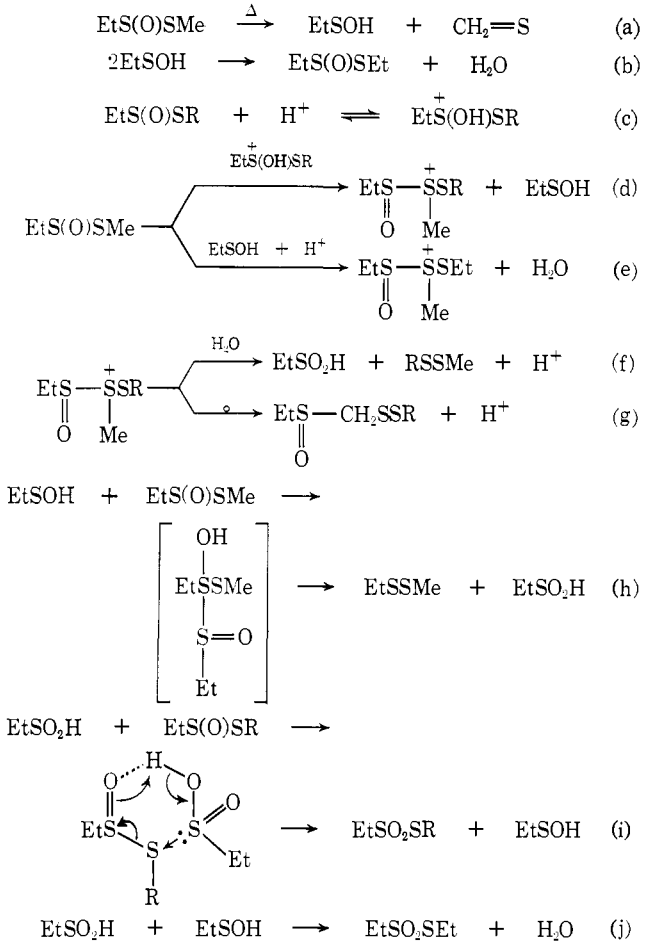
Scheme I. Proposed Mechanism for the Thermal Disproportionation of Methyl Ethanethiolsulfinate



(In the above, R = Me or Et)

tion of an unsymmetrical diaryl thiolsulfinate was found to give a 2:1 mixture of unsymmetrical to symmetrical thiolsulfonate in addition to about 10% of the products resulting from oxygen crossover. The differences in product distribution between our photochemical example (*cf.* Table II, run 10) and the thermal studies of Fava (in our work, more symmetrical products and little oxygen crossover) could be attributable, in the present work, to more pronounced cage effects (lower temperature, more polar substrates) and possible multiplicity restrictions on oxygen crossover *via* a sulfenic anhydride.

Acknowledgment. We thank Messrs. Daniel Kleypas, John O'Connor, and Richard Reudlinger for technical assistance and gratefully acknowledge support from the donors of the Petroleum Research Fund, administered by the American Chemical Society (Grants 1153-G and 4109-B), the Air Pollution Control Office, Environmental Protection Agency (AP-1496-01), and the University of Missouri—St. Louis.

radical absorption. We thank Professor Kochi for performing this experiment.

(13) Visiting Professor at Massachusetts Institute of Technology, 1973–1974. Address correspondence to this author at the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Mass. 02139.

Eric Block,*[13] Stuart W. Weidman

Department of Chemistry, University of Missouri—St. Louis
St. Louis, Missouri 63121

Received April 21, 1973

The Chemistry of Alkyl Thiolsulfinate Esters. V. A Novel Synthesis of α-Heteroatom Substituted Disulfides[1]

Sir:

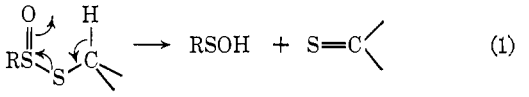
In contrast to α-heteroatom substituted alkyl sulfides, the analogous α-substituted alkyl disulfides (**1**, X = RO, RS, R_2N, halogen, etc.) are a synthetically inaccessible class of compounds whose chemistry has hardly been explored.[2,3] We present here a novel, convenient route to a number of new structures of type **1** (in which X = RS, RS(O), RSO_2) discovered during an investigation of the chemistry of dialkyl thiolsulfinate esters.

$$XCH_2SSR$$
1

Sulfinylsulfonium ions of type **2** have been postulated

$$RS(O)\overset{+}{S}R'R''$$
2

by Kice as intermediates in the reaction of sulfinic acids with disulfides[4a] and sulfides[4b] and in the catalyzed disproportionation of aryl thiolsulfinates.[4c] In view of our recent discovery of a facile intramolecular β-elimination process occurring during thermolysis of alkyl thiolsulfinates (eq 1),[5] it seemed possible that ion



(1)

3, postulated by us as an intermediate in the disproportionation of alkyl thiolsulfinates,[6] might undergo a similar intramolecular elimination process with even greater facility than the thiolsulfinate esters.[7] Sulfinylsulfonium ion **3** might fragment directly, or indirectly *via* ylide **4**, to alkylidenethiosulfonium ion **5** which could be trapped by a nucleophile (X^- or HX:) giving **6**. Another possibility would involve rearrangement of ylide **4** to α-sulfinyl disulfide **7** either in a concerted fashion or by recombination of RSOH and **5** within a solvent cage. In fact, these several possibilities, summarized in Scheme I, represent the options currently favored for the Pummerer rearrangement of an S heterosubstituted sufonium ion such as **3**.[8] We have found that, under the proper reaction conditions,

(1) Presented in part at the 7th Midwest Regional Meeting of the American Chemical Society, St. Louis, Mo., Oct 27–29, 1971, and at the 5th Central Regional Meeting of the American Chemical Society, Cleveland, Ohio, May 13–15, 1973.

(2) Simple systems of type **1** which have been reported include bischloromethyl disulfide,[3a] α-chloromethylalkyl disulfides,[3b] α-alkylthioalkyl disulfides,[3c] 2,4,5,7-tetrathiaoctane,[3d] bismethoxymethyl disulfide,[3e] bishydroxymethyl disulfide[3f] and several N,N-disubstituted bisaminomethyl disulfides.[3f]

(3) (a) H. Brintzinger, K. Pfannstiel, H. Koddebusch, and K. E. Kling, *Chem. Ber.*, **83**, 87 (1950); (b) I. B. Douglass, F. T. Martin, and R. Addor, *J. Org. Chem.*, **16**, 1297 (1951); (c) H. Britzinger and H. Schmahl, *Chem. Ber.*, **87**, 314 (1954); (d) M. R. Altamura, T. Hasselstrom, and L. Long, Jr., *J. Org. Chem.*, **28**, 2438 (1963); (e) J. deLattre, *Bull. Soc. Chim. Belg.*, **26**, 323 (1913); (f) A. Binz, C. Räth, and E. Walter, *Chem. Ber.*, **57B**, 1398 (1924).

(4) (a) J. L. Kice and E. H. Morkved, *J. Amer. Chem. Soc.*, **86**, 2270 (1964); (b) J. L. Kice and E. H. Morkved, *ibid.*, **85**, 3472 (1963); (c) J. L. Kice and J. P. Cleveland, *ibid.*, **95**, 109 (1973).

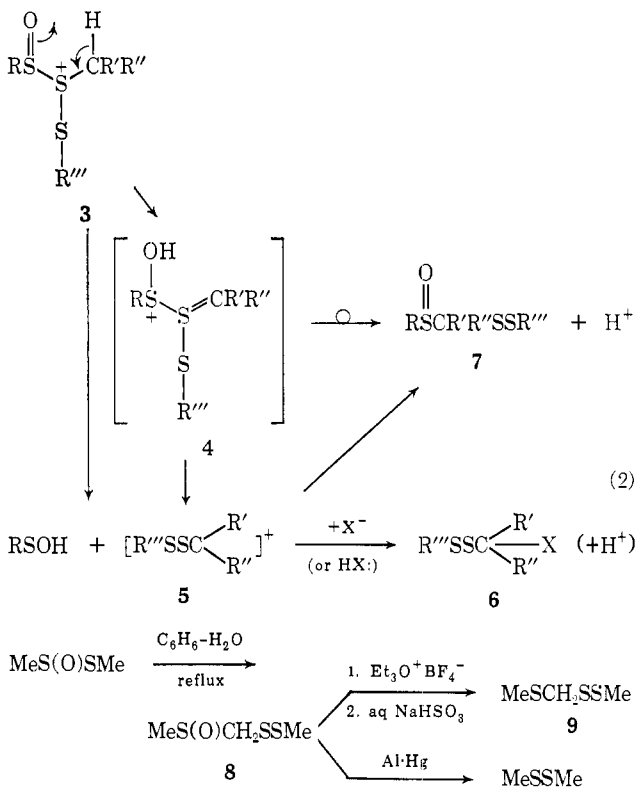
(5) E. Block, *ibid.*, **94**, 642 (1972).

(6) E. Block and S. W. Weidman, *ibid.*, **95**, 5046 (1973).

(7) A similar possibility was considered by Kice in his study of the sulfinic acid–alkyl sulfide reaction to explain formation of alkyl sulfide derived carbonyl compounds.[4b]

(8) C. R. Johnson and W. G. Phillips, *J. Amer. Chem. Soc.*, **91**, 632 (1969).

Scheme I



structures of types **1**, **6**, and **7** are readily produced from dialkyl thiolsulfinate esters, presumably by one or more of the mechanistic pathways of Scheme I.

Thus, a mixture of 200 ml of benzene, 0.348 mol of MeS(O)SMe,[9] and 8 ml of water was refluxed under argon for 52 hr, the reaction mixture was extracted with dilute sulfuric acid and water, the aqueous phase (after saturation with $(NH_4)_2SO_4$) was back-extracted with chloroform, and the dried concentrate was distilled affording 30.2 g (84% yield) of 2,3,5-trithiahexane 5-oxide, $MeS(O)CH_2SSMe$ (**8**) as a pale yellow, water soluble oil: bp (0.13 mm) 85–87°; ir 9.58 μ (S=O); nmr ($CDCl_3$) δ 2.55 (S, 3 H), 2.68 (S, 3 H), 3.97 (AB quartet, J = 6 Hz, 2 H); mass spectrum, m/e 156 (M^+, $C_3H_8S_3O$), 93 ($MeSSCH_2^+$, base peak), 63 ($MeSO^+$, 12%). *Anal.* Calcd for $C_3H_8S_3O$: C, 23.06; H, 5.16. Found: C, 23.41; H, 5.27.

From preparative thin layer chromatography of the distillation residue, minor amounts of products characterized by spectral and analytical means as $MeSO_2CH_2SSMe$ and $MeSCH(MeSO_2)SSMe$ could be obtained. By treatment of **8** with $Et_3O^+BF_4^-$ in CH_2Cl_2 followed by aqueous $NaHSO_3$ at 0°,[10] 2,3,5-trithiahexane, $MeSCH_2SSMe$ (**9**), could be obtained in 86% yield;[11] aluminum amalgam reduction[12] of **8** afforded dimethyl disulfide (see eq 2). The effect of solvent structure on yield of **8** was investigated. In the absence of solvent or in heptane, pyrolysis of MeS(O)SMe at 96° led only to MeSSMe and $MeSO_2SMe$. The yield of **8** from pyrolysis of MeS(O)SMe (at 96°) in anhydrous C_6F_6, benzene, and 1,3,5-trimethylbenzene was, respectively, 24, 40, and 52%. Further details on these reactions are provided in Table I. The aromatic solvent, through interaction of its π electrons with the electrophilic sulfur centers in sulfonium ion **3**, may serve to diminish the amount of **3** going on to disproportionation products (at the expense of sulfinyl disulfide **7**) by blocking attack of water at the sulfinyl sulfur (*cf.* Scheme I, preceding communication[6]).[13] Water, however, also appears to be necessary for the formation of sulfinyl disulfide (see below) although its exact role is not apparent.

To further explore the influence of steric environment at the sulfinyl sulfur in alkyl thiolsulfinates and sulfinylsulfonium ions of type **3** on the relative amounts of sulfinyl disulfide *vs.* disporportionation products, we pyrolyzed methyl *tert*-butanethiolsulfinate, *t*-BuS(O)SMe (**10**).[14–16] Thus, 6 g of **10** and an equal weight of water were vigorously stirred at 96° in an argon atmosphere for 5.5 hr. The addition of ether–pentane to the dried organic layer gave 1.6 g (41% yield) of 2,2-dimethyl-3,5,6-trithiaheptane 3-oxide, *t*-$BuS(O)CH_2SSMe$ (**11**), as a colorless crystalline solid, mp 98.0–99.5° (sublimed): ir 9.68 and 9.74 μ (S=O), nmr ($CDCl_3$) δ 1.30 (S, 9 H), 2.60 (S, 3 H), 3.80 (AB quartet, J = 14 Hz, 2 H); λ_{max} (95% ethanol) 246 (ϵ 443); mass spectrum m/e 198 (M^+, $C_6H_{14}S_3O\cdot^+$), 93 ($MeSSCH_2^+$, 30%) 119 (*t*-$BuSOCH_2^+$, 8%), 142 ($MeSSCH_2SOH\cdot^+$, 3%), 41 ($C_3H_7^+$, base).

Anal. Calcd for $C_6H_{14}S_3O$: C, 36.33; H, 7.11. Found: C, 36.30; H, 7.07.

The other products of the reaction are given in Table I. The pyrolysis of **10** under the same conditions but in the absence of water led to a somewhat lower yield of **11** (27% isolated yield). From our studies with **10**, where even in the absence of aromatic solvent good yields of sulfinyl disulfide result, it can be concluded that product distribution (*i.e.*, rearrangement *vs.* disproportionation) is indeed strongly influenced by the steric environment at the sulfinyl group.

Additional insight into the scope and mechanism of the sulfinyl disulfide synthesis was obtained by studying the pyrolysis of ethyl and methyl ethanethiolsulfinate, EtS(O)SEt (**12**) and EtS(O)SMe (**13**), respectively. Compound **12** afforded 4-methyl-3,5,6-trithiaoctane 3-oxide, EtS(O)CH(Me)SSEt, on pyrolysis, albeit in only fair yield, as a difficultly purified oil. Compound **13** on pyrolysis in benzene gave a complex mixture (*cf.* Table I) of α-sulfinyl and α-sulfonyl disulfides which could, however, be satisfactorily analyzed by combined chromatographic (gc, prep tlc) and spectral (nmr, ms, ir) techniques. Thus, in addition to the expected disproportionation products,[6] there was a fraction containing ~92% α-sulfinyl disulfides, which was essentially a 3:1 mixture of $EtS(O)CH_2SSMe$ (**14**) and $EtS(O)CH_2SSEt$ (**15**) with only minor quantities of EtS(O)-

(9) T. L. Moore and D. E. O'Connor, *J. Org. Chem.*, **31**, 3587 (1966).

(10) C. R. Johnson, C. C. Bacon, and J. J. Rigau, *ibid.*, **37**, 919 (1972).

(11) Compound **9**, a pale yellow oil, had bands in the nmr ($CDCl_3$) at δ 2.23 (s, 3 H), 2.50 (s, 3 H), and 3.86 (s, 2 H); the mass spectrum showed m/e 140 ($C_3H_8S_3$, parent), 93 ($MeSSCH_2^+$, 3%), and 61 ($MeSCH_2^+$, base peak) among others. *Anal.* Calcd for $C_3H_8S_3$: C, 25.68; H, 5.75. Found: C, 26.07; H, 5.71.

(12) E. J. Corey and M. Chaykovsky, *J. Amer. Chem. Soc.*, **87**, 1345 (1965).

(13) H. H. Szmant in "Dimethyl Sulfoxide," Vol. I, S. W. Jacob, E. E. Rosenbaum, and D. C. Wood, Ed., Marcel Dekker, New York, N. Y., 1971, pp 19–20.

(14) Conveniently prepared in 82% yield (after distillation) *via* the condensation of MeSH and *t*-BuSOCl in ether–pyridine at 0°;[15] satisfactory spectral and analytical data are available for this new compound. The sulfinyl chloride is readily available in 95% overall yield from *t*-BuSS-*t*-Bu.[16]

(15) H. J. Backer and H. Kloosterziel, *Recl. Trav. Chim. Pays-Bas*, **73**, 129 (1954).

(16) H. Asakawa, K. Kamiya, and S. Takai, *Takeda Kenkyusho Nempo*, **29**, 610 (1970); *Chem. Abstr.*, **74**, 125603 (1971).

Table I. α-Sulfinyl and α-Sulfonyl Disulfides from Pyrolysis of Alkyl Thiolsulfinate Esters

No.	Thiolsulfinate (% converted)	Conditions	α-Sulfinyl and α-sulfonyl disulfides (% yield)	Other products
1	MeS(O)SMe (~87)	~1.5 *M* in C_6H_6 with 1 equiv H_2O, reflux 52 hr	$MeS(O)CH_2SSMe$ (84),[a] $MeSO_2CH_2SSMe$ (<1)	$MeSCH(MeSO_2)SSMe$ (trace)
2	MeS(O)SMe (~50)	1.3 *M* in C_6H_6 96°, 3 hr[h]	$MeS(O)CH_2SSMe$ (40),[b,d] $MeSO_2CH_2SSMe$	H_2O, MeSSMe, MeSSSMe, $MeSO_2SMe$, $MeSCH_2SSMe$[c]
3	MeS(O)SMe (~50)	1.3 *M* in mesitylene 96°, 3 hr[h]	$MeS(O)CH_2SSMe$ (52),[b,d]	
4	MeS(O)SMe (~50)	0.8 *M* in C_6F_6 96°, 12 hr[h]	$MeS(O)CH_2SSMe$ (24),[b,d]	
5	EtS(O)SEt (~100)	~2 *M* in C_6H_6 96°, 4 hr[h]	EtS(O)CHMeSSEt (~15)[a]	
6	EtS(O)SMe (~90)	~2 *M* in C_6H_6 with 1 equiv H_2O, reflux 23 hr	$EtS(O)CH_2SSMe$ (66.5), $EtS(O)CH_2SSEt$ (22.2), EtS(O)CHMeSSMe (3.1), $EtSO_2CHMeSSMe$ (5.8), $EtSO_2CH_2SSMe$ (1.5), $EtSO_2CH_2SSEt$ (0.2), $EtSO_2CHMeSSEt$ (0.7)[e]	
7	*t*-BuS(O)SMe (~100)	With equal wt H_2O 96°, 5.5 hr, under Ar[i]	*t*-BuS(O)CH_2SSMe (41)[a,f]	*t*-BuSSMe (5), *t*-BuSS-*t*-Bu (9), *t*-$BuSO_2SMe$ (26), *t*-BuS(O)S-*t*-Bu (36)[a,g]
8	*t*-BuS(O)SMe (~100)	Neat, 96°, 5 hr	*t*-BuS(O)CH_2SSMe (27)[a]	Same as Run 7
9	*t*-BuS(O)SMe (~100)	Neat, 96°, with 0.2 equiv CaH_2, 5.5 mm, 5.5 hr[m]	*t*-$BuSO_2CH_2SSMe$ (0.147)[a,j] *t*-BuS(O)CH_2SSMe (11)[a] (0.056)[k]	*t*-BuSS-*t*-Bu (13), *t*-BuS_3-*t*-Bu (3), *t*-$BuSO_2SMe$ (7), *t*-BuS(O)S-*t*-Bu (52)[b,a,l]

[a] Isolated yield. [b] Analysis by quantitative gc. [c] Analysis by gc–ms. [d] These represent the highest absolute yields attainable during the course of the reaction. At higher reactant conversion, sulfinyl disulfide destruction becomes more pronounced. [e] Molar ratios from quantitative gc; analysis by prep tlc followed by ir, nmr, and gc–ms on separate fractions. In this run considerable thiolsulfonate and disulfide was formed with the total product distribution similar to run 8, Table II of procedure communication.[6] [f] 24 mol %. [g] Given as mole per cent of product. [h] In sealed tube. [i] A 35% yield of **11** was realized if the water was replaced by 3.3 *M* acetic acid; very poor yields of **11** were obtained on refluxing a 2 *M* solution of **10** in benzene containing an equimolar amount of water as **10**. [j] Mole per mole of **10**; stoichiometry uncertain so yield cannot be calculated; the vacuum is necessary for complete removal of water. [k] Mole per mole of **10**. [l] **11** and **20** represent 7 and 19 mol % of product, respectively. [m] Similar results were obtained using CaC_2 or CaO instead of CaH_2; when the base but not the the vacuum was omitted, the ratio of **11** to **20** became 6:1, NaH led to poor yields of **11** and **20** while P_4O_{10} caused complete destruction of **10**.

$$t\text{-BuS(O)SMe}\ (\mathbf{10}) \xrightarrow{H_2O\ 96^\circ} t\text{-BuS(O)}CH_2SSMe\ (\mathbf{11}) + t\text{-BuS(O)S-}t\text{-Bu} + t\text{-BuSO}_2SMe + t\text{-BuSSR} \quad (3)$$

$$t\text{-BuS(O)SMe}\ (\mathbf{10}) \xrightarrow{CaH_2\ 96^\circ,\ \text{vacuum}} t\text{-BuS(O)}CH_2SSMe\ (\mathbf{11}) + t\text{-BuSO}_2CH_2SSMe\ (\mathbf{18}) + t\text{-BuS(O)S-}t\text{-Bu} + t\text{-BuS}_n\text{-}t\text{-Bu} + t\text{-BuSO}_2SMe$$

CHMeSSMe (**16**), and ~8% α-sulfonyl disulfides, with the major component being $EtSO_2CHMeSSMe$ (**17**) and about one-fourth as much $EtSO_2CH_2SSMe$ in addition to lesser amounts of other α-sulfonyl disulfides. The results with compound **13** are significant because they exlcude the possibility of a *direct* Pummerer rearrangement of **13** as the source of α-sulfinyl disulfide (since EtS(O)CHMeSSMe, the anticipated major Pummerer product from **13**, is formed to only a minor extent).[17] A direct Pummerer reaction is of course impossible for compound **10**. The origin of α-sulfonyl disulfide is somewhat harder to rationalize although it is certainly not without precedence.[18–20]

In an attempt to elucidate the origin of the α-sulfonyl disulfides, we have subjected thiolsulfinate **10** to pyrolysis in the presence of various added reagents (*cf.* Table I, run 9 and footnote *m*). Surprisingly, with various basic dehydrating agents, 2,2-dimethyl-3,5,6-trithiaheptane 3,3-dioxide, *t*-$BuSO_2CH_2SSMe$ (**18**), becomes the dominant product. Thus, 3.27 g of **10** and 0.16 g of calcium hydride were refluxed under an air-cooled condenser at 5–6 mm in a bath maintained at 96° for 5.5 hr. On addition of ether–pentane to the filtered product followed by cooling, 0.91 g of a practically colorless solid was obtained; nmr analysis indicated the composition **18**, 0.68 g, and **11**, 0.24 g. The other reaction products are indicated in Table I (run 9) and eq 3. Preparative tlc readily separated compounds **11** and **18**. A sublimed sample of **18** had mp 55–56° (corr); nmr ($CDCl_3$) δ 1.45 (S, 9 H), 2.60 (S, 3 H), and 4.13 (S, 2 H); ir 7.78 and 9.03 μ (–SO_2–); mass spectrum *m/e* 214 ($C_6H_{14}S_3O_2$, parent), 93 ($MeSSCH_2^+$, 37%), and 57 ($C_4H_9^+$, base).

Anal. Calcd for $C_6H_{14}S_3O_2$: C, 33.62; H, 6.58. Found: C, 33.40; H, 6.29.

From this result, as well as the observations summarized in Table I (*cf.* footnote *m*) we surmise that water in some manner (perhaps through hydrogen bonding) stabilizes sulfenic acids[21] while rigorous exclusion of water, and perhaps the presence of certain

(17) For an apparent example of a Pummerer rearrangement involving the cyclic thiolsulfinate β-lipoic acid, see I. Saito and S. Fukui, *J. Vitaminol. (Kyoto)*, **12**, 244 (1966).

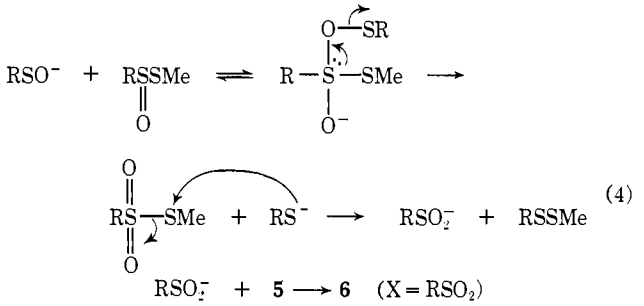
(18) See, for example, G. A. Russell and E. T. Sabourin, *J. Org. Chem.*, **34**, 2336 (1969).

(19) The α-sulfonyl disulfide distribution may reflect the relative stabilities of the alkylidenethiosulfonium ion precursors **5** (Scheme I); an apparently analogous situation occurs in the chlorination of unsymmetrical sulfides.[20] We shall elaborate on this point in the full report.

(20) D. L. Tuleen and T. B. Stephens, *J. Org. Chem.*, **34**, 31 (1969).

(21) For a discussion of factors affecting the stability of sulfenic acids, see J. R. Shelton and K. E. Davis, *Int. J. Sulfur Chem.*, in press. We thank Professor Shelton for a preprint.

basic reagents, would appear to promote conversion of sulfenic acids (sulfenate) to sulfinic acids (sulfinate), *i.e.*, by a sequence of the type shown in eq. 4.[22]



(4)

It may be anticipated that the unique combination of functional groups in α-sulfinyl and α-sulfonyl disulfides will lead to unusual chemical, physical, and perhaps physiological properties. A study of the chemistry of these novel and now readily available compounds is in progress.

Acknowledgment. We gratefully acknowledge support from the donors of the Petroleum Research Fund, administered by the American Chemical Society, the Air Pollution Control Office, Environmental Protection Agency (AP-1496-01), and the University of Missouri—St. Louis.

(22) We thank Professor Kice for this suggestion.

(23) Visiting Professor at Massachusetts Institute of Technology, 1973–1974. Address correspondence to this author at the Department of Chemistry, Massachusetts Institute of Technology, Cambridge, Mass. 02139.

Eric Block,*[23] John O'Connor
Department of Chemistry, University of Missouri—St. Louis
St. Louis, Missouri 63121
Received April 21, 1973

Methylenecyclooctatrienyl Anion, a Cyclic Delocalized Atropic Species

Sir:

The electronic properties of cyclic "$4n + 1$" π-electron systems[1] represent an interesting theoretical problem. Intuitively one might anticipate properties in between those of $4n + 2$ "aromatic" or diatropic systems and $4n$ "antiaromatic" or paratropic systems,[2,3] but experimental evidence is completely lacking.

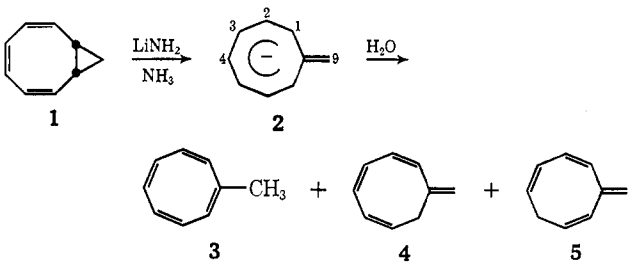
The methylenecyclooctatrienyl anion **2** is of particular interest in this regard since the nonbonding π orbital of the heptatrienyl anion portion of **2** (C_1–C_7) is antisymmetric with respect to the mirror plane through C_4, C_8, and C_9 and consequently does not interact with the orbitals of the exocyclic double bond (which are symmetric with respect to this plane). Thus, even though there is interaction between the symmetric orbitals, the energies of the antibonding levels are expected to balance those of the bonding levels so that there is relatively little transfer of π-electron density into or out of the eight-membered ring.[4] This consideration, along with the greater tendency toward delocalization in an ionic system compared with a polyenic system such as fulvene,[5] suggests that the heretofore unknown anion **2** may be a nearly ideal "$4n + 1$" closed shell π system for study.[6]

We now report that careful treatment of *cis*-bicyclo[6.1.0]nona-2,4,6-triene (**1**) with lithium, sodium, or potassium amide in liquid ammonia at *ca.* $-60°$ produces emerald green solutions of the methylenecyclooctatrienyl anion **2**, which have been characterized by nmr spectroscopy (see Table I).[7,8] The lithium salt of **2** is moderately stable up to about 0° in liquid ammonia, at which point it is irreversibly lost, but is stable for at least 1 hr at room temperature in hexamethylphosphoramide (HMPA).[9] In contrast, the sodium and potassium salts of **2** are rapidly lost at $-60°$ in the presence of excess base.

Table I. Chemical-Shift Data for the Methylenecyclooctatrienyl Anion **2** in Liquid Ammonia at *ca.* $-60°$

Compd	Chemical shift, ppm[a]				
	H_1	H_2	H_3	H_4	H_9
2, Li^+[b]	4.42	5.38	3.80	5.20	5.00
2, Na^+	4.42	5.37	3.78	5.20	4.99
2, K^+	4.41	5.35	3.76	5.18	4.99
2, Li^+ (HMPA)[c]	4.09	5.09	3.50	4.89	4.54
2 (calcd)[d]	4.0	5.5	3.9	5.4	4.9

[a] Trimethylamine ($\delta_{TMS}^{NH_3}$ = 2.135) was used as an internal standard in liquid ammonia and tetramethylsilane (TMS) was employed in hexamethylphosphoramide (HMPA). [b] J_{12} = 12.5 ± 0.2, J_{23} = 10.2 ± 0.4, J_{34} = 10.8 ± 0.4 Hz. [c] In HMPA at 34°. [d] See text.



Addition of **2** in ammonia to pentane–water produced a mixture of 1% **3**,[8a,10] 24.5% **4**,[11] and 74.5% **5**.[12] A

(1) We define these as cyclic delocalized systems in which the atoms of the ring possess essentially $4n + 1$ π electrons in a closed shell configuration.

(2) We use the terms aromatic and antiaromatic advisedly. For recent discussions of the concept of aromaticity, see (a) J.-F. Labarre and F. Crasnier, *Top. Current Chem.*, **24**, 33 (1971); (b) D. Lloyd and D. R. Marshall, *Angew. Chem., Int. Ed. Engl.*, **11**, 404 (1972). For a thermodynamic definition, see (c) M. J. S. Dewar, *Chem. Soc., Spec. Publ.*, No. **21**, 207 (1967).

(3) Atropic molecules possess no net (nmr) ring currents. The terms diatropic and paratropic (possessing diamagnetic and paramagnetic ring currents, respectively) have been defined by P. J. Garratt and F. Sondheimer; see F. Sondheimer, *Accounts Chem. Res.*, **5**, 81 (1972).

(4) Note that this contrasts with the benzyl π system, in which the nonbonding orbital is symmetrical.

(5) P. A. Baron, R. D. Brown, F. R. Burden, P. J. Domaille, and J. E. Kent, *J. Mol. Spectrosc.*, **43**, 401 (1972), and references cited.

(6) G. Boche and D. Martens (*Angew. Chem., Int. Ed. Engl.*, **11**, 724 (1972)) briefly mentioned several related anions but our evidence suggests that these compounds are nonplanar.

(7) Portions of this work were presented at the XXIIIrd International Congress of Pure and Applied Chemistry, Boston, Mass., July 1971, Abstracts, p O-C-7.

(8) For previous reports of the behavior of **1** in strongly basic media, see (a) C. L. Osborn, T. C. Shields, B. A. Shoulders, J. F. Krause, H. V. Cortez, and P. D. Gardner, *J. Amer. Chem. Soc.*, **87**, 3158 (1965); (b) E. A. LaLancette and R. E. Benson, *ibid.*, **87**, 1941 (1965).

(9) Prepared by the treatment of **1** with lithium dimethylamide in hexamethylphosphoramide.

(10) A. C. Cope and H. C. Campbell, *J. Amer. Chem. Soc.*, **74**, 179 (1952).

(11) We thank Professor P. D. Gardner for ir and nmr spectra of **4** (see ref 8a).

(12) Nmr (CCl_4) complex multiplet at δ 6.3–5.4 (6 H, olefinic), singlet, at 4.88 (2 H, H_9), and a complex triplet at 2.99 (2 H, H_5, $J_{45} = J_{56}$ = 7 Hz); uv (hexane) λ_{max} 267 nm (ϵ 9240).