them not to be significantly different at the 3σ level, and suggests that the S(1)–C–S(2) system is delocalized as shown in Figure 1.

Average distances within the icosahedral framework (B–B = 1.79 Å, B–C = 1.71 Å, C–C = 1.63 Å) are in good agreement with those found in such complexes as $(B_9C_2H_{11})Fe(\pi\text{-}C_5H_5)$,[2] $[B_9C_2H_{11}Re(CO)_3]^-$,[3] and $[(B_9C_2H_{11})_2Cu]^{2-}$.[4]

Hydrolysis of $(B_9C_2H_{10})_2CoS_2CH$ can be accomplished by heating in alkaline 50% aqueous ethanol at the reflux temperature for 45 min. The fate of the bridge carbon (which presumably appears as formate ion) has not been specifically investigated. Addition of H_2O_2 and $(CH_3)_4N^+$ or Cs^+ precipitates the purple $[(B_9C_2H_{10})_2CoS_2]^-$ ion, which apparently contains a disulfide bridge linking the icosahedral cages.

Anal. Calcd for $C_4H_{20}B_{18}CoCsS_2$: C, 9.25; H, 3.88; B, 37.59; Co, 11.35; Cs, 25.60; S, 12.31. Found: C, 9.75; H, 4.03; B, 35.43; Co, 11.48; Cs, 26.59; S, 12.57. Average particle weight of $(CH_3)_4N^+$ salt by vapor pressure osmometer (acetonitrile): calcd, 230.1; found, 240. ^{1}H nmr (acetone-d_6, 60 MHz) of $(CH_3)_4N^+$ salt, δ 3.47 (12 H, $(CH_3)_4N^+$) and 4.04 (4 H, cage CH.)

Further details on this and other reactions of the $(B_9C_2H_{11})_2M$ complexes will appear in a future publication.

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(2) A. Zalkin, T. E. Hopkins, and D. H. Templeton, *J. Am. Chem. Soc.*, **87**, 3988 (1965).

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(4) R. M. Wing, *J. Am. Chem. Soc.*, **89**, 5599 (1967).

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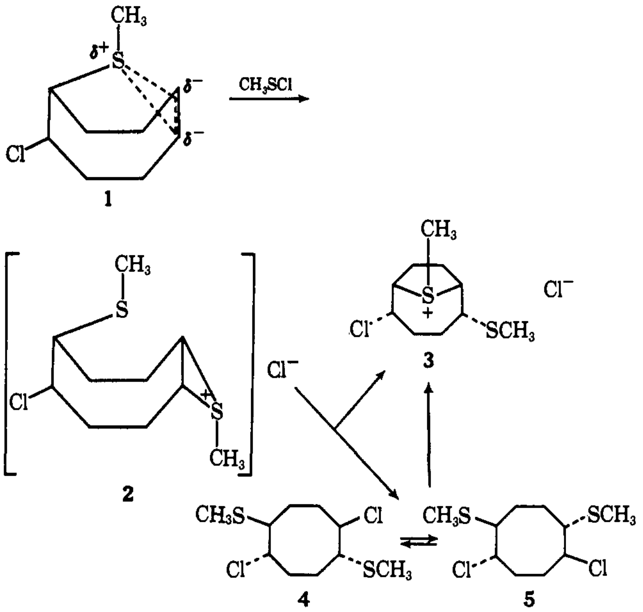
Transannular π-Bond Activation by Sulfur toward Electrophilic Attack

Sir:

A unique case of transannular carbon–carbon bond formation during methanesulfenyl chloride addition to *cis,trans*-1,5-cyclodecadiene has been recently reported.[1] The interaction of a double bond with a cationic center across a ring is well established in this and other ring systems; however, such behavior with an episulfonium ion is unprecedented. It is particularly surprising in the case of the strongly bridging methylthio group since all evidence with such episulfonium ions points toward little charge being developed on carbon.[2]

During attempts to demonstrate a similar transannular carbon–carbon bond formation with 1,5-cyclooctadiene (COD) and methanesulfenyl chloride, an unexpected transannular π-bond activation by the methylthio group was detected which is the subject of the present communication.

Reaction of methanesulfenyl chloride with various amounts of COD ranging from equimolar to 10 *M* excess afforded about 80–90% of diadducts **3–5**, and only 8–13% of monoadduct **1**.[3] This observation is in strong contrast to the highly selective monoadduct formation previously encountered with other dienes.[4] The remarkable propensity for diadduct formation in the present case indicates a considerable activation of the remaining double bond in monoadduct[5] **1** over those in COD toward the attack of sulfenyl chloride.



Apparently a transannular overlapping of the sulfur orbitals with the π bond as depicted in **1** is responsible for this increased nucleophilicity of the double bond. Inspection of a Dreiding model showed that in a twisted tub conformation the sulfur can come within bonding distance above the center of the π bond.

Addition of a second mole of methanesulfenyl chloride must then involve an intermediate such as the episulfonium ion **2**. Ring opening of **2** by chloride in the well-documented *trans* manner[5] would account for the oily diadduct(s) **4** and/or **5** formed in *ca.* 30% yield. More interestingly, intramolecular ring opening of episulfonium ion **2** by the methylthio group results in 2-chloro-5-methylthio-9-methyl-9-thiabicyclo[4.2.1]-nonanesulfonium chloride (**3**), mp 175–177° dec, in *ca.* 50% yield. Mutual isomerization of the oily diadducts **4** and **5** through an episulfonium ion inter-

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(1) J. G. Traynham, G. R. Franzen, G. A. Knesel, and D. J. Northington, Jr., *J. Org. Chem.*, **32**, 3285 (1967).

(2) W. H. Mueller and P. E. Butler, *J. Am. Chem. Soc.*, **88**, 2866 (1966); **90**, 2075 (1968).

(3) All sulfenyl chloride additions during this study were conducted at −20 to −30° with *ca.* 50% methylene chloride solutions of the unsaturate.

(4) W. H. Mueller and P. E. Butler, *Chem. Commun.*, 646 (1966); *J. Org. Chem.*, **33**, 2642 (1968).

(5) The *trans* stereochemical relationship assumed for the monoadduct finds support in similar *trans* additions previously reported in ref 2 and other references cited therein.

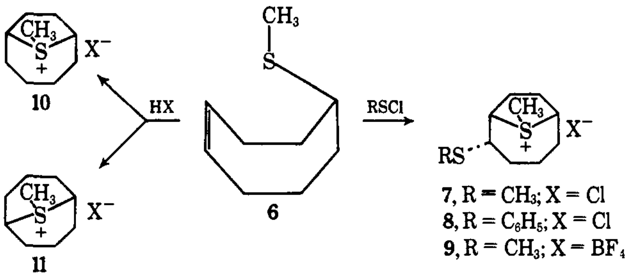
Table I. Nmr Parameters of Bicyclic Sulfonium Ions

Compound[b]	Solvent	Group assignments and chemical shifts,[a] ppm -SCH$_3$	 >$^+$SCH$_3$	 >CHS$^+$<	 >CHS-	 >CHCl
3	SO$_2$	1.96 s	2.78 s	4.37 m	3.25 m	4.50 m
7	SO$_2$	2.08 s	2.74 s	4.28 m	3.18 m	
8	SO$_2$		2.52 s	3.85–4.42 m	3.62 m	
9	CD$_3$CN	2.15 s	2.72 s	4.35 m	3.28 m	
10	SO$_2$		2.51 s	4.18 m		
11	SO$_2$		2.65 s	3.41 m		
11	CF$_3$CO$_2$H		2.99 s	3.77 m		
12	CDCl$_3$	2.16 s			3.01 dq	4.20 dq
13	CDCl$_3$		2.62 s	~4.3 m		

[a] Spectra were determined on a Varian A-60 instrument at ambient temperature. Chemical shifts are measured in parts per million downfield from TMS as internal standard. With SO$_2$ as solvent, CHCl$_3$ (at 7.20 ppm) was used as internal standard. [b] All compounds gave satisfactory elemental analyses.

mediate such as **2** would be expected.[2,6] Consequently slow formation of the crystalline sulfonium chloride **3** should occur. This was indeed observed on standing at room temperature.

The addition of methane- and benzenesulfenyl chloride to 5-methylthiocyclooctene-1 (**6**) was chosen to support the proposed mechanism for the formation of **3** and to aid its structural assignment. The closely related bicyclic sulfonium chlorides **7**, mp 162–164° dec, and **8**, mp 151–152° dec, were isolated in addition to some oily adducts which corresponded to **4** and **5**.



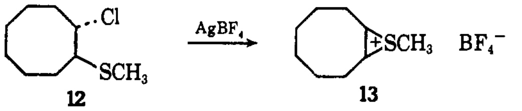
11, **10**, X = Cl or I

Reaction of **7** with silver tetrafluoroborate afforded **9**, mp 103–105° dec.

A more general verification of transannular π-bond activation by the methylthio group as suggested in **1** was obtained from the unusually rapid addition of hydrogen iodide and hydrogen chloride to compound **6**. While sulfenyl chloride additions produced essentially a single sulfonium salt, mixtures of the isomeric products **10** and **11** were obtained with hydrogen halides. Both mixtures, the sulfonium chlorides (mp 184–191° dec) and the sulfonium iodides (mp 198–208° dec), exhibit nearly identical nmr spectra. The chemical shifts of the pertinent signals for the minor product (*ca.* 20–25%) are in excellent agreement with those previously reported for 9-methyl-9-thiabicyclo[3.3.1]-nonanesulfonium iodide (**11**).[7a]

A priori one is tempted to infer a [3.3.1] structure for sulfonium salts **3** and **7–9** from the previously reported formation of this ring system in transannular additions of sulfur dichloride to COD.[7] However, the predominant formation of the [4.2.1] compound **10** in hydrogen halide additions coupled with a comparison of the nmr data in Table I seems convincing evidence in favor of the [4.2.1] ring system. Bridgehead protons appear in general around 4.2–4.4 ppm while they are located *ca.* 0.7 ppm upfield for the [3.3.1]nonane **11**. This sizable deshielding effect seems to be diagnostic for the more strained ring system since it is also found in 7-methyl-7-thiabicyclo[2.2.1]heptanesulfonium iodide[7a] and the corresponding bridged sulfides.[7a,b]

Significant activation of **6** toward methanesulfenyl chloride addition was also observed in competition with cyclooctene. Within the experimental accuracy only **6** (>90%) was consumed from an equimolar mixture of the substrates. The methanesulfenyl chloride–cyclooctene adduct **12** is a nonionic, oily compound which excludes the remote possibility of a stable episulfonium salt rather than the transannular bridging in compounds **3** and **7**. It was, however, possible to generate the stable episulfonium tetrafluoroborate **13**, mp *ca.* 106° dec.



Work to independently synthesize some of these sulfonium salts and thus affirm the [4.2.1] ring system is in progress. Attempts will be made to define the scope of this transannular π-bond activation.

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(7) (a) E. J. Corey and E. Block, *J. Org. Chem.*, 31, 1663 (1966); (b) E. D. Weil, K. J. Smith, and R. J. Gruber, *ibid.*, 31, 1669 (1966); (c) F. Lautenschlaeger, *Can. J. Chem.*, 44, 2813 (1966).

Conversion of Linear Trienes into Bicyclic Boranes *via* Hydroboration–Isomerization and Their Carbonylation. A Simple Synthesis of Angularly Substituted Bicyclic Alcohols

Sir:

We reported recently that certain cyclic polyenes can be readily converted into polycyclic tertiary alcohols *via* hydroboration–carbonylation–oxidation.[1,2] Earlier, Köster and his coworkers reported the syntheses of

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(1) H. C. Brown and E. Negishi, *J. Am. Chem. Soc.*, **89**, 5478 (1967).

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