

The departure from tetrahedral geometry should in turn be greater, the more difficult the ionization of  $RX$  to  $R^+X^-$ . Now the energy ( $\Delta E$ ) required to convert  $RX$  to separated ions  $R^+$  and  $X^-$  in the absence of a solvent is given<sup>30</sup> by

$$\Delta E = E_{RX} + I_R - A_X \quad (10)$$

where  $E_{RX}$  is the  $RX$  bond energy,  $I_R$  the ionization potential of  $R$ , and  $A_X$  the electron affinity of  $X$ . Since bond energies of  $HX$  and  $CX$  bonds run roughly parallel, we would expect on this basis that the relative facility with which a series of alkyl derivatives  $RX$  ( $R$  fixed) ionize should run parallel to the strengths of the acid  $HX$ . Furthermore, this relation should carry over into solution, because the difference in energy of solvation between the ions derived from two members of the first series,  $R^+X^-$  and  $R^+Y^-$ , should be the same as the corresponding difference between  $H^+X^-$  and  $H^+Y^-$ . Since acid strength increases in the order  $HCl < HBr < HI$ , and since all these acids are at least as strong as *p*-toluenesulfonic acid, it is consequently difficult to

(30) M. J. S. Dewar, "The Electronic Theory of Organic Chemistry," Clarendon Press, Oxford, 1949.

explain our results on this basis, for the slopes of the plots indicate that ease of ionization in  $ArCH_2X$  must decrease in the order  $OTs \gg Cl > Br > I$ .

There are two factors that could account for this discrepancy. In the first place, the transition state for solvolysis of  $RX$  is a structure in which the nascent ions  $R^+$  and  $X^-$  are still linked. There will be a coulombic interaction between them which is not taken into account in eq 10. For a given degree of bond breaking, the charges of  $R$  and  $X$  will be presumably much the same for different  $X$ ; the coulombic energy will then decrease with increasing  $RX$  bond length. Since bond length increases rapidly in the order  $CO < CCl < CBr < CI$ , the corresponding decrease in coulombic energy will lead to a decrease in ease of ionization (or partial ionization) along the series.

A second factor is the increase in polarizability of atoms with increasing size, in particular in the order  $O < Cl < Br < I$ . One would expect<sup>30</sup> the energy required to convert the initial alkyl derivative to an  $SN_2$ -like bipyramidal transition state to be less, the more polarizable the leaving group; this effect should again lead to an increased tendency to nucleophilic participation in the series  $O < Cl < Br < I$ .

## The Solvolysis of 2-Arylethyl *p*-Toluenesulfonates<sup>1</sup>

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**Abstract:** The rates of solvolysis of a number of 2-arylethyl *p*-toluenesulfonates,  $ArCH_2CH_2OSO_2C_6H_4$ , where  $ArH$  is an alternant aromatic hydrocarbon, have been measured in acetic acid, formic acid, and trifluoroacetic acid, and the results interpreted in terms of various MO approximations. The reactions take place by two alternative paths, one at a rate independent of the aryl group and the other at a rate which increases with increasing conjugative power of  $Ar$ . Quantitative correlations of the rates of the latter process with appropriate MO parameters support the view that it involves a concerted process in which separation of the toluenesulfonate moiety is accompanied by rearrangement of the cation to a  $\pi$  complex.

In spite of extensive investigations over the last two decades, some controversy still exists concerning the intimate details of aryl participation in the solvolysis of 2-arylethyl derivatives.<sup>4</sup> In a recent preliminary report<sup>3</sup> we described some work which had a bearing on this problem; here we are presenting more complete details and additional rate studies which reinforce our earlier conclusions.

The object of this investigation was to apply a technique which has been used successfully in other connections, *e.g.*, aromatic substitution,<sup>5</sup> nucleophilic

aliphatic substitution,<sup>6</sup> and the Diels–Alder reaction.<sup>7</sup> The idea behind this is to make use of the special properties of alternant hydrocarbons (AH)<sup>8</sup> by studying the relative rates of a number of reactants that differ only by a substituent derived from an AH. Since the atoms in an AH are neutral,<sup>8</sup> such substituents exert no field or inductive effects other than those due to the bond linking the substituent to the rest of the molecule, and the effect of this bond will of course be the same for different AH substituents. Any differences in rate must then be due to resonance interactions, and the special properties of AHs enable such interactions to be estimated with unusual facility. In the present case, the obvious way of applying this technique was to study the rates of solvolysis of 2-arylethyl derivatives  $ArCH_2CH_2X$ , where  $ArH$  is an alternant aromatic hydro-

(1) This work was supported by the Air Force Office of Scientific Research through Grant Number AF-AFOSR-1050-67. A preliminary account has appeared.<sup>3</sup>

(2) N.A.S.A. Trainee, 1965–1968.

(3) M. D. Bentley and M. J. S. Dewar, *J. Amer. Chem. Soc.*, **90**, 1075 (1968).

(4) (a) A. Streitwieser, "Solvolytic Displacement Reactions," McGraw-Hill Book Co., Inc., New York, N. Y., 1962; (b) H. C. Brown, K. S. Morgan, and F. S. Chloupek, *J. Amer. Chem. Soc.*, **87**, 2137 (1965); (c) D. J. Cram, *ibid.*, **88**, 3767 (1964).

(5) M. J. S. Dewar, T. Mole, and E. W. T. Warford, *J. Chem. Soc.*, 3581 (1956).

(6) M. J. S. Dewar and R. J. Sampson, *ibid.*, 2789 (1956).

(7) M. J. S. Dewar and R. S. Pyron, work in course of publication.

(8) See M. J. S. Dewar, "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1969, for a discussion and references.

Table I.  $^{14}\text{C}$  Tracer Studies of Solvolysis for 2-Arylethyl Tosylates

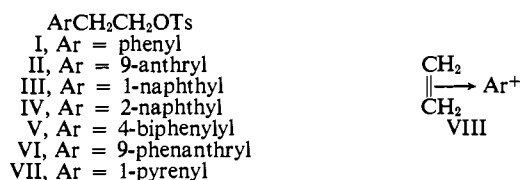
Aryl group	% rearrangement on solvolysis ( $^{\circ}\text{C}$ )			Ref
	Ethanol-acetic acid	90% formic acid	Formic acid	
Phenyl	0.3 (76 $^{\circ}$ )	5.5 (118 $^{\circ}$ )	40 (100 $^{\circ}$ )	a
$\alpha$ -Naphthyl		46 (110.6 $^{\circ}$ )		b
$\beta$ -Naphthyl		34 (110.6 $^{\circ}$ )		b

<sup>a</sup> C. C. Lee, G. P. Slater, and J. W. T. Spinks, *Can. J. Chem.*, **35**, 1417 (1957). <sup>b</sup> C. C. Lee and A. G. Forman, *ibid.*, **43**, 3386 (1965); **44**, 841 (1966).

carbon. If the reaction is unassisted, the rate should be independent of Ar, since in this case there can be no resonance interactions between aryl and the reaction center. If the reaction is assisted, the rate should vary in a predictable way with the nature of the aryl group.

The only measurements of this type that had been reported previously were by Winstein, *et al.*,<sup>9</sup> who studied the solvolysis of 2-phenylethyl (I) and 2-(9'-anthryl)ethyl tosylates (II) in ethanol and in acetic and formic acids. In ethanol, the rates were identical, implying that the reactions took place through  $\text{S}_{\text{N}}2$  attack by solvent, whereas in acetic or formic acid II reacted much faster than I, implying aryl participation at least in the case of II.

Participation by aryl has also been studied in I, and in 2-( $\alpha$ -naphthyl)ethyl (III) and 2-( $\beta$ -naphthyl)ethyl tosylates (IV), by observing the amount of isotopic scrambling in the solvolysis of  $\text{ArCH}_2^{14}\text{CH}_2\text{OTs}$ ; the results are shown in Table I.



It will be seen that phenyl participation is negligible in the ethanolysis of I, in agreement with the conclusions of Winstein, *et al.*,<sup>9</sup> and small in acetic acid; however, the solvolysis of I in formic acid or of III or IV in acetic or formic acids leads to very extensive scrambling, which has been taken as evidence that the major part of the reaction takes place *via* the  $\pi$  complex VIII or a corresponding phenonium ion.<sup>10</sup>

We decided for the reasons indicated above to study the solvolysis of a number of 2-arylethyl tosylates, covering a wide range of predicted reactivity, in a variety of solvents. Here results are reported for I-IV, and for the corresponding 4-biphenyl (V), 9-phenanthryl (VI), and 1-pyrenyl (VII) derivatives. Aryl scrambling in the solvolysis of III and IV was also studied, using the 1,1-dideuterio derivatives.

## Experimental Section

**A. Materials.** Elemental analyses were performed by Galbraith Laboratories, Knoxville, Tenn., and Dr. A. Bernhardt, Max-Planck Institute, Mulheim (Ruhr), West Germany. Melting points were determined with a Thomas-Hoover melting point apparatus and are uncorrected. Nuclear magnetic resonance spectra were measured with a Varian A-60 spectrometer, infrared spectra with a Beckman IR-8 infrared spectrophotometer, and ultraviolet-visible spectra with a Beckman DK-2A spectrophotom-

eter, all at room temperature. All nmr spectra integrated correctly.

**2-Phenylethyl tosylate (I)** was prepared in 57% overall yield from 2-phenylethanol by conversion with sodium hydride in ether to the alkoxide and treatment with *p*-toluenesulfonyl chloride, followed by several crystallizations from ether-pentane: mp 35.5-36.5 $^{\circ}$  (lit.<sup>11</sup> mp 35.5-36.6 $^{\circ}$ , 39.5-40.5 $^{\circ}$ ); nmr spectrum in  $\text{DCCl}_3$  doublet,  $\tau$  2.3 ( $J = 8$  Hz), multiplet, 2.65-2.8, triplets, 5.78, 7.07 ( $J = 7$  Hz), singlet, 7.58.

**2-(2'-Naphthyl)ethyl Tosylate (IV).** Reduction of 2-naphthylacetic acid with lithium aluminum hydride in ether gave 2-(2'-naphthyl)ethanol in 75% yield, white platelets (benzene-hexane), mp 66-67 $^{\circ}$  (lit.<sup>12</sup> mp 67-68 $^{\circ}$ ). The alcohol (2 g) was converted to IV with tosyl chloride (2.44 g) in pyridine (10 ml); recrystallization from benzene-hexane gave IV (2.5 g, 64%); mp 63-64 $^{\circ}$  (lit.<sup>12</sup> mp 75-76 $^{\circ}$ ); nmr spectrum in  $\text{CDCl}_3$  multiplet, 2.2-2.3, triplets, 5.7, 6.92 ( $J = 6$  Hz), singlet, 7.7, intensities in expected ratios.

*Anal.* Calcd for  $\text{C}_{19}\text{H}_{18}\text{O}_3\text{S}$ : C, 69.91; H, 5.56; S, 9.82. Found: C, 70.15; H, 5.66; S, 9.95.

All attempts to raise the melting point failed. In view of this, the analysis and nmr spectrum, and the melting point of the dideuterio derivative (see below), we feel that the previous value<sup>12</sup> must have been wrongly reported.

**1,1-Dideuterio-2-(2'-naphthyl)ethyl Tosylate (IV-1,1- $d_2$ ).** Prepared in the same way as IV, but using  $\text{LiAlD}_4$  in the first step, the product had mp 63.5-64.5 $^{\circ}$ ; nmr spectrum in  $\text{CDCl}_3$ , multiplet  $\tau$  2.15-2.3, singlets, 6.92, 7.69.

*Anal.* Calcd for  $\text{C}_{19}\text{H}_{16}\text{D}_2\text{O}_3\text{S}$ : C, 69.48; (H + D), 6.13; S, 9.70. Found: C, 69.44; (H + D), 5.90; S, 9.89.

**2-(1'-Naphthyl)ethyl Tosylate (III).** Prepared in the same way as IV *via* the corresponding ethanol, mp 59-60 $^{\circ}$  (lit.<sup>13</sup> 58-59.5 $^{\circ}$ ), IV had mp 58-59 $^{\circ}$  (lit. mp 56.8-58 $^{\circ}$ ,<sup>13</sup> 59-60 $^{\circ}$ ); nmr spectrum in  $\text{CDCl}_3$  multiplet,  $\tau$  2-3, triplets, 5.65, 6.62 ( $J = 7$  Hz), singlet, 7.67.

**1,1-Dideuterio-2-(1'-naphthyl)ethyl Tosylate (III-1,1- $d_2$ ).** Prepared in the same way as III but using  $\text{LiAlD}_4$  in the first step, the product had mp 58-59 $^{\circ}$  (lit.<sup>13</sup> mp 58.5-59.5 $^{\circ}$ ); nmr spectrum in  $\text{CDCl}_3$ , multiplet,  $\tau$  2.1-3, singlets, 6.60, 7.58.

**2-(4'-Biphenyl)ethyl Tosylate (V).** Prepared from the corresponding alcohol<sup>14</sup> as before, V separated from benzene-Skellysolve B in white platelets: mp 94.5-95.5 $^{\circ}$ ; nmr spectrum in  $\text{CDCl}_3$ , multiplet,  $\tau$  2.2-3, triplets, 5.77, 7.04 ( $J = 7$  Hz), singlet, 7.63.

*Anal.* Calcd for  $\text{C}_{21}\text{H}_{20}\text{O}_3\text{S}$ : C, 71.70; H, 5.72; S, 9.10. Found: C, 71.60; H, 5.60; S, 8.89.

**2-(9'-Phenanthryl)ethyl Tosylate (VI).** Prepared in the same way as V from 9-bromophenanthrene *via* the lithio derivative, V, after crystallizing twice from benzene-hexane and once from carbon tetrachloride, had mp 103-104 $^{\circ}$ ; nmr spectrum in  $\text{CDCl}_3$ , multiplet,  $\tau$  1.5-2.6, doublet, 3.00 ( $J = 8$  Hz), triplets, 5.58, 6.58 ( $J = 7$  Hz), singlet, 7.72.

*Anal.* Calcd for  $\text{C}_{23}\text{H}_{20}\text{O}_3\text{S}$ : C, 73.37; H, 5.35; S, 8.51. Found: C, 73.46; H, 5.31; S, 8.72.

**2-(1'-Pyrenyl)ethyl Tosylate (VII).** Prepared in the same way as V from 1-bromopyrene,<sup>15</sup> except that a 1:1 mixture of benzene and tetrahydrofuran was used as solvent in the ethylene oxide reaction, VII crystallized from benzene-hexane in cream-colored needles: mp 104.5-105 $^{\circ}$ ;  $\lambda_{\text{max}}$  nm (log  $\epsilon$ ) in cyclohexane 233 (4.12), 244 (4.72), 255 (3.95), 266 (4.29), 277 (4.56), 313 (3.94), 327 (4.33),

(11) (a) S. Winstein, C. R. Lindgren, H. Marshall, and L. L. Ingraham, *J. Amer. Chem. Soc.*, **75**, 147 (1953); (b) H. C. Brown, R. Bernheimer, C. J. Kim, and S. E. Scheppele, *ibid.*, **89**, 370 (1967).

(12) C. C. Lee and A. G. Forman, *Can. J. Chem.*, **44**, 841 (1966).

(13) D. J. Cram and C. K. Dalton, *J. Amer. Chem. Soc.*, **85**, 1260 (1963).

(14) C. C. Lee and A. G. Forman, *Can. J. Chem.*, **43**, 3386 (1965).

(15) J. Colonge and P. Rochas, *Bull. Soc. Chim. Fr.*, 825 (1948).

(16) G. Lock, *Ber.*, **70B**, 929 (1937).

(9) S. Winstein, *et al.*, *J. Amer. Chem. Soc.*, **87**, 3504 (1965).

(10) Note that 50% rearrangement in Table I corresponds to complete scrambling, apart from small possible deviations due to  $^{14}\text{C}$  secondary isotope effects.

Table II. First-Order Rate Constants for the Solvolysis of 2-Arylethyl *p*-Toluenesulfonates in Carboxylic Acids

Ester	—CH <sub>3</sub> COOH (75°)—		—HCOOH (75°)—		—CF <sub>3</sub> COOH (60°)—		—CF <sub>3</sub> COOH <sup>a</sup> (55°)—	
	10 <sup>7</sup> <i>k</i> , sec <sup>-1</sup>	<i>k</i> <sub>rel</sub>	10 <sup>8</sup> <i>k</i> , sec <sup>-1</sup>	<i>k</i> <sub>rel</sub>	10 <sup>5</sup> <i>k</i> , sec <sup>-1</sup>	<i>k</i> <sub>rel</sub>	10 <sup>4</sup> <i>k</i> , sec <sup>-1</sup>	<i>k</i> <sub>rel</sub>
I	2.88 <sup>b</sup>	(1.00)	4.56	(1.00)	8.30 <sup>c</sup>	(1.00)	1.28 <sup>c</sup>	(1.00)
V	3.28	1.14						
IV	3.17	1.10	6.03	1.32	21	2.5	2.6	2.0
VI			14.3	3.14				
III	3.86	1.34	18.0	3.95	40	4.8	9.6	7.5
VII	19.9	6.92	52.7	11.6	340	41	38.0	30
II	116 <sup>b</sup>	40.3	400 <sup>b</sup>	87.7				

<sup>a</sup> Buffered with NaOCCF<sub>3</sub>. <sup>b</sup> Reference 9. <sup>c</sup> Reference 23.

343 (4.53); nmr spectrum<sup>17</sup> in CDCl<sub>3</sub> at 40°, multiplet,  $\tau$  1.8–2.9, doublets, 2.70, 3.40 ( $J = 8$  Hz), triplets, 5.62, 7.00 ( $J = 6$  Hz), singlet, 8.23.

Anal. Calcd for C<sub>25</sub>H<sub>20</sub>O<sub>3</sub>S: C, 74.97; H, 5.03; S, 8.00. Found: C, 75.08; H, 5.16; S, 8.14.

**2-(2'-Naphthyl)ethyl Trifluoroacetate.** Trifluoroacetic anhydride (2 ml) was added to a solution of 2-(2'-naphthyl)ethanol (0.367 g) in dry pyridine (10 ml) at 0°. After 0.5 hr, the mixture was poured into 10% sulfuric acid (100 ml) and the ester isolated with ether as a white powder (0.35 g, 62%), mp 32–34°, raised by recrystallization from pentane to 35–35.5°; nmr spectrum in CDCl<sub>3</sub>, multiplet,  $\tau$  2.1–2.8, triplets, 5.40, 6.83 ( $J = 7$  Hz).

Anal. Calcd for C<sub>14</sub>H<sub>11</sub>O<sub>2</sub>F<sub>3</sub>: C, 62.68; H, 4.14. Found: C, 62.49; H, 4.13.

**Acetic Acid.** A mixture of glacial acetic acid (1 l), acetic anhydride (100 ml), and concentrated sulfuric acid (5 ml) was boiled under reflux and fractionated under argon through a 3-ft Vigreux column. Dry acetic acid was collected at 118° and stored under argon.<sup>19</sup>

**Formic Acid.** Formic acid (Eastman 97%, 1 l.) was stirred 7 days with boron trioxide (50 g) and distilled through a 3-ft Vigreux column under argon. Formic acid was collected at 33–34° (45 mm) and stored under argon. Karl Fisher titration at 0° indicated <0.1% water.<sup>20</sup>

**Trifluoroacetic Acid.** Trifluoroacetic acid (J. T. Baker, 99%) was distilled (bp 71–72°) and trifluoroacetic anhydride (1% w/w) added.

**B. Kinetic Methods.** All kinetic runs were followed to at least 50% conversion, and in most cases to 70% conversion. All obeyed the first-order rate law and first-order rate constants were obtained by the method of least squares, using the CDC 6600 computer at the University of Texas Computation Center and a program written by Dr. J. Hashmall. All kinetic runs were carried out in duplicate, the duplicate rate constants in all cases agreeing to within 3%.

**Acetolysis of Arylethyl Tosylates.** A quantity of arylethyl tosylate sufficient to make an approximately 0.01 *M* solution was weighed into a 50-ml volumetric flask and the flask filled to the mark with dry acetic acid. Aliquots (ca. 5 ml) were sealed into ampoules and placed in an oil thermostat at 75° ± 0.05°. The tubes were removed at timed intervals and quenched in ice-water. Aliquots (4 ml) diluted to ca. 20 ml with glacial acetic acid were titrated<sup>21</sup> with bromophenol blue to a yellow end point with 0.0100 *N* sodium acetate in acetic acid, using a Kimax 5-ml buret graduated in units of 0.01 ml. Since the acetolysis rates were extremely slow, theoretical infinity titrations were used in calculating rate constants.

**Formolysis of Arylethyl Tosylates.** A two-necked 50-ml flask fitted with a septum and a condenser vented through a mercury bubbler, and containing formic acid (50 ml), was equilibrated in a thermostat at 75 ± 0.05°. A tiny vial containing a weighed amount of arylethyl tosylate was quickly introduced. Zero time was taken as the instant the tosylate dissolved (less than 30 sec required) and aliquots were then withdrawn with a syringe at timed intervals, quenched by injecting into a vial at 0°, and allowed to warm to room temperature. An aliquot (1 ml) was added to an erlenmeyer

flask containing dioxane (20 ml) and a saturated solution of bromophenol blue in acetic acid (20 drops). The liberated *p*-toluenesulfonic acid was titrated to a bright yellow end point<sup>22</sup> with 0.01 *N* sodium acetate in glacial acetic acid. After ten half-lives, an aliquot was removed and the infinity titer measured; this always agreed with theory to ±3%.

**Trifluoroacetolysis of Arylethyl Tosylates.** Trifluoroacetolysis presented some special kinetic problems. No titrimetric procedure for analysis of toluenesulfonic acid in trifluoroacetic acid has been reported and the conductance of toluenesulfonic acid in this solvent proved to be quite low. It was decided to follow the formation of toluenesulfonic acid by the appearance of its absorption band at 261 nm. Since the arylethyl tosylates absorbed strongly in this region, the toluenesulfonic acid had to be separated from them. Formation of polymers interfered with sampling and dilution, so they had to be removed completely. The final procedure was as follows.

An aliquot of arylethyl tosylate in methylene chloride was placed in a glass-stoppered test tube and the methylene chloride evaporated in a stream of nitrogen. After equilibration in the thermostat, prethermostated trifluoroacetic acid (0.5 ml) was added, the resulting solution being 0.025 *M* in arylethyl tosylate at  $t = 0$ . After a given time, the tube was removed and quenched in ice-water. Most of the trifluoroacetic acid was removed at 0° in a stream of nitrogen and the residue was transferred with 7% aqueous sodium bicarbonate to a sintered glass funnel and filtered with suction into a 10-ml volumetric flask which was then removed and filled to the mark with 7% aqueous sodium bicarbonate. The contents were extracted twice with 10-ml portions of chloroform. This procedure was repeated for each kinetic point. The sodium *p*-toluenesulfonate was determined from the absorption at 261 nm. A Beer's law plot was shown to be linear over this concentration range so that absorbances were used directly in the rate equation. Rates were measured in the so-called "buffered" systems by a similar procedure except that 0.05 *M* arylethyl tosylate was added to a 0.125 *M* solution of sodium trifluoroacetate in trifluoroacetic acid. It is uncertain whether or not this represents a true buffer; these concentrations were used to be consistent with previous studies.<sup>23</sup>

## Results

The acetolysis and formolysis of the esters studied here seemed to proceed cleanly. The nmr spectra of the products indicated that the acetates and formates were formed quantitatively, without any detectable elimination or polymerization. The corresponding rate constants are shown in Table II.

Complications arose, however, in the case of trifluoroacetic acid. While 2-phenylethyl tosylate reacted cleanly to form exclusively 2-phenylethyl trifluoroacetate, in agreement with Nordlander and Deadman,<sup>23</sup> extensive polymer formation was observed with the other esters. Indeed, after ten half-lives, the sole products isolated were polymer and *p*-toluenesulfonic acid. The weight of the polymer in each case corresponded to that expected for loss of the toluenesulfonate group from the original ester, suggesting that

(17) This spectrum is temperature dependent.<sup>18</sup>

(18) M. D. Bentley and M. J. S. Dewar, *Tetrahedron Lett.*, No. 50, 5043 (1967).

(19) R. H. Jagow, Ph.D. Dissertation, University of California at Berkeley, 1964.

(20) S. Winstein and H. Marshall, *J. Amer. Chem. Soc.*, **74**, 1120 (1952).

(21) S. Winstein and E. Grunwald, *ibid.*, **79**, 827 (1957).

(22) S. Winstein and R. Heck, *ibid.*, **78**, 4805 (1956).

(23) J. E. Nordlander and W. G. Deadman, *ibid.*, **90**, 1590 (1968).

the polymer was, as expected, formed by self-condensation of the arylolefin moiety, *i.e.*,  $(\text{ArC}_2\text{H}_3)_n$ . The proton nmr spectrum of the polymer from 2-(1'-naphthylethyl) *p*-toluenesulfonate was consistent with this, showing two broad bands at  $\tau$  1.8–3.2 and 6.5–7.0.

The solvolyses followed first-order kinetics over at least the first 70% of reaction, when followed by the appearance of *p*-toluenesulfonic acid. This seems to suggest that the acid is produced by solvolysis of the original ester, and the polymer by subsequent condensation of the solvolysis product; for if the polymer were formed by nuclear alkylation, the rate of solvolysis would have been expected to change as alkylation products for the parent *p*-toluenesulfonate accumulated.

Peterson and Tao<sup>24</sup> have shown that *t*-alkyl trifluoroacetates exist in equilibrium with the corresponding olefins in trifluoroacetic acid, and Nordlander and Deadman<sup>23</sup> found that 1-phenyl-2-propyl trifluoroacetate polymerized, probably by elimination to form 1-phenylpropene as intermediate. This, however, could not have been the sole explanation in our case, since when a solution of equimolecular amounts of 2-(2'-naphthylethyl) trifluoroacetate and *p*-toluenesulfonic acid in trifluoroacetic acid was kept overnight at 75°, no polymer was formed. In the same period, IV would have given polymer quantitatively. Evidently the polymerization in the latter case must have preceded formation of the trifluoroacetic ester. Moreover polymer formation could be reduced by "buffering" the solvent with sodium trifluoroacetate; thus IV gave only 2%, and III 13%, of polymer in buffered acid under conditions where the reaction in unbuffered acid gave polymer exclusively, although the more reactive 1-pyrenyl ester, VII, gave polymer quantitatively even in buffered solution. The reactions in buffered acid again followed first-order kinetics accurately and the ratios of the rate constants were similar to those for reactions in trifluoroacetic acid alone; indeed, the observed differences may have been due to the fact that the rates were measured at slightly different temperatures (55° *vs.* 60°). The fact that the relative rates remain constant even when the products differ again suggests that toluenesulfonic acid is produced by a primary solvolysis of the original ester and the polymer by secondary reactions. On this basis, the rate constants in the last two columns of Table II should refer to this primary process.

Nordlander and Deadman<sup>23</sup> have reported complete equilibration of the methylene carbon atoms during trifluoroacetolysis of I. We found a similar complete scrambling in the solvolyses of  $\alpha$ -dideuterated III and IV in buffered trifluoroacetic acid. The proton nmr spectra of the trifluoroacetates formed in these reactions corresponded to a 1:1 mixture of  $\alpha,\alpha'$ - and  $\beta,\beta'$ -deuterio derivatives.

## Discussion

As pointed out in the introduction, the solvolyses of 2-arylethyl *p*-toluenesulfonates of the type studied here seem to take place by two distinct paths, one involving direct attack by the solvent with no aryl participation, the other involving participation by the aryl group. The rates of reactions of the first type should be the

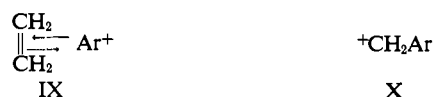
(24) P. E. Peterson and E. V. P. Tao, *J. Org. Chem.*, **29**, 2322 (1964).

same for different aryl groups, since these, being derived from alternant hydrocarbons, are nonpolar. The only possible polar effect would be that due to asymmetry of the  $\text{sp}^2\text{-sp}^3$   $\sigma$  bond linking aryl to the adjacent methylene, and this of course will be the same for different aryls. The assisted reaction should on the other hand be faster, the greater the ability of aryl to participate; on this basis the reactions in formic and trifluoroacetic acid must all be assisted, except possibly that of I, and the esters in Table II have been arranged accordingly in order of increasing efficiency at participation of the aryl group.

The relative rates of the two reactions should depend critically on the solvent, if indeed the aryl-assisted reaction is a typical  $\text{S}_{\text{N}}1$  process involving separation of the *p*-toluenesulfonate group as an anion. The rate of the unassisted reaction, involving as it does nucleophilic attack by solvent, should run parallel to the nucleophilicity of the latter, while the rate of the assisted reaction should be greater, the greater the energy of solvation of the resulting ions. Since solvation in acidic media should involve mainly the anion (*i.e.*,  $\text{C}_6\text{H}_5\text{SO}_3^-$ ), the rate should be greater, the more acidic the solvent.

These conclusions are in complete agreement with the results in Table II. Thus acetic acid is the most nucleophilic and least acidic of the three solvents; only here do we observe rates essentially independent of the aryl group. Only with groups above 1-naphthyl in the participation scale does the rate begin to differ significantly from that of the 2-phenylethyl ester. In the other solvents the reactions are all assisted, except perhaps that of I, and the rate of solvolysis of a given ester increases in the order acetic acid < formic acid < trifluoroacetic acid, the order of increasing acid strength.<sup>25</sup>

In order to discuss the assisted reactions further, it is necessary to assume some structure for the transition state. It seems very likely that the intermediates in these reactions are  $\pi$  complexes or phenonium ions rather than carbonium ions;<sup>4,9</sup> a  $\pi$  complex with an aryl group in the apical position should be stabilized by back-coordination of the  $\pi$  electrons of the ring into the antibonding  $\pi$  MO of the olefin moiety,<sup>8,26</sup> *i.e.*



Now the "normal"  $\pi$  complex dative bond involves an  $\text{sp}^2$   $\sigma$  AO of one of the carbon atoms of Ar; the strength of this bond should be more or less the same for different  $\pi$  complex ions of this type. The reverse  $\pi$  bond on the other hand involves interaction of a *p* AO of the carbon atom with an empty adjacent orbital (the antibonding  $\pi$  MO of the ethylene moiety); the resulting structure is therefore isoconjugate with the corresponding arylmethyl cation X in which the empty

(25) The fact that the rates in "buffered" and "unbuffered" trifluoroacetic acid are similar is not surprising, for it is doubtful if the salt really has much effect on the solvent. Trifluoroacetic acid is not a good ionizing solvent and salts in it are probably largely associated. The sodium trifluoroacetate probably serves to neutralize the *p*-toluenesulfonic acid as it is formed rather than to modify the medium. The increase in rate on addition of sodium trifluoroacetate is presumably due to a secondary salt effect.

(26) M. J. S. Dewar, *Bull. Soc. Chim. Fr.*, **18**, C86 (1951); "The Molecular Orbital Theory of Organic Chemistry," McGraw-Hill Book Co., Inc., New York, N. Y., 1969.

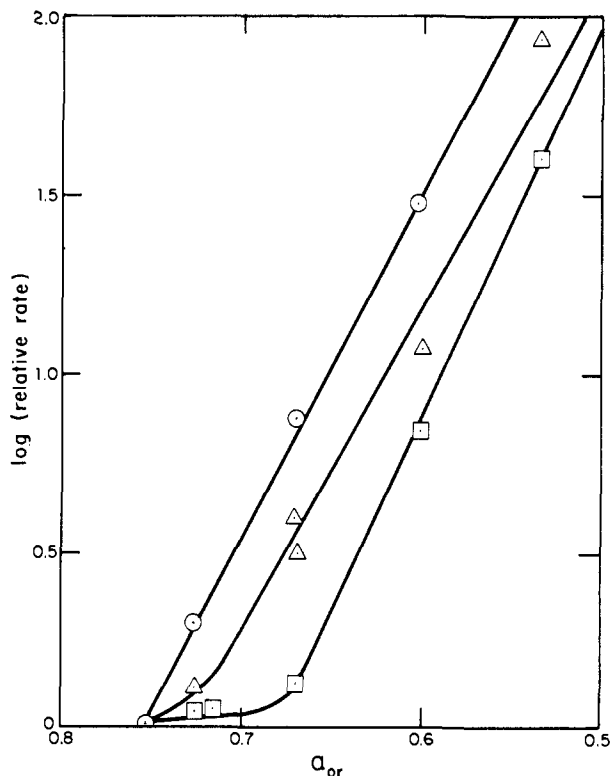


Figure 1. Plot of log (relative rate) vs. NBMO coefficients ( $a_{or}$ ) for solvolysis of 2-arylethyl *p*-toluenesulfonates in trifluoroacetic acid (○), formic acid (Δ), and acetic acid (□).

*p* AO of the methylene carbon plays the same role as the empty antibonding ethylenic MO does in IX. One would therefore expect the stabilities of the two ions to show a similar dependence on the nature of the aryl group. This argument has been applied by Streitwieser<sup>4a</sup> to the reactions of substituted 2-phenylethyl esters; such reactions are, however, difficult to analyze theoretically because of the complications due to the inductive and/or field effects of the polar substituents.

The solvolyses of arylmethyl esters,  $ArCH_2X$ , where  $ArH$  is an AH, have been interpreted very successfully<sup>6,8</sup> in terms of MO theory. In the case of reactions carried out under limiting conditions, *e.g.*, formolysis of chlorides or acetolysis of *p*-toluenesulfonates, there is a good linear relationship between the logarithms of the rate constants and the calculated differences in energy (localization energy) between  $ArCH_2X$  and  $ArCH_2^+$ . The agreement was better<sup>8</sup> for differences calculated by a SCF-MO method, based on the  $\pi$  approximation, than for those estimated by the HMO or PMO (perturbational MO) methods; this of course would be expected since the SCF procedure is known<sup>8</sup> to be much more accurate and reliable. If then a parallel exists, as indicated above, between the solvolysis of  $ArCH_2X$  and the aryl-assisted solvolysis of  $ArCH_2CH_2X$ , one would expect a linear relation between the logarithms of the rate constants of the latter reaction and the corresponding localization energies, and one would expect a better correlation for localization energies calculated by the SCF-MO method.

Figure 1 shows a plot of the logarithms of the relative rates of solvolysis from Table II against the NBMO coefficient ( $a_{or}$ ) in the odd AH  $ArCH_2$ , this being<sup>6,8</sup> a measure in the PMO approximation of the difference in

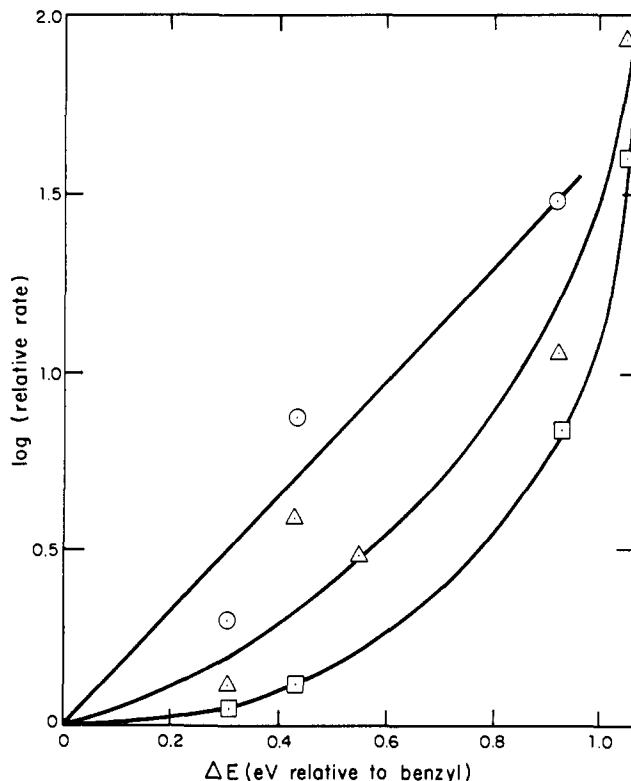


Figure 2. Plot of log (relative rate) vs.  $\Delta E$  for solvolysis of 2-arylethyl *p*-toluenesulfonates in trifluoroacetic acid (○), formic acid (Δ), and acetic acid (□).

energy between  $ArCH_2X$  and  $ArCH_2^+$ . It will be seen that the points for trifluoroacetolysis all lie close to a straight line, while those for formolysis and acetolysis tend to be somewhat curved. (The plot for acetolysis starts with a more horizontal section, corresponding to compounds where the assisted reaction is slower than one involving direct nucleophilic attack by the solvent.)

Figure 2 shows a similar plot in which the energy difference ( $\Delta E$ ) between  $ArCH_2X$  and  $ArCH_2^+$  was estimated directly by the SCF-MO procedure.<sup>8,27</sup> It will be seen that the plots are much *less* linear than those of Figure 1. This is in contrast to the results for solvolysis of arylmethyl derivatives.

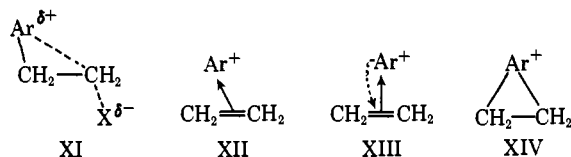
There is therefore a clear distinction between the solvolyses of arylmethyl derivatives, and the assisted solvolyses of analogous 2-arylethyl ones, which is emphasized by two further pieces of evidence. First, the variation in rate is much greater for the limiting solvolyses of arylmethyl derivatives than for the assisted solvolyses of 2-arylethyl ones, even though the latter reactions are much slower; thus the ratio of rates of formolysis for 1-naphthylmethyl chloride and benzyl chloride in moist formic acid at 25° is 382, whereas the corresponding ratio for III and I in trifluoroacetic acid is only 7.5. This suggests that the effect of  $\pi$  bonding in stabilizing the transition state for the former reaction is about three times as great as is the effect of aryl participation in the latter. Secondly, the PMO plots (*cf.* Figure 1) for formolysis of  $ArCH_2Cl$  showed<sup>6,8</sup> a distinction between compounds analogous to  $\beta$ -naphthylmethyl chloride with both positions *ortho* to  $CH_2Cl$  free and compounds analogous to  $\alpha$ -naphthyl-

(27) M. J. S. Dewar and C. de Llano, *J. Amer. Chem. Soc.*, **91**, 789 (1969).

methyl chloride with only one free *ortho* position. On passing to systems where the separation of chloride was assisted to an increasing extent by the nucleophile, the difference between the two types of chloride decreased, becoming zero for the "pure SN2" reactions of the chlorides with iodide ions in dry acetone. As nucleophilic participation by the entering group in the transition state increased, the amount of  $\pi$  bonding between the aryl group and the reaction center correspondingly decreases. Although the explanation given originally<sup>6</sup> for the distinction between " $\alpha$ -naphthyl" and " $\beta$ -naphthyl" types is probably incorrect,<sup>8</sup> the fact that the plots in Figure 1 shows no such distinction does suggest that the arylolefin reactions, like SN2 reactions of arylmethyl derivatives, involve relatively little assistance from the aryl group.

If the  $\pi$ -type interaction between aryl and the reaction center in the transition states for the assisted 2-arylethyl solvolyses is indeed small, the  $\pi$  electrons of the aryl group should be very little perturbed. The structure of the aryl group in the transition state should then resemble that in  $\text{ArCH}_2\text{X}$  more closely than that in  $\text{ArCH}_2^+$ . If so, one would expect<sup>8</sup> the energy of interaction between Ar and the reaction center to be given satisfactorily by first-order perturbation theory, being proportional to the self-polarizability ( $\pi_{rr}$ ) of the anion ( $r$ ) in Ar adjacent to the reaction center. Figure 3 shows logarithms of the relative rates for Table II plotted against  $\pi_{rr}$ ; it will be seen that the portions of the plots corresponding to the assisted reactions are indeed more linear than those in Figures 1 or 2. A further satisfactory feature of Figure 3 is that the points for the benzyl ester (I) lie on the lines for trifluoroacetolysis and formolysis, implying that the reactions of I under these conditions may take place essentially completely by the assisted path. This is consistent with the evidence concerning scrambling of the methylene groups (Table I and ref 23), and similar scrambling has been observed in the formolysis (Table I) and trifluoroacetolysis (reported here) of III and IV. Figure 3 predicts on the other hand that the unassisted reaction should be important in the acetolysis of I and significant for II; this is also in agreement with the evidence in Table I.

The relatively weak participation of aryl in the assisted 2-arylethyl solvolysis, compared with the much larger effects in limiting arylmethyl solvolyses, could be explained in terms of a very unsymmetrical transition state XI in which the aryl group is interacting only weakly with the reaction center. Such a transition state could correspond to a process in which the intermediate  $\pi$  complex is itself unsymmetrical (XII) (*cf.* ref<sup>4b</sup>), or to one in which migration of aryl to the symmetrical bridging position (IX) has only taken place to a small extent.



The objection to this mechanism is that it provides for only a very small overall effect of the aryl group, whereas there are good reasons for believing that the overall effect of aryl must in fact be large. The for-

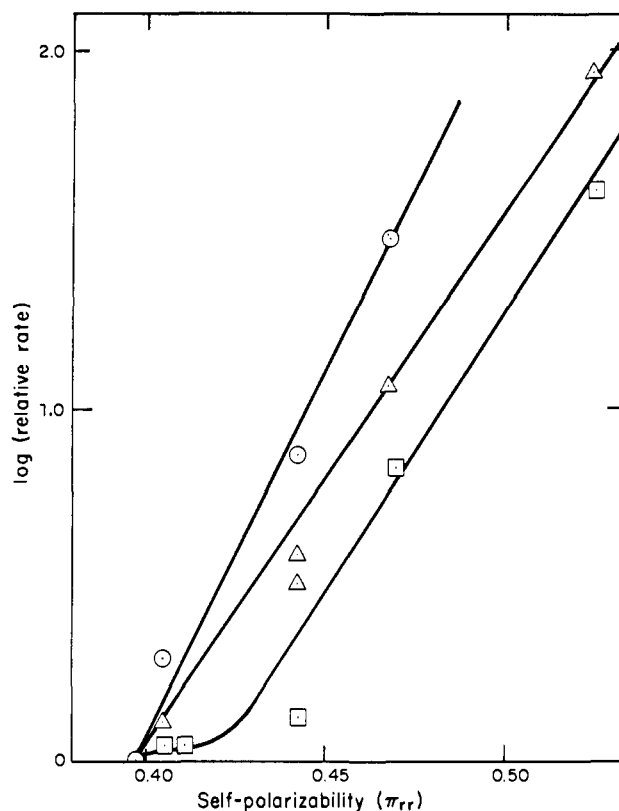


Figure 3. Plot of  $\log$  (relative rate) vs.  $\pi_{rr}$  for solvolysis of 2-arylethyl *p*-toluenesulfonates, in trifluoroacetic acid ( $\circ$ ), formic acid ( $\triangle$ ), and acetic acid ( $\square$ ).

molysis of primary alkyl arylsulfonates is a process of SN2 type, involving Walden inversion,<sup>4a,28</sup> such a process must involve a transition state in which there is very strong bonding of the entering nucleophile to the reaction center. The aryl-assisted solvolysis of an analogous 2-arylethyl ester can compete with the usual solvent-assisted reaction only if the attachment of aryl to the reaction center in the former is as strong as that of solvent to the reaction center in the latter; it therefore seems likely that the *overall* effect of aryl in the aryl-assisted solvolyses of 2-arylethyl esters is large, but that the differences between different aryl groups is less than expected from the apparent analogy between IX and X.

An alternative explanation rests on a more detailed consideration of the  $\pi$  complex IX. In this the  $\pi$ -type interaction, corresponding to back-coordination, involves formation of a  $\pi$  dative bond in which the acceptor orbital is the empty antibonding MO of ethylene. Since this MO has a much higher energy than a carbon 2p AO, the strength of the  $\pi$ -type dative bond in IX should be much less than that of the bond between aryl and methylene in  $\text{ArCH}_2^+$  (X), a situation which could be emphasized by writing the  $\pi$  complex IX as XIII. If the transition state for the assisted 2-arylethyl solvolyses is indeed similar to XIII in structure, the effect of aryl will then arise mainly from the  $\sigma$ -type three-center bond and so be more or less independent of the aryl group. The differences in rates of solvolysis between different arylolefin esters would on the other hand be due to changes in the energy of the

(28) A. Streitwieser Jr., *J. Amer. Chem. Soc.*, 77, 1117 (1955).

relatively weak  $\pi$ -type three center bonds. This interpretation would explain the large overall accelerating effect of aryl, together with the relatively small difference between different aryl groups.

This discussion has been based on the assumption that the intermediate ions are better represented as  $\pi$  complexes (VIII) rather than as phenonium ions (XIV); for a discussion of the relationship between the two representations, see ref 26. It could be that the curvature of the plots in Figure 2 was merely an indication that the ions are better represented as XIV than as VIII. Since XIV is analogous to the intermediates in electrophilic substitution,<sup>26</sup> we would then expect a plot of the logarithms of solvolytic rate constants ( $\log k$ ) vs. localization energies ( $E_{loc}$ ) to be linear. In fact, however, a plot of  $\log k$  vs.  $E_{loc}$ , the latter calculated by our SCF procedure,<sup>27, 29</sup> shows the same curvature as the

(29) C. de Llano, Ph.D. Dissertation, The University of Texas at Austin, 1968.

plots of Figure 2. This of course is not surprising in view of the known<sup>26</sup> relationship between  $E_{loc}$  and  $\Delta E$ .

Not only does this result not support the phenonium ion representation, but it even argues against it, for if the intermediates were phenonium ions, the curvature of the plots of  $\log k$  vs.  $E_{loc}$  would be hard to explain, while the curvature of the plots in Figure 2 can be explained in a reasonable manner if the intermediates are best represented as  $\pi$  complexes.

The conclusions reached here are in agreement with those recently drawn by Schleyer and his collaborators<sup>30</sup> from studies of the rates of solvolysis of substituted 2-phenylethyl esters, using the Hammett relation. These showed in a very elegant way the transition from unassisted reaction with increasing nucleophilicity of the aryl group.

(30) C. J. Lancelot and P. von R. Schleyer, *J. Amer. Chem. Soc.*, **91**, 4291, 4296, 4297 (1969); C. J. Lancelot, J. J. Harper, and P. von R. Schleyer, *ibid.*, **91**, 4294 (1969).

## The Structure of a Halosulfonium Salt. The 1:1 Adduct of Thiophane with Bromine

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**Abstract:** The structure of the 1:1 adduct of thiophane with bromine has been investigated by X-ray (space group Pnma,  $a = 12.326$  (5),  $b = 7.331$  (3),  $c = 8.387$  (3) Å,  $Z = 4$ ,  $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.085$  for 692 observed reflections) and nmr methods. In the solid state the tricoordinate sulfur atom is pyramidal and the S-Br-Br arrangement is linear with S-Br and Br-Br bond lengths of 2.32 and 2.72 Å, respectively. The ring appears planar, but highly anisotropic thermal coefficients were found for the  $\beta$ -carbon atoms. Minimum potential energy calculations suggest that the conformation of the thiophane ring has  $C_2$  symmetry with a low energy barrier between the two enantiomers. Thus, the existence of a statistical distribution between both conformations, perhaps maintained through a dynamic process, provides the most satisfying interpretation of the X-ray results. The nmr data for solutions of the complex suggest rapid inversion of pyramidal coordination and a highly charged sulfur atom. Self-consistent charge extended Hückel calculations indicate a  $+0.34$  charge on sulfur and a  $-0.8$  charge on the terminal bromine, little involvement of sulfur d orbitals, and a very weak Br-Br interaction.

The molecular structure of the metastable adducts formed between organic sulfides and the reactive halogens bromine and chlorine has remained a persistent dilemma. Much of the mystery regarding their structure arises because of their instability with respect to thermal degradation, moisture, or disproportionation. By analogy to structures suggested for sulfur tetrafluoride<sup>3,4</sup> and its organic derivatives<sup>5</sup> and halogenated derivatives of selenium,<sup>6</sup> tellurium,<sup>7</sup> and phos-

phorus,<sup>8</sup> a trigonal-bipyramidal array of groups<sup>9</sup> about sulfur has been considered a possibly stable one,<sup>10</sup> and recently the complex of chlorine with bis(*p*-chlorophenyl) sulfide has been reported to have a trigonal-bipyramidal sulfur atom.<sup>11</sup> On the other hand the lability of protons on the carbons attached to sulfur,<sup>12</sup> the susceptibility of the carbon-sulfur bonds to cleavage forming carbonium ions,<sup>13</sup> and the extreme ease with

11, 782 (1958); G. D. Christofferson and J. D. McCullough, *ibid.*, **11**, 249 (1958).

(8) E. L. Muetterties, W. Mahler, K. J. Packer, and R. Schmutzler, *Inorg. Chem.*, **3**, 1298 (1964); E. L. Muetterties, W. Mahler, and R. Schmutzler, *ibid.*, **2**, 613 (1963).

(9) A thorough review of pentacoordinate species is available: E. L. Muetterties and R. A. Schunn, *Quart. Rev. (London)*, **20**, 245 (1966).

(10) See, for example (a) K. Mislow, T. Simmons, J. T. Melillo, and A. L. Ternay, Jr., *J. Amer. Chem. Soc.*, **86**, 1452 (1964); (b) K. Mislow, *Rec. Chem. Progr.*, **28**, 217 (1967); (c) J. I. Musher, *Angew. Chem. Intern. Ed. Engl.*, **8**, 54 (1969).

(11) N. C. Baenziger, R. E. Buckles, Jr., R. J. Maner, and T. D. Simpson, *J. Amer. Chem. Soc.*, **91**, 5749 (1969).

(12) See, for example: F. G. Bordwell and B. M. Pitt, *ibid.*, **77**, 572 (1955); D. L. Tuleen and T. B. Stephens, *J. Org. Chem.*, **34**, 31 (1969); H. Bohme and H. Gran, *Ann.*, **581**, 133 (1953).

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(3) L. Muetterties and W. D. Phillips, *J. Amer. Chem. Soc.*, **81**, 1084 (1959).

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(5) W. A. Sheppard, *J. Amer. Chem. Soc.*, **84**, 3058 (1962).

(6) J. D. McCullough and G. Hamburger, *ibid.*, **63**, 803 (1941); **64**, 508 (1942); J. D. McCullough and R. E. Marsh, *Acta Crystallogr.*, **3**, 41 (1950).

(7) G. D. Christofferson, R. A. Sparks, and J. D. McCullough, *ibid.*,