-cis*-tricyclo[5.2.1.0^{2,6}]decane (**44**) was prepared by the reaction of 1 g of *exo-cis*-**21**[8] with 0.64 g of *cis*-1,2-dichloroethylene and 3 g of KOH in 35 mL of reluxing EtOH for 4 h. Removal of the EtOH under vacuum followed by hydrolysis, ether extraction, and evaporation gave a white residue purified by column chromatography on Al$_2$O$_3$ using hexane–ethyl acetate (95:5) as eluent to yield 0.80 g (70%) of **44**, mp 50.0–51.5 °C: ^{1}H NMR (CDCl$_3$) δ 5.00 (s, 2 H), 3 85 (d, 2 H, *J* = 1.8 Hz), 2.30 (br s, 2 H), 1.0–2.0 (m, 6 H); ^{13}C NMR (CDCl$_3$) δ 146.7 (s), 100.0 (t), 61.8 (d), 45.4 (d), 32.3 (t), 27.8 (t); IR (CCl$_4$) 2950, 1668, 1565, 1445 cm^{-1}; MS (relative intensity), *m/z* 184.038 10 (100), 93 (71); calcd for C$_9$H$_{19}$S$_2$ 184.03805.

cis-1,3-Cyclopentanediyldithioacetate (**41**) was prepared from *cis*-1,3-cyclopentanediol dimesylate.[43] The dimesylate from 5.3 g of *cis*-1,3-cyclopentanediol was treated with 0.19 mol of CH$_3$COS$^-$Na$^+$ in 300 mL of Me$_2$SO/DMF (1:1) at 60 °C for 10 h. Hydrolysis followed by extraction with CH$_2$Cl$_2$, drying over MgSO$_4$, and removal of the solvent under vacuum gave a residue which was chromatographed on silica gel using hexane/ethyl acetate (9:1) as eluent to yield 8 g of **41** (71%) as a yellow liquid: ^{1}H NMR (CDCl$_3$) δ 3.78 (m, 2 H), 2.30 (s, 6 H), 1.2–2.55 (m, 6 H); IR (neat) 2970, 1680, 1430, 1350, 1240, 1105, 935 cm^{-1}; GCMS (relative intensity), *m/z* 218 (M$^+$, 3.8), 175 (68), 133 (100), 99 (63), 67 (96); HRMS calcd for C$_9$H$_{14}$O$_2$S$_2$ 218.0432, found 218.0436.

1,4-Dithianes, 1,4-Dithiins, and 2,3-Dihydro-1,4-dithiins. 2,5-Dihydroxy-2,5-dimethyl-1,4-dithiane was prepared from chloroacetone and NaSH in H$_2$O, mp 106–109 °C, lit.[44] 109–111 °C. 2,3-Dihydro-1,4-dithiin was prepared from chloroacetaldehyde diethyl acetal and 1,2-ethanedithiol in refluxing C$_6$H$_6$ (23 h) in the presence of a trace of *p*-toluenesulfonic acid, bp 80–100 °C (10 torr), lit.[45] bp 101 °C (29 torr). 5,6-Dimethyl-2,3-dihydro-1,4-dithiiin was prepared from 3-chloro-2-butanone and 1,2-ethanedithiol, bp 50 °C (0.2 torr), lit.[12] bp 113–114 °C (25 torr).

3-*exo*-Chloro-2-norbornanone (0.89 g) was reacted with 0.8 mL of 1,2-ethanedithiol in the presence of a small amount of *p*-toluenesulfonic acid in 35 mL of refluxing toluene for 12 h. The solution was washed with aqueous NaOH and H$_2$O, and the toluene was removed by vacuum distillation. The residue was chromatographed on silica gel with EtOAc/hexane (3:97) as eluent to give 1.12 g (92%) of the 1,3-dithiolane derivative (**25**): ^{1}H NMR (CDCl$_3$) δ 4.1 (d, 1 H, *J* = 2 Hz), 3.25 (d, 4 H), 1.3–2.8 (m, 8 H); IR (neat) 2950, 1450, 1270 cm^{-1}; MS (relative intensity) 220.015 29 (45.4), 192 (100). Calcd for C$_9$H$_{13}$ClS$_2$: 220.01472. Treatment of 0.31 g of **25** with 0.25 g of Al$_2$Cl$_6$ in 10 mL of CH$_2$Cl$_2$ at 0 °C under N$_2$ for 30 min gave, after washing by aqueous

NaOH and H$_2$O, vacuum distillation of the CH$_2$Cl$_2$, and chromatography on silica gel with hexane eluent, a 93% yield (240 mg) of Δ^{2,7}-3,6-dithiatricyclo[6.2.1.0^{2,7}]undecene (**26**) as a colorless oil: ^{1}H NMR (CDCl$_3$) δ 3.3–2.7 (m, 6 H), 1.9–0.9 (m, 6 H); ^{13}C NMR (CDCl$_3$) δ 126.85 (s), 48.08 (d), 43.64 (t), 27.7 (t), 27.27 (t); IR (neat) 2960, 1550, 1440, 1410, 1285 cm^{-1}; MS (relative intensity), *m/z* 184.0386 (41), 156 (100); calcd for C$_9$H$_{12}$S$_2$ 184.038 04.

Δ^{2,7},Δ^{4,5}-3,6-Dithiatricyclo[2.2.1.0^{2,7}]undecadiene (**45**) was prepared from **26** (0.4 g) and 2,3-dichloro-5,6-dicyano-1,4-benzoquinone (0.54 g) in 10 mL of refluxing xylene (16 h). The mixture was filtered, washed with dilute aqueous KOH, and dried. The solvent was removed under vacuum, and the residue was chromatographed on silica gel with hexane eluent to give 0.11 g of **45** (28%) as a pale yellow oil: ^{1}H NMR δ 5.95 (s, 2 H), 2.82 (m, 2 H), 1.0–2.3 (m, 6 H); ^{13}C NMR δ 132.8 (s), 119.4 (d), 48.1 (d), 46.9 (t), 26.4 (t); IR (neat) 3015, 2970, 1525, 1290 cm^{-1}; MS (relative intensity) *m/z* 182.022 45 (M$^+$, 58) 159 (90), 122 (100); calcd for C$_9$H$_{10}$S 182.022 40.

2-Chlorocyclohexanone (0.49 g) and *exo-cis*-bicyclo[2.2.1]heptane-2,3-dithiol[8] (0.59 g) were stirred with a small amount of *p*-toluenesulfonic acid in 100 mL of refluxing C$_6$H$_6$ for 4 h. A mixture of the 1,3-dithiolane derivative **27** and Δ^{4,9}-*cis-exo*-3,10-dithiatetracyclo[10.2.1.0^{2,11}.0^{4,9}]-pentadecane (**28**) was formed. The mixture was treated with 0.50 g of Al$_2$Cl$_6$ in CH$_2$Cl$_2$ at 0 °C for 30 min. After washing with aqueous NaOH and H$_2$O, vacuum removal of the CH$_2$Cl$_2$, and chromatography on silica gel with hexane eluent, a 74% yield (0.65 g) of **28** was obtained as a colorless oil: ^{1}H NMR (CDCl$_3$) δ 3.25 (d, 2 H, *J* = 2 Hz), 2.3 (br s, 6 H), 1.9–1.0 (m, 10 H); ^{13}C NMR (CDCl$_3$) δ 134.54 (s), 57.34 (d), 49.72 (d), 34.91 (t), 33.34 (t), 29.44 (t), 23.59 (t); IR (neat) 2920, 1445, 1300, 1200 cm^{-1}; MS (relative intensity), *m/z* 238.0843 (100), 144 (48); calcd for C$_{13}$H$_{18}$S$_2$ 238.0850.

1,2-Dithiolanes. 1,2-Dithiolane was prepared in C$_6$H$_6$ solution.[21] 1,3-Propanedithiol (2.2 g) was added to a stirred suspension of 6.6 g of Pb(OAc)$_2$ in 150 mL of H$_2$O. After 10 min, the yellow solid that had formed was removed by filtration and dissolved in 200 mL of C$_6$H$_6$. Sulfur was added and the mixture stirred for 30 min. The PbS was removed by filtration, and the C$_6$H$_6$ solution of 1,2-dithiolane was dried over MgSO$_4$. The benzene was removed under vacuum in the mixing cell before reaction with H$_2$SO$_4$ to form the radical cation. 1,2-Dithiolane 1-oxide was prepared by reaction of 1,3-dithiane with Ce^{IV} in CH$_3$CN.[22]

2,5-Dithiabicyclo[4.2.1]non-3-ene (**43**) was prepared by saponification of 1 g of **41** with 2.4 g of KOH in 45 mL of EtOH for 1 h at 30 °C. The mixture was heated to reflux, and 0.44 g of *cis*-1,2-dichloroethylene in 3 mL of EtOH was added. After 6 h of reflux, the EtOH was removed under vacuum and the residue hydrolyzed and extracted with CH$_2$Cl$_2$. the extract was dried and the CH$_2$Cl$_2$ removed under vacuum to give **43** as a residue with only a single peak in GLC: ^{1}H NMR (CDCl$_3$) δ 6.2 (s, 2 H), 3.1–3.4 (m, 2 H), 1.3–2.4 (m, 6 H); ^{13}C NMR (CDCl$_3$) δ 123.2 (d), 44.9 (d), 41.4 (t), 32.7 (t); GCIR 3024, 3001, 2950, 2920, 1539, 1454, 1438, 1276 cm^{-1}; MS (relative intensity), *m/z* 158.0222 (63), 107 (18), 98 (21), 92 (24), 67 (100); calcd for C$_7$H$_{10}$S$_2$ 158.0224.

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