Preparation and Reactions of Stabilized (Dialkylamino)methyloxosulfonium Methylides. Synthesis of 1,3-Oxathiole 3-Oxides[1a]

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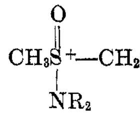
(Dimethylamino)- and (diethylamino)oxosulfonium methylide were treated with acid chlorides, anhydrides, and isocyanates to produce carbonyl-stabilized (dialkylamino)methyloxosulfonium methylides. Stabilized ylides were also prepared by reaction of the simple methylides with methanesulfonyl chloride and ethyl phenylpropiolate. (Dimethylamino)methyloxosulfonium benzoylmethylide and (dimethylamino)methyloxosulfonium acetylmethylide were alkylated at the carbonyl oxygen with trialkyloxonium salts to produce substituted (dialkylamino)methyl(2-alkoxyvinyl)oxosulfonium fluoroborates; the stereochemistry about the carbon–carbon double bond was ascertained by nmr. Acyl-stabilized methylides in this series were found to undergo a unique reaction, catalyzed by cupric sulfate, to yield 5-substituted 1,3-oxathiole 3-oxides.

A wide variety of sulfonium ylides stabilized by strong electron-withdrawing groups on the α carbon have been prepared; the chemistry of these compounds has been the subject of a number of studies.[2] Although these ylides transfer alkylidene groups to only the most reactive of substrates, they have been observed to undergo several interesting rearrangement and decomposition reactions.

The preparation of ylides **1** and **2** are described in the accompanying paper.[3] Here we describe the preparation of a number of stabilized ylides derived from **1** and **2** and compare their chemistry with that of other stabilized sulfonium ylides.



$$\mathrm{CH_3\overset{\overset{O}{\|}}{\underset{\underset{NR_2}{|}}{S^+}}-CH_2^-}$$

1, R = Me
2, R = Et

Preparation of Ylides.—Table I outlines the different stabilized ylides which were prepared; in most of these cases no effort to maximize the yield was made. In the preparation of these stabilized ylides at least 2 equiv of methylide is required, since the product is more acidic than the starting material. In general, the stabilized ylides displayed a fair shelf life; some decomposition was noted when stored for several months at room temperature. The dimethylamino ylide **1** was found to give products with superior crystalline properties, and following this observation only ylide **1** was used in the preparation of stabilized ylides.

Stabilized ylides **3–14** were prepared by reaction of the appropriate substrate with either **1** or **2** in THF at 0°. In the case of the benzoyl ylides, use of the less reactive anhydride as substrate rather than the acid chloride yielded a more manageable product mixture, at least when the diethylamino ylide was used. Several attempts to prepare a formyl-stabilized derivative were unsuccessful. While **12** could be prepared by reaction of **1** with mesyl chloride, *p*-nitrobenzenesulfonyl chloride gave no identifiable product.

TABLE I
STABILIZED YLIDES

Substrate	Stabilized ylide	No.	Yield, %
Benzoic anhydride	$\mathrm{Ph\overset{\overset{O}{\|}}{C}-\bar{C}HX}$	**3**	53
Phenyl isocyanate	$\mathrm{PhNH\overset{\overset{O}{\|}}{C}-\bar{C}HX}$	**4**	83
Benzoyl chloride	$\mathrm{Ph\overset{\overset{O}{\|}}{C}-\bar{C}HY}$	**5**	60
Phenyl isocyanate	$\mathrm{PhNH\overset{\overset{O}{\|}}{C}-\bar{C}HY}$	**6**	75
Acetic anhydride	$\mathrm{CH_3\overset{\overset{O}{\|}}{C}-\bar{C}HY}$	**7**	65
p-Chlorobenzoyl chloride	$\mathrm{\textit{p}\text{-}ClPh\overset{\overset{O}{\|}}{C}-\bar{C}HY}$	**8**	65
p-Nitrobenzoyl chloride	$\mathrm{\textit{p}\text{-}NO_2Ph\overset{\overset{O}{\|}}{C}-\bar{C}HY}$	**9**	82
Trifluoroacetic anhydride	$\mathrm{CF_3\overset{\overset{O}{\|}}{C}-\bar{C}HY}$	**10**	31
Phenylacetyl chloride	$\mathrm{PhCH_2\overset{\overset{O}{\|}}{C}-\bar{C}HY}$	**11**	52
Methanesulfonyl chloride	$\mathrm{CH_3SO_2\bar{C}HY}$	**12**	58
Ethyl phenylpropiolate	$\mathrm{EtO_2CCH{=}CPh\bar{C}HX}$	**13**	38
Ethyl phenylpripolate	$\mathrm{EtO_2CCH{=}CPh\bar{C}HY}$	**14**	55

$$\mathrm{X = \overset{\overset{O}{\|}}{\underset{\underset{NEt_2}{|}}{S^+}}-CH_3} \qquad \mathrm{Y = \overset{\overset{O}{\|}}{\underset{\underset{NMe_2}{|}}{S^+}}-CH_3}$$

The formation of **13** and **14** parallels that of similar reactivity observed when dimethyloxosulfonium methylide was used.[4] Thus, in these systems proton transfer of the initial adduct takes precedence over cyclopropene formation.[5]

O-Alkylation of Stabilized Ylides.—It has been reported by Bestmann[6] that carboethoxymethylenetriphenylphosphorane could be successfully O-alkylated with thiethyloxonium fluoroborate. A variety of stabilized sulfur ylides had previously been C-alkylated with methyl iodide, and the O-alkylation of dimethylsulfonium benzoylmethylide with trimethyl-

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(1) (a) Part XL in the series "Chemistry of Sulfoxides and Related Compounds." We gratefully acknowledge support by the National Science Foundation (GP 19623). (b) National Science Foundation Graduate Trainee, 1968–1971.

(2) (a) A. W. Johnson and R. T. Amel, *J. Org. Chem.*, **34**, 1240 (1969); (b) H. Nazaki, D. Tunemoto, S. Matubana, and K. Kondo, *Tetrahedron*, **23**, 545 (1967); (c) K. W. Ratts and A. H. Yao, *J. Org. Chem.*, **31**, 1689 (1966); (d) B. M. Trost, *J. Amer. Chem. Soc.*, **89**, 138 (1967); (e) W. E. Truce and G. D. Madding, *Tetrahedron Lett.*, 386 (1966); (f) G. B. Payne, *J. Org. Chem.*, **33**, 3517 (1968).

(3) C. R. Johnson and P. E. Rogers, *ibid.*, **38**, 1793 (1973).

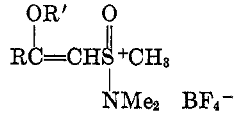
(4) C. Kaiser, B. M. Trost, J. Beeson, and J. Weinstock, *ibid.*, **30**, 3972 (1965).

(5) E. J. Corey and M. Jautelat, *J. Amer. Chem. Soc.*, **89**, 3912 (1967).

(6) H. J. Bestmann, R. Saalfrank, and J. P. Snyder, *Angew. Chem., Int. Ed. Engl.*, **8**, 216 (1969).

oxonium fluoroborate has been reported.[7] For these reasons it seemed that it would be worthwhile to O-alkylate several of the acylides prepared in this study.

Using trimethyl- and triethyloxonium fluoroborate it was possible to O-alkalylate the benzoyl- and acetyl-stabilized ylides **5** and **7**. The reactions were performed at 0° in methylene chloride in the presence of excess sodium carbonate. In all the cases studied,

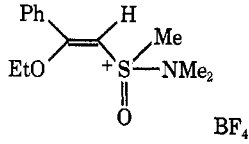


$$\mathrm{R\overset{OR'}{C}{=}CH\overset{O}{\underset{NMe_2}{S}}{}^{+}CH_3\ \ BF_4^-}$$

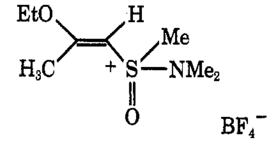
15, R = Ph; R′ = Et
16, R = Ph; R′ = Me
17, R = Me; R′ = Et
18, R = Me; R′ = Me

mixtures of diastereomeric vinyl salts were obtained; in several cases these isomers could be separated by fractional crystallization.

It seems valid to assume that the *Z* isomer of **15** and **16** should be the more favored thermodynamically, because a phenyl group has a larger steric requirement than either an ethoxy or a methoxy group. For similar reasons the *E* isomer of **17** and **18** should be favored.



15 *Z* diastereomer

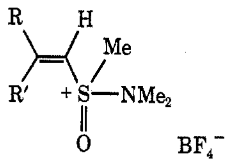


17 *E* diastereomer

Using the values of Pascuel, Meier, and Simon,[8] approximate shifts of the vinyl proton in each of these systems were estimated. These calculations indicated that the vinyl proton of the *Z* isomer of **15** and **16** would appear further downfield than that of the *E* isomer, and that the vinyl proton of the *E* isomer of **17** and **18** appear at lower field than that of the *Z* isomer (Table II).

TABLE II

VINYL ETHER SALTS

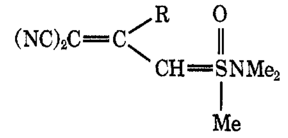


Compd	Isomer	R	R′	% at equil	Calcd vinyl shift	Obsd vinyl shift
15	*Z*	Ph	OEt	68	4.37	3.71
15	*E*	OEt	Ph	32	4.12	3.56
16	*Z*	Ph	OMe	73	4.37	3.74
16	*E*	OMe	Ph	27	4.12	3.52
17	*Z*	Me	OEt	12	3.74	3.36
17	*E*	OEt	Me	88	3.93	3.56
18	*Z*	Me	OMe	10	3.74	3.42
18	*E*	OMe	Me	90	3.93	3.64

Pure isomers or mixtures of different composition than that at equilibrium were stirred in methylene chloride in the presence of sodium carbonate. In all four systems it was found that after an extended period of time the isomer with the least shielded vinyl proton dominated. On this basis structural assignments were made.

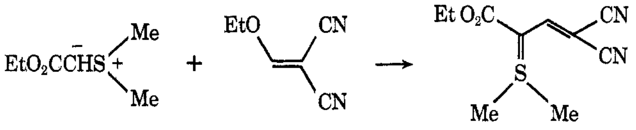
These vinyl ether salts were treated with the anions of several active methylene compounds; it was hoped that this would represent a route to substituted cyclopropyl ethers.[9,10] Initial efforts were made using diethyl and dimethyl malonate. Sodium alkoxides were used as bases, and the reactions were first run at room temperature and later at 50°. Nmr spectra of the crude products offered no evidence for the existence of cyclopropanes. These spectra did indicate that methyl benzoate was present when sodium methoxide was used as a base in reactions with phenylvinyl ethers. It was also noted that in the presence of a sodium methoxide the salt **15** was converted to **16**.

Salts **15** and **17** were found to react smoothly with the anion of malononitrile to give, as expected, the stabilized ylides **19** and **20**, respectively, rather than



19, R = Ph
20, R = Me

cyclopropane. A third allylide identified only on the basis of its nmr spectrum was obtained from the reaction of **15** and methyl cyanoacetate. Payne has observed the formation of allylide **22** in the reaction of



22

(dimethylsulfuranylidene)acetate (**21**) with ethoxymethylenemalononitrile.[2f] There are obvious similarities between Payne's system and the one under study.

It appears that steric factors prevented the addition of the anions of diethyl and dimethyl malonate to the β carbon. Electron donation by the ether oxygen may have also reduced the electrophilic nature of that carbon. The smaller anions derived from malononitrile and methyl cyanoacetate were able to overcome these obstacles, but the elimination of a molecule of alcohol rather than sulfinamide was the reaction pathway followed.

Conversion to 1,3-Oxathiole 1-Oxides.—In a study of dimethylsulfonium phenacylide, Trost[2d] observed that it was stable in refluxing benzene, chloroform, or cyclohexene. He found, however, that tribenzoylcyclopropane (**24**) was obtained in high yield when

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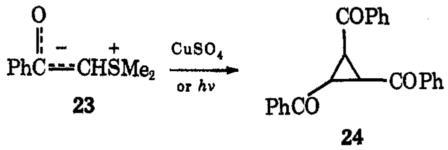
[7] S. H. Smallcombe, R. J. Holland, R. H. Fish, and M. C. Caserio, *Tetrahedron Lett.*, 5987 (1968).

[8] C. Pascual, J. Meier, and W. Simon, *Helv. Chim. Acta*, **49**, 164 (1966).

[9] (a) J. Gosselck, L. Beress, and H. Schenk, *Angew. Chem., Int. Ed. Engl.*, **5**, 596 (1966); (b) J. Gosselck, H. Albrecht, F. Dost, H. Schenk, and G. Schmidt, *Tetrahedron Lett.*, 995 (1968); (c) J. Gosselck and G. Schmidt, *ibid.*, 2615 (1969); (d) G. Schmidt and J. Gosselck, *ibid.*, 3445 (1969).

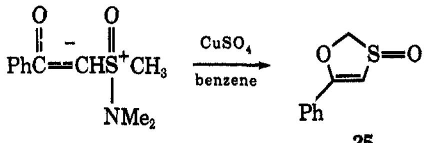
[10] C. R. Johnson and J. P. Lockard have reported [*Tetrahedron Lett.*, 4589 (1971)] that (dimethylamino)phenyl(2-phenylvinyl)oxosulfonium fluoroborate undergoes reactions with active methylene compounds to give cyclopropanes. Gosselck and coworkers[9] had shown that simple vinyl sulfonium salts reacted with the anions of active methylene compounds to give cyclopropanes.



23 **24**

a solution of the ylide was refluxed in cyclohexene in the presence of excess anhydrous copper sulfate. This cyclopropane was also obtained on irradiation of a benzene solution of the ylide with an Hanovia high-pressure mercury lamp using a Pyrex filter. On this basis it was suggested that benzoylcarbene was a common intermediate in both reactions.

A very different result was observed when the benzoyl-stabilized ylide **5** was stirred with 2 equiv of anhydrous cupric sulfate in cyclohexene or benzene. A crystalline solid identified as 5-phenyl-1,3-oxathiole 3-oxide (**25**) was obtained in high yield.

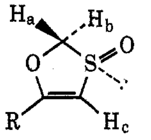


5 **25**

It was found that several other acylides also rearranged cleanly to the corresponding 1,3-oxathiole 3-oxides. In the examples studied, the stabilized ylides were stirred in refluxing benzene, cyclohexene, or toluene for approximately 33 hr in the presence of 2 equiv of cupric sulfate. The 1,3-oxathiole 3-oxides (**25**, **26**, **27**) could be isolated as crystalline solids, while **28** and **29** were isolated as oils. These sulfoxides were stable at room temperature, but were decomposed quickly by traces of acid (Table III).

TABLE III

1,3-OXATHIOLE 3-OXIDES

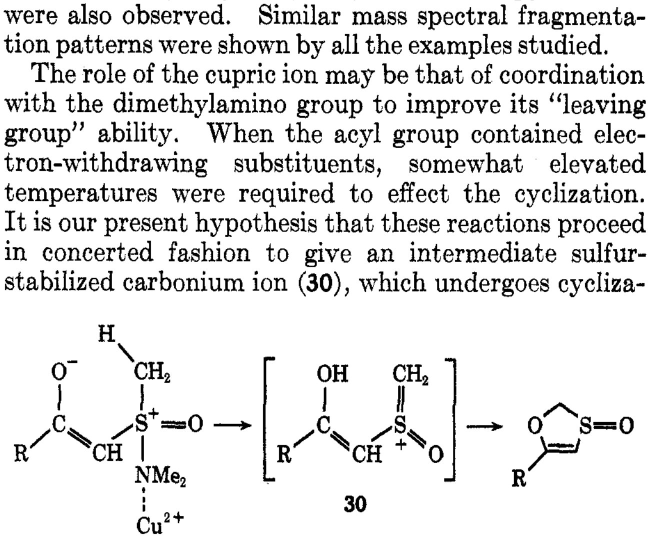


Compd	R	Yield, %	Nmr, ppm (*J*, Hz) H_a[a]	H_b[a]	H_c[b]
25	Ph	84	5.63 (11)	5.1 (11)	6.75
26	*p*-ClPh	80	5.54 (12)	5.0 (12)	6.65
27	*p*-NO_2Ph	79	5.65 (12)	5.1 (12)	6.95
28	CH_3	80	5.35 (12)	4.9 (12)	6.05
29	$PhCH_2$	64	5.25 (12)	4.8 (12)	6.00

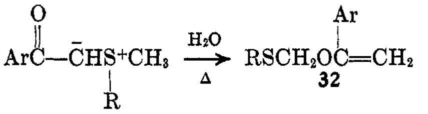
[a] Doublets. [b] Singlets.

The infrared spectra of these compounds all displayed a sulfoxide absorption in the 1020–1040-cm^{-1} region. The nmr spectra of this ring system were very characteristic. In all cases the vinyl proton appeared as a singlet at approximately δ 6.0–6.8, while the diastereotopic protons on the carbon flanked by the sulfoxide and ether appeared as AB quartets between δ 4.5 and 5.0. The doublet at lower field was assigned to the proton cis to the sulfoxide oxygen.[11] The mass spectrum of **25** showed a parent ion of *m/e* 180 and displayed major peaks corresponding to the loss of oxygen and formaldehyde. Peaks assumed to be the phenacylium ion, phenylacetylene, and the tropylium ion were also observed. Similar mass spectral fragmentation patterns were shown by all the examples studied.

The role of the cupric ion may be that of coordination with the dimethylamino group to improve its "leaving group" ability. When the acyl group contained electron-withdrawing substituents, somewhat elevated temperatures were required to effect the cyclization. It is our present hypothesis that these reactions proceed in concerted fashion to give an intermediate sulfur-stabilized carbonium ion (**30**), which undergoes cyclization. Regardless of the mechanism, these reactions show a characteristic of a Pummerer reaction—a sulfur is reduced and an adjacent carbon is oxidized.[12] In Pummerer reactions, which are more typical at the "sulfin" oxidation stage, carbonium ions stabilized by an adjacent sulfur are believed to be key intermediates. A close analogy to the present reaction is from the work of Ratts and Yao[13] in which acyl-stabilized ylides (**31**) were found to rearrange to enol ethers (**32**) in refluxing water.



30



$$\mathrm{ArC(=O)\bar{C}H(R)S^+CH_3 \xrightarrow[\Delta]{H_2O} RSCH_2OC(Ar){=}CH_2}$$

31 **32**

In the case of **5**, refluxing in aqueous solution resulted principally in hydrolysis to benzoic acid, but traces of oxathiole could be detected by nmr.

A survey of the literature revealed no previous examples of 1,3-oxathiole 3-oxides. Several examples of this ring system at the sulfide and sulfone oxidation stages have been reported.[14] Several attempts were made to oxidize **25** using peracetic acid, hydrogen peroxide, sodium metaperiodate, 1-chlorobenzotriazole,[15] and Collins reagent.[16] The media of the first three attempts were acidic, and under these conditions the oxathiole ring decomposed The Collins procedure yielded some recovered starting material, but an nmr of the crude product showed no peaks which might be assigned to the sulfone. The nmr of the crude product from the attempted oxidation with 1-chlorobenzotriazole in methanol indicated that Cl and MeO had added across the double bond. Sodium borohydride will reduce alkoxysulfonium salts to sulfides.[17] Nowever, several attempts to prepare the methoxysulfonium salt of the

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[11] R. G. D. Cooper, P. V. DeMarco, J. C. Cheng, and N. D. Jones, *J. Amer. Chem. Soc.*, **91**, 1408 (1969).

[12] C. R. Johnson and W. G. Phillips, *ibid.*, **91**, 682 (1969).

[13] K. W. Ratts and A. N. Yao, *J. Org. Chem.*, **33**, 70 (1968).

[14] (a) K. Dickore, *Justus Liebigs Ann Chem.*, **671**, 139 (1964); (b) K. Nozaki, M. Yakaku, and Y. Hayashi, *Tetrahedron Lett.*, 2303 (1967); (c) G. Ottmann, G. D. Vickers, and H. Hooks, *J. Heterocycl. Chem.*, **4**, 527 (1967); (d) K. Hirai, *Tetrahedron Lett.*, 1137 (1971); (e) W. Drenth and H. J. DeGruitjen, *Recl. Trav. Chim. Pays-Bas*, **89**, 379 (1970).

[15] W. D. Kingsbury and C. R. Johnson, *Chem. Commun.*, 365 (1969).

[16] (a) J. C. Collins, W. W. Hess, and F. J. Frank, *Tetrahedron Lett.*, 3363 (1968); (b) R. Ratcliffe and R. Rodehurst, *J. Org. Chem.*, **35**, 4000 (1970).

[17] C. R. Johnson and W. G. Phillips, *ibid.*, **32**, 3233 (1967).

oxathiole failed because trace amounts of acid present in the alkylating agents catalyzed the decomposition of the ring.

Experimental Section[18]

(Diethylamino)methyloxosulfonium (*N*-Phenylcarbamoyl)-methylide (4).—The ylide **2**[3] (9.7 mmol) in 20 ml of THF was cooled in an ice bath and 1.0 g (8.4 mmol) of phenyl isocyanate was added in 5 ml of THF. The reaction was allowed to warm to room temperature and stir for 24 hr. The solvent was evaporated at reduced pressure and the residue was stirred with methylene chloride. The salts were filtered off and the methylene chloride was evaporated.[19] The crude product was chromatographed over a short column of alumina eluting with 50:50 benzene–chloroform to give 1.85 g (83%) of **4** as a crystalline solid: mp 114° (benzene–pentane); ir ($CHCl_3$) 3420, 1630, 1580, 1320 cm^{-1}; nmr ($CDCl_3$) δ 7.7–7.0 (m, 6, aryl and NH), 3.8 (s, 1, CH), 3.65–3.2 (q, 4, NCH_2), 3.31 (s, 3, SCH_3), 1.45–1.05 (t, 6, CH_3).

Anal. Calcd for $C_{13}H_{20}N_2O_2S$: C, 58.18; H, 7.51. Found: C, 58.45; H, 7.72.

(Dimethylamino)methyloxosulfonium (*N*-Phenylcarbamoyl)-methylide (6).—The ylide **1** (18.5 mol) in 30 ml of THF was cooled in an ice bath and 2.0 g (0.0168 mol) of phenyl isocyanate in 10 ml of THF was added over a period of 30 min. The crude product[19] was a crystalline solid, and recrystallization from benzene–pentane gave 3.1 g (75%) of **6**: mp 146–147°; ir ($CHCl_3$) 3430, 1630, 1590 cm^{-1}; nmr ($CDCl_3$) δ 7.9–6.8 (m, 6, aryl and NH), 3.64 (s, 1, CH), 3.28 (s, 3, SCH_3), 2.88 (s, 6, NCH_3).

Anal. Calcd for $C_{11}H_{16}N_2O_2S$: C, 54.98; H, 6.71. Found: C, 55.03; H, 6.99.

(Diethylamino)methyloxosulfonium Benzoylmethylide (3).—The ylide **2** (0.044 mol) in 100 ml of THF in a 250-ml three-necked flask equipped with a mechanical stirrer was cooled in an ice bath and 4.52 g (0.02 mol) of benzoic anhydride in 30 ml of THF was added over the period of 1 hr. The reaction was allowed to warm to room temperature and stirred for 4 hr. The crude product[19] was stirred with 500 ml of ether, which was decanted from a small amount of insoluble material and reduced to $^1/_2$ its volume, and on cooling 2.7 g (53%) of a crystalline solid, mp 90.5–91°, was obtained: ir ($CHCl_3$) 1590, 1550, 1370 cm^{-1}; nmr ($CDCl_3$) δ 8.0–7.2 (2 m, 5, aryl), 4.9 (s, 1, CH), 3.6–3.15 (q, 4, NCH_2), 3.54 (s, 3, SCH_3), 1.35–1.05 (t, 6, CCH_3).

Anal. Calcd for $C_{13}H_{19}NO_2S$: C, 61.63; H, 7.56. Found: C, 61.68; H, 7.64.

The ylide **3** was also prepared from **2** (15 mmol) and benzoyl chloride (7 mmol) in THF at 0°. The product (66% as a yellow oil) had spectral properties identical with those of **3** (above) and could be obtained in crystalline form from ether–pentane.

(Dimethylamino)methyloxosulfonium Benzoylmethylide (5).—The ylide **1** in 120 ml of THF was cooled in an ice bath and 8.0 g (0.0592 mol) of benzoyl chloride in 20 ml of THF was added over the period of 30 min. The reaction was allowed to warm to room temperature and was stirred for a total of 5 hr. The crude product[19] was stirred with 1 l. of ether, which was decanted from a small amount of insoluble material, and then reduced to $^1/_2$ its volume. On cooling, 8.0 g (60%) of a crystalline solid, mp 80–81°, was obtained: ir ($CHCl_3$) 1585, 1540, 1370 cm^{-1}; nmr ($CDCl_3$) δ 8.0–7.2 (2 m, 5, aryl), 4.83 (s, 1, CH), 3.44 (s, 3, SCH_3), 2.77 (s, 6, NCH_3).

Anal. Calcd for $C_{11}H_{15}NO_2S$: C, 58.64; H, 6.71. Found: C, 58.62; H, 6.93.

(Dimethylamino)methyloxosulfonium Acetylmethylide (7).—The ylide **1** (65 mmol) in 80 ml of THF was cooled in an ice bath and 3 g (0.0296 mol) of acetic anhydride in 20 ml of THF was added over the period of 1 hr. The crude product[19] was stirred with 300 ml of ether which was decanted from a small amount of insoluble material and then on cooling yielded 3.2 g (65%) of crystalline product: mp 46–46.5°; ir ($CHCl_3$) 1575, 1375 cm^{-1}; nmr ($CDCl_3$) δ 4.52 (s, 1, CH), 3.4 (s, 3, SCH_3), 2.92 (s, 6, NCH_3), 1.97 (s, 3, CCH_3).

Anal. Calcd for $C_6H_{13}NO_2S$: C, 44.15; H, 8.03. Found: C, 43.87; H, 8.31.

The ylide **1** was also treated with acetyl chloride. The crude product was chromatographed over alumina eluting first with methylene chloride and then chloroform to give 58% of a yellow oil which gave spectra identical with those of ylide **7** (above). The use of acetic anhydride is preferred, since it seems to give a cleaner product.

(Dimethylamino)methyloxosulfonium *p*-Chlorobenzoylmethylide (8).—The ylide **1** (68.5 mmol) in 80 ml of THF was cooled in an ice bath and *p*-chlorobenzoyl chloride (5.4 g, 31 mmol) in 20 ml of THF was added over a period of 30 min. The reaction was stirred for 6 hr at 0° and then allowed to warm to room temperature overnight. The crude product[19] was dissolved in 200 ml of ether, filtered, and cooled to give, with periodic additions of pentane, 5.2 g (65%) of a crystalline solid: mp 61–62°; ir (KBr) 1590, 1545, 1390, 1350, 1170, 1070, and 835 cm^{-1}; nmr ($CDCl_3$) δ 7.9–7.3 (q, 4, aryl), 4.85 (s, 1, CH), 3.54 (s, 3, SCH_3), 2.99 (s, 6, NCH_3).

Anal. Calcd for $C_{11}H_{14}ClNO_2S$: C, 50.86; H, 5.43. Found: C, 50.67; H, 5.55.

(Dimethylamino)methyloxosulfonium *p*-Nitrobenzoylmethylide (9).—The ylide **1** was treated with *p*-nitrobenzoyl chloride in the manner described above for **8**. The crude product was recrystallized from benzene–pentane to give 82% of a yellow solid: mp 108–109.5°; ir (KBr) 1550, 1520, 1340, 1170, 1080, and 890 cm^{-1}; nmr ($CDCl_3$) δ 8.2–7.8 (q, 4, aryl), 4.9 (s, 1, CH), 3.6 (s 3, SCH_3), 2.95 (s, 6, NCH_3).

Anal. Calcd for $C_{11}H_{14}N_2O_4S$: C, 48.88; H, 522. Found, C. 48.67; H, 5.34.

(Dimethylamino)methyloxosulfonium Trifluoroacetylmethylide (10).—The **1** (68.5 mmol) was treated with trifluoroacetic anhydride (30 mmol). The crude product was dissolved in ether and on cooling and the addition of pentane 1.9 g (31%) of **10** as a crystalline solid, mp 41.5–43°, was obtained: ir (KBr) 1600, 1250, 1180, 1090, 935, and 890 cm^{-1}; nmr ($CDCl_3$) δ 4.8 (s, 1, CH), 3.54 (s, 3, SCH_3), 3.0 (s, 6, NCH_3).

Anal. Calcd for $C_6H_{10}F_3NO_2S$: C, 33.18; H, 4.64. Found: C, 33.07; H, 4.71.

(Dimethylamino)methyloxosulfonium Phenacetylmethylide (11).—A solution of the ylide **1** (68.5 mmol) was treated with phenylacetyl chloride (4.8 g, 31 mmol) at 0°. The crude product[19] was taken up in ether and with periodic additions of pentane 3.8 g (52%) of a crystalline solid, mp 60–61°, was obtained: ir (KBr) 1570, 1370, 1180, 1090, and 930 cm^{-1}; nmr ($CDCl_3$) δ 7.3 (s, 5, aryl), 4.1 (s, 1, CH), 3.48 (s, 2, CH_2), 3.37 (s, 3, SCH_3), 2.82 (s, 6, NCH_3).

Anal. Calcd for $C_{12}H_{17}NO_2S$: C, 60.22; H, 7.16. Found: C, 60.44; H, 7.16.

(Dimethylamino)methyloxosulfonium Methanesulfonylmethylide (12).—A solution of the ylide **1** in 80 ml of THF solution was cooled in an ice bath, and 2.6 g (0.226 mol) of methanesulfonyl chloride in 15 ml of THF was added. The reaction was allowed to stir at 0° for 5 hr and then warmed to room temperature overnight. A crystalline solid (2.6 g, 58%), mp 80.5–81.5°, was obtained from benzene–pentane: ir (KBr) 1280, 1200, 1110, 1020, and 950 cm^{-1}; nmr ($CDCl_3$) δ 3.83 (s, 1, CH), 3.18 (s, 3, SCH_3), 3.08 (s, SO_2CH_3), 3.0 (s, 6, NCH_3).

Anal. Calcd for $C_5H_{13}NO_3S_2$: C, 30.13; H, 6.58. Found: C, 30.34; H, 6.82.

(Diethylamino)methyloxosulfonium (3-Carboethoxy-2-phenyl)-allylide (13).—The ylide **2** in 10 ml of THF was cooled to 0° and ethyl phenylpropiolate (1.0 g, 5.6 mmol) in 4 ml of THF was added over a period of 10 min. The reaction mixture was stirred overnight. The crude product[19] was chromatographed on silica gel eluting first with benzene and then with chloroform to give 0.720 g (38%) of a yellow oil. A crystalline solid, mp 98–99°, was obtained from chloroform–hexane: ir ($CHCl_3$) 1665, 1520, 1150, 1100, 995 cm^{-1}; nmr ($CDCl_3$) δ 7.67–7.15 (m, 5, aryl), 5.93 (s, 1, CH), 4.82 (s, 1, CH), 4.4–3.97 (q, 2, OCH_2), 3.43–2.75 (m, 4, NCH_2), 1.46–1.08 (t, 3, CH_3), 0.96–0.70 (t, 6, CH_3).

Anal. Calcd for $C_{17}H_{25}NO_3S$: C, 63.13; H, 7.97. Found: C, 63.47; H, 7.95.

(Dimethylamino)methyloxosulfonium (3-Carboethoxy-2-phenyl)allylide (14).—The ylide **1** was treated with ethyl phenylpropiolate. Recrystallization from ether–pentane yielded 55% of a solid: mp 89–91°; ir ($CHCl_3$) 1650, 1525, 1240 cm^{-1}; nmr ($CDCl_3$) δ 7.6–7.16 (m, 5, aryl), 5.8 (s, 1, CH), 4.78 (s, 1, CH), 4.34–3.92 (q, 2, OCH_2), 2.94 (s, 3, SCH_3), 1.4–1.1 (t, 3, CH_3).

Anal. Calcd for $C_{15}H_{21}NO_3S$: C, 60.99; H, 7.16. Found: C, 60.97; H, 7.08.

Reaction of Ylide 5 with Triethyloxonium Fluoroborate.—A solution of 3.0 g (13.3 mmol) of the benzoyl-stabilized ylide **5**

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(18) For general details see Experimental Section of ref 3.

(19) In the preparation of stabilized ylides, all of the crude products were isolated in the manner described for **4**.

was dissolved in 100 ml of methylene chloride and stirred in an ice bath under a cover of nitrogen. Triethyloxonium fluoroborate (7.5 g, 0.037 mol) was added and the reaction was allowed to stir. After 30 min, tlc indicated that some starting material was present. The reaction was kept alkaline by the addition of 4.0 g (0.037 mol) of sodium carbonate. One hour later, 2.5 g of triethyloxonium fluoroborate was added, and the reaction was allowed to stir for 3 hr. The reaction mixture was poured into 100 ml of water, which was extracted with 250 ml of methylene chloride. The methylene chloride was dried and removed at reduced pressure to give 4.1 g (90%) of crude product. A mixture of two isomers was obtained from this reaction, but the ratio of the two isomers varied from reaction to reaction. These two isomers could be separated by fractional crystallization, and on the basis of nmr spectra, structural assignments were made. (*Z*)-(Dimethylamino)methyl(2-ethoxy-2-phenylvinyl)oxosulfonium fluoroborate (**15-*Z***) had mp 108.5–110°; ir (Nujol) 1705 (w), 1690 (w), 1650 (s), 1140–1020 cm^{-1} (BF_4^-); nmr ($CDCl_3$) δ 7.5 (s, 5, aryl), 6.18 (s, 1, vinyl), 4.64–4.18 (q, 2, CH_2), 3.5 (s, 3, SCH_3), 2.8 (s, 6, NCH_3), 1.66–1.30 (t, 3, CH_3).

Anal. Calcd for $C_{13}H_{20}BF_4NO_2S$: C, 45.77; H, 5.91. Found: C, 45.54; H, 6.13.

(*E*)-(Dimethylamino)methyl(2-ethoxy-2-phenylvinyl)oxosulfonium fluoroborate (**15-*E***) had mp 63–64°; ir (Nujol) 1700 (w), 1690 (m), 1655 (m), 1140–1020 cm^{-1} (BF_4^-); nmr ($CDCl_3$) δ 7.6 (s, 5, aryl), 5.94 (s, 1, vinyl), 4.4–4.0 (q, 2, CH_2), 3.77 (s, 3, SCH_3), 3.12 (s, 6, NCH_3), 1.58–1.07 (t, 3, CH_3).

Anal. Calcd for $C_{13}H_{20}BF_4NO_2S$: C, 45.77; H, 5.91. Found: C, 46.01; H, 5.95.

Reaction of Ylide 5 with Trimethyloxonium Fluoroborate.—Ylide **5** was treated with trimethyloxonium fluoroborate in a manner similar to that described above using triethyloxonium fluoroborate to give 1.25 g (85%) of a mixture of two vinyl ether fluoroborate salts. This mixture could not be separated, but it was possible on the basis of later work to assign a structure to each isomer. (*Z*)-(Dimethylamino)methyl(2-methoxy-2-phenylvinyl)oxosulfonium fluoroborate (-**16*Z***) had nmr ($CDCl_3$) δ 7.5 (s, 5, aryl), 6.24 (s, 1, vinyl), 4.17 (s, 3, OCH_3), 3.57 (s, 3, SCH_3), 2.74 (s, 6, NCH_3).

(*E*)-(Dimethylamino)methyl(2-methoxy-2-phenylvinyl)oxosulfonium fluoroborate (**16-*E***) had nmr ($CDCl_3$) δ 7.53 (s, 5, aryl), 5.93 (s, 1, vinyl), 3.95 (s, 3, OCH_3), 3.78 (s, 3, SCH_3), 3.1 (s, 6, NCH_3).

Anal. (as mixture) Calcd for $C_{12}H_{18}BF_4NO_2$: C, 44.06; H, 5.54. Found: C, 43.82; H, 5.50.

Reaction of Ylide 7 with Triethyloxonium Fluoroborate.—A mixture (50% yield) of two isomeric vinyl ether fluoroborate salts was obtained. This mixture could never be completely separated, but on the basis of the nmr spectrum, structural assignments could be made. (*Z*)-(Dimethylamino)methyl(2-ethoxy-2-methylvinyl)oxosulfonium fluoroborate (**17-*Z***) had nmr ($CDCl_3$) δ 5.77 (s, 1, vinyl), 4.64–4.27 (q, 2, OCH_2), 3.60 (s, 3, SCH_3), 3.07 (s, 6, NCH_3), 2.32 (s, 3, CCH_3), 1.6–1.3 (t, 3, CH_2CH_3).

(*E*)-(Dimethylamino)methyl(2-ethoxy-2-methylvinyl)oxosulfonium fluoroborate (**17-*E***) had nmr ($CDCl_3$) δ 5.98 (s, 1, vinyl), 4.4–4.0 (q, 2, OCH_2), 3.62 (s, 3, SCH_3), 3.10 (s, 6, NCH_3) 2.32 (s, 3, CCH_3), 1.6–1.3 (t, 3, CH_2CH_3). The mixture was converted to the tetraphenylborate salt by exchange with sodium tetraphenylborate.

Anal. (as mixture of monohydrated tetraphenylborate salts). Calcd for $C_{32}H_{40}BNO_3S$: C, 72.58; H, 7.61. Found: C, 72.56; H, 7.87.

Reaction of Ylide 7 with Trimethyloxonium Fluoroborate.—The components of this mixture could never be completely separated. (*Z*)-(Dimethylamino)methyl(2-methoxy-2-methylvinyl)oxosulfonium fluoroborate (**18-*Z***) had nmr ($CDCl_3$) δ 5.67 (s, 1, vinyl), 4.04 (s, 3, OCH_3), 3.60 (s, 3, SCH_3), 3.04 (s, 6, NCH_3), 2.32 (s, 1, CCH_3). (*E*)-(Dimethylamino)methyl(2-methoxy-2-methylvinyl)oxosulfonium fluoroborate (**18-*E***) had nmr ($CDCl_3$) δ 5.94 (s, 1, vinyl), 3.97 (s, 3, OCH_3), 3.64 (s, 3, SCH_3), 3.10 (s, 6, NCH_3), 2.32 (s, 3, CCH_3).

Anal. (as mixture of tetraphenylboroate salts). Calcd for $C_{31}H_{36}BNO_2S$: C, 74.84; H, 7.29. Found: C, 74.36; H, 7.44.

(Dimethylamino)methyloxosulfonium (3,3-Dicyano-2-phenyl)allylide (19).—A solution of 100 mg (1.47 mmol) of malononitrile was stirred in 7 ml of methanol under a cover of nitrogen; 1.5 ml (1.5 mmol) of 1 *M* sodium methoxide was added. Over a period of 10 min, 480 mg (1.46 mmol) of salt **16** dissolved in 10 ml of methanol was added. The reaction mixture was allowed to stir at room temperature for 5 hr, and then was worked up by pouring it into water and extracting with methylene chloride. The methylene chloride was dried and evaporated to give 390 mg of crude product. The ylide **19** (300 mg, 75%) as a crystalline solid, mp 180–184° dec, was obtained from methylene chloride–pentane: ir ($CHCl_3$) 2200, 1460, 1430, 980, 830 cm^{-1}; nmr ($CDCl_3$) δ 7.43 (s, 5, aryl), 5.0 (s, 1, CH), 3.48 (s, 3, SCH_3), 2.58 (s, 6, NCH_3).

Anal. Calcd for $C_{14}H_{15}N_3OS$: C, 61.51; H, 5.53. Found: C, 61.25; H, 5.67.

(Dimethylamino)methyloxosulfonium (3,3-Dicyano-2-methyl)-allylide (20).—In a similar manner malononitrile anion and salt **17** gave **20** (59%): mp 146–147°; ir ($CHCl_3$) 2170, 1480, 990 cm^{-1}; nmr ($CDCl_3$) δ 4.74 (s, 1, CH); 3.11 (s, 3, SCH_3), 2.97 (s, 6, NCH_3), 2.3 (s, 3, CCH_3).

Anal. Calcd for $C_9H_{13}N_3OS$: C, 51.16; H, 6.20. Found: C, 50.94; H, 6.34.

(Dimethylamino)methyloxosulfonium (3-Carbomethoxy-3-cyano-2-phenyl)allylide.—A solution of 150 mg (1.5 mmol) of methyl cyanoacetate was stirred in 10 ml of methanol with 1.6 mmol of sodium methoxide. The vinyl salt **15** (500 mg, 1.5 mmol) was dissolved in 3 ml of methanol and added. The reaction mixture immediately darkened and was allowed to stir at room temperature for 24 hr. The reaction mixture was poured into water and extracted with methylene chloride. The methylene chloride was dried and evaporated. The residue was taken up in a small amount of methylene chloride and 140 mg (30%) of a crystalline solid, mp 205–206°, was obtained following the addition of pentane: ir (KBr) 2200, 1660, 1450, and 1120 cm^{-1}; nmr ($CDCl_3$) δ 7.45 (s, 5, aryl), 6.6 (s, 1, CH), 3.85 (s, 3, OCH_3), 3.0 (s, 3, SCH_3), 2.6 (s, 6, NCH_3).

Equilibration of Salts 15-*Z* and 15-*E*.—A solution of 100 mg (0.294 mmol) of pure **15-*E*** was stirred in 5 ml of methylene chloride with 100 mg (0.95 mmol) of sodium carbonate at room temperature for 5 days. The reaction mixture was poured into water and extracted with methylene chloride. Nmr analysis of the product indicated that 32% of the product was **15-*E*** and 68% was **15-*Z***. When a pure sample of **15-*Z*** was subjected to similar equilibrating conditions, an identical product mixture was obtained.

Equilibration of Other Salts.—In a manner similar to that described above for **15** the equilibrium composition for other salts were found to be as follows: **16**, 27% *E* and 73% *Z*; **17**, 88% *E* and 12% *Z*; **18**, 90% *E* and 10% *Z*.

5-Phenyl-1,3-oxathiole 3-Oxide (25).—Anhydrous cupric sulfate (2.8 g, 0.0175 mol) was added to a solution of 2.0 g (8.9 mmol) of the benzoyl-stabilized ylide **5** in 60 ml of benzene. The reaction mixture was stirred at 80° for 30 hr. The copper salts were filtered off and washed with 75 ml of methylene chloride. The solvent was evaporated and 1.34 g (84%) of **25** as a crystalline solid, mp 108–109°, was obtained from benzene–pentane: ir (KBr) 1605, 1565, 1060, and 1020 cm^{-1} (s); nmr ($CDCl_3$) δ 8.0–7.3 (m, 5, aryl), 6.75 (s, 1, vinyl), 5.63 (d, 1, J = 11 Hz, CHSO), 5.1 (d, 1, J = 11 Hz, CHSO).

Anal. Calcd for $C_9H_8O_2S$: C, 59.98; H, 4.47. Found: C, 59.71; H, 4.58.

5-*p*-Chlorophenyl-1,3-oxathiole 3-Oxide (26).—The *p*-chlorobenzoyl stabilized ylide **8**, 1.0 g (3.85 mmol), was stirred with 1.23 g (7.7 mmol) of anhydrous cupric sulfate in 50 ml of toluene at 110° for 30 hr. At this time the copper salts were filtered off and washed with 100 ml of dichloromethane. The solvent was evaporated to give 0.69 g (80%) of **26** as a crystalline solid: mp 122–123° (benzene–pentane); ir (KBr) 1590, 1550, 1470, 1390, 1320, and 1070–1020 cm^{-1} (s); nmr ($CDCl_3$) δ 7.9–7.3 (q, 4, aryl), 6.65 (s, 1, vinyl), 5.54 (d, 1, J = 12 Hz, CHSO), 5.0 (d, 1, J = 12 Hz, CHSO).

Anal. Calcd for $C_9H_7ClO_2S$: C, 50.36; H, 3.29. Found: C, 50.59; H, 3.52.

5-*p*-Nitrophenyl-1,3-oxathiole 3-Oxide (27).—A solution of 1.0 g (3.7 mmol) of the *p*-nitrobenzoyl stabilized ylide **9** in 50 ml of toluene was stirred with 1.2 g (7.4 mmol) of anhydrous cupric sulfate. After 30 hr at 110° the copper salts were filtered off and washed with 100 ml of methylene chloride. The solvent was evaporated and 0.66 g (79%) of **27** was obtained as a crystalline solid: mp 169–170° (methylene chloride–pentane); ir (KBr) 1580, 1540, 1340, and 1050 cm^{-1}; nmr ($CDCl_3$) δ 8.5–7.8 (q, 4, aryl), 6.95 (s, 1, vinyl), 5.65 (d, 1, J = 11 Hz, CHSO), 5.10 (d, 1, J = 11 Hz, CHSO).

Anal. Calcd for $C_9H_7NO_4S$: C, 48.00; H, 3.13. Found: C, 48.29; H, 3.33.

5-Methyl-1,3-oxathiole 3-Oxide (28).—A solution of 0.5 g (3.06 mmol) of the acetyl-stabilized ylide **7** was stirred with 0.98 g (6 mmol) of anhydrous copper sulfate at 70° for 36 hr. The insoluble salts were filtered off and washed with methylene chloride to give 300 mg (80%) of **28**: ir (film) 1620, 1050-1030 cm^{-1}; nmr ($CDCl_3$) δ 6.05 (s, 1, vinyl), 5.35 (d, 1, J = 12 Hz, CHSO), 4.9 (d, 1, J = 12 Hz, CHSO), 2.2 (s, 3, CH_3). This product displayed a mass spectrum in accord with the assigned structure.

Registry No.—**1**, 38709-75-0; **2**, 38421-38-4; **3**, 38709-77-2; **4**, 38709-78-3; **5**, 38709-79-4; **6**, 38709-80-7; **7**, 38709-81-8; **8**, 38709-82-9; **9**, 38709-83-0; **10**, 38709-84-1; **11**, 38709-85-2; **12**, 38709-87-4; **13**, 38709-88-5; **14**, 38709-89-6; **15-*Z***, 38708-52-0; **15-*E***, 38708-53-1; **16-*Z***, 38708-54-2; **16-*E***, 38708-55-3; **17-*Z***, 38780-33-5; **17-*E***, 38708-56-4; **17-*Z*** tetraphenylborate salt, 38811-40-4; **17-*E*** tetraphenylborate salt, 38704-60-8; **18-*Z***, 38708-57-5; **18-*E***, 38708-58-6; **18-*Z*** tetraphenylborate salt, 38704-61-9; **18-*E*** tetraphenylborate salt, 38704-62-0; **19**, 38709-90-9; **20**, 38709-91-0; **25**, 38709-92-1; **26**, 38709-93-2; **27**, 38709-94-3; **28**, 38709-95-4; **29**, 38709-96-5; phenyl isocyanate, 103-71-9; benzoic anhydride, 93-97-0; benzoyl chloride, 98-88-4; acetic anhydride, 108-24-7; acetyl chloride, 75-36-5; *p*-chlorobenzoyl chloride, 122-01-0; trifluoroacetic anhydride, 407-25-0; phenylacetyl chloride, 103-80-0; methanesulfonyl chloride, 124-63-0; ethyl phenylpropiolate, 2216-94-6; triethyloxonium tetrafluoroborate, 368-39-8; trimethyloxonium tetrafluoroborate, 420-37-1; sodium tetraphenylborate, 143-66-8; (dimethylamino)methyloxosulfonium (3-cyano-3-carbomethoxy-2-phenyl)allylide, 38709-99-8.

Conformationally Rigid Organosulfur Molecules. Derivatives of 4-Thiatricyclo[4.2.1.$0^{3,7}$]nonane and 4-Thiatricyclo[4.3.1.$0^{3,7}$]decane[1]

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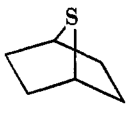
The reaction of sodium sulfide with the epoxy brosylates **4** and **12** provided *exo*-2-hydroxy-4-thiatricyclo[4.2.1.$0^{3,7}$]nonane (**5**) and *exo*-2-hydroxy-4-thiatricyclo[4.3.1.$0^{3,7}$]decane (**13**), respectively. Compound **5** has been oxidized to the corresponding hydroxy sulfone **14**, to sulfoxides **15a** and **15b**, and to keto sulfide **17**. Reduction of the latter compound with sodium borohydride gave the endo hydroxy sulfide **16**. Reduction of **17** by hydrazine and base yielded sulfide **18**. Compound **13** was converted to the keto sulfide **19**, which upon reduction with sodium borohydride gave the epimeric alcohol **20**.

Conformationally rigid organosulfur molecules provide substrates which are useful in studies pertaining to stereochemistry and intramolecular interactions.[2,3] Examples of systems presently available for such studies are sulfides **1**[4] and **2**.[5] We now report several additions, namely *exo*-2-hydroxy-4-thiatricyclo[4.2.1.$0^{3,7}$]nonane (**5**) and *exo*-2-hydroxy-4-thiatricyclo[4.3.1.$0^{3,7}$]decane (**13**) along with several derivatives.



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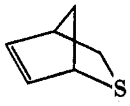

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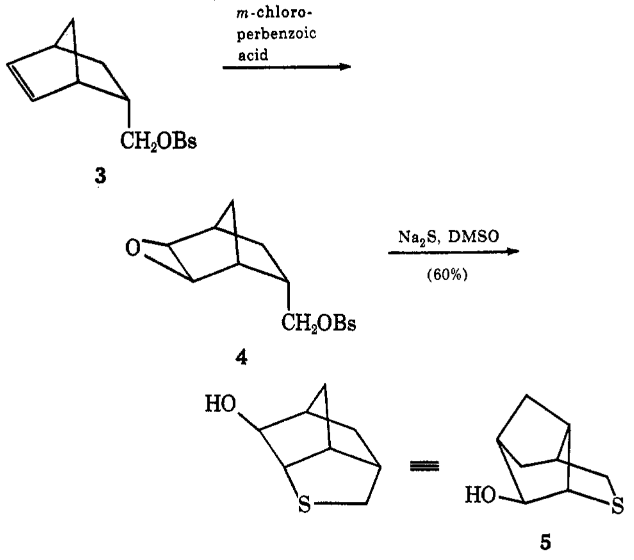
The synthesis of compound **5** is outlined in Scheme I. The reaction of sodium sulfide with epoxy brosylate **4** is thought to lead to intermediate **6** by initial displacement of the brosyl group. This postulate is supported by experiments of Gray and Heitmeier,[6] which demonstrated that exo norbornyl epoxides are resistant to opening on treatment with lithium aluminum hydride. From intermediate **6** C–O cleavage could occur at either C_2 or C_4, leading to either sulfide alcohol **5** or **7**, respectively. Studies of Dreiding models indicated that attack at C_2 would involve more strain than attack at C_4; therefore, *a priori*, sulfide alcohol **5** was expected to be the product of this reaction. In fact, a stable, waxy solid was obtained in 60% yield, which, upon acetylation followed by desulfurization, afforded *exo*-2-acetoxy-5-*endo*-methylbicyclo[2.2.1]heptane (**8**). Sulfide alcohol **7** would have led to *exo*-2-acetoxy-*endo*-6-methylbicyclo[2.2.1]heptane (**9**).

SCHEME I

SYNTHESIS OF

exo-2-HYDROXY-4-THIATRICYCLO[4.2.1.$0^{3,7}$]NONANE (5)[a]



[a] Bs = *p*-bromobenzenesulfonyl.

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[1] Part XLI in the series "Chemistry of Sulfoxides and Related Compounds." We gratefully acknowledge support by the National Science Foundation (GP 19623).

[2] For reviews of this subject, see N. J. Leonard, *Rec. Chem. Progr.*, **17**, 24, (1956); L. N. Ferguson and J. C. Nadi, *J. Chem. Educ.*, **42**, 529 (1965).

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