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(20) *trans*-Mo(CO)₄(PMe₃)₂ and other products have been observed in the reaction of Mo₂Me₄(PMe₃)₄ with CO in refluxing toluene. Cotton, F. A.; Darensbourg, D. J.; Kolthammer, B. W. S. Southwest-Southeast American Chemical Society Regional Meeting, New Orleans, L.A., Dec 10-13, 1980; INOR 235.

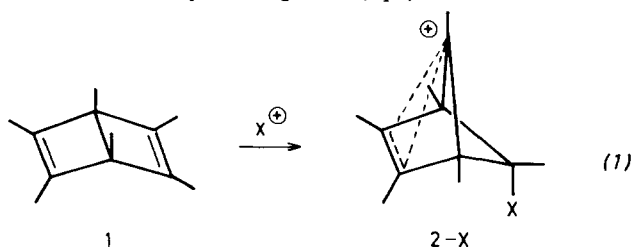
Sulfenium Ion Addition to Hexamethyl(Dewar benzene). A Case for a Hypervalent Sulfonium Ion Intermediate

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The addition of electrophiles to hexamethyl(Dewar benzene) (1) induces its transformation to reactive intermediates that provide a rich array of rearrangement products.¹ In the addition of hetero atom derived electrophiles, i.e., halonium ions, the pivotal intermediate is the bicyclo[2.2.1]hexenyl cation (2), the formation of which is initiated by addition to a double bond from the endo face of 1 followed by rearrangement (eq 1).^{1,2} We find now that



reaction of 1 with sulfenium ion (RS⁺) equivalents involves a significant deviation from this course of reaction.

Phenylsulfenyl chloride (3) and 1 were mixed in equimolar amounts at -120 °C in CH₂Cl₂ under an N₂ atmosphere. The solution became homogeneous at -70 °C and the ¹H NMR spectrum taken immediately revealed in the methyl region three new singlets of equal intensity at δ 1.49, 1.57, and 1.67 (the absorptions for 1 are found at δ 1.55 and 1.05).³ Within 10 min the ¹H NMR spectrum becomes complex, but after warming to room temperature a clean spectrum is obtained which arises from 1 (48% yield) and dichloride 5, formed in 31% yield. The latter is known to be the end product of the chlorination of 1.^{2b} Diphenyl disulfide is also formed.

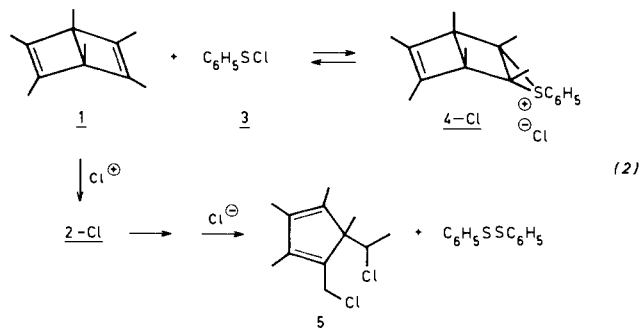
An abbreviated scheme consistent with these observations is given in eq 2. The intermediate immediately formed at low temperature is assigned structure 4-Cl (endo attack, exo orientation of phenyl substituent) consistent with the normal reaction course of sulfenyl halides.⁴ The complicated spectrum that soon appears is probably the consequence of subsequent formation of covalent adducts. However, the formation of 4, as well as any adducts, must be reversible. This is indicated by the failure to obtain sulfur

(1) Review: Hogeveen, H.; Kwant, P. W. *Acc. Chem. Res.* **1975**, *8*, 413 and references cited therein.

(2) (a) Hogeveen, H.; Volger, H. C. *Recl. Trav. Chim. Pays-Bas* **1968**, *87*, 385, 1042; **1969**, *88*, 353. (b) Hogeveen, H.; Kwant, P. W.; Schudde, E. P.; Wade, P. A. *J. Am. Chem. Soc.* **1974**, *96*, 7518. (c) Paquette, L.; Krow, G. *Ibid.* **1969**, *91*, 6107.

(3) For comparison purposes in 2-Cl the methyl absorptions are found at δ 1.64 (3 H), 1.71 (6 H), 1.97 (3 H), and 2.30 (6 H). See: Schaefer, W.; Hellmann, H. *Angew. Chem.* **1967**, *79*, 566.

(4) See, for example: Smit, W. A.; Zefirov, N. S.; Bodrikov, I. V.; Krimer, M. Z. *Acc. Chem. Res.* **1979**, *12*, 282. These authors also discuss the problem whether thiiranium salts have a covalent sulfurane structure or an ionic structure as drawn for 4-Cl.



containing stable adducts as well as by the recovery of 48% of the starting material 1. The other half of the starting material (1) is ultimately irreversibly consumed by chlorination via a chloronium ion from 3.⁵ Reversible thiiranium ion formation has been previously demonstrated by us.⁶

The chloride counterion in 4 is clearly too nucleophilic. Phenylbis(thiophenyl)sulfonium hexachloroantimonate (6) has the less nucleophilic diphenyl disulfide as the leaving group.⁷ On treatment of 1 with 6 in CH₂Cl₂ (this was the only suitable solvent found) a solid formed at low temperatures, but at -60 °C the solution became homogeneous. In the methyl region four new singlets were observed in the ¹H NMR spectrum (60 MHz) at δ 1.10 (3 H), 1.37 (6 H), 1.43 (6 H), and 1.51 (3 H). A small and variable amount of 1 remained; the phenyl absorptions were obscured by diphenyl disulfide. On warming the three absorptions at δ 1.37, 1.43, and 1.51 broaden and coalesce at -43 °C. At -30 °C the spectrum consists of two sharp singlets at δ 1.43 (15 H) and 1.10 (3 H). These spectra are shown in Figure 1. Owing to the limited solubility and stability we have been unable to obtain ¹³C NMR spectra. Above -20 °C the spectrum broadens irreversibly, but after standing for some hours the sharp absorption for hexamethylbenzene appears. A rationalization for these observations is given in eq 3.

At low temperatures 4-SbCl₆ is formed as a solid that at -60 °C rearranges to 7, which is a single geometrical isomer with the phenyl group oriented toward the five-membered ring.⁸ That the structure of the ion is 7 and not 2-SC₆H₅, which has the same symmetry, is shown by the high field positions of the methyl groups in the ¹H NMR spectrum.⁹ Moreover, this structural assignment is in agreement with the observation that quenching with (C₂H₅)₃N gives in 45% yield tricyclic alkene 9¹⁰ as shown in eq 3. This is

(5) With 2 equiv of 3, addition to both double bonds of 1 occurs to give a product: ¹H NMR δ 1.46 (s, 12 H), 1.60 (s, 6 H), and 7.25-7.50 (br abs, 10 H). This is apparently a dithiiranium salt derived from addition of phenylsulfenium ion to both double bonds of 1. The C_{2v} symmetry apparent from the ¹H NMR spectrum is consistent with endo-endo or exo-exo addition.

(6) Bolster, J. M.; Kellogg, R. M. *J. Chem. Soc., Chem. Commun.* **1978**, 630.

(7) Gybin, A. S.; Smit, W. A.; Bogdanov, V. S.; Krimer, M. Z.; Kakyarov, J. B. *Tetrahedron Lett.* **1980**, 383.

(8) No indication for a second isomer could be found from the 360-MHz ¹H NMR spectrum. Examination of models indicates that the isomer drawn has the phenyl group in the least hindered position. The formation of only one of two possible isomers of a thiiranium ion has been observed previously. See, for example: Reynolds, P.; Zonnebelt, S.; Bakker, S.; Kellogg, R. M. *J. Am. Chem. Soc.* **1974**, *96*, 3146. Capozzi, G.; De Lucchi, O.; Lucchini, V.; Modena, G. *Tetrahedron Lett.* **1975**, 2603.

(9) The carbon bound methyl groups in the methyl sulfonium salt of *cis*-2,4-dimethylthietane absorb at δ 1.64 (Trost, B. M.; Schinski, W. L.; Chen, F.; Mantz, I. B. *J. Am. Chem. Soc.* **1971**, *93*, 676), which value should be compared with the chemical shifts for 2-Cl cited in ref 3.

(10) As has been shown (Hogeveen, H.; Zwart, L. *Israel. J. Chem.*, in press) ¹³C NMR spectroscopy provides a powerful tool for structural assignments of these types of compounds. The characteristic chemical shifts are sp² carbon atoms 135-165 ppm; cyclopropane quaternary atoms 29-36 ppm; cyclobutane quaternary atoms 48-60 ppm; bicyclobutane quaternary atoms 19-32 (nonbridgehead) and 37-47 ppm (bridgehead atoms) and the methyl groups 1.5-4 ppm (nonbridgehead connected methyl groups) and 4-9 ppm (bridgehead connected methyl groups). Spectra for 9: ¹H NMR (CDCl₃) δ 0.91 (s, 3 H), 1.05 (s, 3 H), 1.18 (s, 3 H), 1.22 (s, 3 H), 1.34 (s, 3 H), 4.32 (s, 1 H), 4.35 (s, 1 H), 7.1-7.5 (m, 5 H); ¹³C NMR (CDCl₃) δ 4.2 (CH₃), 6.1 (CH₃), 6.4 (CH₃), 7.4 (CH₃), 20.4 (CH₃), 40.0 (C), 44.6 (C), 48.7 (C), 60.2 (C), 62.1 (C), 85.2 (sp² CH₂), 126.2 (aromatic CH, 2x), 127.6 (aromatic C), 128.0 (aromatic CH, 2x), 136.1 (aromatic CH), 158.1 (sp² C).

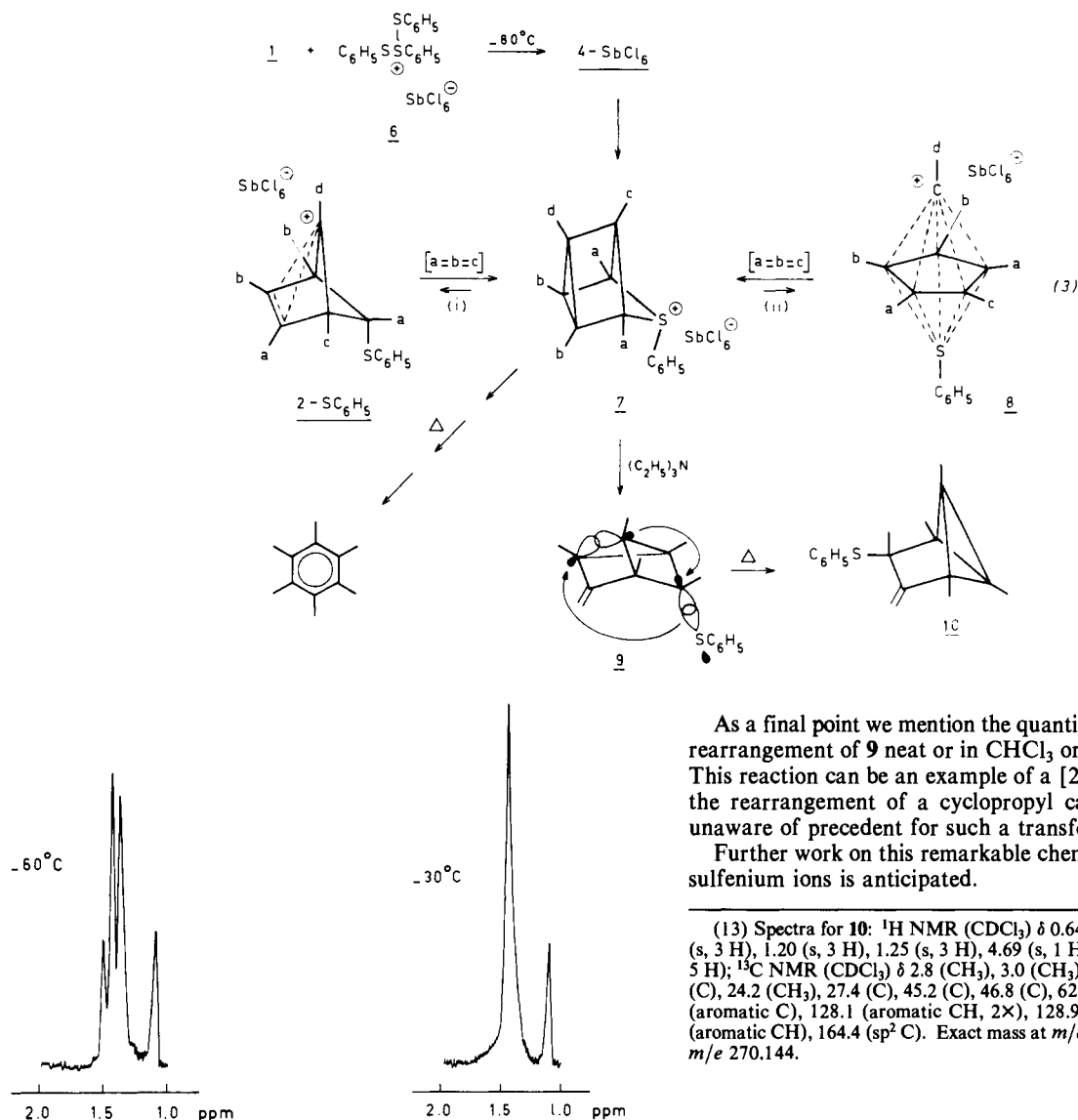
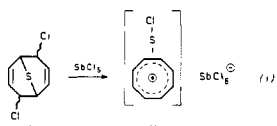


Figure 1. 60-MHz spectrum of (a) **7** at -60°C ; and (b) **8/2-SC₆H₅** at -30°C . Both samples in CH_2Cl_2 solution.

a simple β -elimination product of the sulfonium salt **7**.

The spectral behavior of **7**, as described above, is consistent with a rapid automerization of sulfonium salt **7** via cation **2-SC₆H₅** or, indistinguishably, the highly symmetrical hypervalent sulfonium ion **8**. Either description leads to the observed degeneracy of five methyl groups (see i and ii in eq 3). The data now in hand are not sufficient to allow a decision between those two possibilities. The structure **8**, if it truly exists, can in formal sense be viewed as the pyramidal dication that we have previously described¹ to which a sixfold bonded thiolate ligand has been added opposite to the sixfold bonded carbon atom.^{11,12}

(11) In 1966 in a lecture at Princeton University Lautenschlager suggested that II could arise from I (eq i) on treatment with SbCl_5 . There have been no further reports on this. See: Mueller, W. A. *Angew. Chem.* **1969**, *81*, 475.



(12) See also: (a) Ross, J. A.; Seiders, R. P.; Lemal, D. M., *J. Am. Chem. Soc.* **1976**, *98*, 4327. (b) Kwart, H.; George, T. J. *Ibid.* **1977**, *99*, 5215. (c) Vincent, J. A. J. M.; Schipper, P.; de Groot, Ae.; Buck, H. M. *Tetrahedron Lett.* **1975**, 1989. (d) Kwart, H.; King, K. G.; "d-Orbitals in the Chemistry of Silicon, Phosphorus and Sulfur"; Springer-Verlag: Heidelberg, 1977.

As a final point we mention the quantitative room temperature rearrangement of **9** neat or in CHCl_3 or CH_2Cl_2 to **10** (eq 3).¹³ This reaction can be an example of a $[2 + 2]$ cycloaddition in the rearrangement of a cyclopropyl carbinyl sulfide; we are unaware of precedent for such a transformation.

Further work on this remarkable chemical behavior of **1** with sulfenium ions is anticipated.

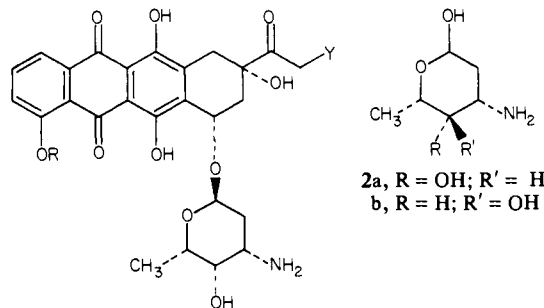
(13) Spectra for **10**: ^1H NMR (CDCl_3) δ 0.64 (s, 3 H), 0.92 (s, 3 H), 1.05 (s, 3 H), 1.20 (s, 3 H), 1.25 (s, 3 H), 4.69 (s, 1 H), 4.82 (s, 1 H), 7.1-7.5 (m, 5 H); ^{13}C NMR (CDCl_3) δ 2.8 (CH_3), 3.0 (CH_3), 6.0 (CH_3), 7.0 (CH_3), 23.9 (C), 24.2 (CH_3), 27.4 (C), 45.2 (C), 46.8 (C), 62.4 (C), 99.2 (sp^2CH_2), 127.9 (aromatic C), 128.1 (aromatic CH, 2 \times), 128.9 (aromatic CH, 2 \times), 136.2 (aromatic CH), 164.4 (sp^2C). Exact mass at m/e 270.143; calcd for $\text{C}_{18}\text{H}_{22}\text{S}$, m/e 270.144.

A Chiral Synthesis of L-Acosamine and L-Daunosamine via an Enantioselective Intramolecular $[3 + 2]$ Cycloaddition

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Anthracycline antibiotics adriamycin (**1a**), daunomycin (**1b**), and carminomycin (**1c**) are highly effective against a wide variety of tumors. The dose-limiting toxicity of these substances has



1a, R = CH_3 ; Y = OH
1b, R = CH_3 ; Y = H
1c, R = Y = H

sparked intensive research in the areas of synthesis of modified