Timing of Bond Formation and Breaking in Nucleophilic Substitution at Dicoordinate Sulfur. Effect of the Basicity of Entering and Leaving Groups in the Reaction of Oxygen Nucleophiles with *para*-Substituted Phenyl Sulfenate Esters[1a]

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Abstract: The effect of the basicity of entering and leaving groups on the reaction of hydroxide and *para*-substituted phenoxide ions with *para*-substituted phenyl triphenylmethanesulfenic acid esters has been measured. The kinetic data plotted in a Brønsted fashion against the pK_a of the conjugate acid of the nucleophile and the leaving group, respectively, yield good linear relations characterized by $\beta = 0.25$ and $\beta = -0.97$. These values are discussed in terms of the timing of bond formation and breaking at the rate-determining transition state and interpreted as evidence of a synchronous SN2 displacement at sulfur.

A direct nucleophilic displacement reaction can conceivably take place in either of two mechanistically distinct processes. The first is a one-step synchronous process, the familiar SN2 mechanism of the English school, where bond formation and rupture are included in the same transition state. The second is a two-step addition–elimination process (recently labeled S$_A$N by Kosower[2]) where bond formation precedes bond breaking while a metastable intermediate is formed along the reaction path. Neglecting charges, the two mechanisms are summarized below where

$$\text{S}_\text{N}2 \quad \text{N:} + \text{Y-X} \longrightarrow [\text{N----Y----X}] \longrightarrow \text{N-Y} + \text{X:}$$

$$\text{S}_\text{A}\text{N} \quad \text{N:} + \text{Y-X} \rightleftharpoons [\text{N--Y—X}] \rightleftharpoons$$
$$\text{N-Y-X} \longrightarrow [\text{N—Y--X}] \longrightarrow \text{N-Y} + \text{X:}$$

transition states are shown in brackets.

Except in the few fortunate cases where the intermediate accumulates in solution to the point where it can be isolated[3] or detected by physical methods,[4] as is the case for nucleophilic aromatic substitution,[5] the two processes are kinetically equivalent. Their distinction must then rest on indirect evidence which is not always clear-cut.

Nevertheless, countless examples of substitutions are recorded in the literature, which can be classified into one or the other class. Thus, from organic chemistry, it is common notion that direct substitution at saturated carbon belongs to the SN2 class, while many substitutions at unsaturated carbon, whether acyl, aromatic, or vinyl, can be confidently assigned to the S$_A$N class.

These examples point out the fact that for an element of the second row, carbon, the S$_A$N mechanism may operate where the reaction center is part of a π system and may form a σ bond with the nucleophile without expanding its valence shell, but it does not operate for saturated carbon where it would imply a metastable pentacovalent species.

This leads us to consider the duality of mechanism for direct displacement in other organic systems where the electrophilic center may be a saturated atomic species for which valence shell expansion is more easily accessible. To remain in areas of wide interest to organic chemistry we will bring to attention the third row atoms, particularly silicon, phosphorus, and sulfur, whose saturated organic compounds are often involved in direct nucleophilic substitution at the heteroatom.

As for silicon and phosphorus, the pattern which emerges from the enormous wealth of factual information available is that, although most observations can be accounted for in terms of the more common SN2 mechanism, in numerous cases definitive proof has been reached of the operation of the S$_A$N mechanism.[6]

In contrast, at the present time the situation concerning sulfur is much less conclusive in regard to the possibility of the operation of the S$_A$N mechanism since the existing evidence is adequately fitted in terms of the SN2 mechanism.[7,8]

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(1) (a) The financial support of C. N. R., Rome, and du Pont de Nemours International S.p.A. is gratefully acknowledged; thanks are due to E. N. I. Rome for the loan of a stopped-flow spectrophotometer; (b) on leave from the University of Bari; (c) author to whom correspondence should be addressed at the Ecole de Chimie, Laboratoire de Chimie Organique, Université de Genève, Geneva, Switzerland.

(2) E. M. Kosower, "Introduction to Physical Organic Chemistry," John Wiley & Sons, Inc., New York, N. Y., 1968, p 65.

(3) J. Meisenheimer, *Ann.*, **313**, 242 (1902).

(4) (a) R. Foster and D. L. Hammick, *J. Chem. Soc.*, 2154 (1954); (b) R. Foster, C. A. Fyfe, P. H. Emslie, and M. I. Foreman, *Tetrahedron*, **23**, 227 (1967); (c) K. L. Servis, *J. Amer. Chem. Soc.*, **89**, 1508 (1968).

(5) For a discussion on the detection of intermediates in nucleophilic aromatic substitution see J. Miller, "Aromatic Nucleophilic Substitution," Elsevier Publishing Co., Amsterdam, 1968, p 10 ff.

(6) A survey of the pertinent literature is outside the scope of this article. Excellent recent publications exist to which the interested reader may refer. For substitution at silicon: (a) L. O. Sommer, "Stereochemistry, Mechanism, and Silicon," McGraw-Hill Book Co., Inc., New York, N. Y., 1964, p 88 ff, for example; (b) for substitution at phosphorus, see R. F. Hudson, "Structure and Mechanism in Organo Phosphorus Chemistry," Academic Press, London, 1965, Chapters 3 and 8; (c) F. H. Westheimer, *Accounts Chem. Res.*, **1**, 70 (1968).

(7) For a recent review see: E. Ciuffarin and A. Fava, *Progr. Phys. Org. Chem.*, **6**, 81 (1968).

(8) While the present research was being completed several reports appeared relevant to the question of formation of a metastable inter-

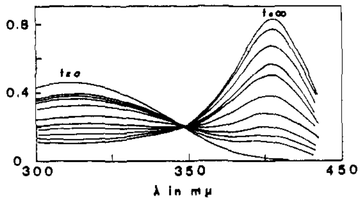

Figure 1. Change of the absorption spectrum for the alkaline hydrolysis of *p*-nitrophenyl triphenylmethylsulfenic ester. The wavelength scale on the Unicam SP800 uv spectrophotometer is compressed at 350 mμ as indicated.

The more significant evidence comes from the consideration of the structural effect on the sulfur substrate, which appears to be very meager; Hammett treatment of kinetic data for nucleophilic substitution at sulfenyl sulfur yields values of ρ which are positive but usually small, less than unity. The relevant evidence has been recently summarized.[7] Since then other reports have appeared confirming this general trend.[9-11] The low values of ρ seem to indicate that only little negative charge is dispersed from the reaction center toward the adjacent aromatic system. This is contrary to what might be expected for the S_AN mechanism. In fact, for certain substitutions at silicon or phosphorus centers where the operation of the S_AN mechanism has been evidenced, very high values of ρ have been found.[12]

Whatever the case may be it is obvious that more factual information is needed in order to put on less uncertain bases the question of the operation of the S_AN mechanism for sulfur. From the discussion which ensues, it will be clear that, in the lack of physical evidence for an intermediate, the next best evidence would be the knowledge of the relative extent of bond making and breaking at the rate-determining transition state. This goal can be achieved, on a roughly quantitative or at least qualitative basis, through the study of the rate effect resulting from some systematic structural variation of the nucleophile and of the leaving group. The approach consists of the determination of the Brønsted coefficients, β, for both entering and leaving groups. As Hudson[13] has shown in his fundamental papers, these coefficients are closely related to the extent of charge transfer from the nucleophile and to the leaving group, hence to the structure of the transition state.

We have undertaken a systematic investigation aimed at determining the coefficients for entering and leaving groups for sulfur substrates.

In this first paper we report kinetic data concerning the displacement by oxygen nucleophiles, hydroxide, and *para*-substituted phenoxides, of a series of *para*-substituted phenyl sulfenate esters, as an example of substitution at dicoordinated sulfur. Subsequent papers will deal with tri- and tetracoordinated sulfur.

Results

The rates of reaction of *para*-substituted phenyl triphenylmethylsulfenic esters, RSOPhY, with hydroxide ion and *para*-substituted phenoxides, have been measured at 25° in 45% aqueous dioxane (weight per cent of dioxane). All esters, Y = *p*-NO_2, *p*-Cl, H, and *p*-CH_3, were stable under experimental conditions. Attempts to prepare aryl sulfenate esters with the organic portion attached to sulfur different from triphenylmethyl were all unsuccessful. In the presence of nucleophiles the esters reacted according to eq 1. In each case the

$$X^- + RSOPhY \longrightarrow RSX + YPhO^- \qquad (1)$$

phenoxide formed during the reaction was unambiguously identified by its characteristic band in the uv spectrum. The amount of phenoxide formed was always equivalent to 100% reaction. The ester formed in the transesterification reactions (X^- = phenoxide) was also identified by its uv spectrum after extraction of the phenoxide with 5% bicarbonate solution in a few sample cases, namely for the *p*-CH_3, *p*-Cl, and *p*-H phenyl esters. Its concentration was consistent with that expected for 100% reaction after correction for hydrolysis.

In the hydrolysis reactions ($X = OH^-$), sulfenic acids are one of the reaction products. Such compounds are very unstable and can be isolated only in very special circumstances.[14,15] However, that the reaction follows eq 1 can be gathered from the following observations. Some of the slowest reactions were followed by recording the whole uv spectrum at different times. One of these series of spectra is shown in Figure 1. The final spectrum is identical with that of the corresponding phenoxide at the same pH and all the curves go through an isosbestic point. Thus it could be shown that only the sulfenic ester and the phenoxide absorb in that region. Since the rate of disappearance of the sulfenic ester parallels that of formation of phenoxide, the hydrolysis reaction thus measured suffers no interference from parasite reactions or subsequent decomposition of the sulfenic ester.

The order of reaction is unity in substrate and all the nucleophiles. The reactions were all measured under pseudo-first-order conditions and were linear up to 90% completion. The data are reported in Tables I and II. The reaction is specific base catalyzed since the rate was independent of the buffer concentration (Table II).

At the lowest hydroxide ion concentrations, in order to avoid any possible interference from atmospheric carbon dioxide, buffer solutions have been used and the hydroxide concentration was calculated from the pH value measured with a glass electrode. In every other case the hydroxide was titrated with standard hydrochloric acid solution.

The pH values shown in the tables are clearly different from those reported in the literature for the same buffers in aqueous solutions. However, the response of the glass electrode is linear in a large range of pH values

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mediate in nucleophilic substitution at sulfur: (a) E. Ciuffarin and G. Guaraldi, (*J. Amer. Chem. Soc.*, **91**, 1745 (1969)) and E. Ciuffarin and F. Griselli (*ibid.*, in press) actually propose that the intermediate could either be a pentacovalent sulfur species or a tetracovalent sulfur cation in a discrete ion pair intermediate; (b) B. M. Trost, R. LaRochelle, and R. C. Atkins (*ibid.*, **91**, 2175 (1969)) and B. M. Trost, W. L. Schinski, and I. B. Mants (*ibid.*, **91**, 4320 (1969)) outrightly propose a pentacovalent intermediate; (c) R. Tang and K. Mislow (*ibid.*, **91**, 5644 (1969)) on the other hand present evidence which in our opinion speaks strongly against formation of an intermediate. The case in question, a nucleophilic substitution on a four-membered sulfur heterocycle, would be a most likely one for intermediate formation.

(9) J. L. Kice and J. M. Anderson, *J. Org. Chem.*, **33**, 3331 (1968).

(10) E. N. Givens and H. Kwart, *J. Amer. Chem. Soc.*, **90**, 378, 386 (1968).

(11) C. Brown and D. R. Hogg, *Chem. Commun.*, 38 (1967).

(12) Reference 6a, p 127 ff.

(13) R. F. Hudson, *Chimia*, **16**, 173 (1963); (b) R. F. Hudson and G. Klopman, *J. Chem. Soc.*, 1062 (1962); (c) R. F. Hudson and G. Loveday, *ibid.*, 1068 (1962).

(14) T. C. Bruice and R. T. Markiw, *J. Amer. Chem. Soc.*, **79**, 3150 (1957).

(15) W. Jenny, *Helv. Chim. Acta*, **41**, 317, 326 (1958).

Table I. Substituent Effect on the Entering Group[a]

$Ph_3CSOPhNO_2\text{-}p + X^- \longrightarrow Ph_3CSOX + p\text{-}NO_2PhO^-$

X^-	Concn, $M \times 10^4$	$k' \times 10^4$, sec^{-1}	$k_{OH}' \times 10^4$, sec^{-1} [b]	$(k' - k_{OH}')/[X\text{-}PhO^-]$, $M^{-1}\ sec^{-1}$
$p\text{-}CH_3PhO^-$	7.15	1.34	0.34	0.140
$p\text{-}CH_3PhO^-$	12.9	2.43	0.34	0.162
$p\text{-}CH_3PhO^-$	17.0	3.06	0.34	0.160
$p\text{-}CH_3OPhO^-$	20.4	3.08	0.96	0.104
$p\text{-}CH_3OPhO^-$	25.6	3.58	0.96	0.102
$p\text{-}CH_3OPhO^-$	39.6	5.02	0.96	0.103
PhO^-	16.0	2.34	0.34	0.125
PhO^-	23.8	3.37	0.34	0.127
PhO^-	38.5	5.12	0.34	0.124
PhO^-	46.0	6.03	0.34	0.124
$p\text{-}ClPhO^-$	71.8	7.22	0.96	0.0871
$p\text{-}ClPhO^-$	76.0	7.70	0.96	0.0886
$p\text{-}ClPhO^-$	82.0	8.35	0.96	0.0901
$p\text{-}BrPhO^-$	23.0	3.61	1.05	0.111
$p\text{-}BrPhO^-$	32.6	4.66	1.05	0.111
$p\text{-}BrPhO^-$	42.0	5.69	1.05	0.110
$p\text{-}CH_3COPhO^-$	118	6.80	3.22	0.0303
$p\text{-}CH_3COPhO^-$	142	7.58	3.22	0.0307
$p\text{-}CH_3COPhO^-$	184	8.88	3.22	0.0307
$p\text{-}CH_3COPhO^-$	245	10.8	3.22	0.0309

[a] Substrate concentration 4–7 × 10^{-5} M. [b] From Table III.

Table II. Substituent Effect on the Leaving Group

$Ph_3CSY^a + OH^- \longrightarrow Ph_3CSOH + Y^-$

Y	$[OH^-] \times 10^4$ M	pH[b]	$k_{OH}' \times 10^4$, sec^{-1}	k_{OH}, M^{-1} sec^{-1}
$p\text{-}O_2NPhO^-$	0.093[c]	10.71	0.330	3.55
$p\text{-}O_2NPhO^-$	0.097[c]	10.73	0.338	3.48
$p\text{-}O_2NPhO^-$	0.293[c]	11.20	0.962	3.28
$p\text{-}O_2NPhO^-$	0.322[c]	11.25	1.05	3.26
$p\text{-}O_2NPhO^-$	0.945[c]	11.72	3.22	3.41
$p\text{-}O_2NPhO^-$	2.72[c]	12.18	9.35	3.44
$p\text{-}O_2NPhO^-$	2.72[c]	12.18[e]	9.24	3.40
$p\text{-}O_2NPhO^-$	2.72[c]	12.18[f]	9.26	3.40
$p\text{-}O_2NPhO^-$	3.15[c]	12.24	11.0	3.49
$p\text{-}O_2NPhO^-$	4.38[c]	12.38	15.6	3.56
$p\text{-}O_2NPhO^-$	5.14[c]	12.45	17.8	3.46
$p\text{-}O_2NPhO^-$	233[d]		787	3.38
$p\text{-}O_2NPhO^-$	400[d]		1330	3.33
$p\text{-}ClPhO^-$	547[d]		17.0	0.0310
$p\text{-}ClPhO^-$	944[d]		27.9	0.0295
PhO^-	547[d]		3.86	0.00706
PhO^-	944[d]		6.98	0.00739
$p\text{-}CH_3PhO^-$	818[d]		2.75	0.00336
$p\text{-}CH_3PhO^-$	2150[d]		7.37	0.00343
$p\text{-}CH_3PhO^-$	2350[d]		8.25	0.00351

[a] Substrate concentration 4–7 × 10^{-5} M. [b] Buffers are made with borax, 0.0081 M, and the appropriate amount of NaOH or HCl. [c] Calculated from pH. [d] Titrated. [e] Buffer diluted two times. [f] Buffer diluted ten times.

as shown by Haas[16] in various water–dioxane mixtures. Moreover, the correction to be applied, due to the concentration of buffer, was a very minor one. The ionic product of water was taken as 1.809 × 10^{-16} as measured by Harned[17] for 45% aqueous dioxane. The correctness of the above assumptions was confirmed by our own experiments. In fact, two runs were performed with a high OH^- concentration with p-nitrophenyl ester. The reactions were very fast and were followed with a stopped-flow apparatus. The concentrations were determined by titration. The specific rate constants (k_{OH}) thus obtained are equal within experimental error to those obtained with buffers where the hydroxide concentration was calculated from the pH and followed with a conventional recording spectrophotometer (see Table I).

With phenoxide ions as nucleophiles, hydrolysis was unavoidable. However, the rate of hydrolysis could be calculated from the specific rate constant (k_{OH}) or measured by extrapolation at zero phenoxide concentration. The two values were identical within experimental error. The order in phenoxide was thus calculated after subtraction of the contribution to the rate due to hydrolysis. The concentrations of the phenoxides were determined spectrophotometrically after careful calibration.

The use of aqueous dioxane was necessary in order to be able to dissolve all the reagents and buffers. The particular mixture, *i.e.*, 45%, was chosen because such a mixture was already well characterized in the literature.

The pK values[18] reported in Table III are those measured in water since they are not known in the solvent mixture used in this paper. However, the relative dissociation constants are generally little dependent on medium.[19] It is then permissible to compare reaction velocities in one medium with dissociation constants in another medium.[19c] In any case, no matter what the absolute values of β are, the really significant datum, in relation to the transition state structure, is the β value for the nucleophile relative to that for the leaving group.

Table III. Summary of the Second-Order Rate Constants and the pK Values for Different Entering and Leaving Groups

$Ph_3CSY + X^- \longrightarrow Ph_3CSX + Y^-$

X^-	Y	pK (entering group)	pK (leaving group)	k_2, M^{-1} sec^{-1} [a]
$p\text{-}CH_3COPhO^-$	$p\text{-}O_2NPhO^-$	8.05	7.15	0.031
$p\text{-}BrPhO^-$	$p\text{-}O_2NPhO^-$	9.34	7.15	0.11
$p\text{-}ClPhO^-$	$p\text{-}O_2NPhO^-$	9.38	7.15	0.089
PhO^-	$p\text{-}O_2NPhO^-$	9.92	7.15	0.13
$p\text{-}CH_3OPhO^-$	$p\text{-}O_2NPhO^-$	10.21	7.15	0.10
$p\text{-}CH_3PhO^-$	$p\text{-}O_2NPhO^-$	10.26	7.15	0.15
HO^-	$p\text{-}O_2NPhO^-$	15.74	7.15	3.4
HO^-	$p\text{-}ClPhO^-$	15.74	9.38	0.030
HO^-	PhO^-	15.74	9.86	0.0072
HO^-	$p\text{-}CH_3PhO^-$	15.74	10.26	0.0034

[a] Average.

Discussion

The significance of the kinetic data summarized in Table III is best appreciated when the results are reported as Brønsted plots as in Figures 2 and 3. Good linear correlations appear to hold between the log of the rate constants and the pK_a of the conjugate acid of the nucleophile, in the experiments where the leaving group (p-nitrophenoxide) was held constant (β = 0.25), or the conjugate acid of the leaving group, when the nucleophile (hydroxide) was held constant (β = −0.97).

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[16] L. G. Van Uitert and G. G. Haas, *J. Amer. Chem. Soc.*, **75**, 451 (1953).

[17] H. S. Harned and L. D. Fallon, *ibid.*, **61**, 2377 (1939).

[18] G. B. Barlin and D. D. Perrin, *Quart. Rev.* (London), **20**, 75 (1966).

[19] (a) J. F. P. J. Dippy, *Chem. Rev.*, **25**, 151 (1939); (b) S. M. Petrov and Y. I. Umanskii, *Zh. Fiz. Khim.*, **41**, 1374 (1967); *Chem. Abstr.*, **68**, 6919g (1968); (c) J. E. Leffler and E. Grunwald, "Rates and Equilibria of Organic Reactions," John Wiley & Sons, Inc., New York, N. Y., 1963, p 242.

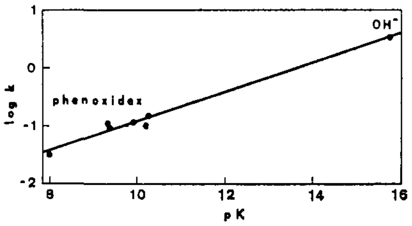


Figure 2. Logarithm of the rate constants for the reaction of nucleophiles with *p*-nitrophenyl triphenylmethylsulfenic ester as a function of the basicity of the nucleophile.

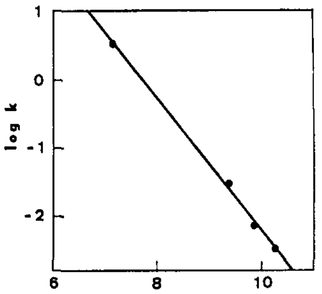
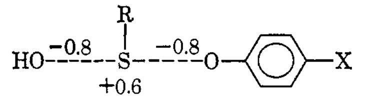


Figure 3. Logarithm of rate constants for the alkaline hydrolysis of *para*-substituted phenyl triphenylmethylsulfenic esters as a function of the pK_a of the leaving group.

The signs of the Brønsted coefficient, positive for the nucleophile, negative for the leaving group, are as expected for a nucleophilic substitution; *i.e.*, the rate increases either with increasing the basicity of the nucleophile or with decreasing the basicity of the leaving group. Moreover, the excellent linearity of the plots through wide pK_a ranges (8 pK units for the nucleophile, 3 pK units for the leaving group) makes sure that, for this type of substitution at sulfur, nucleophilic reactivity and leaving group mobility closely parallel basicity. This finding legitimates the use of the dissociation of the conjugate acid as a model for heterolysis of the sulfur-to-leaving group bond and, conversely, for the formation of the nucleophile-to-sulfur bond. Under these circumstances the Brønsted coefficients can be used with some confidence as a criterion for gauging the *relative* extent of charge transfer, initial to transition state, from the nucleophile and to the leaving group. Our results establish the fact that, for the particular substitution under investigation, bond breaking ($\beta = -0.97$) is far more advanced than bond formation ($\beta = 0.25$). This finding can only be consistent with a one-step process (S_N2) contrary to the idea of a pentacovalent intermediate along the reaction path (S_AN). In fact in the latter case, no matter which transition state is rate determining, that for bond formation or that for bond breaking, β for the leaving group could never exceed β for the nucleophile.

Although we are fully aware of the limitations of this treatment and of the extrathermodynamic relationships in general, particularly since all our measurements were made at a single temperature,[20] we can hardly resist the temptation to develop a little further the implications of our findings. If, following Jencks and Gilchrist[21] and with the same provisions they express (footnote 27 of ref 21), we assume that in "symmetric" displacements the coefficients for entering and leaving group are complementary; the fractional charge transfers can be estimated. Thus, according to our data the nucleophile would have donated $0.25/(0.97 + 0.25) = 0.2$ charge unit, while the leaving group would have accepted $0.97/(0.97 + 0.25) = 0.8$ charge unit.

If this is so the reaction center would carry a net *positive* charge amounting to 0.6 charge unit. The picture emerging out of this analysis is that of a transition state very "loose" indeed, much more than it could ever be imagined. Most likely, however, this picture is not general for substitution at sulfur and may well represent a rather extreme case.[22] In fact several factors may be at play to drive the particular reaction under investigation toward predominance of bond breaking. In the first place the protic solvent is expected to depress tremendously the reactivity of the oxygen nucleophile[23] while it may assist the departure of the oxygen leaving group through an electrophilic "pull." A second factor which may be important is the nature of the organic moiety bound to the reaction center, the triphenylmethyl group. In view of the enormous steric effects prevailing in substitution at sulfur,[7,24] it is to be expected that the very bulky Ph_3C- group adjacent to the reaction center will exert an exceedingly high steric hindrance for the transition state to assume the favored collinear geometry,[24a] thus favoring exceptionally long bonds of nucleophile and leaving group to reaction center. However, a very recent investigation on the alkaline hydrolysis of cyclic sultones,[25] for which a strong steric acceleration had been established,[26] has yielded a β value of -0.6 for the leaving group, thus indicating a large extent of bond breaking also in this transition state.



$$\mathrm{HO}\overset{-0.8}{- - - - -}\underset{+0.6}{\overset{\overset{\displaystyle\mathrm{R}}{|}}{\mathrm{S}}}\overset{-0.8}{- - - - -}\mathrm{O}-\mathrm{C_6H_4}-\mathrm{X}$$

These few simple considerations already allow a perspective on the work that would be needed to make the approach adopted in this work deeply significant. It amounts to verifying in a systematic fashion the effect on the Brønsted coefficients of such factors as solvent, steric compression at the reaction center, effective electronegativity of the reaction center, nature of the nucleophilic atom, and leaving group atom. It is a staggering amount of work, comparable to or greater than that which has been, and still is, carried out for carbonyl displacement reaction.[21,27]

For the time being we may guess that the greater chances for the S_AN mechanism to be evinced are with good nucleophiles and poor leaving groups (accounting for the effect that the solvent may have on these factors) and for highly electronegative and unhindered reaction

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(20) Reference 19c, Chapter 9.

(21) W. P. Jencks and M. Gilchrist, *J. Amer. Chem. Soc.*, **90**, 2622 (1968).

(22) It may be noted incidentally that such a transition state would predict a high structural effect on the substrate with large negative ρI

(23) J. Miller and A. J. Parker, *J. Amer. Chem. Soc.*, **73**, 117 (1961); A. J. Parker, *Quart. Rev.* (London), **16**, 163 (1962).

(24) (a) A. Fava and A. Iliceto, *J. Amer. Chem. Soc.*, **80**, 3478 (1958); (b) K. Mislow, *Rec. Chem. Progr.*, **28**, 217 (1967).

(25) O. R. Zaborsky and E. T. Kaiser, *J. Amer. Chem. Soc.*, **92**, 860 (1970).

(26) E. T. Kaiser, I. R. Katz, and T. F. Wulfers, *ibid.*, **87**, 3781 (1965); E. T. Kaiser and O. R. Zaborsky, *ibid.*, **90**, 4626 (1968).

(27) For review see: (a) W. P. Jencks, *Progr. Phys. Org. Chem.*, **2**, 63 (1964); (b) S. L. Johnson, *Advan. Phys. Org. Chem.*, **5**, 237 (1967).

Table IV. Summary of Analysis Data, Melting Points, and Spectral Characteristics of Triphenylmethylsulfenyl Phenyl Esters ($Ph_3CSOPh\text{-}X\text{-}p$)

X	Mp, °C		%					λ_{max}, mμ	ϵ_{max}
			C	H	S	N	Cl		
H	92.5–93.5	Found	81.44	5.37	8.70			276[a]	2,524
		Calcd	81.48	5.47	8.70				
NO_2	161–162	Found	72.48	4.62	7.80	3.68		308	11,220
		Calcd	72.61	4.63	7.76	3.39			
Cl	116.5–117	Found	74.44	4.70	8.00		8.83	274[a]	2,297
		Calcd	74.52	4.75	7.96		8.80		
CH_3	96–97	Found	81.83	5.83	8.40			284[a]	2,804
		Calcd	81.63	5.80	8.38				

[a] Shoulder.

centers. It is worth noting that the only two cases[8] where formation of a pentacovalent intermediate has been postulated meet at least some of these requirements.

Experimental Section

Materials. Pure, peroxide-free *p*-dioxane was prepared according to the method described by Vogel,[28] kept over sodium under nitrogen atmosphere, and distilled immediately before use. Deionized water was distilled from potassium permanganate. Reagent grade sodium hydroxide, hydrochloric acid, and borax were used without further purification. All commercial phenols, *i.e.*, *p*-Cl, *p*-Br, H, *p*-CH_3, and *p*-OCH_3, have been purified by repeated sublimations and had good melting points. *p*-Acetylphenol was kindly provided by Professor Da Re and purified by sublimation; mp, 110°.[29]

All the sulfenyl esters have been prepared according to the method of Vorländer and Mittag.[30] Yields in purified product ranged from 20 to 40% and no attempts have been made to increase them. Table IV is a summary of analysis data, melting points, and spectral characteristics.

Kinetic Methods. The reactions were followed at the appropriate wavelength corresponding to the maximum absorption of the product phenoxide by a spectrophotometric technique at 25.0 ± 0.1° with a SP 800 Unicam spectrophotometer. The faster reactions were followed with a Durrum stopped-flow apparatus. All reactions were studied under pseudo-first-order conditions.

Boric acid–borate buffers have been prepared according to Bates.[31] pH measurements were performed with a Metrohm Herisau pH meter equipped with XL glass electrode.

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Mechanistic Features of the Base-Induced Decomposition of Dibenzosemibullvalene 1-Carboxaldehyde Tosylhydrazone

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Abstract: The decomposition of dibenzosemibullvalene 1-carboxaldehyde tosylhydrazone (**7a**) and its α-d_1 analog (**7b**) with several bases was examined under a variety of conditions. In each case, only 3,4-benzofluorene (**8**) and terminal allene **9** were produced and the ratio of these hydrocarbons was consistently found to be approximately 2:1. Decomposition of **7b** under aprotic conditions gave rise to **8** containing deuterium only at the methylene position; likewise, **9** contained covalently bound deuterium uniquely at the terminal allene position. The locations of the isotope were established by nmr spectroscopy. Base-induced rearrangement of **7a** with *n*-butyllithium in diglyme, followed by quenching of the reaction mixture with deuterium oxide afforded **8** with greater than 80% d_1 incorporation; allene **9** contained no measurable deuterium. When decomposed in ethylene glycol-d_2, both **8** and **9** were found to be dideuterated at the methylene and terminal allene positions, respectively. The reaction mechanisms which best correlate with these results are presented. It is concluded that the unique geometry of the semibullvalene nucleus in **7** results in rearrangement of the derived carbene principally by a pathway which involves an unprecedented 1,3-aryl shift to what is formally a *trans*-disposed carbon atom.

The capability of the bullvalene molecule (**1**) to undergo rapid and reversible Cope rearrangements and thereby scramble in phantasmagoric fashion the constituent cyclopropyl, vinyl, and bridgehead carbon atoms has no equal in the realm of organic chemistry.[2] The capability of each carbon in bullvalene to partition

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