Episulfonium Salts. II. Detection of an Unusual Intermediate in the Reaction of a Stable Episulfonium Salt with Chloride Ion[1]

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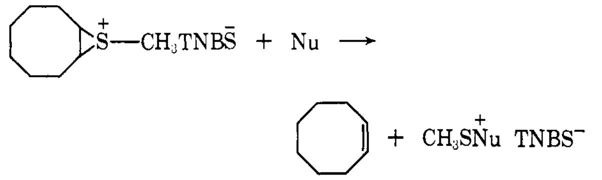
Abstract: The reaction between cyclooctene-S-methylepisulfonium 2,4,6-trinitrobenzenesulfonate, **1**, and tetraphenylarsonium chloride in perdeuterionitromethane was studied by nmr spectrometry. An unusual intermediate was shown to be present by the rise and decay of a signal which could be attributed to its S-methyl group. Solutions of the intermediate, 9-chloro-9-methyl-9-thiabicyclo[6.1.0]nonane, **3**, were stable for at least 30 min at −5°. Decomposition of **3** to *trans*-1-chloro-2-(methylthio)cyclooctane, **2**, was accomplished by the addition of excess chloride ion at −5°, or by warming to room temperature. Extended Hückel MO calculations on 1-chloro-1-methyl-1-thiacyclopropane, **4** (a model for **3**), were carried out in order to explore possible bonding schemes for this intermediate.

On the basis of both kinetic and stereochemical evidence, the known *trans* ionic addition of sulfenyl halides to alkenes has been postulated to involve episulfonium cations as intermediates.[4] Recent studies of the reaction of methanesulfenyl and benzenesulfenyl chloride with alkenes[5,6] and allenes[7] have attempted to correlate the direction of ring opening of the proposed episulfonium intermediate with various steric and electronic factors present in the olefinic substrates. Until recently, however, no comprehensive study of the reaction of a stable episulfonium salt with nucleophiles has been reported. The results of that study[8] showed that the sulfur atom of cyclooctene-S-methylepisulfonium 2,4,6-trinitrobenzenesulfonate (**1**) has the remarkable ability to coordinate with a wide variety of both charged and uncharged nucleophilic species, resulting in the production of cyclooctene and a sulfenyl compound (eq 1).



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Reactive sulfenyl compounds such as methanesulfenyl chloride, which would be formed when **1** reacts with chloride ion (eq 1, Nu = Cl^-, $TNBS^-$ = 2,4,6-trinitrobenzenesulfonate anion), were trapped by a large excess of cyclohexene that was present in the system.

The production of quantitative yields of cyclooctene and 1-chloro-2-(methylthio)cyclohexane from the reaction of **1** with chloride ion in the presence of cyclohexene suggested that it should be of interest to study this reaction by nmr techniques in the absence of a methanesulfenyl chloride interceptor. Thus, this technique might allow the direct observation of methanesulfenyl chloride or another intermediate. If another intermediate were formed, it might be possible to obtain its entire nmr spectrum at low temperature. This paper describes the results which were obtained from an nmr study of the reaction between **1** and tetraphenylarsonium chloride.

Results

Equivalent amounts of 0.25 *M* solutions of **1** and tetraphenylarsonium chloride in perdeuterionitromethane were mixed at room temperature in an nmr tube. The 60-MHz nmr spectrum, which was immediately recorded at 37°, showed two clearly defined singlets at 122 and 128 Hz downfield from TMS. The upfield singlet was the stronger in intensity immediately after mixing. Seven minutes after mixing, the intensities of the two signals were approximately equal. After 15 min, the signal at 122 Hz had disappeared and the resulting spectrum was superimposable on that of 1-chloro-2-(methylthio)cyclooctane (**2**). The nmr spectrum of **2** showed a singlet at 128 Hz attributable to the S-methyl group. At no time during the reaction period could a signal at 158 Hz be detected for the methyl group of **1** or at 171 Hz for methanesulfenyl chloride. Furthermore, no signal could be detected in the olefinic region of the spectrum, a fact which indicates the absence of cyclooctene.

The two initial solutions were then cooled to −5° before mixing. Again, equivalent amounts of each were added to an nmr tube. The spectrum, obtained at −5° (Figure 1, top), showed no detectable signal at 128 Hz. These solutions were stable for periods up to 30 min at −5° with no evidence of a signal that would indicate the presence of **2**. If the solution were taken from the nmr spectrometer and allowed to warm to room temperature, the spectrum of **2** slowly appeared. Alternatively, the addition of a 20% excess of chloride ion immediately produced the spectrum of **2** at −5° (Figure 1, center). At higher spectrum amplitudes, signals at 158 and 150 Hz (H_2O) were detected, but no signal was observed that would indicate the presence of either cyclooctene or methanesulfenyl chloride.

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[1] This work was supported by the National Science Foundation under Grant No. GP-8594.

[2] U. S. Public Health Service Environmental Sciences Trainee, 1967–1969.

[3] To whom inquiries should be directed.

[4] (a) N. Kharasch and C. M. Buess, *J. Am. Chem. Soc.*, **71**, 2724 (1949); (b) N. Kharasch and A. J. Havlik, *ibid.*, **75**, 3734 (1953); (c) W. L. Orr and N. Kharasch, *ibid.*, **75**, 6030 (1953); (d) D. R. Hogg and N. Kharasch, *ibid.*, **78**, 2728 (1956).

[5] W. A. Thaler, W. H. Mueller, and P. E. Butler, *ibid.*, **90**, 2069 (1968).

[6] W. H. Mueller and P. E. Butler, *J. Org. Chem.*, **33**, 2111, 2643 (1968).

[7] W. H. Mueller and P. E. Butler, *ibid.*, **33**, 1533 (1968).

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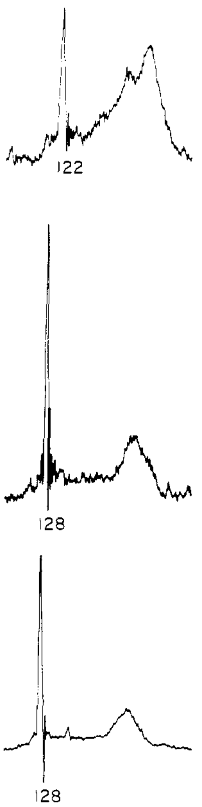


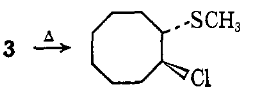
Figure 1. The 60-MHz spectra (in CD_3NO_2) of cyclooctene-S-methylepisulfonium 2,4,6-trinitrobenzenesulfonate in the presence of chloride ion: top, stoichiometric amounts at −5°; center, excess chloride ion at −5°; bottom, 1-chloro-2-(methylthio)cyclooctane at −5°.

Discussion

A consideration of the nmr data can lead only to the conclusion that an intermediate, **3**, was formed during the reaction between **1** and chloride ion. The fate of this intermediate can be adequately described by eq 2–5.

$$1 + Cl^- \xrightarrow{-5°} 3 \qquad (2)$$

$$3 \underset{K_{eq}<<1}{\rightleftharpoons} CH_3SCl + \qquad (3)$$

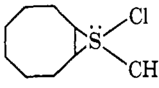


$$3 \xrightarrow{\Delta} \qquad (4)$$

2

$$3 + Cl^- \xrightarrow{-5°} 2 \qquad (5)$$

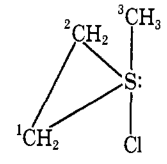
It is of interest to note that the broad, unresolved multiplet upfield from the methyl signal of **3** is nearly superimposable on a similar signal found in the nmr spectrum of **1**. It therefore appears that the cyclooctyl portion of **1** remains essentially undisturbed in the process described by eq 2. The position of the signal for the methyl group of **3** is highly indicative that the process of bringing a chloride ion up to **1** puts more electron density on this methyl group than on the methylthio group of **2**. These data are consistent with the previously reported observation[8] that the sulfur atom of **1** shows a marked tendency for coordination with nucleophiles. Furthermore, the remarkable stability of **3** and the apparently high electron density on its methyl carbon atom are inconsistent with an ion pair formulation for its structure. Any proposed structure for **3** must therefore include some bond formation between sulfur and chlorine. The structure 9-chloro-9-methyl-9-thiabicyclo[6.1.0]nonane is consistent with all existing data.



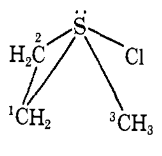
3

Compounds containing quadrivalent sulfur atoms are not unknown in the literature of organosulfur chemistry. Some examples of known compounds include the SF_4 molecule, and alkyl- and arylsulfur trichlorides and trifluorides.[9–12] Moreover, tetravalent sulfur intermediates have been proposed in the chlorinolysis of both thioethers[13,14] and arenesulfenyl chlorides.[15]

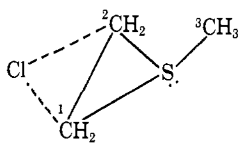
In order to gain a fuller understanding of the bonding about the sulfur atom of **3** and the possible role that the sulfur 3d orbitals might play in its stability, LCAO–MO calculations were carried out on a number of model "compounds," **4a**, **4b**, **4c**, **5**, and **6**, using a modification of the extended Hückel molecular orbital theory developed by Hoffmann.[16–18] This theory has enjoyed some success in the calculation of the correct geometries of the pentavalent phosphorus chlorofluorides.[17]



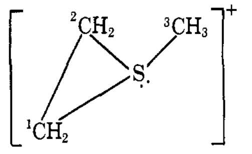
4a



4b



4c



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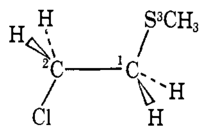

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In extended Hückel calculations the diagonal Hamiltonian matrix elements (H_{ii}) are usually estimated from atomic valence state ionization energies (VSIE's). In our calculations, the VSIE's were obtained from the tables of Basch, Viste, and Gray[19] and were corrected for the calculated atomic charge. All off-diagonal Hamiltonian matrix elements (H_{ij}) were estimated by the Wolfsberg–Helmholz approximation with K =

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(9) K. R. Brower and I. B. Douglass, *J. Am. Chem. Soc.*, 73, 5787 (1951).

(10) I. B. Douglass, K. R. Brower, and F. T. Martin, *ibid.*, 74, 5770 (1952).

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(19) H. Basch, A. Viste, and H. B. Gray, *Theoret. Chim. Acta*, 3, 458 (1965).

1.75.[20] The overlap matrix was calculated from the Clementi double ζ functions[21] for the atomic orbitals of each atom of the model "compounds" and their cartesian coordinates using the method of Rettig and Drago.[22] Preliminary calculations were carried out using an overlap matrix that was calculated from Slater functions and included the 3d orbitals using the same method. The overlap matrix was computed only once for each calculation and was not adjusted for changes in molecular charge distribution as the molecule was iterated to charge self-consistency.

By using the modified program of Hoffmann, with the Clementi overlap basis set included, it was possible to calculate the overlap matrix, set up the Hamiltonian matrix, solve the secular equation, and carry out a Mulliken population analysis[23] on each hypothetical model.

Structures **4a** and **4b** are models for a hypothetical 1-chloro-1-methyl-1-thiacyclopropane having two possible geometries about sulfur: trigonal bipyramidal (**4a**) and square pyramidal (**4b**); **4c** is a model for an ion pair prior to the opening of an ethylene-S-methylepisulfonium cation by chloride ion; **5** is a model for the episulfonium cation itself; and **6** is a model for the ring-opened product. Bond distances (in Ångströms) in **4** and **5** were C–H, 1.09; C–S, 1.80; S–Cl, 1.99; C–C, 1.48; and in **4c** were C–Cl, 1.77. In **6**, all distances were the same, except that the carbon–carbon distance was lengthened to 1.54 Å. In the pseudo-square-pyramidal case, **4b**, the CH_3SCl bond angle was 110°, with the plane containing these atoms bent down from the ring plane by 105°. The geometry of **4c** was chosen such that the chlorine atom was in the plane of the ring and the methyl group was placed at an angle of 54.5° out-of-the-ring plane. The geometry of **5** was the same as **4c** but with the chlorine atom removed. All bond angles in **6** were 109.5°.

Unhybridized s and p orbitals were used for the calculations reported here (*vide infra*) because the early calculations for the various structural types (**4a**, **4c**, **5**) showed that the 3d orbitals appeared as a nonbonding set. Furthermore, the total electronic energy of each system did not change appreciably when the 3d orbitals were not included. These findings are consistent with the findings of other authors[18,24–27] that 3d orbitals make negligible contributions to bonding in compounds of the later third row elements. However, the same authors have shown that calculated charge distributions and dipole moments must be treated with some reservations in calculations which do not include the 3d orbitals. It seems that the 3d contribution for third row elements lies mainly in small $3d_\pi$–p_π interactions which provide higher electron densities for the second row atom.

The calculations reported in the present paper were carried out on **4a**–**c**, **5**, and **6** without the inclusion of the sulfur 3d orbitals because the main interest centered upon a description of bonding in these models, rather than on more quantitative descriptions of molecular properties.

The calculations show that **4a**–**c** and **5** can be formed from a series of multicenter molecular orbitals. The form of these orbitals does not appear to change when the 3d orbitals of sulfur are included in the calculations. The sulfur–chlorine bond in **4a** and **4b** appears to have some ionic character. The calculated charges on the carbon, sulfur, and chlorine atoms are included in Table I. It is of interest to note that the trend in calculated charges for the S-methyl group (C-3) follows nearly that which would be expected from the nmr data on the reaction of **1** with chloride ion as the presence of **1**, then **3**, and finally **2** is recorded.

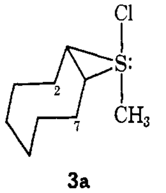
Table I. Calculated Charge Densities and Total Energies for Species **4**, **5**, and **6**

Species	Charges C(1)	C(2)	C(3)	S	Cl	Total energy, eV
4a	0.054	0.054	−0.053	0.271	−0.330	−499
4b	−0.051	−0.038	0.024	0.278	−0.159	−511
4c	0.028	0.028	0.054	0.155	−0.234	−489
5	0.127	0.127	0.107	0.350		−460
6	0.032	0.059	0.017	−0.040	−0.083	−514

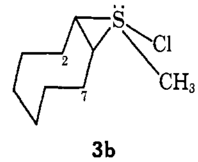
Table I also includes the calculated sum of all one-electron energies for the model compounds. These data indicate a calculated order of stability of **6** > **4b** ≫ **4a** ≫ **4c**. The episulfonium cation is not included in this order because of the absence of the chlorine atom. The numbers must also be taken with some reservation, as the calculations do not explicitly include electron–electron or nuclear repulsion terms. However, if the numbers can be taken only as being indicative of a trend, then the same trend is also apparent in the Mulliken overlap populations calculated for **4a**, **4b**, and **4c**.

The overlap population has been proposed[23] as a measure of bond strength. Positive and negative overlap populations correspond to bonding and antibonding interactions, respectively. The overlap populations between sulfur and chlorine indicate a weakly antibonding interaction in **4a** and a bonding interaction in **4b**. On the other hand, the overlap populations between chlorine and the ring carbons of **4c** are indicative of strongly antibonding interaction.

The fact that the calculations reveal that **4b** is the most stable "isomer" of **4** on the basis of total electronic energy is quite interesting from another standpoint. Models of **3** indicate that an arrangement about sulfur similar to **4a** (**3a**) would give rise to unfavorable van der Waals interactions between the hydrogen atoms bound to the 2- and 7-carbon atoms and either the methyl group or the chlorine atom. These constraints are removed assuming a geometry similar to that of **4b**



3a



3b

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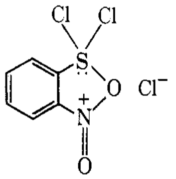
(**3b**). Thus, the observation of **3** due to its remarkable stability arises from a fortunate combination of electronic and steric factors.

The existence of a species such as **3**, which is a compound containing the elements of cyclooctene and methanesulfenyl chloride (with some ionic character in the sulfur–chlorine bond), raises some doubts about the universal role of episulfonium salts in the ionic additions of sulfenyl halides to olefins. Furthermore, the result depicted by eq 5 in which **3** apparently is subjected to nucleophilic attack by chloride ion at carbon to give **2** (the product of *trans* addition of methanesulfenyl chloride to cyclooctene) raises further doubts about the accepted mechanism of sulfenyl halide additions.

After Kharasch's work on the addition of 2,4-dinitrobenzenesulfenyl chloride to alkenes, his proposal of episulfonium salts as intermediates[4] was generally accepted. Although no further kinetic studies have been reported on the addition of sulfenyl halides that do not contain an *o*-nitro group, the assumption has been accepted that the intermediacy of episulfonium salts applied to all such additions. The role of the *o*-nitro group in stabilizing the 2,4-dinitrobenzenesulfenium cation was described,[28] but a bonding interaction between oxygen of a nitro group and sulfur of an episulfonium salt has not been postulated, even though bonding capacities remain optimum.

The possible role of an *o*-nitro group is best seen in the work of Givens and Kwart[15] on the chlorinolysis of 2-nitrobenzenesulfenyl chlorides, in which an ion pair having the structure **7** has been postulated as a key intermediate. In view of the remarkable affinity of the sulfur of **1** for nucleophilic centers, it would seem that the episulfonium salt postulated by Kharasch[4] might be represented by structure **8** (eq 6) instead of a "free" episulfonium salt, **9**.



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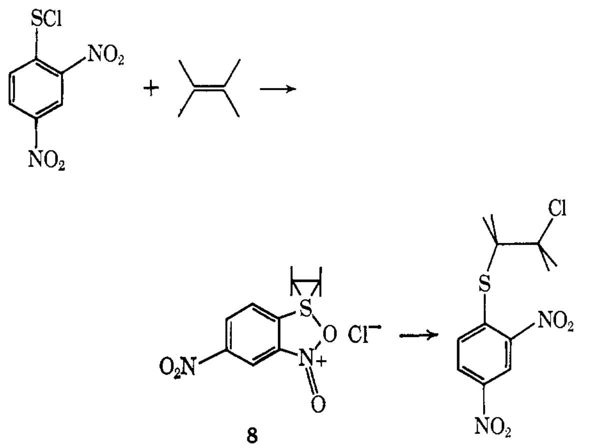

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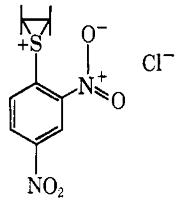

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Although it is difficult to generalize from our system to other episulfonium salts (or to extend the experimental study because of their present unavailability), the question of the mechanism of additions of sulfenyl compounds to alkenes must be reopened. It is imperative that the role of episulfonium salts in these reactions under a variety of conditions be examined. Of paramount importance is the effect of solvent dielectric constant on the rates and rate laws of the addition to alkenes of sulfenyl halides which do not have *o*-nitro groups, because "free" and "nucleophile coordinated" episulfonium cations might be differentiated by such studies.

Experimental Section

Cyclooctene-S-methylepisulfonium 2,4,6-trinitrobenzenesulfonate was prepared according to the method of Pettitt and Helmkamp.[29]

Nmr spectra were recorded on a Varian Associates A-60 nmr spectrometer. Temperature calibration was accomplished by observing the chemical shift of the hydroxyl proton of methanol as it varied with temperature. Molecular orbital calculations were carried out on an IBM 360/50 computer.

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