Degenerate Interconversions of Sulfonium Ions Involving Intramolecular Nucleophilic Displacement by Neighboring Sulfide Sulfur. The Question of an Intermediate in the SN2 Displacement[1]

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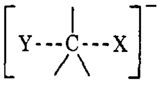
Abstract: The generation of a potential benzylic cation α to the 9 position of anthracenes, which are substituted with arylthio substituents at the 1 and 8 positions, results in formation of cyclic sulfonium ions, 2-thioniaaceanthrenes **3**, **4**, and **5**. The rapid degenerate rearrangement of these sulfonium ions, with the central carbon alternating in attachment to the two flanking arylthio substituents, the "bell-clapper rearrangement," has been studied kinetically employing nmr line-shape analysis, both directly using peaks assigned to substituents on the arylthio rings and indirectly using peaks for methyl substituents on the central carbon. The cis–trans isomerization responsible for coalescence of these methyl peaks is 75% as fast as the bell-clapper rearrangement followed directly, and orders of magnitude faster than the cis–trans isomerization of sulfonium ion **2**, which lacks the neighboring arylthio substituent. This is in accord with the suggestion that the same phenomena are reflected in both rate processes. The conclusion that this intramolecular nucleophilic displacement proceeds by a mechanism near the SN2 extreme is supported by the following observations. The rate of this rearrangement is insensitive to substitution on the central carbon, to gegenion nucleophilicity, and substitution on the anthracene ring. The acceleration seen upon going to more polar media or higher dilution is ascribed to loss of ground-state stabilization associated with gegenion placement in the ion pair. Effects of polar substituents on the arylthio rings (ρ 1.03) are also consistent with predominant ground-state stabilization of the cyclic sulfonium ions. The methanolysis of 2-thioniaaceanthrene cations, involving attack at the 6 position, is 18-fold faster for **3a**, with its neighboring arylthio substituent, than for **2**, which lacks such a substituent. Implications of this observation with respect to the possible intermediacy of a pentacoordinate carbon species are discussed.

The 1953 Doering–Zeiss[3] mechanism for solvolysis suggested the possibility that the SN2 displacement proceeds through a metastable intermediate (**1**) in



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which both entering nucleophile Y and leaving group X are bound to the pentacoordinate central carbon.

Winstein's elusive[4] merged mechanism for substitution and elimination, which received considerable attention a few years ago,[5] employed such an intermediate, common to both substitution and elimination. A somewhat related hypothesis involving solvated ion-pair intermediates in the SN2 reaction has recently been championed by Sneen.[6]

Pentacoordinate carbon species **1** differs from CH_5^+ and its analogs, which were first encountered in mass spectrometry,[7] and more recently obtained by the protonation of alkanes in super acids,[8] in that these cationic species involve electron deficient bonds, which can give pentacoordination at carbon with a bonding scheme involving only the eight valence electrons of carbon. Such electron-deficient bonds are represented by dotted lines in the structures usually drawn for nonclassical carbonium ions.[9]

The bonding in **1**, also represented here by dotted lines, is electron rich, rather than electron deficient, involving two more electrons than are normally accommodated in the valence shell of the central carbon. Analogous hypervalent[10] species in which the central atom is from the second or higher row of the periodic table are well known. Theoretical treatments of bonding in hypervalent compounds of xenon[11] (XeF_2), halogen[12] (ICl_2^-, etc.), sulfur[13] (SF_4 and the sulfuranes), and phosphorus[14] (PCl_5 and the phosphoranes) are qualitatively in accord with that proposed by Rundle[15] for such compounds. In this scheme, the two most electronegative ligands at the hypervalent center prefer-

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(2) From the Ph.D. Thesis of R. J. B., University of Illinois, 1971. Fellowship support from the University of Illinois, the Proctor and Gamble Co., the National Science Foundation, and the National Institutes of Health is gratefully acknowledged.

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(11) J. G. Malm, H. Selig, J. Jortner, and S. A. Rice, *Chem. Rev.*, **65**, 199 (1965).

(12) E. E. Havinga and E. H. Wiebenga, *Recl. Trav. Chim. Pays-Bas*, **78**, 724 (1959).

(13) R. D. Willet, *Theor. Chim. Acta*, **2**, 393 (1964).

(14) A. Rauk, L. C. Allen, and K. Mislow, *J. Amer. Chem. Soc.*, **94**, 3035 (1972); J. B. Florey and L. C. Cusachs, *ibid.*, **94**, 3040 (1972); R. Hoffmann, J. M. Howell, and E. L. Muetterties, *ibid.*, **94**, 3047 (1972), and references cited in these works.

(15) R. J. Hach and R. E. Rundle, *ibid.*, **73**, 4321 (1951); R. E. Rundle, *ibid.*, **85**, 112 (1963); R. E. Rundle, *Surv. Progr. Chem.*, **1**, 81 (1963).

Table I. Chemical Shifts (δ) for Substituted 2-Thioniaaceanthrene Cations (**2**, **3**, **4**, and **5**) in Trifluoroacetic Acid at −10°

Assignment	Chemical shift for compound										
	2[a,c]	**3a**[d]	**3b**[d]	**3d**[c]	**4a**[b,e]	**4b**[e]	**4c**[e]	**4d**[e]	**4e**[e]	**5b**[c]	**5b**[e]
3-H		8.21	8.12	8.23	8.1	8.11	8.17	8.0	8.15		
4-H		7.98	7.94	7.47	7.8	7.86	7.91	7.84	7.94		
5-H		8.62	8.58	8.61	8.6	8.70	8.7	8.72	8.70		
R_3	8.89	9.03	8.95	9.00	3.26	3.27	3.31	3.30	3.23		
7-H		8.43	8.33	8.36	8.6	8.66	8.7	8.72	8.56		
8-H		7.80	7.60	7.5	7.8	7.75	7.78	7.70	7.70		
9-H		8.21	8.12	8.23	8.1	8.06	8.17	8.0	8.03		
R_1	2.52	2.99	2.94	2.95	6.43	6.42	6.4	6.58	6.34		
R_2	2.08	2.50	2.48	2.48	6.10	6.05	6.04	6.27	5.98	6.21	6.24
Y			2.48	1.34		2.45	2.32	1.35	3.96	2.44	2.51
			2.29	1.21		2.16	2.05	1.21	3.84	2.19	2.20

[a] 30° in ethylene carbonate. [b] −20° in $SOCl_2$. [c] X = BF_4. [d] X = trifluoroacetate (TFATE). [e] X = Cl.

entially[16] occupy apical positions of a trigonal bipyramid in which the three equatorial positions are occupied by the least electronegative ligands and/or lone pairs of electrons. The apical bonds in such structures are viewed as three-center four-electron bonds which are rather well described in MO's using the central atom p_z orbital and a p orbital from each ligand. Two electrons occupy the bonding MO of this set and two are in the approximately nonbonding MO, putting electron density only on the ligands. Most of the theoretical treatments point to relatively small bonding contributions from d orbitals and outer s orbitals. This suggests the possibility that hypervalent species might exist with central atoms from below the second row of the periodic table, atoms in which low-lying d orbitals are not available. Indeed, the Pimentel[17] theory of the hydrogen bond suggests that such symmetrically hydrogen-bonded species as HF_2^- might properly be viewed as hypervalent compounds of hydrogen.

During the course of the research of this paper, which was designed as a search for a hypervalent carbon species, accounts continued to appear of explorations of the energy surfaces for the S_N2 reaction, using both theoretical[18,19] and experimental[20,21] approaches.

The reaction of $Fe_3(CO)_{12}$ with 1-pentyne gives a small amount of a compound in which a carbon atom was shown, in the X-ray crystal structure, to be bonded to five iron atoms in a pyramidal cage-like structure.[22] There have been no reports of pentacoordinate carbon compounds analogous to **1**, however, species which clearly involve hypervalent bonding of the type of interest here.

Experimental Section

New compounds were prepared as described in the accompanying paper.[23] Varian A-60A, A-56/60, HA-100, and HR-220 nmr spectrometers were employed, using the Varian temperature controller, with calibration, for the rate studies. Chemical shifts are quoted relative to internal tetramethylsilane.

Curve-fitting techniques were used to obtain rate constants using a computer program[24] to obtain a least-squares fit to the experimental curves using the equations of Gutowsky and Holm.[25] Exchange processes were followed at several temperatures using nmr peaks of methyl groups in **3**, **4**, and **5** as probes. Rate constants quoted for 25° were obtained from a least-squares Arrhenius treatment of all the data for five or six kinetic runs over a temperature range of 15–35°.

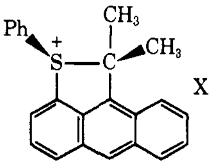
The methanolyses of 2-thioniaaceanthrene cations (**2** and **3b**) were followed for at least 3 half-lives at various temperatures. Methanol solutions of known concentrations of **2** and **3b** were placed in a 5-cm path length, temperature-regulated uv cell and the absorbance of the kinetic sample was recorded *vs.* time at the absorption maximum near 410 nm using a Cary 14 recording spectrophotometer.

The temperature of the cell was regulated by a circulating temperature bath maintaining a temperature within ±0.1°.

Solutions of **4a** (X = Cl) in methanol-*d* or **4b** (X = Cl) in TFA-*d* showed no decrease in the intensity of the methylene proton peaks near δ 6.4 and 6.1 upon standing at room temperature for several hours.

Results

The synthesis and characterization of several substituted thioniaaceanthrenes (**2**, **3**, **4**, and **5**) are described in the preceding paper.[23] Proton chemical shift data important in this paper are recorded in Table I.



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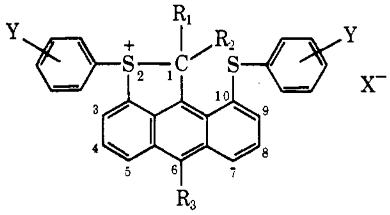

3, $R_1 = R_2 = CH_3$; $R_3 = H$
4, $R_1 = R_2 = H$; $R_3 = CH_3$
5, $R_1 = R_2 = H$; $R_3 = Ph$
a, Y = H
b, Y = 4-CH_3
c, Y = 3-CH_3
d, Y = 4-$C(CH_3)_3$
e, Y = 4-OCH_3

Room-temperature nmr spectra of **2** show that the two methyl groups, the one cis to the sulfonium phenyl and the other trans, are indeed nonequivalent (Δδ *ca.* 0.5 ppm). Coalescence of these two peaks is

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(16) E. L. Muetterties and R. A. Schunn, *Quart. Rev., Chem. Soc.*, **20**, 245 (1966); R. J. Gillespie, *J. Chem. Educ.*, **47**, 18 (1970).

(17) G. C. Pimentel, *J. Chem. Phys.*, **19**, 446 (1951).

(18) J. P. Lowe, *J. Amer. Chem. Soc.*, **93**, 301 (1971), and references therein.

(19) R. Gleiter and R. Hoffmann, *Tetrahedron*, **24**, 5899 (1968).

(20) R. Breslow, L. Kaplan, and D. LaFollette, *J. Amer. Chem. Soc.*, **90**, 4056 (1968).

(21) L. Tenud, S. Faroog, J. Seibl, and A. Eschenmoser, *Helv. Chim. Acta*, **53**, 2059 (1970). We wish to thank Professor Eschenmoser for acquainting us with this work prior to its publication.

(22) E. H. Bray, L. F. Dahl, W. Hübel, and D. L. Wampler, *J. Amer. Chem. Soc.*, **84**, 4633 (1962).

(23) R. J. Basalay and J. C. Martin, *ibid.*, **95**, 2565 (1973).

(24) The Fortran computer program CURVE2 prepared by J. Jonas, A. Allerhand, and H. S. Gutowsky, *J. Chem. Phys.*, **42**, 396 (1965), performs the line-shape analysis for an uncoupled exchanging AB system with equal populations at sites A and B. This program was modified to allow the option of a dichotomous search for a best fit of calculated curves to experiment varying not only the exchange rate but also the chemical shift difference between A and B and/or the peak width.

(25) H. S. Gutowsky and C. H. Holm, *J. Chem. Phys.*, **25**, 1228 (1956).

Table II. Rates of Degenerate Exchange Reactions of 2-Thioniaaceanthrene Cations from Nmr Line-Shape Analysis

Kinetic series	Compd (X)	Solvent	Concn, *M*	$k_{25°}$, sec^{-1} [a]	ΔH^*, kcal/mol	ΔS^*, eu	Temp range (°C)
1	**3d** (BF_4)	TFA	0.40	106[b]	13.0 ± 0.5	−5.7 ± 1.9	2.5 to 21
2	**3d** (BF_4)	TFA	0.40	138[c]	12.6 ± 0.5	−6.6 ± 2.0	−8 to 8
3	**4b** (Cl)	TFA	0.30	37[c]	12.2 ± 0.7	−10.6 ± 2.4	20 to 37
4	**4b** (Cl)	$SOCl_2$	0.53	28[c]	9.8 ± 0.7	−19.1 ± 2.2	14 to 32
5	**4b** (Cl)	CH_3OH	0.30	9 1[c]	15.3 ± 0.7	3.0 ± 2.2	30 to 50
6	**4b** (BF_4)	TFA	0.54	25[c]	14.2 ± 0.6	−4.4 ± 1.9	25 to 45
7	**4c** (Cl)	TFA	0.35	72[c]	15.6 ± 0.5	2.3 ± 1.8	10 to 30
8	**4d** (Cl)	TFA	0.14	61[c]	11.9 ± 0.5	−10.4 ± 1.8	0 to 20
9	**4d** (Cl)	TFA	0.07	67[c]	12.0 ± 0.5	−9.8 ± 1.7	−5 to 15
10	**4d** (Cl)	TFA	0.03	72[c]	10.7 ± 0.5	−14.2 ± 1.7	−5 to 15
11	**4d** (Cl)	$COCl_2$	0.50	41[c]	11.2 ± 0.7	−13.5 ± 2.6	−3 to 10
12	**4e** (Cl)	TFA	0.50	18[c]	14.3 ± 0.7	−4.9 ± 2.4	18 to 34
13	**4e** (Cl)	$SOCl_2$	0.50	25[c]	14.5 ± 0.5	−3.4 ± 1.7	14 to 36
14	**5b** (Cl)	TFA	0.41	40[c]	15.8 ± 0.8	1.7 ± 2.7	14 to 29
15	**5b** (BF_4)	TFA	0.42	42[c]	14.6 ± 0.5	−2.0 ± 1.7	21 to 42
16	**3a** (TFATE)	TFA	0.40	188[b]	19.9 ± 0.6	−5.7 ± 1.9	6 to 23
17	**3a** (TFATE)	$C_2H_2Cl_4$	0.40	108[b]	13.5 ± 0.3	−4.1 ± 0.1	−7 to 30

[a] Calculated from the listed activation parameters. [b] Following coalescence of *gem*-dimethyl peaks. [c] Following coalescence of methyl peaks from substituent Y.

Table III. Rate Constants[a] for Methanolysis (k_M) and Elimination (k_E) for **2** (X = BF_4) and **3a** (X = TFATE)

Temp, °C	**2** (X = BF_4)		**3a** (X = TFATE)	
	10^5k_M	10^5k_E	10^5k_M	10^5k_E
60	8.2 ± 0.1[b]	1.2 ± 0.1		
50	3.0 ± 0.06[c]	0.56 ± 0.06	53.4 ± 0.3[d]	2.5 ± 0.3
40			16.3 ± 0.1[d]	1.0 ± 0.1
30			4.88 ± 0.04[d]	0.36 ± 0.04

[a] Sec^{-1}. [b] 5.06×10^{-5} *M*. [c] 7.05×10^{-5} *M*. [d] 8.90×10^{-5} *M*.

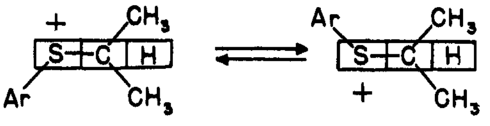
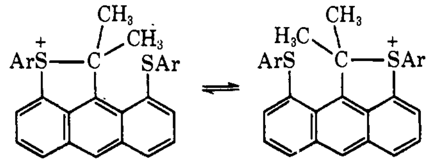


Figure 1. View from within the plane of the anthracene nucleus of the degenerate rearrangement of **2**.

not complete, even at 200°. Sulfonium ion **3a** shows only a single peak for the two analogous methyl groups under the same condition, but the spectrum is strongly temperature dependent giving two methyl peaks at low temperature. This is interpreted in terms of a degenerate intramolecular displacement on the C-1 of **3**,



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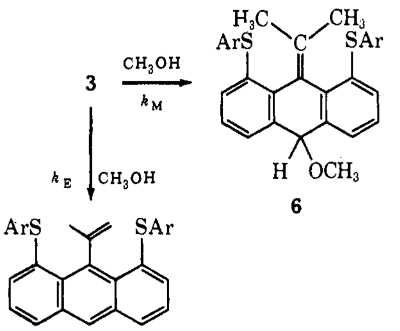
a mechanism which we have called the "bell-clapper" mechanism.[1] This interpetation is confirmed by the observation for **3b–e** of related nmr phenomena involving nonequivalence of meta and para substituent methyl peaks at low temperature.

The rates of exchange listed in Table II were obtained by curve-fitting techniques for the substituent methyl peaks and, in one case (series 1), for the *gem*-dimethyl groups.

The accompanying paper[23] describes evidence for attack of nucleophiles at the 6 position of sulfonium ion **3** (at the 10 position as the anthracene ring is usually numbered). Kinetic studies of the methanolysis to give **6** were carried out following the disappearance of the chromophore of **3** with λ_{max} near 410 nm.



The experimental first-order rate constant for disappearance of sulfonium ion is factored, in Table III, into rate constants for methanolysis (k_M) and for olefin-forming elimination (k_E). Product ratios, determined spectrophotometrically, are the source of nearly all of the error quoted for the rate constants.

Discussion

The nmr spectrum of sulfonium ion **2** shows two methyl peaks, for methyl groups cis and trans to the sulfonium phenyl substituent. Coalescence of these two peaks is nearly, but not quite, complete at 200°. Figure 1 shows a bird's-eye view (in the plane of the anthracene nucleus) of this process.

The rate of cis–trans isomerization indicated by this nmr result is comparable to that reported[26] for the pyramidal inversion of sulfonium ion **7** (k = 20 sec^{-1}

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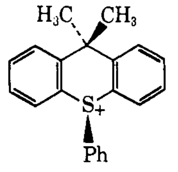
(26) K. K. Anderson, M. Cinguini, and N. E. Papanikoloan, *J. Org. Chem.*, **35**, 706 (1970).



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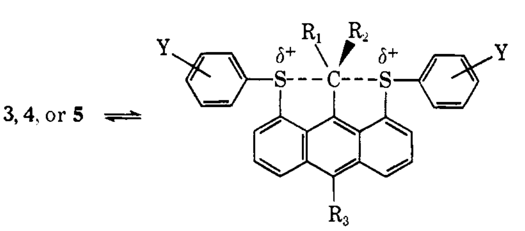
at 200° in benzophenone) as reflected in the coalescence of its methyl peaks.

It is also to be compared with the racemization rate reported[27] for *tert*-butylethylmethylsulfonium perchlorate in ethanol ($k = 4.7 \times 10^{-4}$ sec^{-1} at 50°), which is also postulated[27] to involve simple pyramidal inversion. The mechanism for the process pictured in Figure 1 could therefore well be such a pyramidal inversion, not involving the breaking of S–C bonds.

Our reasons for undertaking these studies lay in the desire to seek evidence for an intermediate in an SN2 type displacement in a system designed to favor such an intermediate. The degenerate rearrangements of sulfonium ions **3**, **4**, and **5**, if proceeding through a mechanism of the SN2 type, would proceed through an intermediate or transition state, **8**, which is favored by entropy and angle strain considerations over analogous species in intermolecular reactions.



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The single methyl peak seen for solutions of **3** at room temperature would be consistent with the predominance of *trans*-**8**, in which the two methyl groups are equivalent. That this is not the proper interpretation is clearly demonstrated by the temperature dependence studies of Table II. The low temperature spectra were in every case entirely compatible with the unsymmetrical sulfonium ions structures **3**, **4**, and **5**, with no evidence for the symmetrical hypervalent species **8** in the nmr.

Mechanism of Rearrangement of 3, 4, and 5. The three sorts of degenerate rearrangements which might be responsible for the temperature dependence of the spectra of **3**, **4**, and **5** are shown as paths A, B, and C in Figure 2. For a compound such as **3d**, the interconversion of methyl groups R_1 and R_2, which leads to coalescence of the corresponding nmr peaks, is effected by processes B and C, but not A (R_1 is cis to the sulfonium aryl group before and after reaction). The *p*-*tert*-butyl groups of **3d** are interconverted by reactions A and B but not reaction C.

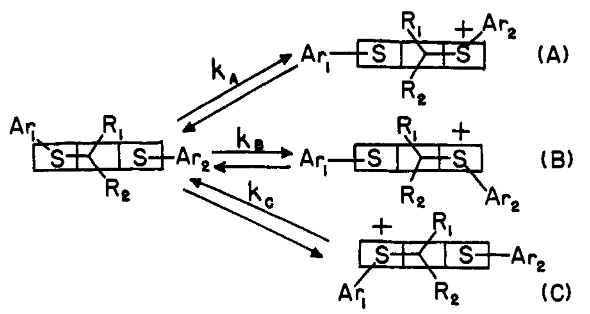
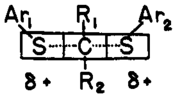
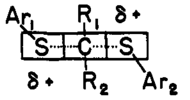


Figure 2. View parallel to the plane of the anthracene ring of the interconversion processes (A, B, and C) of 2-thioniaaceanthrene cations **3**, **4**, and **5**.

The rate constant $k_B + k_C$ for interconversion of R_1 and R_2 in **3d** (series 1, Table II, $k_{25} = 106$ sec^{-1}) is smaller than the corresponding sum $k_A + k_B$ for the interconversion of Ar_1 and Ar_2 (series 2, Table II, $k_{25} = 138$ sec^{-1}). Obviously path B must be followed more often than path A (a factor of 3.3 more often if k_C is negligibly small). The transition state, or closely resembling intermediate, for a nucleophilic displacement mechanism for path B (*trans*-**8**) is likely to be more favored on steric grounds than that for path A (*cis*-**8**), in which both aryl groups are on the same side of the molecule, in a manifestation of the buttressing effect.[28]



cis-**8**



trans-**8**

The pyramidal inversion mechanism for path C would be expected,[26,27] upon the basis of data discussed earlier in this paper, to be much too slow to contribute appreciably to the observed coalescence of peaks for **3**, **4**, and **5**. We are, therefore, justified in neglecting possible contributions from path C.

Comparisons of the exchange rate for **3d** (X = BF_4), in series 2, Table II, with those for **4d** (X = Cl) in series 8, 9, and 10, must consider three differences in structure: (a) the difference in primary alkyl ($R_1 = R_2 = H$) and tertiary alkyl ($R_1 = R_2 = CH_3$), (b) the difference in anion (chloride or fluoroborate), and (c) the difference in the 6-substituent ($R_3 = H$ or $R_3 = CH_3$). The first of these factors is most important.

If the reaction were to proceed by a mechanism resembling the SN1 extreme, the dissociation of sulfonium ion **3d** to something resembling a tertiary carbonium ion, then one would expect the reaction of **3d** to be much faster than that of **4d**, which would involve a transition state resembling a primary carbonium ion. The stabilizing effect of an α-methyl substituent, when compared to hydrogen, in an ionization reaction is very large. The limiting α-CH_3/H rate ratio in the 2-adamantyl system has been reported to be 10^8. Compound **3d**, with two α-CH_3 groups, is only approximately twofold faster than the primary alkyl analog, **4d**. This suggests a transition state with little positive charge on the central (bell-clapper) carbon.

A comparison of k_{25} from series 3, 6, 14, and 15 shows that 6-phenyl substituted **5b**, with either chloride or fluoroborate gegenion in TFA, is only slightly different (*ca.* 30% acceleration) from **4b** with its 6-methyl substituent. This lack of sensitivity to substitution at position 6 suggests[29] a very small transition state

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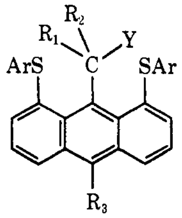
[27] D. Darwish and G. Tourigny, *J. Amer. Chem. Soc.*, **88**, 4303 (1966).

[28] F. H. Westheimer in "Steric Effects in Organic Chemistry," M. S. Newman, Ed., Wiley, New York, N. Y., 1956, p 552.

[29] The ΔF of ionization of diphenylmethylcarbinol to give diphenylmethylcarbonium ion in acid is 5 kcal/mol less negative than for the analogous reaction leading to triphenylcarbonium ion; G. A. Olah and P. v. R. Schleyer, "Carbonium Ions," Vol. I, Wiley-Interscience, New York, N. Y., 1968, p 104.

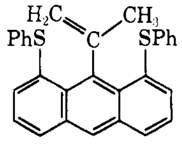
charge at this position. Although the bell-clapper carbon is benzylic and formally in position to be conjugated with this substituent at C-6, the benzylic group is, at least in the sulfonium precursor, twisted by 90° from the plane of the anthracene ring.

These same sets of data show that there is little difference in rate between the sulfonium salt with chloride gegenion and with the much less nucleophilic fluoroborate gegenion. This rules out a mechanism for rearrangement involving reversible formation of **9**, or other neutral species, formed by nucleophilic attack on the sulfonium ion. The nonidentity of the exchange rates measured by line-shape analyses of the *gem*-dimethyl group and of the aromatic substituent methyl peaks also argues against a SN1 type mechanism in which the tertiary alkyl cation exists for times long with respect to the rate of rotation about the aromatic C–S bonds.



9

Other alternative mechanisms for this rearrangement which must be considered include those which would involve loss of a proton from sulfonium ion **3**, **4**, or **5** to give **10** and from sulfonium ion **3** to give **11**. Both of these mechanisms were ruled out by deuterium exchange studies. The protonation of **10** to give **3a** (X = TFATE), when carried out in TFA-*d*, results in the incorporation of only 1 deuterium atom/molecule of **3a** and no further incorporation of deuterium was seen on further standing in this same solvent under conditions showing rapid degenerate rearrangement. Similarly, all mechanisms involving **11** as an intermediate in the rearrangement were ruled out by the observation that no deuterium exchange was observed for **4a** (X = Cl) in methanol-*d*, or for **4b** (X = Cl)in TFA-*d*.



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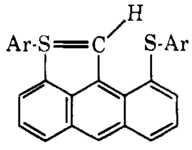
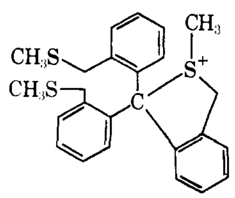


11

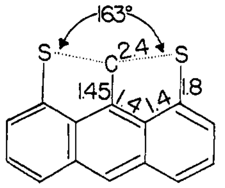
These observations all point to the conclusion that the degenerate bell-clapper rearrangement of these sulfonium ions proceeds by way of a transition state resembling that of the SN2 mechanism for nucleophilic displacements. This is to be contrasted with the finding of Breslow, Kaplan, and LaFollette[20] that the degenerate rearrangements observed for **12**, and a series of related sulfonium salts, proceed through a mechanism of the SN1 type.



12

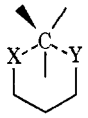
The anthracene-related series of compounds used in our work provides a more rigid geometry, very like that of transition state (or intermediate) **8**, thus favoring the SN2 over the SN1 mechanism. During the course of our work, Gleiter and Hoffmann[19] independently suggested the use of the anthracene nucleus as a rigid framework for anchoring substituents whose interactions might lead to stable hypervalent species.

Geometric model **13** was constructed using a C–S single bond length of 1.8 Å, intermediate between that in suitably chosen models for the C–S bonds in aromatic sulfides[30] and sulfonium ions[31] and a C(carbonium)–C(aromatic) bond length of 1.45 Å[32] and assuming all bond angles from the anthracene nucleus to be 120°. In the absence of bond-angle deformations the hypervalent C–S distance is 2.4 Å. One might expect the normal bond length for such a hypervalent bond to be longer than the normal C–S single bond (1.8 Å).[30] An elongation of 0.2 Å, similar to that seen for the hypervalent S–O bonds in dialkoxydiarylsulfuranes,[33] would lead to the reasonable prediction of a hypervalent C–S bond length of *ca.* 2 Å. An in-plane bending of the bond from the anthracene to sulfur by about 13° brings the sulfur to within this distance of the central carbon.



13

The fact that the C–S bond is longer than the C–C bond prevents the attainment of the preferred[21] colinear arrangement for the central carbon and the two apical sulfur atoms involved in the hypervalent bond of this transition state or intermediate. The facility with which this intramolecular nucleophilic displacement proceeds is to be contrasted with the results of Tenud, Faroog, Seibel, and Eschenmoser[21] from studies of rearrangement reactions which might have been expected to proceed by intramolecular nucleophilic displacement *via* a five- or six-membered ring cyclic transition state. In every case which these workers investigated these rearrangements were shown[21] to proceed by a competing intermolecular process. The deviation from linearity which the geometry of six-ring transition state **14** imposes on the X–C–Y bond apparently represents prohibitive strain. Our system, effectively an eight-membered ring (see partial struc-



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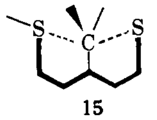

15

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(30) H. Bowen, J. Donohue, O. Kennard, P. Wheatley, and D. Whiffen, *Chem. Soc., Spec. Publ.*, **No. 11**, M230 (1958).

(31) A. Lopez-Castro and M. R. Truter, *Acta Crystallogr.*, **17**, 465 (1964).

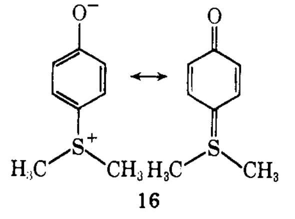
(32) A. H. Gomes De Mesquita, C. H. MacGillarry, and K. Eriks, *ibid.*, **18**, 437 (1965).

(33) I. C. Paul, J. C. Martin, and E. F. Perozzi, *J. Amer. Chem. Soc.*, **94**, 5010 (1972).

ture **15**), in which the deviation from linearity is only about 17°, allows the facile reactions of Table II. The symmetric bending of the apical C–S bonds, which is enforced by the geometry of our system, is related to the deformation of the trigonal bipyramid which provides the low energy[14] route, *via* the tetragonal pyramidal geometry, for the Berry[34] mechanism for pseudorotation of pentacoordinate hypervalent species such as phosphoranes. This deformation of the transition state is expected to be accompanied by an opening of the R_1–C–R_2 angle, providing a possible explanation for the small acceleration seen upon going from $R_1 = R_2 = H$ to $R_1 = R_2 = CH_3$.

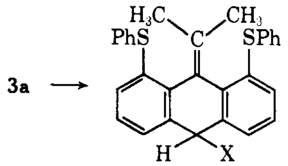
The rates of rearrangement in Table II are relatively insensitive to solvent. For example, **4b** (X = Cl) (in series 3 and 5) shows a rate in the less polar methanol (Kosower *Z* factor, 83.6)[35] about one-third that in the more polar TFA (*Z* = 103.4).[35] The rate for **3a** (X = TFATE) is 40% slower in tetrachloroethane than in TFA (series 16 and 17). For the reaction of a starting material with a positive charge largely localized on sulfonium sulfur proceeding through a transition state such as **8**, with more diffuse charge, the dependence on solvent polarity which one would predict is opposite to that seen. The observation (series 8, 9, and 10) that in a single solvent the rate constant increases with decreasing concentration suggests that the solvent and concentration effects can be related to the degree of ion pairing. In the less polar solvents extensive ion pairing stabilizes the ground state, in which the negative gegenion is associated with the positively charged sulfonium center, relative to the transition state in which the electrostatic interaction with the diffuse charge is less important.

The degenerate rearrangements of cations **4** in thionyl chloride solvent showed only small dependence on polar substituent constants. In the more polar TFA, however, in which ion pairing is less extensive, the rates were well correlated with σ^+ (correlation coefficient 0.963, compared with 0.807 *vs.* σ) to give a ρ value of 1.04. This is in accord with the idea that the principle substituent effect is associated with stabilization of the ground-state sulfonium ion. The $p\pi$–$d\pi$ conjugative interaction of sulfonium sulfur with electron π-donor substituents has been argued by Bordwell and Boutan[36] from their acidity constant measurements of substituted phenols, including **16**. This might lead one to expect a correlation with σ^+, rather than σ, as is seen. The nucleophilic attack of aqueous hydroxide ion on the methyl groups of aryldimethylsulfonium perchlorates is, however, correlated[37] with σ, to give a ρ value of 1.60. The direct resonance interaction with the O^- substituent in **16** may call into play resonance effects not important for the less effective π-donor substituents such as the methoxy group.



16

Solvolysis. The preceding section builds a strong case for the hypothesis that the degenerate rearrangements of **3**, **4**, and **5** proceed by a path resembling the SN2 mechanistic extreme. Although attempts at direct observation of a possible symmetrical intermediate, **8**, in these intramolecular nucleophilic displacements were unsuccessful, the question remains open of whether a very small amount of such a metastable high energy species might be present. The traditional approach to establishing the intermediacy of such a high-energy species is to employ trapping techniques, adding a species which reacts differently with the intermediate than with the low-energy ground states in equilibrium with it. In this context, we were very intrigued by the observation that **3a** (X = Cl) could not be isolated because of its rapid conversion to **17** (X = Cl). This observation was expanded to show a general susceptibility of ions **3** to nucleophilic attack on the anthracene ring to form derivatives of type **17**.



17

The primary alkyl sulfonium ions **4** and **5** showed no such reactions and the sulfonium ion **2**, which lacks a neighboring thiophenyl substituent, reacted much more slowly. This suggested the interesting possibility that this reaction might in fact represent the trapping of a high energy hypervalent intermediate of type **8**.

The specific reaction chosen for quantitative study was the reaction with nucleophilic solvent methanol to give **6**. The rate constants in Table III show that the reaction of **3a** with solvent methanol is much slower than the degenerate rearrangement of **3a**. If the methanolysis reaction is indeed trapping **8** it is doing so much too inefficiently to allow us to find conditions in which the rate of reaction with nucleophile equals the rate of formation of the trapped intermediate. Our arguments for the trapping postulate must, at present, be much less direct than such a situation would permit.

The methanolysis of **3a** (X = TFATE) is 18-fold more rapid than that of **2** (X = BF_4). Any mechanism for the reaction must account in some way for this remarkable accelerating effect of the second thiophenyl substituent in **3a**. The difference in gegenions (BF_4 *vs.* TFATE) is unlikely to be the source of any appreciable fraction of this difference, since the same qualitative order of reactivity (**3a** > **2**) was seen for other gegenions as well. One explanation would invoke the attack on the symmetrical intermediate **8** in the bell-clapper rearrangement of **3a**. No analogous intermediate is available for **2**. The failure to trap analogous intermediates in the rearrangement of ion **4** or **5** could reflect either the higher energy of the symmetrical intermediate in which the central carbon is primary, reducing the concentration of trappable species, or steric hindrance to the attack of nucleophile by the 6 substituent in these ions.

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(34) R. S. Berry, *J. Chem. Phys.*, 32, 933 (1960); *Rev. Mod. Phys.*, 32, 447 (1960).

(35) E. M. Kosower, "An Introduction to Physical Organic Chemistry," Wiley, New York, N. Y., 1968, p 301.

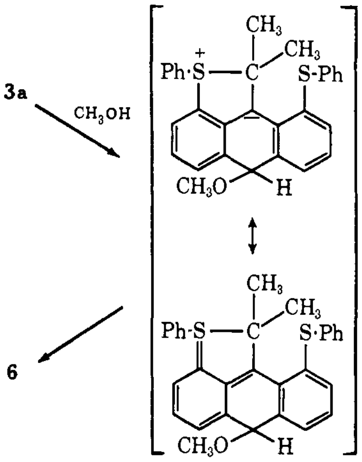
(36) F. G. Bordwell and P. J. Boutan, *J. Amer. Chem. Soc.*, 78, 87 (1956).

(37) J. K. Coward and W. D. Sweet, *J. Org. Chem.*, 36, 1337 (1971).

Although the transition state for the degenerate rearrangement has been shown to have little more positive charge on the central carbon than does the corresponding ground state, it is possible that intermediate **8** might have more such positive charge than does the transition state. This would result in greater stability for tertiary **8** ($R_1 = R_2 = CH_3$) than for primary **8** ($R_1 = R_2 = H$). The transition state for the reaction of methanol with **8** involves a twisting of the *gem*-dimethyl group about the C–aryl bond by 90° to give **6**. The steric interactions between these methyl groups and the flanking sulfurs must be large and unfavorable in this twisting process. The steric influence of the second thiophenyl group of **3a** would therefore be expected to slow the methanolysis of **3a** relative to that of **2**, whether attack of methanol is on **3a** or on intermediate **8**. The accelerating effect of this thiophenyl substituent must therefore be an electronic effect, either through-bond or through-space. A possible through-space nucleophilic involvement of both sulfur atoms in stabilizing a transition state leading directly to **6**, while avoiding the intermediacy of **8**, must be considered. It is, however, less appealing than the route involving the trapping of **8** because of the much greater degree of concertedness demanded by such a formulation.

Although the degenerate rearrangement has been shown to proceed by an SN2 type mechanism, it is possible that the solvolysis proceeds by a mechanistically distinct SN1 type process. Referee 1 has suggested that the intermediate benzylic cation from **3a** in such a process, by virtue of its stabilization by symmetrical intramolecular solvation by the two thiophenyl groups, would be more easily formed than the analogous cation from **2**, which would be intramolecularly solvated by sulfur on one face and intermolecularly by solvent on the other. This description of the intermediate form **3a** is in fact reducible to the description of the hypervalent intermediate **8** for some definitions of the term "solvation." The C–S bonds are largely ionic in the hypervalent bonding picture of **8**, as they would be in a symmetrical intramolecularly solvated carbocation. If one arbitrarily defines solvation as an interaction lacking covalent character, then perhaps the two possible descriptions of the intermediate could be differentiated on the basis of differences in the directional character of the C–S bonds.

In one alternative formulation, the attack of nucleophile directly on **3a** to give **18** could be slightly accelerated by the somewhat greater electron withdrawing effect (σ 0.13)[38] of the phenylthio substituent relative to that of the hydrogen of **2**.



18

Further work now underway[39] will test the tentative conclusion that this reaction does, in fact, involve the trapping of an intermediate of structure **8**, a hypervalent carbon(V) derivative.

Acknowledgment. This work was supported in part by grants from the National Science Foundation (GP-30491X and a grant for the purchase of a 220-MHz nmr spectrometer). We wish to acknowledge helpful discussions with Mr. William Work.

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(38) L. J. Kaplan and J. C. Martin, *J. Amer. Chem. Soc.*, **95**, 793 (1973); W. A. Sheppard and R. W. Taft, *ibid.*, **94**, 1919 (1972).

(39) Unpublished results of Mr. William Work.