Substitution Reactions of Alkanesulfonyl Derivatives: Direct Substitution vs. Elimination–Addition Mechanisms in Substitution Reactions of Alkyl α-Disulfones

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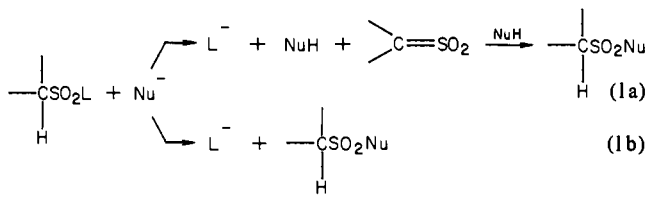
Abstract: The reactions of a series of alkyl and aralkyl α-disulfones, RSO_2SO_2R (R = Me, *n*-Bu, *i*-Pr, $ArCH_2$), with a variety of nucleophiles in aqueous dioxane have been examined. Both rates of reaction and whether a given reaction takes place by an elimination–addition (sulfene intermediate) or a direct substitution (attack of nucleophile on SO_2 group of α-disulfone) mechanism have been determined. The great majority of substitution reactions of alkyl α-disulfones take place via an elimination–addition mechanism (eq 3a), with formation of a sulfene from the α-disulfone being rate determining. Only when the nucleophile is one, like azide ion, that is weakly basic while still being a good nucleophile is direct substitution the preferred pathway. Even with azide the reaction pathway changes to elimination–addition when the acidity of the hydrogens on the carbon adjacent to the sulfonyl group is increased sufficiently, as in $(PhCH_2SO_2)_2$. Comparison of rates of elimination of α-disulfones $(R'CH_2SO_2)_2$ with rates of base-catalyzed hydrogen exchange of the corresponding trifluoromethyl sulfones $R'CH_2SO_2CF_3$ indicates that formation of sulfenes from α-disulfones involves either an irreversible E1cB or a very E1cB-like E2 mechanism, a conclusion that is also supported by the observed variation of the rate of elimination of $RR'CHSO_2SO_2R''$ with changes in R and R'. Comparison of the behavior of an alkyl α-disulfone with that of the corresponding alkanesulfonyl chloride reveals that changing Y in RCH_2SO_2Y from RSO_2 to Cl causes direct substitution to be able to compete much more effectively with elimination–addition. Kinetic studies show that this arises because, for a given nucleophile, (a) elimination–addition is 5–10 times slower for the alkanesulfonyl chloride than for the α-disulfone while (b) the rate of direct substitution is 5–10 times faster for the sulfonyl chloride. The origin of these rate differences is discussed and explained.

Ever since the classic work of King and Durst[1] and Truce et al.[2] it has been recognized that some nucleophilic substitutions of alkanesulfonyl derivatives take place by an elimination–addition mechanism (eq 1a) involving a sulfene intermediate rather than by attack of the nucleophile on the sulfonyl group (eq 1b) and direct substitution of Nu for L.

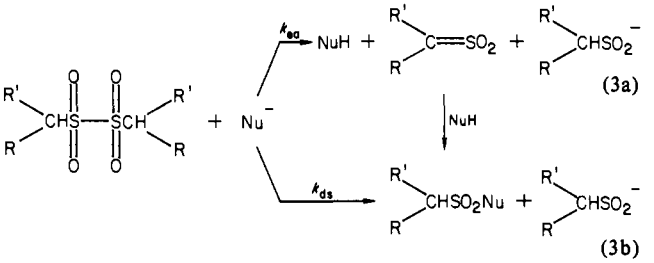


Almost nothing is known about the chemistry of alkyl α-disulfones, RSO_2SO_2R, but the fact that they have been shown[3a] to be one of the products of the reaction of photochemically excited sulfur dioxide with hydrocarbons (RH), a reaction of interest[3] to those concerned with atmospheric chemistry and the environment, suggests they merit more attention than they have previously received. Their aryl counterparts, $ArSO_2SO_2Ar$, undergo substitution (eq 2) readily with a wide range of nucleophiles,[4] their

$$ArSO_2SO_2Ar + Nu^- \rightarrow ArSO_2Nu + ArSO_2^- \qquad (2)$$

reactivity in such reactions being comparable to that of sulfonyl chlorides.[5] This suggests that high reactivity toward nucleophiles will also be one of the salient characteristics of the chemical behavior of alkyl α-disulfones.

Since aryl α-disulfones have no hydrogen on the carbon adjacent to the sulfonyl group, the substitutions in eq 2 perforce proceed by direct substitution at the sulfonyl group. Alkyl α-disulfones, on the other hand, provided they have an α-hydrogen, should be able to undergo nucleophilic substitution either by an elimination–addition (ea, eq 3a) or by a direct substitution pathway (ds, eq 3b).



In the present work we have examined the reactions of a series of alkyl α-disulfones with a variety of nucleophiles, determining both reaction rates and whether a given reaction takes place by elimination–addition or direct substitution. These data allow one to assess the effect of changes in (a) nucleophile and (b) alkyl group structure on k_{ea} and k_{ds}. One thereby obtains a more systematic and precise picture of the effect of such changes on the rates for the two competing substitution mechanisms for reactive alkanesulfonyl derivatives than has been available from the studies of alkanesulfonyl chlorides reported to date.[6] We have also determined the behavior of an alkanesulfonyl chloride RSO_2Cl vis-à-vis the corresponding α-disulfone RSO_2SO_2R and from this discovered that a change in leaving group from Cl^- to RSO_2^- has a significantly different effect on k_{ds} than it has on k_{ea}. Other experiments have permitted one to decide which of the various possible elimination mechanisms (E2, $E1cB_i$, or $E1cB_r$) operates for sulfene formation from α-disulfones.

Results

Substitution Reactions of α-Disulfones. Reaction of various α-disulfones RSO_2SO_2R (R = Me, *n*-Bu, *i*-Pr, and $PhCH_2$) with different nucleophiles was studied in 60% dioxane (v/v). The

(1) King, J. F.; Durst, T. *J. Am. Chem. Soc.* **1964**, *86*, 287.
(2) Truce, W. E.; Campbell, R. W.; Norell, J. R. *J. Am. Chem. Soc.* **1964**, *86*, 288.
(3) (a) Penzhorn, R. D.; Steiglitz, L.; Filby, W. G.; Gunther, K. *Chemosphere* **1973**, *3*, 111. (b) Sidebottom, H. W.; Badcock, C. C.; Jackson, G. E.; Calvert, J. G.; Reinhardt, G. W.; Damon, E. K. *Environ. Sci. Technol.* **1972**, *6*, 72. (c) Groblicki, P. J.; Nebel, G. J. "The Photochemical Formation of Aerosols in Urban Atmospheres"; Elsevier: Amsterdam, 1971; p 241.
(4) (a) Kice, J. L.; Legan, E. *J. Am. Chem. Soc.* **1973**, *95*, 3912. (b) Kice, J. L.; Kasperek, G. J.; Patterson, D. *Ibid.* **1969**, *91*, 5516.
(5) Rogne, O. *J. Chem. Soc. B.* **1970**, 1056.
(6) (a) King, J. F. *Acc. Chem. Res.* **1975**, *8*, 10. (b) King, J. F.; Lee, T. W. S. *J. Am. Chem. Soc.* **1969**, *91*, 6524. (c) King, J. F.; Kang, Y. I. *Chem. Commun.* **1975**, 52.

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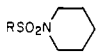
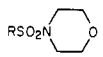
Table I. Deuterium Incorporation in Substitution Products in Reactions of Alkyl α-Disulfones in 60% Dioxane–40% D_2O[a]

nucleophile	struct of substn product analyzed	no. of Ds on α-C to SO_2 group in RSO_2Nu			
		R = *n*-Bu	R = Me	R = *i*-Pr	R = $PhCH_2$
piperidine		1.03 ± 0.02			
morpholine		1.05 ± 0.07	1.02 ± 0.03	1.0 ± 0.1	0.96 ± 0.05
glycine ethyl ester	RSO_2NHCH_2COOEt	1.0 ± 0.1			
OD^-	RSO_3^-	1.01 ± 0.04			
AcO^-	RSO_3^-	1.00 ± 0.03			
N_3	RSO_2N_3	0.00 ± 0.05	<0.1	0.0 ± 0.1	0.71 ± 0.08

[a] All data are for reaction of α-disulfone RSO_2SO_2R having the R group indicated with the nucleophile shown at 25 °C, except for the reaction with acetate where a temperature of 50 °C was used.

Table III. Rate Constants for Reaction of Nucleophiles with Alkyl α-Disulfones at 25 °C in 60% Dioxane

R for RSO_2SO_2R	k_2, M^{-1} s^{-1}, for Nu^- + RSO_2SO_2R[a] with the following nucleophiles					
	OH^-	piperidine	morpholine	GEE[b]	AcO^-	N_3^-
Me			70 (ea)			1.45 (ds)
n-Bu	1.4×10^4 (ea)	56 (ea)	1.05 (ea)	0.13 (ea)	0.004 (ea)	0.14 (ds)
i-Pr	1.6×10^3 (ea)	8.0 (ea)	0.27 (ea)			0.021 (ds)
$PhCH_2$				94 (ea)	4.2 (ea)	5.2 (ea)
p-$CH_3C_6H_4CH_2$				51 (ea)		
p-$ClC_6H_4CH_2$				4.1×10^2 (ea)		
m-$ClC_6H_4CH_2$				7.1×10^2 (ea)		

[a] Pathway used for substitution: (ea) = elimination–addition, (ds) = direct substitution. [b] GEE = glycine ethyl ester.

nucleophiles used were piperidine, morpholine, and glycine ethyl ester (three amines of differing base strength), OH^- and AcO^- (two oxyanions of greatly different basicity), and azide ion (an anion of base strength comparable to acetate but of much greater nucleophilicity). All except acetate yield substitution products RSO_2Nu that are stable under the reaction conditions used. The mixed anhydride RSO_2OAc that is presumably formed initially in the reaction with acetate is hydrolyzed to give the sulfonate RSO_3^-. Product isolation experiments (see Experimental Section) showed that the expected substitution products were formed in the various α-disulfone–nucleophile reactions.

Incorporation of Deuterium into Substitution Product in Reactions of α-Disulfones. In the presence of D_2O any substitution of an alkyl α-disulfone $(R'CH_2SO_2)_2$ that proceeds via an elimination–addition pathway and a sulfene intermediate will yield a substitution product, $RCHDSO_2Nu$, having a deuterium on the carbon adjacent to the sulfonyl group (eq 4a). On the other hand,

$$(R'CH_2SO_2)_2 \xrightarrow[Nu^-]{k_{ea}} R'CH{=}SO_2 \xrightarrow[D_2O]{Nu^-} R'CHDSO_2Nu \quad (4a)$$

$$(R'CH_2SO_2)_2 \xrightarrow[Nu^-]{k_{ds}} R'CH_2SO_2^- + R'CH_2SO_2Nu \quad (4b)$$

a direct substitution mechanism (eq 4b) will result in a product, $R'CH_2SO_2Nu$, having no deuterium on that carbon. The extent of deuterium incorporation can be determined easily in most cases from the integrated NMR spectrum of the substitution product.

Reaction of *n*-butyl α-disulfone with the various nucleophiles in 60% dioxane–40% D_2O led to deuterium incorporation in the substitution product as indicated in the third column of Table I. In all cases except the reaction with azide ion, the substitution product has exactly one atom of deuterium on the carbon adjacent to the sulfonyl group. In the product from the reaction with azide ion there is none. Thus although the reaction of N_3^- with *n*-butyl α-disulfone is a direct substitution, all of the other substitution reactions of this α-disulfone occur exclusively by the elimination–addition pathway.

To see if a change in the nature of the alkyl group would alter the mechanism used for substitution, we reacted methyl, isopropyl, and benzyl α-disulfones with (a) morpholine (an "elimination–addition" nucleophile with *n*-$BuSO_2SO_2Bu$-*n*) and (b) azide ion (a "direct substitution" nucleophile with *n*-$BuSO_2SO_2Bu$-*n*). The results, shown in the last three columns of Table I, indicate that the substitutions with morpholine all remain elimination–addition reactions. On the other hand, while the reactions of azide with methyl and isopropyl α-disulfone remain direct substitutions, that of N_3^- with benzyl α-disulfone occurs principally via the elimination–addition mechanism. A change in mechanism from direct substitution to elimination–addition with a change in structure of the alkyl group from CH_3 to $PhCH_2$ has also been observed[6c] in the reaction with pyridine of methanesulfonyl and phenylmethanesulfonyl chlorides.

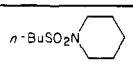
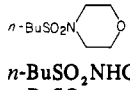
Kinetics of the Reactions of Nucleophiles with Alkyl α-Disulfones. The kinetics of the reactions of various of the nucleophiles with the different alkyl α-disulfones were studied spectrophotometrically (either by conventional or stopped-flow techniques) in 60% dioxane under conditions where the nucleophile was always present in a large stoichiometric excess over the α-disulfone. When either an amine or acetate ion was the nucleophile, buffers of the nucleophile and its conjugate acid were employed. The disappearance of the α-disulfone followed good first-order kinetics in every case; the experimental first-order rate constants, k_1, for the various runs can be found in Table II.[7] The slope of a plot of k_1 vs. [nucleophile] gives the second-order rate constant, k_2, for each particular α-disulfone–nucleophile reaction; the k_2's for the different reactions are given in Table III.

The data on deuterium incorporation in the substitution products given earlier enable one to specify whether the measured k_2 for a particular α-disulfone–nucleophile reaction represents the rate constant (k_{ea}) for an elimination–addition reaction (eq 3a) or, alternatively, is one (k_{ds}) for a direct substitution (eq 3b). Those k_2's in Table III that are rate constants for an elimination–addition process are indicated by ea after the numerical value of k_2; those that are rate constants for a direct substitution process are followed by ds.

Incorporation of Deuterium into Substitution Product in Reactions of 1-Butanesulfonyl Chloride. 1-Butanesulfonyl chloride, *n*-$BuSO_2Cl$, was allowed to react in 60% dioxane–40% D_2O with each of the nucleophiles that had been shown (Table I) to react with *n*-butyl α-disulfone exclusively via an elimination–addition mechanism. Isolation of the substitution products and determination of the extent of deuteration of the carbon adjacent to the sulfonyl group were carried out in the same fashion as in the reactions of the α-disulfone. The results are shown in Table IV.

(7) See the paragraph at the end of paper regarding supplementary material.

Table IV. Deuterium Incorporation in Substitution Products in Reactions of 1-Butanesulfonyl Chloride in 60% Dioxane–40% D_2O[a]

nucleophile	struct of substn product analyzed	no. of Ds on α-C to SO_2 group in n-$BuSO_2Nu$
piperidine		0.72 ± 0.05
morpholine		0.15 ± 0.05
glycine ethyl ester	n-$BuSO_2NHCH_2COOEt$	0.24 ± 0.15
OD^-	n-$BuSO_3^-$	0.97 ± 0.04
AcO^-	n-$BuSO_3^-$	0.27 ± 0.06

[a] All data are for 25 °C, except for acetate ion where a temperature of 50 °C was used.

Table VI. Rate Constants for Reaction of Nucleophiles with Sulfonyl Chlorides at 25 °C in 60% Dioxane

nucleophile	k_2, M^{-1} s^{-1}, for Nu^- + RSO_2Cl[a] R = n-Bu	R = Ph
OH^-	4.0×10^3 (ea)	
morpholine	1.0	
$EtOOCCH_2NH_2$	0.095	2.1 (ds)
AcO^-	0.025 (50 °C)	0.015 (ds)
N_3^-		6.2 (ds)

[a] Pathway used for substitution: (ea) = elimination–addition, (ds) = direct substitution. Where no symbol is shown, the reaction proceeds by a mixture of both pathways.

One sees that, while the reaction with hydroxide ion still occurs exclusively by an elimination–addition mechanism, the substitutions involving the other nucleophiles all lead to significantly less deuteration than in the case of the α-disulfone. In the case of acetate, morpholine, and glycine ethyl ester, the data indicate that *most* of the substitution product is being formed by direct substitution. Direct substitution is clearly much more competitive in rate with elimination–addition in substitution reactions of n-$BuSO_2Cl$ than it is in reactions of $(n\text{-}BuSO_2)_2$.

Kinetics of Reactions of Nucleophiles with Sulfonyl Chlorides. The kinetics of the reactions of selected nucleophiles with 1-butanesulfonyl chloride and benzenesulfonyl chloride in 60% dioxane were followed spectrophotometrically by using the same reaction conditions as for the α-disulfones. The disappearance of the sulfonyl chloride followed good first-order kinetics in each case; experimental first-order rate constants, k_1, for the different runs may be found in Table V.[7] Second-order rate constants, k_2, obtained from the slope of a plot of k_1 vs. [nucleophile] are given in Table VI. Those for reactions involving $PhSO_2Cl$ naturally represent rates for direct substitution processes. That for reaction of OH^- with n-$BuSO_2Cl$ is for an elimination–addition. However, since the data in Table IV indicate that elimination–addition and direct substitution are competitive in rate for reaction of the other nucleophiles with n-$BuSO_2Cl$, the measured k_2's for their reactions represent the *sum* of k_{ea} and k_{ds} for the system in question. For this reason no symbol in parentheses has been placed after these particular k_2's in Table VI.

Rates of Deuterium Exchange of Benzyl and n-Butyl Trifluoromethyl Sulfones. Alkyl trifluoromethyl sulfones, $RCH_2SO_2CF_3$, undergo base-catalyzed exchange of the protons in the CH_2 group in acetonitrile–D_2O via the mechanism shown in eq 5. The rate of exchange can be followed by NMR and the

$$RCH_2SO_2CF_3 + B \xrightarrow{k_B} BH^+ + RC^-HSO_2CF_3 \xrightarrow{D_2O} RCHDSO_2CF_3 \quad (5)$$

rate constant, k_{exch}, equal to $k_B[B]$, determined. Study of the acetate-catalyzed exchange of $PhCH_2SO_2CF_3$ at 25 °C in 1:1 AcO^-–AcOD buffers in 70% CD_3CN–30% D_2O gave the following results ([AcO^-], k_{exch}): 0.01 M, 0.42×10^{-4} s^{-1}; 0.02 M, 0.78×10^{-4} s^{-1}; 0.04 M, 1.41×10^{-4} s^{-1}. From a plot of k_{exch} vs. [AcO^-] the second-order rate constant, k_{OAc}, for the acetate-catalyzed exchange of $PhCH_2SO_2CF_3$ under these conditions is 3.1×10^{-3} M^{-1} s^{-1}.

The much slower acetate-catalyzed exchange of n-$PrCH_2SO_2CF_3$ was also studied in the same medium at 50 °C ([AcO^-], k_{exch}): 0.015 M, 1.4×10^{-6} s^{-1}; 0.02 M, 1.7×10^{-6} s^{-1}. From a plot of k_{exch} v. [AcO^-], one estimates that k_{OAc} for acetate-catalyzed exchange of n-$PrCH_2SO_2CF_3$ at 50 °C in this medium is $\sim 6 \times 10^{-5}$ M^{-1} s^{-1}. Due to the very slow rate of exchange in these reactions this rate constant is probably somewhat less accurate than the one for benzyl trifluoromethyl sulfone.

An attempt was also made to measure the rate of exchange of n-$PrCH_2SO_2CF_3$ in the presence of 0.002 M OD^- at 25 °C in 70% CD_3CN–30% D_2O, but under those conditions the rate was so rapid that exchange was complete by the time (~45 s) needed to mix the solutions of sulfone and OD^-, insert the tube into the probe, and determine the integrated intensities of the CH_3 and CH_2SO_2 signals in the NMR spectrum of the sample. This means that under those conditions $k_{exch} \geq 0.069$ s^{-1} and that $k_{OD} = k_{exch}/[OD^-]$ is greater than 35 M^{-1} s^{-1}.

Discussion

The results in Table I show that the great majority of nucleophilic substitution reactions of alkyl α-disulfones take place via an elimination–addition mechanism (eq 3a) with a sulfene as an intermediate. Only when the nucleophile is one like azide ion that is weakly basic while at the same time being a good nucleophile does one see reaction proceeding by direct substitution. Even with azide, when the acidity of the hydrogens on the carbon adjacent to the sulfonyl group is increased sufficiently, as in $(PhCH_2SO_2)_2$, the preferred pathway for substitution changes to elimination–addition.

The k_2 values in Table III for the reaction of n-butyl α-disulfone with all nucleophiles except azide ion provide information on how the rate constant for eq 3a, k_{ea}, varies with nucleophile. Given that the role of the nucleophile in the k_{ea} step is to remove a proton from the carbon α to the sulfonyl group, a correlation of nucleophile reactivity with basicity of the nucleophile might be anticipated. This is found to be the case. A plot of log k_{ea} values for $(n\text{-}BuSO_2)_2$ vs. pK_a (in H_2O) of the nucleophiles is linear with a slope (β) of about 0.6. A β value of this magnitude indicates that in the transition state, transfer of the proton from the α-disulfone to the nucleophile has proceeded to a significant extent. It is comparable to the β values reported for the elimination of HBr from 2-phenylethyl bromide[8] (0.54) and for the base-catalyzed formation of $PhCH{=}SO_2$ from 2,4-dinitrophenyl phenylmethanesulfonate[9,10] (0.6).

Mechanism of Sulfene Formation from Alkyl α-Disulfones. A priori, three mechanisms are possible for sulfene formation from α-disulfones: (1) a reversible E1cB mechanism (eq 6, $k_{ii} < k_{-i}[BH^+]$); (2) an irreversible E1cB mechanism (eq 6, $k_{ii} > k_{-i}[BH^+]$); (3) an E2 mechanism (eq 7).

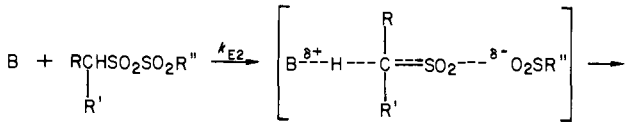
$$B + RR'CHSO_2SO_2R'' \underset{k_{-i}}{\overset{k_i}{\rightleftharpoons}}$$

$$BH^+ + RR'C^-{-}SO_2SO_2R'' \xrightarrow{k_{ii}} RR'C{=}SO_2 + R''SO_2^- \quad (6)$$

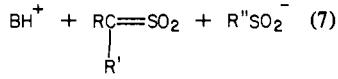
$$(ElcB_r,\ k_{ii} < k_{-i}[BH^+];\ ElcB_i,\ k_{ii} > k_{-i}[BH^+])$$

The reversible E1cB mechanism can definitely be ruled out. In an $E1cB_r$ mechanism the carbanions $RR'C^-SO_2SO_2R''$ formed

(8) Hudson, R. F.; Klopman, G. *J. Chem. Soc.* **1964**, 5.
(9) Davy, M. B.; Douglas, K. T.; Loran, J. S.; Steltner, A.; Williams, A. *J. Am. Chem. Soc.* **1977**, *99*, 1196.
(10) Recent work by Thea, Harun, and Williams[11] indicates that the Brønsted relation for this reaction actually has a slope of +1.0 for weak bases and one of about +0.3 for stronger bases; in the earlier study[9] there were too few data points to reveal this break in the slope. Since our data for n-butyl α-disulfone are also for only a limited number of bases, it seems more appropriate to compare our results with the earlier reported[9] "average" β for sulfene formation from 2,4-dinitrophenyl phenylmethanesulfonate.
(11) Thea, S.; Harun, M. G.; Williams, A. *J. Chem. Soc., Chem. Commun.* **1979**, 717.

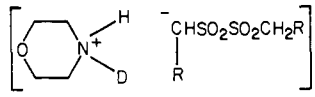


transition state



(7)

by step k_i revert to α-disulfone (step k_{-i}) faster than they eliminate sulfinate ion (step k_{ii}). In D_2O with such a mechanism extensive exchange of hydrogens on the α-carbon in the starting material would therefore occur prior to reaction to form substitution product, and one would find that the substitution products from the reactions involving methyl, *n*-butyl, or benzyl α-disulfones would have significantly more than one deuterium atom on the α-carbon to the sulfonyl group. From Table I one can see that this is not the case. Especially noteworthy are the reactions of these α-disulfones with morpholine. In D_2O the nitrogen atom of morpholine is deuterated, and the ion pair formed upon removal of a proton from these α-disulfones will have structure **1**. Because



1

of the deuterium already present on nitrogen in **1**, exchange of D for H on the α-carbon can take place directly in **1**. There is no need for BH^+ to diffuse away and be replaced by BD^+, as would be the case if a tertiary amine was being used as the base. Even if step k_{-i} is faster than diffusion, i.e., an $E1cB_r$ (ion pair) mechanism, one should still get exchange of H by D in the starting material prior to reaction to form substitution product in this particular case. The fact that this is not observed allows one to rule out any type of $E1cB_r$ mechanism for sulfene formation from α-disulfones.

The distinction between the irreversible E1cB and E2 mechanisms is that in the E2 mechanism the breaking of the C–H and S–S bonds is synchronous, while in the $E1cB_i$ mechanism breaking of the C–H bond precedes cleavage of the S–S bond. An unequivocal decision between $E1cB_i$ and E2 mechanisms is frequently not easy. One way to attempt it is through use of the "leaving group effect". In an $E1cB_i$ mechanism step k_i is rate-determining, and the only influence that the leaving group (in this case $R''SO_2^-$) should have on k_{ea} is through its inductive effect on the ease of removal of a proton from the α-carbon to the SO_2 group. On the other hand, in the normal E2 mechanism, where the S–S bond is substantially broken in the rate-determining transition state, the energy of that transition state should be lower than for the $E1cB_i$ process, and the reaction should be faster than expected from the simple inductive effect of the leaving group on removal of a proton from the α-carbon.

To use this probe one must be able to estimate reasonably accurately what the inductive effect of $R''SO_2$ on k_i would be. The determination of k_B for eq 5 for removal of a proton from $RCH_2SO_2CF_3$ when B is AcO^- (R = Ph or *n*-Pr) was outlined in the Results. Rate constant k_i for removal of a proton from $(RCH_2SO_2)_2$ under the same reaction conditions should be related to k_{OAc} as shown in eq 8, where ρ^* is the reaction constant for

$$\log k_i^{OAc}(RCH_2SO_2)_2 = \log k_{OAc}(RCH_2SO_2CF_3) + \rho^*(\sigma_{R''SO_2} - \sigma^*_{CF_3}) + \log 2 \quad (8)$$

removal of a proton from RCH_2SO_2Y by AcO^-, and the log 2 term is the statistical factor needed to take into account that there are two equivalent sites in the α-disulfone from which a proton can be removed.

The σ^* values for $CH_3SO_2CH_2$ (+1.32) and CF_3CH_2 (+0.92) are known.[12a] Given the usual attenuation factor (1/2.8) associated with insertion of a CH_2 group, this would make $\sigma^*_{CH_3SO_2} = +3.69$, $\sigma^*_{CF_3} = +2.57$, and $\sigma^*_{R''SO_2} - \sigma^*_{CF_3} = +1.1$; the same value for $(\sigma^*_{R''SO_2} - \sigma^*_{CF_3})$ is also obtained by using the reported[12b] σ_I values for CH_3SO_2 and CF_3 and the relationship $\Delta\sigma^* = 6.2\Delta\sigma_I$.

For removal of a proton from $PhCH_2SO_2OAr$ by Et_3N in D_2O–dimethoxyethane, ρ is +1.9,[13a] while $\rho = +2.8$ has been reported[13b] for the OD^--catalyzed exchange of the proton adjacent to the sulfonyl group in an aryl alkyl sulfone, $ArSO_2CH$. These results indicate that ρ^* for removal of a proton from RCH_2SO_2Y by acetate ion will certainly be quite large and positive. Just how large depends on one's view regarding the most appropriate way to estimate ρ^* from the ρ values for these other reactions, but a ρ^* of at least +2.8 seems indicated. By use of eq 8 and $\rho^* = +2.8$ the estimated k_i's for the α-disulfones and acetate in 70% CD_3CN–30% D_2O are as follows: $(PhCH_2SO_2)_2$, 25 °C, 7.5 M^{-1} s^{-1}; $(n\text{-}BuSO_2)_2$, 50 °C, 0.15 M^{-1} s^{-1}. The *measured* rate constants (k_{ea}) for reaction of acetate with these two α-disulfones under the same conditions are as follows: $(PhCH_2SO_2)_2$, 25 °C, $k_{ea} = 6.5$ M^{-1} s^{-1}; $(n\text{-}BuSO_2)_2$, 50 °C, 0.03 M^{-1} s^{-1}. In neither case is k_{ea} larger than k_i as estimated from eq 8. This indicates that the leaving group $R''SO_2$ has no significant effect on the rate of sulfene formation from the α-disulfone beyond its expected inductive effect on the ease of proton removal. The results therefore point to an $E1cB_i$ mechanism (eq 6, $k_{ii} > k_{-i}[BH^+]$) for formation of sulfenes from α-disulfones.[12c]

In this connection one should note that Davy et al.[9] in their study of sulfene formation from aryl phenylmethanesulfonates, $PhCH_2SO_2OAr$, concluded that, when the pK_a of ArO^- is very low, k_{ii} for loss of ArO^- from PhC^-HSO_2OAr may become so rapid ($>10^{13}$ s^{-1}) that the "lifetime" of the carbanion is less than a vibration frequency, and the mechanism, which would otherwise be $E1cB_i$, is forced to become concerted in the sense that no discrete carbanion intermediate can be present on the reaction coordinate. Such a mechanism can be considered to be an extreme example of an E1cB-like E2 reaction, having an unusually "unsymmetrical" timing for bond cleavage. Given that the α-disulfone eliminations also involve a leaving group of low pK_a, if the conclusions of Davy et al.[9] about the magnitude of k_{ii} for PhC^-HSO_2OAr are in fact correct, which some doubt,[14] sulfene formation from α-disulfones would then presumably also be an $E1cB_i$ reaction where the extreme magnitude of k_{ii} precludes a finite lifetime for the carbanion intermediate and forces the reaction to be in actuality a *very* E1cB-like E2 reaction.

Variation in k_{ea} for α-Disulfones with Alkyl Group Structure. From the data in Table III the typical variation in k_{ea} with variation in alkyl group structure would seem to be that shown in the first line of Table VII. This reactivity pattern for sulfene formation from $RR'CHSO_2SO_2R''$ is very different from that for a classic E2 reaction, the EtO^--induced elimination of HBr from $RR'CHCH_2Br$[15] (second line of Table VII). On the other hand,

(12) (a) Taft, R. W. "Steric Effects in Organic Chemistry"; Newman, M., Ed.; Wiley: New York, 1956; p 595. (b) Exner, O. "Advances in Linear Free Energy Relationships"; Chapman, N. B., Shorter, J., Eds; Plenum Press: London and New York, 1972; pp 37–38. (c) Use of a larger value for ρ^* than +2.8 would, of course, increase the values of k_i estimated for the α-disulfones from eq 8. Since even with $\rho^* = +2.8$ $k_i \geq k_{ea}$, use of a larger ρ^* would not alter the conclusion reached, namely, that the rate of elimination of the α-disulfone is not any faster than would be expected from the inductive effect of the leaving group on the acidity of the protons α to the sulfonyl group.

(13) (a) King, J. F.; Beatson, R. P. *Tetrahedron Lett.* **1975**, 973. (b) Hogeveen, H.; Maccagnani, G.; Montanari, F.; Taddei, F. *J. Chem. Soc.* **1964**, 4101.

(14) Professor J. F. King (private communication) does not feel that k_{ii} for $PhC^-HSO_2OC_6H_3$-2,4-NO_2 is necessarily $\geq 10^{13}$ s^{-1}, as Davy et al.[9] believe. From the evidence that the carbanion $PhC^-HSO_2OC_6H_3$-2-Cl-4-NO_2 can be successfully trapped in 80% dimethoxyethane (DME)–20% H_2O by 0.07 M Et_3NH^+, King concludes that k_{ii} for this intermediate is $\leq 10^9$ s^{-1} in 80% DME–20% H_2O. Since the equation given by Davy et al.[9] predicts that k_{ii} for the carbanion from the 2,4-dinitro ester should be only about 500 times larger than this, King estimates that in 80% DME–20% H_2O k_{ii} for $PhC^-HSO_2OC_6H_3$-2,4-NO_2 is $\leq 5 \times 10^{11}$ s^{-1} (well below the vibration limit), and the carbanion should have a finite lifetime in that medium. Since there is no a priori reason why k_{ii} in water (the solvent used by Davy et al.[9]) should be much larger than k_{ii} in 80% DME–20% H_2O, King feels that his results[13a] raise doubts about whether the conclusions given by Davy et al. regarding the lifetime of the carbanion in water are in fact correct.

Table VII. Effect of Alkyl Group Structure on Rates of Various Elimination Reactions

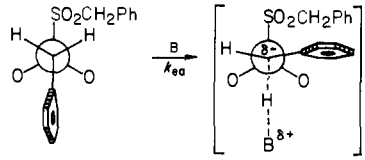
reaction			$k/k_{R=H,R'=n\text{-}Pr}$[c]		
			R = R' = H	R = R' = Me	R = H, R' = Ph
$RR'CHSO_2SO_2R''$	$\xrightarrow[B:,\ 60\%\ dioxane,\ 25\ ^\circ C]{k_{ea}}$	$RR'C{=}SO_2$	70	0.15	9×10^2
$RR'CHCH_2Br$	$\xrightarrow[EtOH,\ 55\ ^\circ C]{EtO^-}$	$RR'C{=}CH_2$[a]	0.45	2.4	1.6×10^2
$RR'CHCH_2N^+Me_3$	$\xrightarrow[EtOH,\ 104\ ^\circ C]{EtO^-}$	$RR'C{=}CH_2$[b]	25	0.6	3.3×10^4

[a] Data are from ref 14. [b] Data are from ref 15 and 16. [c] Ratio is 1.0 for R = H and R' = *n*-Pr.

for methyl, *n*-butyl, and isopropyl α-disulfones the change in k_{ea} with change in alkyl group structure is similar to although somewhat greater in magnitude than the change in rate with alkyl group structure found[16] for the Hofmann elimination of quaternary ammonium salts $RR'CHCH_2N^+Me_3$ (third line of Table VII), an elimination normally considered to be an E1cB-like E2 reaction. The variation in k_{ea} with alkyl group structure thus provides further support for the idea that sulfene formation from α-disulfones takes place by either an $E1cB_i$ or a *very* E1cB-like E2 mechanism.

One notes, however, that in the elimination involving the α-disulfone a phenyl group provides about 30-fold less rate enhancement than does the corresponding structural change in the Hofmann elimination. We believe the probable reason for the smaller acceleration provided by phenyl in the elimination involving th α-disulfone is as follows.

On the basis of the X-ray crystal structure of phenyl α-disulfone,[17] the preferred conformation for benzyl α-disulfone might be expected to be as in **2** (Newman projection along C–S bond).



2 **3**

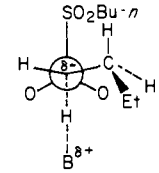
The required geometry for removal of a proton from a carbon adjacent to a sulfonyl group is known[18] to be one in which the hydrogen lies on the bisector of the angle *between* the two oxygens of the sulfonyl group. That being the case, the required conformation for the transition state for sulfene formation from benzyl α-disulfone will be as shown in **3**.

In the elimination of the quaternary ammonium salt the replacement of *n*-Pr by Ph results in a 33 000-fold rate increase, primarily because of the ability of the phenyl group to stabilize by resonance the partial negative charge on the adjacent carbon and thereby lower the energy of the transition state. For the benzyl α-disulfone elimination, examination of molecular models suggests that the decrease in energy of the transition state due to resonance stabilization of the negative charge when R' = Ph will be partially offset by the fact that going from **2** to **3** introduces, if the phenyl group is to be positioned in **3** so that it can provide maximum stabilization of the negative charge by overlap with the π system of the ring, an energetically significant, unfavorable steric interaction between the phenyl group and one of the oxygens on the adjacent SO_2 group. Because of this unfavorable steric interaction, the change from R' = *n*-Pr to Ph leads to a 30-fold smaller increase in rate in the α-disulfone system than in the elimination involving the quaternary ammonium salt. In *n*-butyl α-disulfone the fact that the last two carbons of the propyl group can be bent back away from the oxygen (see **4**) eliminates any unfavorable steric interaction of the *n*-propyl group with this sulfonyl oxygen.

Table VIII. Effect of Alkyl Group Structure on Rates of Direct Substitution at Different Electrophilic Centers

reaction	$k/k_{R=n\text{-}Bu}$[c]	
	R = Me	R = *i*-Pr
$RSO_2SO_2R + N_3^- \rightarrow RSO_2N_3 + RSO_2^-$	10	0.15
$RCH_2Br + EtO^- \rightarrow RCH_2OEt + Br^-$[a]	4.3	0.15
$RS\text{-}SO_3^- + {}^*SO_3^{2-} \rightarrow R{}^*S\text{-}SO_3^- + SO_3^{2-}$[b]	3.3	0.03

[a] Reference 19. [b] Reference 20. [c] Ratio is 1.0 for R = *n*-Bu.



4

A plot of log k_{ea} for the reaction of glycine ethyl ester with the various $(ArCH_2SO_2)_2$ in Table III vs. σ indicates that the ρ value associated with this reaction is +2.3. This measured ρ value, of course, represents the sum of the two separate ρ values associated with (1) substituents in the ring attached directly to the carbon from which the proton is being removed and (2) substituents in the distant aromatic ring of the $ArCH_2SO_2$ leaving group; i.e., $\rho_{obsd} = \rho_1 + \rho_2$. The ρ value ($\rho_1$) associated with the proximate Ar group should clearly be much larger than the one (ρ_2) associated with the distant Ar group. Just how much larger cannot be specified precisely, but it seems likely that $\rho_1 \geq +1.9$, while $\rho_2 \leq +0.4$.

A value for ρ_1 in this range is comparable to the values ($\rho = +1.83$,[11] $\rho^- = +2.35$[13a]) that have been reported for the pyridine-catalyzed formation of $ArCH{=}SO_2$ from 2,4-dinitrophenyl phenylmethanesulfonates in 80% dimethoxyethane–20% water as solvent, a reaction that is thought to proceed via either an $E1cB_i$[13a] or a very E1cB-like E2[9,11] mechanism. That ρ_1 for sulfene formation from the α-disulfones, as induced by another weakly basic amine (glycine ethyl ester) in a comparable solvent medium (60% dioxane), is similar to ρ for this elimination involving the 2,4-dinitrophenyl phenylmethanesulfonates provides additional support for the view that sulfene formation from α-disulfones involves either an $E1cB_i$ or a very E1cB-like E2 mechanism.

Note that despite the other evidence clearly indicating their E1cB character, neither of these sulfene-forming eliminations of $ArCH_2SO_2Y$ deriatives exhibits as large a positive ρ value as do E1cB-like E2 eliminations of 2-phenylethyl derivatives such as $ArCH_2CH_2N^+Me_3$. The discussion in ref 11 of the changes in effective charge on various atoms that are thought to occur on going from the reactants to the transition state in sulfene-forming reactions may provide a possible explanation.

Variation in k_{ds} for α-Disulfones with Alkyl Group Structure. The variation in rate with alkyl group structure for the reaction of azide ion with methyl, *n*-butyl, and isopropyl α-disulfones indicates how the rate, k_{ds}, for a direct substitution reaction is influenced by the nature of the alkyl group. It is interesting to

(15) Dhar, M. L.; Hughes, E. D.; Ingold, C. K.; Masterman, S. *J. Chem. Soc.* **1948**, 2055.
(16) (a) Banthorpe, D. V.; Hughes, E. D.; Ingold, C. K. *J. Chem. Soc.* **1960**, 4054. (b) Saunders, W. H.; Bushman, D. G.; Cockerill, A. F. *J. Am. Chem. Soc.* **1968**, *90*, 1775.
(17) Kiers, C. T.; Vos, A. *Recl. Trav. Chim. Pays-Bas* **1972**, *91*, 126.
(18) (a) Corey, E. J.; König, H.; Lowrey, T. H. *Tetrahedron Lett.* **1962**, 515. (b) Bordwell, F. G.; Phillips, D. D.; Williams, J. M. *J. Am. Chem. Soc.* **1968**, *90*, 426. Bordwell, F. G.; Doomes, E. *J. Org. Chem.* **1974**, *39*, 2526.

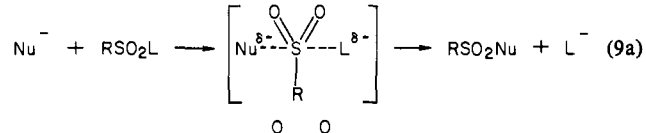
see how this compares with the variation in rate with the same change in alkyl group structure for substitutions at other electrophilic centers. This is done in Table VIII. The data show that the variation for the α-disulfone–azide reaction is quite similar to what is observed in either an S_N2 substitution at the CH_2 group of RCH_2Br[19] or a nucleophilic displacement at the dicoordinate sulfur of a Bunte salt, $RSSO_3^-$.[20] The variation in k_{ds} for RSO_2SO_2R with changes in the steric requirements of R is clearly unexceptional when compared with other direct substitutions where the reaction goes through a transition state (or intermediate) where the entering and leaving groups occupy the apical positions of a trigonal bipyramid.

Comparison of the data in Tables VII and VIII shows that for methyl, *n*-butyl, and isopropyl α-disulfones the change in k_{ds} with alkyl group structure is approximately the same as the change in k_{ea}. For this reason, changing the alkyl group from *n*-butyl to either methyl or isopropyl should not normally alter the path (elimination–addition or direct substitution) by which a given nucleophile reacts with the three alkyl α-disulfones.

Comparison of Nucleophilic Substitutions of Alkyl α-Disulfones and Alkanesulfonyl Chlorides. It is apparent from comparison of the data in Table IV for *n*-$BuSO_2Cl$ with those in Table I for *n*-$BuSO_2SO_2Bu$-*n* that changing Y in *n*-$BuSO_2Y$ from RSO_2 to Cl enables direct substitution (k_{ds}) generally to compete much more effectively with elimination–addition (k_{ea}). Rate data reveal that this arises from the fact that, for a reaction with a given nucleophile, k_{ea} for *n*-$BuSO_2Cl$ is significantly slower than k_{ea} for *n*-$BuSO_2SO_2Bu$-*n*, while at the same time k_{ds} for a sulfonyl chloride is considerably faster than k_{ds} for the corresponding α-disulfone. Specifically, since reaction of hydroxide ion with both substrates is seen from Tables I and IV to be cleanly elimination–addition, the rate constants for reaction of OH^- with *n*-$BuSO_2Cl$ (Table VI) and $(n\text{-}BuSO_2)_2$ (Table III) show that for this nucleophile $k_{ea}(RSO_2Cl)/k_{ea}(RSO_2SO_2R) = 0.25$. One might expect that with less reactive, and presumably therefore more selective, nucleophiles this ratio would be somewhat smaller; values of $k_{ea}(RSO_2Cl)/k_{ea}(RSO_2SO_2R) \simeq 0.1$–$0.25$ would seem indicated. Comparison of the rate constants for reaction of $PhSO_2Cl$ with several nucleophiles (Table IV) with those for reaction of $PhSO_2SO_2Ph$ under the same conditions[4a] provides information relevant to $k_{ds}(RSO_2Cl)/k_{ds}(RSO_2SO_2R)$.[21] They indicate that $k_{ds}(RSO_2Cl)/k_{ds}(RSO_2SO_2R)$ is typically 5–10. Taken together these data on k_{ea} and k_{ds} suggest that in general k_{ds}/k_{ea} for $RSO_2Cl \simeq (20\text{–}100)(k_{ds}/k_{ea})$ for RSO_2SO_2R. From this one can see how a direct substitution mechanism can be the dominant pathway for the reaction of the alkanesulfonyl chloride with certain nucleophiles (morpholine, glycine ethyl ester, acetate) while the same nucleophiles react with the α-disulfone entirely via elimination–addition. The fact that stronger bases than morpholine react with the sulfonyl chloride either exclusively (OH^-) or predominantly (piperidine) by elimination–addition requires that k_{ea} be more sensitive to nucleophile basicity than is k_{ds}. That such should be the case is not unexpected.

It is not surprising that $k_{ea}(RSO_2Cl) < k_{ea}(RSO_2SO_2R)$. We saw earlier that in either an $E1cB_i$ or a very E1cB-like E2 mechanism the effect of the leaving group on the rate is determined by its inductive effect on the ease of proton removal from the α-carbon to the sulfonyl group. Since $\sigma^*_{ClCH_2}$ (+1.05) is less than $\sigma^*_{CH_3SO_2CH_2}$ (+1.32), RSO_2 will be inductively a stronger electron-withdrawing group than Cl, and removal of a proton from the α-carbon should be faster in the α-disulfone than in the sulfonyl chloride, in line with $k_{ea}(RSO_2Cl) < k_{ea}(RSO_2SO_2R)$. On the basis of $\sigma^*_{RSO_2} - \sigma^*_{Cl}$ and the sort of ρ^* that would seem reasonable for proton removal, one would have anticipated a considerably smaller value for $k_{ea}(RSO_2Cl)/k_{ea}(RSO_2SO_2R)$ than the one actually found; i.e., the sulfonyl chloride seems to undergo elimination quite a bit faster than would be predicted for an $E1cB_i$ mechanism. Since we noted earlier that eliminations where the bond to the leaving group is broken to a significant degree in the rate-determining transition state show a faster rate than the one predicted from the purely inductive effect of the leaving group on the ease of proton removal, this may indicate that the elimination of the alkanesulfonyl chloride is a *less* E1cB-like E2 reaction than the elimination of the α-disulfone and that in its transition state the S–Cl bond is cleaved to a significant degree. Such a shift in mechanism on changing the leaving group from RSO_2 to Cl can be rationalized on the basis that, although Cl has a weaker acidifying effect than RSO_2 on the hydrogens on the α-carbon, Cl^- should be a better leaving group than RSO_2^- (HCl is a considerably stronger acid than RSO_2H).

In considering why $k_{ds}(RSO_2Cl)$ is greater than $k_{ds}(RSO_2SO_2R)$, one should first take note of the two different views regarding the normal mechanism for direct substitution at sulfonyl sulfur. Williams[22] and Rogne[23] believe such substitutions involve concerted bond making and bond breaking (eq 9a), while others like Ciuffarin[24] believe that they proceed by a stepwise mechanism (eq 9b) with an intermediate **5** on the reaction coordinate.



5

In the concerted mechanism (eq 9a) there is obviously appreciable negative charge on the leaving group, L, in the transition state, and since Cl^- is more stable than RSO_2^-, one would clearly expect a $k_{ds}(RSO_2Cl) > k_{ds}(RSO_2SO_2R)$.

Because Cl^- and RSO_2^- are very good leaving groups, stepwise mechanisms in the system under consideration here would presumably be ones where $k_b > k_{-a}$, and attack of the nucleophile on the substrate (step k_a) would be rate determining. At first sight, it might seem that $k_{ds}(RSO_2Cl) > k_{ds}(RSO_2SO_2R)$ could not be reconciled with a mechanism of this type and that the data could be construed as evidence in favor of the concerted mechanism. However, in an intermediate like **5** the entering and leaving groups should be bonded to the sulfonyl group by four-electron, three-center (hypervalent) bonds.[25] Such bonds are quite different[26] from ordinary bonds, and in **5** there will be appreciable partial negative charge on both Nu and L. The intermediate **5** from the sulfonyl chloride (L = Cl) where that negative charge is on chlorine should be of somewhat lower energy and be more easily formed than the one from the α-disulfone (L = RSO_2) where the partial negative charge is on RSO_2. Thus the stepwise mechanism can also adequately account for the fact that $k_{ds}(RSO_2Cl)$ is greater than $k_{ds}(RSO_2SO_2R)$.

Experimental Section

Preparation and Purification of Materials. ***n*-Butyl α-Disulfone.** 1-Butanesulfinic acid was synthesized from *n*-butylmagnesium bromide and sulfur dioxide by using the procedure of Houlton and Tartar.[27] The sulfinic acid was neutralized with sodium hydroxide, and evaporation of

(19) Streitweiser, A., Jr. "Solvolytic Displacement Reactions"; McGraw-Hill: New York, 1962; p 12.
(20) Fava, A.; Iliceto, A. *J. Am. Chem. Soc.* **1958**, *80*, 3478.
(21) Unfortunately k_{ds} for reaction of azide ion with *n*-$BuSO_2Cl$ could not be measured accurately spectrophotometrically; k_{ds} for other nucleophiles and *n*-butyl α-disulfone are not accessible because those nucleophiles react with the α-disulfone entirely by the elimination–addition pathway. For these reasons we have had to use $k_{ds}(PhSO_2Cl)/k_{ds}(PhSO_2SO_2Ph)$ values and make the plausible assumption that these should approximate $k_{ds}(n\text{-}BuSO_2Cl)/k_{ds}(n\text{-}BuSO_2SO_2\text{-}n\text{-}Bu)$ reasonably well.
(22) Deacon, T.; Farrar, C. B.; Sikkel, B. J.; Williams, A. *J. Am. Chem. Soc.* **1978**, *100*, 2525.
(23) Rogne, O. *J. Chem. Soc. B* **1971**, 1855.
(24) Ciuffarin, E.; Senatore, L.; Isola, M. *J. Chem. Soc., Perkin Trans. 2*, **1972**, 468.
(25) Kice, J. L. *Adv. Phys. Org. Chem.*, in press.
(26) Perozzi, E. F.; Martin, J. C.; Paul, I. C. *J. Am. Chem. Soc.* **1974**, *96*, 6735.
(27) Houlton, H. G.; Tartar, H. V. *J. Am. Chem. Soc.* **1938**, *60*, 544.

the neutralized solution gave sodium 1-butanesulfinate, IR (KBr), strong band at 960–1020 cm^{-1} (SO_2^-). Oxidation of the sulfinate with cobalt(III) sulfate following the procedure of Denzer et al.[28] gave, after recrystallization from benzene–ethanol, *n*-butyl α-disulfone: 31% yield; mp 58–59 °C (lit.[29] mp 59–60 °C); IR (KBr) strong absorption at 1339 and 1102 cm^{-1} (>SO_2); NMR ($CDCl_3$) δ 0.99 (t, 6 H), 1.53 (sextet, 4 H), 1.99 (quintet, 4 H), 3.46 (t, 4 H).

Methyl α-Disulfone. Methanesulfonyl chloride (Aldrich) was reduced to sodium methanesulfinate by treatment with sodium sulfite in an aqueous solution which was kept slightly alkaline throughout the course of the reaction. At the end of the reaction the water was removed, and the residue was thoroughly dried. Treatment of the residue with absolute methanol allowed the sulfinate to be separated from methanol-insoluble salts, and removal of the methanol gave pure sodium methanesulfinate: 95% yield; mp 279–281 °C; IR (KBr) strong band at 960–1040 cm^{-1} (SO_2^-). After oxidation of the methanesulfinate with cobalt(III) sulfate via the same procedure[28] as in the *n*-butyl case, the α-disulfone was removed from the reaction mixture by extraction with methylene chloride. Removal of the methylene chloride and recrystallization from absolute ethanol gave methyl α-disulfone: 10% yield; mp 169–171 °C (lit.[30] mp 167–168 °C); IR (KBr) strong bands at 1305–1325 and 1105 cm^{-1} (>SO_2); NMR ($CDCl_3$) δ 3.33 (s).

Isopropyl α-Disulfone. Isopropyl disulfide (Aldrich; 4.69 g, 0.03 mol) was dissolved in 30 mL of chloroform, and a solution of *m*-chloroperbenzoic acid (12.2 g, 0.06 mol) in 200 mL of chloroform was added at 0 °C with stirring. The reaction mixture was then allowed to warm to room temperature and stand for 5 h. The *m*-chlorobenzoic acid was filtered off, and the filtrate was washed with 5% sodium bicarbonate and then dried (Na_2SO_4). After removal of the chloroform the residue was purified by column chromatography on silica gel. The fraction eluted with benzene was pure isopropyl 2-propanethiolsulfonate: 2.46 g (45%); IR (neat) 1312 and 1117 cm^{-1} (s, >SO_2); NMR ($CDCl_3$) δ 1.43, 1.44, 1.49, 1.51 (pair of d, 12 H), 3.36 (m, 1 H), 3.68 (m, 1 H). The product appears to be identical with that synthesized by Field and co-workers[31] by another procedure.

The thiolsulfonate (2.68 g, 14.7 mmol) and 6.6 g (32.4 mmol) of 85% *m*-chloroperbenzoic acid were dissolved in 100 mL of methylene chloride, and the solution was allowed to stand at room temperature for 1 week. The precipitate of *m*-chlorobenzoic acid was filtered off, and the filtrate was washed with 5% sodium bicarbonate and then dried ($MgSO_4$). The residue after removal of the solvent was chromatographed on silica gel by using benzene as eluent. From the chromatography, isopropyl α-disulfone (1.49 g, 47%) was obtained as a liquid. Purification of the α-disulfone by distillation was not attempted since spectral and elemental analyses indicated that the material as obtained from the chromatography was already of high purity: IR (neat) 1325–1331 and 1081–1108 cm^{-1} (s, >SO_2); NMR ($CDCl_3$) δ 1.56 (d, 12 H), 3.96 (septet, 2 H). Anal. Calcd for $C_6H_{14}O_4S_2$: C, 33.63; H, 6.58; S, 29.92. Found: C, 33.92; H, 6.65; S, 30.18.

Benzyl α-Disulfone. Benzyl α-toluenethiolsulfonate[32] (1.3 g, 4.7 mmol) and 2.21 g of 85% *m*-chloroperbenzoic acid were dissolved in 70 mL of methylene chloride, and the solution was allowed to stand for 4 days at room temperature. The workup followed the same procedure used in the synthesis of isopropyl α-disulfone. The residue after removal of the methylene chloride was recrystallized from benzene–ethanol, giving 0.45 g (31%) of benzyl α-disulfone: mp 178–180 °C; IR (KBr) >SO_2 absorptions at 1336, 1315, and 1105 cm^{-1}; NMR ($CDCl_3$) δ 4.46 (s, 4 H), 7.43 (s, 10 H). Anal. Calcd for $C_{14}H_{14}O_4S_2$: C, 54.20; H, 4.55; S, 20.67. Found: C, 54.12; H, 4.61; S, 20.75.

***p*-Chlorobenzyl α-Disulfone.** *p*-Chlorobenzyl disulfide[33] (10.6 g, 0.035 mol) and 13.8 g of 85% *m*-cloroperbenzoic acid were dissolved in methylene chloride (200 mL), and the solution was allowed to stand at room temperature for 14 h. After the same workup procedure as that used in the other *m*-chloroperbenzoic acid oxidations, the residue, which TLC showed contained at least four compounds, was chromatographed on silica gel. *p*-Chlorobenzyl (4-chlorophenyl)methanethiolsulfonate (1.42 g, 12%) was eluted with benzene. It was recrystallized from ethanol: mp 125–127 °C; IR (KBr) 1320 and 1120 cm^{-1} (SO_2); NMR ($CDCl_3$) δ 4.05 (s, 2 H) 4.19 (s, 2 H), 7.1–7.5 (m, 8 H).

The thiolsulfonate (0.50 g, 1.44 mmol) and 1.2 g of 85% *m*-chloroperbenzoic acid (5.8 mmol) were dissolved in 40 mL of methylene chloride, and the solution was allowed to stand at room temperature for 5.5 days. After the standard workup procedure the residue was recrystallized from absolute ethanol, giving 0.19 g (34%) of *p*-chlorobenzyl α-disulfone: mp 184–185 °C; IR (KBr) strong bands at 1340, 1160, and 1110 cm^{-1} (>SO_2 groups); NMR ($CDCl_3$) δ 4.54 (s, 4 H), 7.38 (8 H). Anal. Calcd for $C_{14}H_{12}Cl_2O_4S_2$: C, 44.35; H, 3.19; S, 16.88. Found: C, 44.60; H, 3.35; S, 16.72.

***p*-Methylbenzyl α-Disulfone.** *p*-Methylbenzyl disulfide[33] (8 g, 29 mmol) and 12.2 g of 85% *m*-chloroperbenzoic acid were dissolved in 140 mL of methylene chloride, and the solution was allowed to stand for 5 h at room temperature. After the usual workup the residue was chromatographed on silica gel. *p*-Methylbenzyl (4-methylphenyl)methanethiolsulfonate was eluted with benzene and recrystallized from ethanol: mp 83–84 °C; 0.75 g (9%); IR (KBr) 1320 and 1110 cm^{-1} (>SO_2); NMR ($CDCl_3$) δ 2.34 (s, 3 H), 2.36 (s, 3 H), 4.02 (s, 2 H), 4.20 (s, 2 H), 7.20 (8 H).

Oxidation of this thiolsulfonate (0.63 g, 2.07 mmol) with *m*-chloroperbenzoic acid (8.2 mmol) in methylene chloride with a reaction time of 36 h gave, after recrystallization from ethanol, 0.44 g (63%) of *p*-methylbenzyl α-disulfone: mp 162–163 °C; IR (KBr) 1340, 1160, and 1115 cm^{-1} (>SO_2); NMR ($CDCl_3$) δ 2.39 (s, 6 H), 4.45 (s, 4 H), 7.16–7.38 (m, 8 H). Anal. Calcd for $C_{16}H_{18}O_4S_2$: C, 56.79; H, 5.36; S, 18.92. Found: C, 56.69; H, 5.38; S, 18.79.

***m*-Chlorobenzyl α-Disulfone.** *m*-Chlorobenzyl disulfide was synthesized from *m*-chlorobenzyl chloride (Aldrich) by using the general procedure for the synthesis of symmetrical disulfides from alkyl halides developed by Milligan and Swan.[34] From 24.3 g (0.15 mol) of the chloride there was obtained, after purification of the crude disulfide by chromatography on silica gel, 12.8 g (54%) of the disulfide: NMR ($CDCl_3$) δ 3.57 (s, 4 H), 7.0–7.5 (m, 8 H).

The disulfide (9.6 g, 30.5 mmol) and 13.6 g of 85% *m*-chloroperbenzoic acid were dissolved in 150 mL of chloroform, and the solution was allowed to stand at room temperature for 21 h. After the usual workup the residue was purified through column chromatography on silica gel. *m*-Chlorobenzyl (*m*-chlorophenyl)methanethiosulfonate, which was eluted with benzene, was recrystallized from ethanol: mp 46–49 °C; 2.26 g (21%); IR (KBr) 1315–1325, 1121 cm^{-1} (>SO_2); NMR ($CDCl_3$) δ 4.07 (s, 2 H), 4.21 (s, 2 H), 7.1–7.5 (m, 8 H).

The thiolsulfonate (0.92 g, 2.66 mmol) was then oxidized with *m*-chloroperbenzoic acid (10.6 mmol) in methylene chloride (35 mL) as solvent. After 5 days at room temperature, the reaction mixture was worked up in the usual manner, and the residue was recrystallized from ethanol, affording 0.27 g (27%) of *m*-chlorobenzyl α-disulfone: mp 168–170 °C; IR (KBr) 1342, 1326, 1164, 1115 cm^{-1} (>SO_2); NMR ($CDCl_3$) δ 4.52 (s, 4 H), 7.2–7.5 (m, 8 H). Anal. Calcd for $C_{14}H_{12}Cl_2O_4S_2$: C, 44.35; H, 3.19; S, 16.88. Found: C, 44.18; H, 3.39; S, 16.67.

Other Reagents. *n*-Butyl trifluoromethyl sulfone and benzyl trifluoromethyl sulfone were prepared and purified as described by Hendrickson and co-workers.[35] 1-Butanesulfonyl chloride (Eastman) and benzenesulfonyl chloride (Eastman) were purified by distillation under reduced pressure. The various amines, dioxane, and the other reagents used were purified as previously described.[4a] Deuterium oxide (Wilmad, 99.8 atom % D) was used without further purification. Perchloric acid-*d* was prepared by addiing 5 g of 70% perchloric acid to 10 mL of D_2O, evaporating the solution to about 6 mL volume, and then repeating the dilution with 10 mL of D_2O and subsequent evaporation three more times. Titration indicated that the concentration of perchloric acid-*d* in the final solution was 8.0 N.

Reaction of Amines with α-Disulfones. Product Isolation and Deuterium Incorporation Experiments. The α-disulfone (1 mmol) in 5–10 mL of anhydrous dioxane was added rapidly with stirring to a solution of the amine (3 mmol) and its conjugate acid (3 mmol) in 10–20 mL of 30% dioxane–70% water (either H_2O or D_2O), and the solution was allowed to stand at room temperature for a period of time just sufficient for complete reaction. The solution was then poured into approximately 5 times its volume of water, and the resulting mixture was extracted several times with either ether or methylene chloride. The extracts were washed with dilute hydrochloric acid (to remove excess amine) and water and dried (Na_2SO_4), and the solvent was removed under reduced pressure at room temperature. After being subjected to an oil-pump vacuum at room temperature to remove any traces of dioxane, the residue was purified and identified, and, for the runs in dioxane–D_2O, the extent of

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deuteration of the carbon α to the sulfonyl group in the substitution product was determined by NMR. The results of the different α-disulfone–amine reactions are summarized below.

1-(Butylsulfonyl)piperidine [0.12 g (59%); mp 42–43 °C (lit.[36] mp 42–43 °C)] was obtained by recrystallization (benzene–hexane) of the residue from the reaction of piperidine with *n*-butyl α-disulfone: NMR ($CDCl_3$) δ 0.95 (t, 3 H, CH_3), 1.63 (m, 10 H), 2.90 (t, 2 H, CH_2SO_2), 3.25 (m, 4 H). Deuteration of the carbon α to the sulfonyl group in the product from the reaction in dioxane–D_2O was determined from the ratio of the integrated intensities of the signals at δ 2.90 and 0.95.

1-(Butylsulfonyl)morpholine [0.11 g (55%): mp 40 °C (lit.[37] mp 39 °C] was obtained on recrystallization (benzene–petroleum ether) of the residue from the reaction of morpholine and *n*-butyl α-disulfone: NMR ($CDCl_3$) δ 0.97 (t, 3 H, CH_3), 1.25–1.8 (m, 4 H), 2.92 (t, 2 H, CH_2SO_2), 3.27 (m, 4 H), 3.76 (m, 4 H). The extent of the deuteration of the α-carbon of the product from the reaction in dioxane–D_2O was determined from the relative intensities of the triplets at δ 2.92 and 0.97.

The residue from the reaction of glycine ethyl ester and *n*-butyl α-disulfone was a liquid (0.14 g, 63%) that infrared and NMR spectra showed must have the structure $EtOOCCH_2NHSO_2Bu$-*n*: IR (neat) 3300–3320 (NH), 1750, 1205 (C(O)O), 1325, 1135 cm^{-1} (>SO_2); NMR ($CDCl_3$) δ 0.95 (t, 3 H, CH_3, in *n*-Bu), 1.31 (t, 3 H, CH_3 in Et), 1.5–2.0 (m, 4 H), 3.13 (t, 2 H, CH_2SO_2), 3.96 (s, 2 H, $CH_2C(O)$), 4.27 (q, 2 H, CH_2O). For the reaction in dioxane–D_2O the extent of deuteration of the α-carbon was determined from the relative intensities of the signals centered at δ 3.13 and 0.95.

1-(Methylsulfonyl)morpholine [0.07 g (44%); Mp 96 °C (lit.[38] mp 92–94 °C)] was obtained from recrystallization (ethanol) of the residue from the reaction of morpholine with methyl α-disulfone: NMR ($CDCl_3$) δ 2.81 (s, 3 H), 3.23 (m, 4 H), 3.80 (m, 4 H). Deuteration of the methyl group in the product from the reaction in dioxane–D_2O was determined from the ratio of the integrated intensities of the signals at δ 2.81 and 3.23.

1-(Benzylsulfonyl)morpholine [0.164 g (68%); mp 175–177 °C (lit.[38] mp 174–175 °C)] was obtained upon recrystallization (ethanol) of the residue from the reaction of benzyl α-disulfone with morpholine: NMR ($CDCl_3$) δ 3.10 (m, 4 H), 3.62 (m, 4 H), 4.24 (s, 2 H), 7.42 (s, 5 H). The extent of deuteration of the methylene group adjacent to sulfonyl group in the product from dioxane–D_2O was determined from the relative intensity of the signals at δ 4.24 and 7.42. In a separate experiment, undeuterated 1-(benzylsulfonyl)morpholine showed no deuteration of the CH_2SO_2 group when allowed to stand in a 1:1 morpholine–morphilineH$^+$ buffer in 60% dioxane–40% D_2O for the same period of time used for the rection of the α-disulfone with morpholine.

The reaction of isopropyl α-disulfone with morpholine gave a liquid residue of 1-(isopropylsulfonyl)morpholine (0.08 g, 41%). The identity of the product was established by IR and NMR comparison with a known sample:[38] NMR ($CDCl_3$) δ 1.35 (d, 6 H), 3.37 (m, 5 H), 3.75 (m, 4 H). The degree of deuteration of the carbon α to the sulfonyl group in the product group in the product from dioxane–D_2O was estimated by comparing the integrated intensity of the multiplet centered at δ 3.37 ($CHSO_2$ plus $(CH_2)_2N$) with that of the doublet at δ 1.35 $(CH_3)_2CH$).

Reaction of Azide Ion with α-Disulfones. Product Isolation and Deuterium Incorporation Experiments. The reactions were carried out and worked up exactly the same way as those involving the amines except that sodium azide only (2 mmol), and none of its conjugate acid, was employed. During the workup the wash of the methylene chloride extracts with dilute hydrochloric acid was omitted. All of the sulfonyl azides except α-toluenesulfonyl azide are liquids, and their thermal instability precludes their purification by distillation. However, the residues remaining after removal of methylene chloride and any traces of dioxane appear, as judged by IR and NMR spectral comparisons with knowns, to be quite pure samples of sulfonyl azides. The results of the different α-disulfone–azide ion reactions are given below.

The residue from the reaction of azide ion with *n*-butyl α-disulfone was 1-butanesulfonyl azide;[39] 0.15 g (91%); IR (neat) 2117 (N_3), 1360, 1190, 1151 cm^{-1} (>SO_2); NMR ($CDCl_3$) δ 0.98 (t, 3 H), 1.67 (m, 4 H), 3.36 (t, 2 H). The ratio of the integrated intensities of the signals at δ 3.36 and 0.95 was the same for the product of the reaction in dioxane–D_2O as for the one from dioxane–H_2O.

Reaction of methyl α-disulfone with azide gave methanesulfonyl azide;[40] 0.086 g (71%); NMR ($CDCl_3$) δ 3.30 (s). The NMR spectrum of the product from the reaction in dioxane–D_2O showed, after scale expansion, *no* indication of any detectable splitting of the δ 3.30 singlet into a triplet, as would be the case of there had been any significant deuteration of the methyl group.

The residue from the reaction of the isopropyl α-disulfone was an oil whose infrared spectrum [2120 (N_3), 1350 and 1143 cm^{-1} (>SO_2)] and NMR ($CDCl_3$) [δ 1.51 (d, 6 H), 3.53 (septet, 1 H)] indicated it to be 2-propanesulfonyl azide (0.09 g, 60% yield). The relative intensities of the two signals at δ 3.53 and 1.51 were unchanged when dioxane–D_2O was used as the reaction solvent.

α-Toluenesulfonyl azide [0.10 g (52%); mp 53–54.5 °C (lit.[40] mp 54 °C)] was obtained upon recrystallization from ethanol of the residue from the reaction of benzyl α-disulfone with N_3^-: NMR ($CDCl_3$) δ 4.55 (s, 2 H), 7.47 (s, 5 H). The degree of deuteration of the α-carbon in the product from the reaction in dioxane-D_2O was determined from the relative intensities of these two NMR signals. That azide ion is able to trap $PhCH{=}SO_2$ in dioxane–water to yield the sulfonyl azide was demonstrated by allowing benzyl α-disulfone (1 mmol) to react with tertiary amine, *N*-methylimidazole (2 mmol), in the presence of sodium azide (1 mmol) in 60% dioxane–40% D_2O. The workup of the reaction gave α-toluenesulfonyl-α-*d* azide: 0.76 mmol (76%); NMR ($CDCl_3$) δ 4.55 (s, 1 H), 7.47 (s, 5 H).

Reaction of Sodium Deuteroxide with *n*-Butyl α-Disulfone. A solution of *n*-butyl α-disulfone (1.0 mmol) in 9 mL of dioxane was rapidly added with efficient stirring to a solution of 2.0 mmol of NaOD in 8 mL of D_2O plus 3 mL of dioxane. After 5 min the solution was evaporated nearly to dryness under reduced pressure at room temperature. The residue was dissolved in 5 mL of water, and the solution was acidified to pH <1 with 2 N sulfuric acid and then extracted three times with 10 mL-portions of ether. (That this extraction will remove 1-butanesulfinate, as 1-butanesulfinic acid, from 1-butanesulfonate had been demonstrated in a trial experiment using equal amounts of sodium 1-butanesulfinate and 1-butanesulfonate.) The aqueous solution was then neutralized to pH 7 with concentrated potassium hydroxide, and the water was removed under reduced pressure. The solid residue was transferred to an extraction thimble in a Soxhlet extractor and extracted for 6 h with ethanol. The ethanol extract was concentrated to 10–15 mL under reduced pressure and cooled. The potassium 1-butanesulfonate-1-*d* (0.056 g, 32%) that crystallized was filtered off and dried: NMR (D_2O) δ 0.84 (t, 3 H), 1.15–1.80 (m, 4 H), 2.87 (t, 1 H); IR (KBr) strong bands at 1214 and 1180 cm^{-1} (SO_3^-).

Reaction of Acetate Ion with *n*-Butyl α-Disulfone. The α-disulfone (2.0 mmol) was allowed to react with sodium acetate (8.0 mmol) at 50 °C under nitrogen in a 4:1 acetate–acetic acid buffer in 60% dioxane–40% D_2O. After the reaction the solution was diluted with 1.5 times its volume of water and evaporated to a volume of 5 mL under reduced pressure at room temperature. It was then acidified and worked up in the fashion described for the reaction of deuterioxide with the α-disulfone, yielding 0.135 g (38%) of potassium 1-butanesulfonate-1-*d* whose infrared and NMR spectra matched those of the sample from the reaction of OD^- with *n*-butyl α-disulfone.

Reaction of 1-Butanesulfonyl Chloride with Nucleophiles. Product Isolation and Deuterium Incorporation Experiments. The reactions of 1-butanesulfonyl chloride with the various nucleophiles were carried out by using the same procedures employed for the corresponding reactions of *n*-butyl α-disulfone. The extent of deuteration of the α-carbon of the substitution products from the reactions in dioxane–D_2O was also determined in the same manner as in the reactions of α-disulfone. The yields of substitution product isolated from the various reactions were as follows (nucleophile, substitution product, yield): piperidine, 1-(butylsulfonyl)piperidine, 41%; morpholine, 1-(butylsulfonyl)morpholine, 54%; glycine ethyl ester, n-$BuSO_2NHCH_2COOEt$, 81%; sodium deuterioxide, potassium 1-butanesulfonate, 85%; sodium acetate, potassium 1-butanesulfonate, yield not determined.

Procedure for Kinetic Runs. In the runs that were followed by conventional spectrophotometry 3.5 mL of a 60% dioxane solution containing the desired concentration of the nucleophile and, where appropriate, its conjugate acid was placed in a 1-cm spectrophotometer cell in the thermostated cell compartment of a spectrophotometer. Once the solution had reached thermal equilibrium, the reaction was initiated by the addition (via microsyringe) and rapid mixing of 10–35 μL of a solution of the α-disulfone or sulfonyl chloride dissolved in anhydrous dioxane. The change in absorbance with time was then followed at an appropriate wavelength. Wavelengths used were as follows: *n*-butyl α-disulfone, 230 nm; isopropyl α-disulfone, 240 nm; methyl α-disulfone, 225 nm; benzyl α-disulfone, 250 nm; *p*-methylbenzyl α-disulfone, 246 nm; 1-butanesulfonyl chloride, 225 and 230 nm; benzenesulfonyl chloride, 255 and 270 nm.

In those runs that were so rapid that they had to be followed by stopped-flow spectrophotometry a solution of the α-disulfone or sulfonyl chloride in 60% dioxane, prepared immediately prior to use, was placed

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in one of the reservoir syringes of a Durrum-Gibson Model D-110 stopped-flow spectrophotometer, and a solution of the nucleophile (and, where appropriate, its conjugate acid) in 60% dioxane was placed in the other reservoir syringe. After the reactants were mixed, the course of the reaction was then monitored on the storage oscilloscope at an appropriate wavelength. These wavelengths were the same as those used for runs employing conventional spectrophotometry. For those α-disulfones whose kinetics were followed only by stopped-flow spectrophotometry the wavelengths were as follows: *p*-chlorobenzyl α-disulfone, 246 nm; *m*-chlorobenzyl α-disulfone, 250 nm.

Pseudo-first-order rate constants for each run were determined from the slope of a plot of log $(A_t - A_\infty)$ vs. time. All plots showed excellent linearity, and duplicate runs showed excellent reproducibility.

Deuterium-Exchange Reactions of Trifluoromethyl Sulfones. The alkyl trifluoromethyl sulfone $RCH_2SO_2CF_3$ (R = *n*-Pr or Ph; 10–20 mg) was dissolved in 1 mL of 70% CD_3CN–30% D_2O containing the desired concentrations of sodium acetate and acetic acid, and the solution was placed in an NMR tube and kept at constant temperature. At appropriate time intervals the integrated NMR spectrum of the solution was measured, and from this the extent to which the protons on the methylene group adjacent to the sulfonyl function had undergone exchange with the deuterium of the solvent was determined. For the *n*-butyl sulfone the ratio of the integrated intensity of the signal for the methyl group to that for the hydrogens on the carbon α to the sulfonyl group was used to measure the degree of exchange. In the case of the benzyl sulfone the ratio of the integral for the aromatic protons of the phenyl group to the integral for the methylene group protons was employed.

That exchange in the presence of $[OD^-] = 0.002$ M was too fast to be able to be followed by the NMR procedure was shown by the fact that when *n*-butyl trifluoromethyl sulfone (60 mg), dissolved in 1 mL of 70% CD_3CN–30% D_2O, was placed in an NMR tube and 20 μL of a 0.1 N stock solution of sodium deuterioxide in D_2O was added, exchange of the protons on the carbon adjacent to the sulfone group was complete by the time (45 s) the NMR spectrum could be determined.

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Supplementary Material Available: Tabulation of results of individual kinetic runs with α-disulfones (Table II) and sulfonyl chlorides (Table V) (3 pages). Ordering information is given on any current masthead page.

Reactions of (9-Anthryl)arylmethyl Chloride and Its Homologues with Nucleophiles under Solvolytic Conditions. Notable Effects of Reaction Conditions and Substituents on the Reaction Sites

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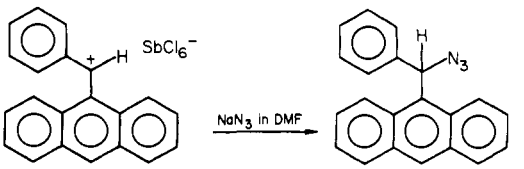
Abstract: The reactions of (9-anthryl)arylmethyl chlorides **2a–e** (the substituents are *p*-MeO, *p*-Me, H, *p*-Cl, and *m*-Cl), the corresponding bromides **3b–d** (the substituents are *p*-Me, H, and *p*-Cl), and the antimonate salts **4b-e** (the substituents are *p*-Me, H, *p*-Cl, and *m*-Cl) with several nucleophiles have been examined. When **2** was allowed to react with sodium ethoxide, ethanol in the presence of triethylamine, sodium azide in aqueous DMF, and sodium borohydride in aqueous diglyme, a mixture of anthracene derivatives and compounds with a quinoidal structure was obtained. The yield of the quinoidal product increased as the substituent became increasingly electron withdrawing. The reaction of the bromide **3** gave also a mixture of an anthracene derivative and the quinoidal compound; the product composition was almost the same as that obtained by the reaction of **2**. By contrast, the preferential formation of the anthracene derivatives was observed in the reactions of the antimonate salt **4** with the same nucleophiles. When **2** was treated with sodium borohydride in trifluoroacetic acid, only the anthracene hydrocarbon was isolated. The reaction of 9-(diphenylmethylene)-10-chloro-9,10-dihydroanthracene (**6a**) under the same conditions, however, yielded predominantly the thermodynamically less stable quinoidal compound **28a**. When (10-methylanthracen-9-yl)benzyl chloride (**9a**) was allowed to react with several nucleophiles, the corresponding quinoidal compounds were obtained in good yields. However, the reactions of (10-phenylanthracen-9-yl)benzyl chloride (**9b**) and the corresponding antimonate salt **11b** gave mainly the anthracene derivatives. In the case of 9-benzylidene-10-isopropyl-10-chloro-9,10-dihydroanthracene (**9c**), the product composition remarkably depends on the nucleophilicity of reagent; sodium ethoxide, a powerful nucleophile, attacks predominantly the benzylic site. In contrast, the quinoidal compound **30c** was the main product when ethanol was the nucleophile. A mechanism which emphasizes the role of a tight ion pair for attack by a nucleophile on the ring site and that of a free ion (and a solvent-separated ion pair) for attack on the benzylic site has been proposed to explain the effects of reaction conditions and the substituents on the reaction sites.

Recently we reported[1,2] that the reaction of (9-anthryl)benzyl hexachloroantimonate (**4c**) with the nucleophiles H_2O, ^-OH, MeOH, ^-OMe, EtOH, ^-OEt, ^-Oi-Pr, and $^-N_3$ gave exclusively products with the anthracene structure by attack of a nucleophile on the benzylic site (eq 1). By contrast, the reaction of (9-anthryl)benzyl chloride (**2c**) with the same nucleophiles in protic solvents yielded a mixture of anthracene derivatives and com-



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