were carefully purified by fractional distillation at normal pressure. Boiling points (uncorrected) and pmr data (CCl_4, TMS) are reported below for the ethers synthesized: **1b**, bp 7° (lit.[28] bp 6.6°, cor); δ 3.33 (CH_2CH_3, q, $J_{HCH} = 7.0$ Hz), 3.23 (CH_3, s), 1.13 (CH_2CH_3, t); **1c**, bp 31° (lit.[29] bp 31° (752 mm)); δ 3.36 ($CH(CH_3)_2$, septet, $J_{HCH} = 6.1$ Hz), 3.20 (CH_3, s), 1.09 ($CH(CH_3)_2$, d); **1d**, bp 53–54° (lit.[30] bp 55–56° (769 mm)); δ 3.10 (CH_3, s), 1.12 ($C(CH_3)_3$, s).

pK_{BH^+} Measurements. Solutions of bases (*ca.* 0.05 *M*) were made in sulfuric acid solution (0.5–18.6 *M*) containing Me_3NH^+ (0.05 *M*) as reference.

Care was taken to make the solutions just before measurements since decomposition of some substrates was observed on standing in acid solution. In particular, compounds **3** and **4** suffer decomposition before any degree of protonation could be observed. No detailed analysis of the products deriving from such reaction has been so far accomplished. Attempts to slow down this decomposition by working under nitrogen or with carefully degassed solutions were unsuccessful. Therefore, only $\Delta\nu_B$ values are reported for these substrates. Methyl *tert*-butyl ether (**1d**) also decomposes very fast. By running the spectra within 45 sec after mixing with acids we measured $\Delta\nu$ values up to 8.7 *M* H_2SO_4.

With the other compounds the decomposition is much slower and therefore measurements were made up to 18.6 *M* H_2SO_4. However, $\Delta\nu_{BH^+}$ values had to be computed, since even at this acid concentration protonation was not complete.

The computation was made on the basis of eq 2, by expressing $\Delta\nu$ as a function of $\Delta\nu_B$, H_0, $\log [H^+]$, $\Delta\nu_{BH^+}$, ϕ, and pK_{BH^+}. The last three terms were varied by 1% increments until the best fit between calculated and experimental $\Delta\nu$ values was found through the least-squares analysis reported by Sillen.[31] This treatment cannot be used for **1d** because of the small range of protonation experimentally observable.

By plotting $\Delta\nu_{BH^+}$ for **1a–c** *vs.* Taft's σ^*, we obtained a curve from which a value of −98.5 has been extrapolated for **1d**.

Data were treated as before.[10]

Acknowledgment. We are indebted to Professor K. Yates for informing us of the work cited in ref 24 prior to publication.

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[28] V. N. Ipatieff and R. L. Burwell, Jr., *J. Amer. Chem. Soc.*, **63**, 969 (1941).

[29] P. G. Stevens and S. A. V. Deans, *Can. J. Res., Sect. B*, **17**, 290 (1939).

[30] L. C. Bateman, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 881 (1938).

[31] L. G. Sillen, *Acta Chem. Scand.*, **18**, 1085 (1964), and previous papers.

Bond Scission in Sulfur Compounds. VIII.[1] Reaction of Aryl Chlorosulfates with Anionic Nucleophiles

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Abstract: Reaction of phenyl chlorosulfate, and of *p*-nitrophenyl chlorosulfate, with some anionic nucleophiles is found to give rise to phenol, and *p*-nitrophenol, quantitatively. Kinetic data for the reactions have been obtained in 1% aqueous ethanol (acetate buffers). The observed reactivity order is $S_2O_3^{2-} > CN^- > I^- > SO_3^{2-} \gg Br^-, Cl^-, F^-, AcO^-$. Several possible mechanisms are considered but the one involving nucleophilic displacement at chlorine is strongly favored. On that basis, the results show the halogen center to be a "soft" electrophilic site toward nucleophilic attack. Discussion of activation parameters is also given.

The occurrence of three electrophilic centers in chlorosulfates, carbon, sulfur, and chlorine, renders the $ROSO_2Cl$ substrates of considerable interest since nucleophiles may potentially react at one or several of these centers.[2] It will be recalled that studies from our laboratory have shown that, typically, alkyl chlorosulfates undergo attack at carbon (OSO_2Cl^- leaving group),[3a] while attack at sulfur (Cl^- leaving group) is only a minor process.[3b] Evidence for a possible fragmentation process, $R\cdots OSO_2\cdots Cl$, has also been presented.[3c] On the other hand, we found no evidence of displacement at chlorine in reaction of alkyl chlorosulfates with common nucleophilic reagents.

Aryl chlorosulfates were chosen for further investigation since with these substrates nucleophilic displacement at aromatic carbon should be unlikely,[4] thus increasing the likelihood that attack at the sulfur or chlorine site would become a possibility. It was found in fact that phenyl chlorosulfate reacts with methoxide ion in methanol concurrently through S–O and S–Cl bond scission, that is by attack at sulfur with comparable aryloxy and chlorine leaving group tendencies.[5a] *p*-Nitrophenyl chlorosulfate reacts by the same modes, though the S–O scission process becomes more important in accord with the greater leaving group ability of *p*-nitrophenoxide ion.[5b] Thus chlorine as an electrophilic site still remained elusive.

It seemed possible that significant change in the nucleophilic reagent could induce a change in mechanism of reaction in the aryl chlorosulfates series. Hence a study was initiated of phenyl chlorosulfate and of *p*-nitrophenyl chlorosulfate with a variety of nucleophiles, characterized by varied polarizability, with the view that differentiation between the sulfur and chlorine centers might become feasible; the results of this study are now

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[1] Part VII: E. Buncel, A. Raoult, and J. F. Wiltshire, *J. Amer. Chem. Soc.*, **95**, 799 (1973).

[2] E. Buncel, *Chem. Rev.*, **70**, 323 (1970).

[3] (a) E. Buncel and J. P. Millington, *Can. J. Chem.*, **43**, 547 (1965); (b) *ibid.*, **47**, 2145 (1969); (c) *ibid.*, **43**, 556 (1965).

[4] (a) J. F. Bunnett and R. E. Zahler, *Chem. Rev.*, **49**, 273 (1951); (b) E. Buncel, A. R. Norris, and K. E. Russell, *Quart. Rev., Chem. Soc.*, **22**, 123 (1968); (c) J. Miller, "Aromatic Nucleophilic Substitution," Elsevier, Amsterdam, 1968.

[5] (a) E. Buncel, L. I. Choong, and A. Raoult, *J. Chem. Soc., Perkin Trans. 2*, 691 (1972); (b) E. Buncel and A. Raoult, *Can. J. Chem.*, **50**, 1907 (1972); (c) E. Buncel and A. Raoult, *J. Chem. Soc., Chem. Commun.*, 210 (1973).

reported. Some of the rate data, pertaining to phenyl chlorosulfate, have already been given in abbreviated form.[5c] Our results are of a highly unusual nature, if in fact displacement at sulfur does occur. On the other hand, the results strongly suggest that we are actually observing nucleophilic displacement at chlorine, for which we have been able to obtain the first quantitative reactivity data.

Experimental Section

The method for preparation of phenyl chlorosulfate[5a] and of *p*-nitrophenyl chlorosulfate[5b] has already been described. All the inorganic salts used were reagent grade. Solutions of the salts were prepared using triply distilled water. Solutions of the chlorosulfates were made up in ethanol which had been dried and distilled.

The reactions of aryl chlorosulfates with various nucleophilic reagents were carried out under pseudo-first-order conditions in 1% aqueous ethanol in an acetate buffer (pH 4.6–5.5) with the anionic reagent present in large excess. Runs were initiated by the addition, with a syringe, of a stock solution of substrate in ethanol (0.05 ml) to an aqueous solution (4.95 ml) of the reagent in buffered medium, contained in a thermostated cuvette (20-mm path length) in the cell compartment of a Unicam SP 800 spectrophotometer. The mixing techniques used have been described elsewhere.[5a] In the case of fast reactions, the formation of phenol was monitored at 270 nm and that of *p*-nitrophenol at 317 nm. Slower reactions were followed by repeated scanning over the region 225–400 nm. Full spectra were taken at the completion of reaction in all cases. In some typical instances, the pH of solutions was determined before and after a run was completed and shown not to vary by more than 0.02 pH unit at most.

Pseudo-first-order rate constants (k_{obsd}) were calculated from the linear plots of log ($A_\infty - A_t$) *vs.* time, where A_t and A_∞ are the absorbances at 270 nm (or 317 nm) at time t and at the completion of reaction. Rates measured over a range of anion concentration yielded the second-order rate constant k_{Nu}. Plots of log k_{obsd} *vs.* log [Nu] were linear and of slope equal to unity. Activation parameters were obtained from the appropriate linear plots as described elsewhere.[5a]

Table I. Reaction of Phenyl Chlorosulfate with Anionic Reagents in 1% Ethanol–99% Water (v/v) at 25°

	Reagent/ concn, mol l.$^{-1}$	[Substrate], mol l.$^{-1}$	pH[a]	$10^3 k_{obsd}$,[b] sec^{-1}	k_{Nu},[c] M^{-1} sec^{-1}
NaI	2.0×10^{-3}	2.5×10^{-5}	5.06	24.8	15.9
				25.3	
	4.0×10^{-3}			52.0	
	2.0×10^{-3}	2.0×10^{-4}		30.4	
				30.7	
	4.0×10^{-3}			59.8	
				59.8	
			4.65	59.8	
				60.9	
			5.45	59.8	
				62.1	
	8.0×10^{-3}		5.06	127	
				126	
	2.0×10^{-3}	4.0×10^{-4}		34.1	
				33.7	
	4.0×10^{-3}			69.0	
Na_2SO_3[d]	5.0×10^{-3}	2.0×10^{-4}	5.45	0.421	2.55
	1.0×10^{-2}			0.735	
	1.5×10^{-2}			1.05	
	2.0×10^{-2}			1.49	
				1.44	
	2.0×10^{-2}		5.06	0.625	
	3.0×10^{-2}		5.45	2.16	
NaCN[d]	1.5×10^{-3}		5.50	1.50	4300
	2.0×10^{-3}			1.87	
	3.0×10^{-3}			2.55	

[a] Acetate buffer, with concentration of acetate 0.05 *M*, except for the sodium cyanide reaction where the acetate was 0.097 *M*. [b] Corrected for solvolysis. [c] Calculated from plots of k_{obsd} *vs.* concentration of nucleophile. [d] Total reagent concentration; the actual concentration of nucleophile at a given pH was calculated using the pK_a values 7.0 for HSO_3^- and 9.3 for HCN.

Table II. Reaction of *p*-Nitrophenyl Chlorosulfate with Anionic Reagents in 1% Ethanol–99% Water (v/v) at 25°

	Reagent/ concn, mol l.$^{-1}$	[Substrate], mol l.$^{-1}$	pH[a]	$10^3 k_{obsd}$,[b] sec^{-1}	k_{Nu},[c] M^{-1} sec^{-1}
NaI	2.5×10^{-4}	5×10^{-5}	5.06	55.2	212
	5.0×10^{-4}			105	
				111	
				111	
	1.0×10^{-3}			207	
	1.5×10^{-3}			320	
Na_2SO_3[d]	5.0×10^{-3}		5.45	2.70	14.6
	1.0×10^{-2}			4.47	
	2.0×10^{-2}			8.85	
	3.0×10^{-2}			12.6	
	3.0×10^{-2}	10^{-5}		11.5	
NaCN[d]	1.0×10^{-3}	5×10^{-5}	5.50	4.17	24100
	2.0×10^{-3}			7.71	
	3.0×10^{-3}			11.6	
	2.0×10^{-3}	10^{-5}		7.25	

[a,b,c,d] As for Table I.

Results

The reaction of phenyl, or *p*-nitrophenyl, chlorosulfate with anions in aqueous acetate buffer was characterized in all cases by the appearance of a spectral absorption typical of phenol, or *p*-nitrophenol, which were produced quantitatively. With the slower runs, where it was possible to scan the entire spectrum throughout the course of reaction, an isosbestic point was observed. This rules out the buildup of an intermediate of appreciable lifetime, provided such an intermediate possesses spectral characteristics different from both substrate and product and is not in rapid equilibrium with either. In the case of *p*-nitrophenyl chlorosulfate, the rate of disappearance of substrate (followed at 260 nm) yielded a rate constant equal to that obtained when following the appearance of *p*-nitrophenol.

Quantitative data were obtained for cyanide, iodide, and sulfite ions and are given in Table I for phenyl chlorosulfate and Table II for *p*-nitrophenyl chlorosulfate. Plots of log k_{obsd} *vs.* log [Nu] gave straight lines of slope equal to unity, establishing the reaction to be first order in nucleophile. In the case of the Na_2SO_3 reagent, the reacting species was shown to be SO_3^{2-}, rather than HSO_3^-, in the following manner.[6] Phenyl chlorosulfate was allowed to react with sodium sulfite at two different pH values (5.06 and 5.45) but keeping the reagent concentration constant (0.02 *M*). Using the Henderson–Hasselbach equation, the amount of reagent present in the conjugate acid and base forms could be calculated, from the known pK_a, at each of the two pH values. The observed first-order rate constants could hence be used to calculate second-order rate coefficients with respect to sulfite ion, yielding the values 2.66 and 2.71 M^{-1} sec^{-1} for the two media. The constancy of the second-order rate coefficient with respect to the concentration of sulfite ion establishes that this species, and not bisulfite ion, is the reactive entity toward phenyl chlorosulfate. In addition to the anions for which rate data are recorded in Tables I and II, the

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(6) (a) W. P. Jencks and J. Carriuolo, *J. Amer. Chem. Soc.*, **82**, 1778 (1960); (b) A. Raoult and M. Vilkas, *Bull. Soc. Chim. Fr.*, 3315 (1968).

Table III. Rate Data and Activation Parameters in Reaction of Phenyl Chlorosulfate (PCS) and *p*-Nitrophenyl Chlorosulfate (*p*-NPCS) with Sodium Iodide and Sodium Sulfite in 1% Ethanol–99% Water (v/v) Acetate Buffers[a]

Reaction	[Substrate], mol l.$^{-1}$	[Reagent], mol l.$^{-1}$	Temp, °C	$10^3 k_{obsd}$,[b] sec^{-1}	k_{Nu}, M^{-1} sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	$\Delta F^{\ddagger}$, kcal/mol
PCS + NaI	2×10^{-4}	2×10^{-3}	15.1	14.6 13.5	7.02			
			25.0	30.4 30.7	15.9	13.5	−7.8	15.9
			35.0	67.9 69.2	34.3			
PCS + Na_2SO_3[c]	2×10^{-3}	2×10^{-2}	15.1	0.66 0.71	1.20			
			25.0	1.49 1.44	2.55	10.9	−20.0	17.0
			35.0	2.48 2.59	4.40			
p-NPCS + NaI	5×10^{-5}	5×10^{-4}	15.4	51.5 53.3	105			
			25.0	105 111	212	12.3	−6.6	14.3
			35.0	216 221	437			
p-NPCS + Na_2SO_3[c]	5×10^{-5}	2×10^{-2}	15.2	4.35 4.35	7.57			
			25.0	8.85	14.6	11.5	−14.5	15.9
			35.0	15.2 18.9	29.2			

[a] For the iodide reaction the pH was 5.06, while for the sulfite reaction the pH was 5.45. The acetate concentration was 0.05 M throughout. [b] Corrected for solvolysis. [c] Total concentration of sodium sulfite is given (see text).

following further information was obtained. The thiosulfate ion reacted at a rate too fast to be measurable by the present technique. Bromide, chloride, and fluoride ions did not enhance the hydrolysis rate measured over that in the acetate buffer alone. Additional rate data were obtained to allow some activation parameters to be determined and these are recorded in Table III.

Discussion

Reaction of phenyl chlorosulfate, or *p*-nitrophenyl chlorosulfate, with the anionic reagents has been found to give rise to phenol, or *p*-nitrophenol, as the only observable product in a facile process. The overall reaction may be depicted by the equation

$$ArOSO_2Cl + 2H_2O \xrightarrow{Nu^-} ArOH + H_2SO_4 + HCl \qquad (1)$$

For both substrates the order of nucleophilic reactivity is $S_2O_3^{2-} > CN^- > I^- > SO_3^{2-} \gg Br^-, Cl^-, F^-, AcO^-$. The problem posed by these observations is, what is the reaction pathway leading to phenolic product and how can one explain this reactivity order?

A number of possible mechanisms are worthy of consideration. Perhaps the most straightforward explanation might be that initial attack occurs at the sulfur center (Cl^- leaving) and that the $ArOSO_2Nu$ produced becomes rapidly hydrolyzed to $ArOSO_3H$ which subsequently would yield ArOH. However, this pathway can be ruled out since aryl hydrogen sulfates are known to be stable in neutral medium, though at much lower pH values an acid-catalyzed process becomes effective giving rise to phenolic product.[7] Alternatively, the initially formed $ArOSO_2Nu$ species could undergo further attack at sulfur with preferential displacement of ArO^-. This appears to be unlikely as a general mechanism since it would require, for instance in the case of $Nu^- = I^-$, a leaving group order $PhO^- < Cl^-$ in the first stage and $PhO^- > I^-$ in the second stage, which cannot be justified.

The second possibility is that reaction proceeds by attachment of nucleophile to the sulfur center with initial formation of a pentacoordinate intermediate which breaks down solely by expulsion of phenoxide ion, rather than of chloride ion. However, in view of the elusive nature of pentacoordinate intermediates (there is no *positive* proof for such species in reaction at sulfonyl centers)[8] such a mechanism is not regarded as probable.

Thirdly we consider the possibility that reaction occurs by direct synchronous displacement at sulfur with expulsion of phenoxide ion. However, the implied leaving group order, $PhO^- \gg Cl^-$, has not previously been observed in nucleophilic substitution reactions.[9] While we cannot exclude this pathway on the basis of the present results, if such a mechanism were to obtain then many accepted ideas of nucleophilic reactivity[9,10] would have to be questioned as applicable only to systems where a "normal" leaving group order is followed. Bearing in mind the fact that the sulfonyl center has been termed "hard,"[8b] if reaction occurred at this center in the $ArOSO_2Cl$ series then one would have predicted high reactivity by relatively nonpolarizable

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[7] (a) J. L. Kice and J. M. Anderson, *J. Amer. Chem. Soc.*, **88**, 5242 (1966); (b) S. J. Benkovic and P. A. Benkovic, *ibid.*, **88**, 5504 (1966); (c) E. J. Fendler and J. H. Fendler, *J. Org. Chem.*, **33**, 3852 (1968).

[8] (a) E. Ciuffarin and A. Fava, *Progr. Phys. Org. Chem.*, **6**, 81 (1968); (b) J. L. Kice, G. J. Kasperek, and D. Patterson, *J. Amer. Chem. Soc.*, **91**, 5516 (1969); (c) W. A. Pryor and K. Smith, *ibid.*, **92**, 2731 (1970); (d) J. H. Smith, T. Inoue, and E. T. Kaiser, *ibid.*, **94**, 3098 (1972).

[9] (a) E. S. Gould, "Mechanism and Structure in Organic Chemistry," Holt, Rinehart and Winston, New York, N. Y., 1959, Chapter 8; (b) C. K. Ingold, "Structure and Mechanism in Organic Chemistry," 2nd ed, Cornell University Press, Ithaca, N. Y., 1969, Chapter 7.

[10] (a) J. O. Edwards and R. G. Pearson, *J. Amer. Chem. Soc.*, **84**, 16 (1962); (b) R. G. Pearson, *ibid.*, **85**, 3533 (1963); (c) R. G. Pearson and J. Songstad, *ibid.*, **89**, 1827 (1967).

nucleophiles. However, the actual results point to an opposite reactivity order.

The final mechanism considered is nucleophilic displacement at chlorine. This process would yield initially phenyl sulfite ion which would then decompose to phenol and bisulfite ion. The latter is expected to be oxidized by the pseudo-halogen formed in the first stage of reaction, yielding bisulfate and chloride ions and regenerating the anionic nucleophiles. The overall reaction sequence is then

$$\mathrm{ArOSO_2Cl + Nu^- \longrightarrow ArOSO_2^- + ClNu} \qquad (2)$$

$$\mathrm{ArOSO_2^- + H_2O \longrightarrow ArOH + HSO_3^-} \qquad (3)$$

$$\mathrm{NuCl + HSO_3^- + H_2O \longrightarrow Nu^- + Cl^- + HSO_4^- + 2H^+} \qquad (4)$$

Nucleophilic substitution at halogen centers has not been investigated extensively hitherto and there appear to be no quantitative data given in the literature for displacement at chlorine. It is significant, however, that in those cases where displacement at halogen has been observed (or proposed), nucleophiles of high polarizability have been found to be the most effective.[11] For instance, the reaction of sulfonyl chlorides with nucleophiles such as Ph_3P, I^-, and SO_3^{2-} gives products which are indicative of reaction at the chlorine center.[11b,c] Another example is the reaction of halide ions with stilbene dibromides in DMF where the reactivity order $I^- > Br^- > Cl^- > Sn^{2+} >$ DMF was found for attack at bromine.[12] Other cases described in the literature[13] are in accord with the high polarizability principle; our own data are fully accommodated thereby. Thus a general picture emerges of univalent halogen as a "soft" electrophilic site.

The question need also be posed whether or not phenyl chlorosulfate and the *p*-nitro derivative react by a common mechanism. Germane to this point is the plot of the logarithm of the second-order rate constants for reaction of nucleophiles with phenyl chlorosulfate *vs.* the logarithm of the second-order rate constants for the *p*-nitrophenyl chlorosulfate reaction which is linear and has unit slope. While it would be desirable to extend the number of points on this graph beyond the three that are currently available, the linear relationship may be regarded as meaningful. This type of correlation has been considered as a way of normalizing dispersion factors in nucleophilic reactivity studies for two different substrates reacting by the same mechanism.[14]

Lastly we consider the significance of the activation parameters, which are presented in Table III. It is seen that, with both substrates, the iodide ion reaction is characterized by a smaller $\Delta F^{\ddagger}$ than the sulfite ion reaction. However, $\Delta H^{\ddagger}$ for the I^- reaction is larger than that for the SO_3^{2-} reaction while $\Delta S^{\ddagger}$ is more positive for the former, so that on balance the $T\Delta S^{\ddagger}$ term favors the iodide ion reaction. The more negative $\Delta S^{\ddagger}$ value in the sulfite reaction points to greater transition state solvation compared to the iodide reaction, relative to the initial states. This conclusion is in accord with the larger solvation requirements by the electronegative oxygens of the sulfite moiety, which should be more likely to persist in the transition state. Thus in forming the transition state the desolvation of iodide ion will be larger than that of sulfite ion.

Of further interest is comparison of activation parameters in the present system with those obtained in the methanolysis of the aryl chlorosulfates.[5a,b,15] In the latter reaction the S–Cl scission pathway was characterized by $\Delta S^{\ddagger}$ values ranging from -11 to -14 eu, while the S–O scission pathway had the $\Delta S^{\ddagger}$ values $+7$ to $+9$ eu. It is apparent that while the former range of values fit into a region of normally observed $\Delta S^{\ddagger}$ for displacement of chloride ion in bimolecular processes, the reaction leading to phenol is characterized by an unusual $\Delta S^{\ddagger}$; this was ascribed to the operation of a stereoelectronic effect.[5a,b] For the present purposes we merely wish to contrast the pathways leading to phenol in the methanolysis system, characterized by a positive $\Delta S^{\ddagger}$, with the reaction of the anionic reagents described herein, which has negative $\Delta S^{\ddagger}$. This contrast lends further support to the notion discussed in this paper that the mechanistic pathways in the two reaction types are different.

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(11) (a) J. F. Bunnett, *Annu. Rev. Phys. Chem.*, **14**, 271 (1963); (b) F. Muth in "Houben Weyl, Methoden der Organischen Chemie," Vol. 9, 4th ed, E. Muller, Ed., Georg Thieme Verlag, Stuttgart, 1955, p 306; (c) T. Durst and M. J. O'Sullivan, *J. Org. Chem.*, **35**, 2043 (1970).

(12) W. K. Kuroka and S. I. Miller, *J. Org. Chem.*, **35**, 4034 (1970).

(13) (a) J. P. Freeman, *J. Amer. Chem. Soc.*, **82**, 3869 (1960); (b) J. F. Ahrens, *Recl. Trav. Chim. Pay-Bas*, **82**, 183 (1963); (c) M. C. Verplaegh, L. Donk, H. J. T. Bos, and W. Drenth, *ibid.*, **90**, 765 (1971); (d) J. F. Bunnett, *Accounts Chem. Res.*, **5**, 139 (1972); (e) J. I. Dickstein and S. I. Miller, *J. Org. Chem.*, **37**, 2168 (1972).

(14) (a) M. J. Gregory and T. C. Bruice, *J. Amer. Chem. Soc.*, **89**, 2121 (1967); (b) S. L. Johnson, *Advan. Phys. Org. Chem.*, **5**, 237 (1967).

(15) It is noted that the reaction media in the two cases are not identical, so that strict comparison is not possible. However, it is unlikely that on changing from methanolic medium to aqueous medium *relative* solvation effects should change significantly.