Acknowledgment. We thank the NSF for a departmental grant used to purchase the NMR spectrometer used in this work. We also thank Chevron for a fellowship (G.S.G.) and the Equal Opportunity Fund of UCB for a fellowship (V.V.M). V. W. Day is a Camille and Henry Dreyfus Teacher–Scholar.

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(20) *trans*-$Mo(CO)_4(PMe_3)_2$ and other products have been observed in the reaction of $Mo_2Me_4(PMe_3)_4$ 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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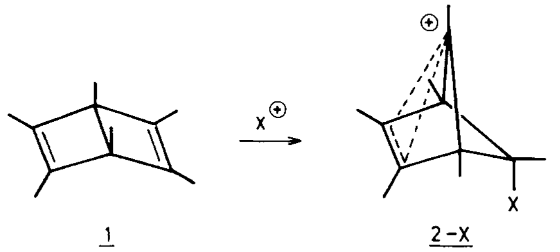
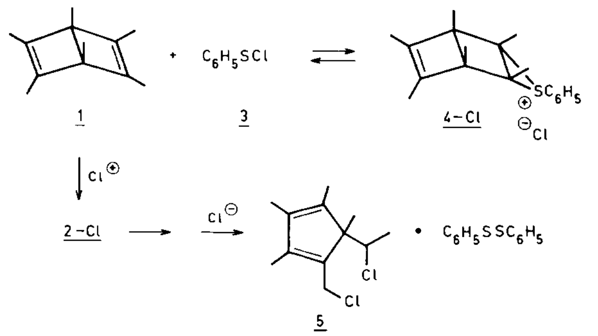
The addition of electrophiles to hexamethyl(Dewar benzene) (**1**) induces its transformation to reactive intermediates that provide a rich array of rearrangement products.[1] In the addition of hetero atom derived electrophiles, i.e., halonium ions, the pivotal intermediate is the bicyclo[2.2.1.]hexenyl 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.



(1)

Phenylsulfenyl chloride (**3**) and **1** were mixed in equimolar amounts at −120 °C in CH_2Cl_2 under an N_2 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 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]



(2)

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 CH_2Cl_2 (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 ^{13}C 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**-$SbCl_6$ 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**-SC_6H_5, 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 $(C_2H_5)_3N$ gives in 45% yield tricyclic alkene **9**[10] as shown in eq 3. This is

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(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.

(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: Raynolds, 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) ^{13}C NMR spectroscopy provides a powerful tool for structural assignments of these types of compounds. The characteristic chemical shifts are sp^2 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 ($CDCl_3$) 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); ^{13}C NMR ($CDCl_3$) δ 4.2 (CH_3), 6.1 (CH_3), 6.4 (CH_3), 7.4 (CH_3), 20.4 (CH_3), 40.0 (C), 44.6 (C), 48.7 (C), 60.2 (C), 62.1 (C), 85.2 (sp^2 CH_2), 126.2 (aromatic CH, 2×) 127.6 (aromatic C), 128.0 (aromatic CH, 2×), 136.1 (aromatic CH), 158.1 (sp^2 C).

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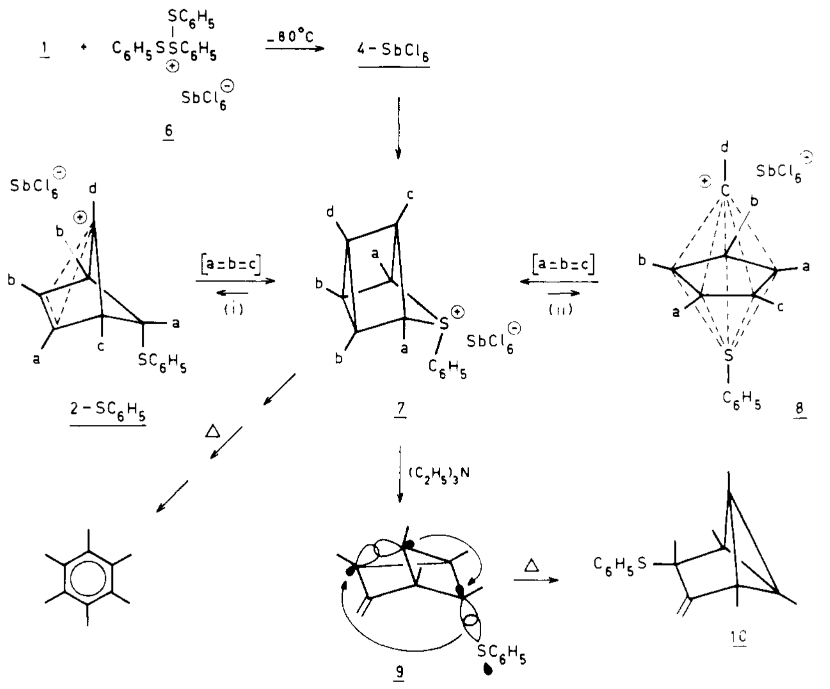

(3)

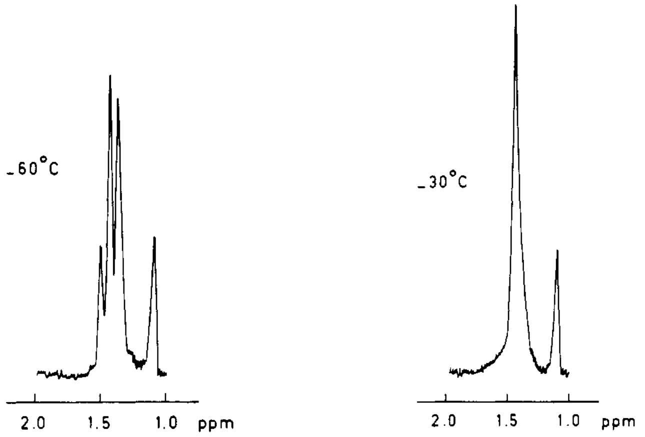

Figure 1. 60-MHz spectrum of (a) **7** at −60 °C; and (b) **8**/**2**-SC$_6$H$_5$ at −30 °C. Both samples in CH$_2$Cl$_2$ solution.

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**-SC$_6$H$_5$ 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 described[1] to which a sixfold bonded thiolate ligand has been added opposite to the sixfold bonded carbon atom.[11,12]

As a final point we mention the quantitative room temperature rearrangement of **9** neat or in CHCl$_3$ or CH$_2$Cl$_2$ to **10** (eq 3).[13] This reaction can be an example of a [$2_s + 2_a$] 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.

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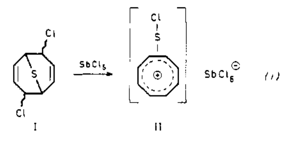
(11) In 1966 in a lecture at Princeton University Lautenschlager suggested that II could arise from I (eq i) on treatment with SbCl$_5$. There have been no further reports on this. See: Mueller, W. A. *Angew. Chem.* **1969**, *81*, 475.



(i)

(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.

(13) Spectra for **10**: ^{1}H 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^2 CH$_2$), 127.9 (aromatic C), 128.1 (aromatic CH, 2×), 128.9 (aromatic CH, 2×), 136.2 (aromatic CH), 164.4 (sp^2 C). Exact mass at *m/e* 270.143; calcd for C$_{18}$H$_{22}$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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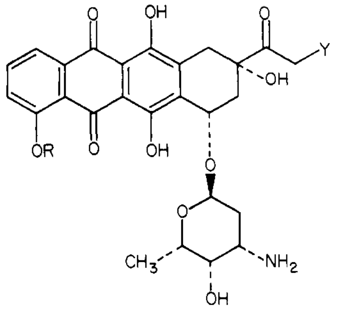
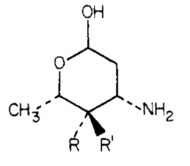
Anthracycline antibiotics adriamycin (**1a**), daunomycin (**1b**), and carminomycin (**1c**) are highly effective against a wide variety of tumors. The dose-limiting toxicity of these substances has sparked intensive research in the areas of synthesis of modified



1a, R = CH$_3$; Y = OH
b, R = CH$_3$; Y = H
c, R = Y = H



2a, R = OH; R' = H
b, R = H; R' = OH

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