(20 ml). The suspension was extracted with carbon tetrachloride (2 × 10 ml) and the carbon tetrachloride layers were washed with water and dried. Solvent was removed by rotary evaporation. Residual dioxane was removed by pumping on the samples (0.1 mm, 48 hr). Samples were dissolved in 500 μl of $CDCl_3$ and the exchangeable hydrogen was integrated. The aromatic protons were used as an internal standard. Four integrations of the proton and standard were performed in each case. Rate constants were determined by plotting the natural logarithm of the remaining proton against time, using a least-squares method. Second-order rate constants were determined by dividing the first-order rate constants by the base strength.

The validity of the integration method was checked by preparation of a calibration curve for α-chlorobenzyl isopropyl sulfone. Mixtures of 0, 25, 50, and 75 deuterated material were prepared by mixing together appropriate weights of undeuterated and fully deuterated (at the site of exchange) substrate. These mixtures were then dissolved in 500 μl of chloroform-*d* and integrated in a manner identical with that used in the rate determinations. The per cent of deuterium in the sample (by weight) was plotted against the per cent of deuterium in the sample by integration to give a straight line (r = 0.997) of slope 1.06 ± 0.05.

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Registry No.—**3**, 34009-00-2; **7**, 51392-16-6; $PhCDBrSO_2CD(CH_3)_2$, 51392-17-7; $PhCHBrSO_2CH(CH_3)_2$, 35500-99-3.

References and Notes

(1) F. G. Bordwell and M. D. Wolfinger, *J. Amer. Chem. Soc.*, **93**, 6303 (1971). J. R. Jones (private communication) has found relative rates of about (1.0):10^2:10^4 in the rates of tritium exchange in NaOMe–MeOH for the series *p*-$ClC_6H_4SO_2CHMe_2$, *p*-$ClC_6H_4SO_2CH_2Me$, *p*-$ClC_6H_4SO_2CH_3$. Experimental details are given in the Ph.D. Dissertation of Mark D. Wolfinger, Northwestern University, 1968.

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(3) (a) F. G. Bordwell and J. M. Williams, Jr., *J. Amer. Chem. Soc.*, **90**, 435 (1968); (b) see F. G. Bordwell and M. D. Wolfinger, *J. Org. Chem.*, **39**, 2521 (1974), for additional examples.

(4) We have commented elsewhere on the rarity of the one-stage mechanism for 1,3-eliminations.[5]

(5) (a) F. G. Bordwell, *Accounts Chem. Res.*, **3**, 281 (1970); (b) F. G. Bordwell and B. B. Jarvis, *J. Amer. Chem. Soc.*, **95**, 3585 (1973). See also F. G. Bordwell and E. Doomes, *J. Org. Chem.*, **39**, 2531 (1974).

(6) D. A. Schexnayder, Ph.D. Dissertation, Northwestern University, 1968, observed *ca.* a 1400-fold increase in the rate of exchange of $PhSO_2CH_2Cl$ *vs.* $PhSO_2CH_3$ in NaOMe–MeOD at 25°.

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(8) F. G. Bordwell and J. Almy, *J. Org. Chem.*, **38**, 575 (1973).

(9) The ρ for $ArSO_2CH_2CO_2H$ is 0.253,[10] as compared to 0.237 for $ArCH_2CH_2CO_2H$.[10] (Our earlier estimate was based on a transmission coefficient of 2.8 for SO_2.)

(10) D. J. Pasto, D. McMillan, and T. Murphy, *J. Org. Chem.*, **30**, 2688 (1965).

(11) An alternative possibility, which we believe to be less likely, is facilitation of ionization and solvent exchange at the methine position by a 1,3 proton shift of the type $Ph\bar{C}ClSO_2CHMe_2 \rightarrow PhCHClSO_2\bar{C}Me_2$.

(12) See ref 3b for additional data on the effects of methyl substitution on the rate of Ramberg–Bäcklund reactions.

Solvent and Substituent Effects in the Ramberg–Bäcklund Reaction

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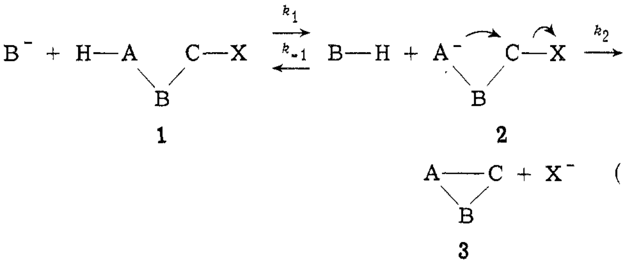
The effects of increasing the proportion of nonaqueous solvent on the rate of reaction of $PhCHBrSO_2CH_2Ph$ with lyate ion in mixtures of water with 1,2-dimethoxyethane, dioxane, ethanol, or methanol have been found to be remarkably similar to those observed earlier under similar conditions with ethylene chlorohydrin. Deuterium exchange studies indicate that with $ArCH_2SO_2CH_2X$ (**4**) and $ArCHXSO_2CH_3$ (**5**), as well as with $ArCHXSO_2CH_2Ar$ (**6**), equilibrium concentrations of α' carbanions are formed prior to halide loss. The overall ρ values for alkene formation from **4**, **5**, and **6** range from +1.29 to +3.43. Analysis shows that ρ for halide ion loss is negative for **4** and slightly positive for **5** and **6**. Methyl substitution at the α position of **4** or the α' position of **5** causes surprisingly little change in the overall rate of alkene formation. The k^{Br}/k^{Cl} leaving group effects for **4**, **5**, and **6** in 40% aqueous dioxane ranged from 169 to 207. All of these observations are shown to be consistent with a mechanism wherein equilibrium concentrations of α' carbanions are formed in the first step and these carbanions participate in a nucleophilic displacement in a second, rate-limiting step.

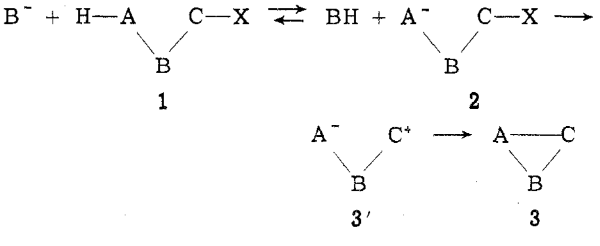
A variety of stepwise mechanisms can be visualized for base-promoted 1,3-elimination of H-X from a system H-A-B-C-X with consequent formation of a three-membered ring.[2] In the most common mechanism (1), deprotonation by a base, B^-, generates an anion (2) from which X^- is eliminated by an intramolecular nucleophilic displacement initiated by atom A. (Either k_1 or k_2 can be rate limiting, depending on the system.)



(1)

Numerous examples are known where A is O, N, C, S, P, etc., and B and C are carbon atoms.[3,4]

The presence of a negative charge in 2 would be expected to enhance greatly the tendency for X to ionize without direct participation by the nucleophilic atom A^-. If one or more groups capable of stabilizing a carbonium ion, such as Ar, R, or RO, are present on the atom holding X, it would not be surprising, then, to find that the mechanism has changed to one where a dipolar ion intermediate (3′) is produced in the second step (mechanism 2).



(2)

Examples where the evidence indicates that a type 2 mechanism obtains, at least in some instances, include (a) α-lactone formation by solvolysis of $ArCHXCO_2H$ in

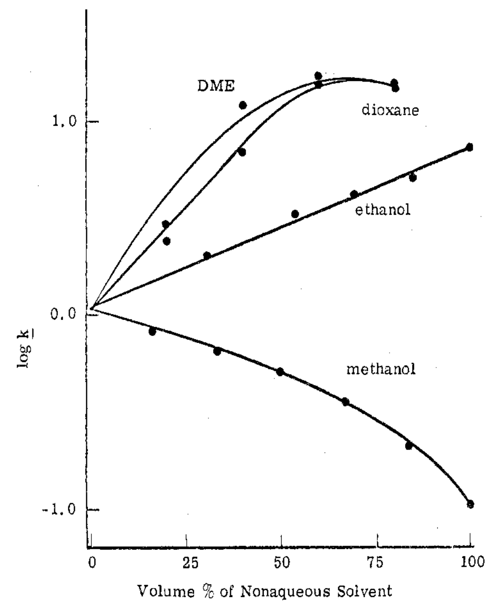


Figure 1. Plot of log *k* for the reaction of α-bromobenzyl benzyl sulfone with lyate ion in various solvent media *vs.* the volume per cent of nonaqueous solvent.

aqueous base[5] and (b) cyclopropanone formation during Favorskii rearrangements of $ArCH_2COCHXCH_3$, $Ar_2CX\text{-}COCH_3$, and the like.[6]

The reaction of 2-haloalkanols with aqueous alkali to form epoxides probably utilize both types of mechanisms. When the halogen is primary or secondary the evidence points to participation by the oxide ion.[7] When the halogen is tertiary, however, the rates calculated for ionization under the influence of the negative charge of the oxide ion are 1 to 3 orders of magnitude faster than the observed rates.[8] Mechanism 2 appears likely, therefore, when the halogen is tertiary.

In earlier studies we have shown that 1,3-dehydrohalogenation of an α-halo sulfone of the type $PhCH_2SO_2CHXPh$ by a base such as sodium methoxide in methanol (Ramberg-Bäcklund reaction) usually occurs by mechanism 1 with k_2 (episulfone formation) being rate limiting.[10] It was of interest to use additional probes to test this mechanism and at the same time to investigate its generality. To this end we have (a) determined the effect of solvent changes on the rates for $PhCH_2SO_2CHXPh$ (X = Cl and Br), (b) determined the effects of meta and para substituents on the rates for $ArCH_2SO_2CH_2X$ (**4**), $ArCHXSO_2CH_3$ (**5**), and $ArCHXSO_2CH_2Ar'$ (**6**), and (c) determined the effect on the rates of methyl substitution α to the halogen in **4** and **5** and α to the phenyl group (α' position) in **5**.

Results

Solvent effects on the rates of reaction of α-bromobenzyl benzyl sulfone were determined in basic aqueous 1,2-dimethoxyethane (DME), dioxane, ethanol, and methanol solutions containing amounts of nonaqueous solvent ranging from 100% down to as low as 16% by volume. The results are summarized in Figure 1.[11] α-Chlorobenzyl benzyl sulfone responded similarly to these solvent changes, except that the aqueous DME and dioxane mixtures showed a more nearly linear increase in rate with increasing volume per cent of nonaqueous solvent.[11]

The desired substituted-benzyl bromomethyl sulfones, $ArCH_2SO_2CH_2Br$ (**4**), were prepared from the benzyl chlorides *via* the arylmethylsulfonylacetic acids, $ArCH_2SO_2CH_2CO_2H$. The latter were subjected to brominative decarboxylation[12] and the resulting benzyl dibromomethyl sulfones were reduced with potassium sulfite.[12,13] This method was used also to prepare α-bromobenzyl benzyl sulfones of the type $ArCHBrSO_2CH_2Ph$ and $PhCH_2SO_2CHBrAr$, and for $PhCHBrSO_2CH_3$.[12] The remaining α-halo sulfones were prepared by halogenation of the appropriate sulfides, followed by oxidation (see Experimental Section).

Rates for $ArCH_2SO_2CH_2Br$ (**4**), $ArCHBrSO_2CH_3$ (**5**), and $ArCHBrSO_2Ar'$ (**6**) reacting with hydroxide ion in 40% (v/v) dioxane-water or methoxide in methanol were determined spectrophotometrically and/or titrimetrically by methods described earlier.[10] The results are summarized in Table I.

Spectrophotometric rates for some members in series **4** and **5** were difficult to determine because the change in absorption between starting sulfone and styrene product was small. For this reason the rates in methanol were determined titrimetrically. Spectrophotometric rate constants for **4** with Ar = $3\text{-}BrC_6H_4$, $3\text{-}FC_6H_4$, and C_6H_5 were found to be 11% higher, 5.6% higher, and 6% lower, respectively, than the corresponding titrimetric rates.

The calculated σ constant for $p\text{-}NO_2$ in series **4**, based on the rate constant and using the line defined by the other points, was 1.21, which agrees well with $\sigma^-{}_{p\text{-}NO_2}$ (1.27).

The rate for 3-bromo-4-methoxybenzyl bromomethyl sulfone was somewhat slower than anticipated by assum-

Table I
Second-Order Rate Constants for the Reaction of $ArCH_2SO_2CH_2Br$ (4), $ArCHBrSO_2CH_3$ (5), and $ArCH_2SO_2CHXAr'$ (6) with Base in 60% (v/v) Dioxane–Water or Methanol

Halo sulfone	Temp, °C	Solvent-base	k_H,[a] M^{-1} sec^{-1}	ρ_{obsd}	r
$ArCH_2SO_2CH_2Br$	25.1	40% dioxane–H_2O	$8.08 \pm 0.04 \times 10^{-2}$	1.47[b,c]	0.992
$ArCH_2SO_2CH_2Br$	25.0	Methanol	$1.35 \pm 0.04 \times 10^{-3}$	1.47[c,d]	0.999
$ArCHBrSO_2CH_3$	50.0	40% dioxane–H_2O	$2.54 \pm 0.05 \times 10^{-3}$	1.29[b,e]	0.978[f,g]
$ArCHBrSO_2CH_3$	25.0	40% dioxane–H_2O	1.24 ± 10^{-4} (calcd)		
$ArCHBrSO_2CH_3$	50.0	Methanol	$1.83 \pm 0.12 \times 10^{-4}$	1.29[d,e]	0.996[f]
$ArCH_2SO_2CHBrPh$	24.9	Methanol	$6.79 \pm 0.06 \times 10^{-2}$	2.31[b,h]	0.993
$ArCHBrSO_2CH_2Ph$[n]	24.9	Methanol	$6.79 \pm 0.06 \times 10^{-2}$	1.51[b,i]	0.990[f,j]
$ArCH_2SO_2CHClPh$	25.0	40% dioxane–H_2O	$2.65 \pm 0.01 \times 10^{-2}$	2.19[b,k]	0.995
$ArCHClSO_2CH_2Ph$	25.0	40% dioxane–H_2O	$2.65 \pm 0.01 \times 10^{-2}$	1.64[b,l]	0.993[f]
$ArCHClSO_2CHAr$	25.0	40% dioxane–H_2O	$2.65 \pm 0.01 \times 10^{-2}$	3.43[b,m]	0.990[f]
$ArCHClSO_2CH_2Ar$	38.9	Methanol	$2.40 \pm 0.03 \times 10^{-3}$	3.32[b,m]	0.993[f]

[a] Rate for Ar = Ph. [b] Spectrophotometric rates. [c] $3\text{-}NO_2$, 3-Br, 3-F, 4-Cl, $3\text{-}Br\text{-}4\text{-}OCH_3$, $3\text{-}CH_3$, and $4\text{-}CH_3$ substituents. [d] Titrimetric rates. [e] $3\text{-}NO_2$, 3-F, 4-Cl, $3\text{-}CH_3$, and $4\text{-}CH_3$ substituents. [f] σ normal values were used. [g] Omission of the 4-Cl point gave $\rho = 1.27$ with $r = 0.998$. [h] 3-F, 4-Cl, $3\text{-}CH_3$, and $4\text{-}CH_3$ substituents. [i] $4\text{-}NO_2$, $3\text{-}NO_2$, 3-Cl, 4-Cl, 4-F, $3\text{-}CH_3$, and $4\text{-}CH_3$ substituents. [j] Omission of 4-F point gave $\rho = 1.55$ with $r = 0.999$. [k] 3-F, 4-Cl, and $4\text{-}OCH_3$ substituents. [l] $4\text{-}NO_2$, $3\text{-}NO_2$, 3-F, and 4-Cl substituents were used. [m] $4\text{-}NO_2$, $3\text{-}NO_2$, 3-F, 3-Cl, $3\text{-}CH_3$, $4\text{-}CH_3$ and $4\text{-}OCH_3$ substituents. [n] Registry no., 19217-59-5.

ing additive 3-Br and 4-OCH$_3$ σ constants. The additive value is 0.28 when the σ^n constant is used for p-OCH$_3$ (-0.111),[14] 0.12 when the Hammett σ constant is used, and -0.39 when the σ^+ constant is used for p-OCH$_3$. A value of 0.05 is needed to fit the rate of the line.

α-Bromobenzyl methyl sulfone (5) underwent complete exchange at the α' position in 200 sec. Under these conditions the Ramberg-Bäcklund reaction was less than 15% complete, indicating that a preequilibrium is established.

Discussion

Solvent Effects. The effects of increasing the proportion of nonaqueous solvent on the rates of reaction of PhCHBrSO$_2$CH$_2$Ph with lyate ion brought out in Figure 1 are remarkably similar to the effects of similar solvent changes observed for the reaction of ClCH$_2$CH$_2$OH with lyate ion under similar conditions.[15] The similarity in behavior of the two systems with changing solvents suggests a similarity in mechanism, supporting the assignments of mechanism 1 in each system that have been made previously.[7,10] The increased rate observed on increasing the concentration of 1,2-dimethoxyethane or dioxane in the solvent is presumably due to a decrease in solvation of anion 2 by water and a consequent increase in nucleophilicity of this oxide ion or carbanion. The progressive decrease in rate with increasing methanol concentration conceivably could be due to a greater acidity of methanol than water,[16] but additional factors are no doubt also involved.

Influence of Phenyl and Aryl Substituents. Earlier work has shown that in MeONa-MeOD deuterium exchange at the α' position is essentially complete for PhCH$_2$SO$_2$CHBrPh (6, Ar = Ph) prior to loss of Br$^-$.[10] A preequilibrium involving the α' position is clearly established here and this must be true for PhCH$_2$SO$_2$CH$_2$Br (4), where bromide ion release is 50-fold slower at 25° than for 6 (Table I). Proton abstraction from the α' (methyl) position of PhCHBrSO$_2$CH$_3$ (5) is *ca.* 10^4 slower than from the α' (benzylic) positions of 4 or 6.[17] Nevertheless, the present study shows that deuterium exchange is essentially complete at the α' position, prior to loss of Br$^-$, in this instance also. The correspondence between titrimetric and spectrophotometric rates for 4 shows the halide loss, and not episulfone decomposition, is rate limiting. Comparable data have been obtained with 6.[10]

Information concerning the step in mechanism 1 wherein halogen is lost (k_2) can be gleaned from relative rates and substituent effects for isomers 4 and 5. According to mechanism 1, when k_2 is rate limiting, the rate ratio for halogen loss from 4 and 5 should be given by

$$k_2^{(4)}/k_2^{(5)} = K_{\mathrm{eq}}^{(5)}/K_{\mathrm{eq}}^{(4)} \times k_{\mathrm{obsd}}^{(4)}/k_{\mathrm{obsd}}^{(5)}$$

where $K^{(4)}{}_{\mathrm{eq}}$ and $K^{(5)}{}_{\mathrm{eq}}$ are the equilibrium constants for the first (equilibrium) step. The pK for PhCH$_2$SO$_2$CH$_3$ in dimethyl sulfoxide (DMSO) is *ca.* 4 units higher than for PhCH$_2$SO$_2$CH$_3$.[19] Assuming a similar difference for 5 and 4 gives a $K^{(5)}{}_{\mathrm{eq}}/K^{(4)}{}_{\mathrm{eq}}$ ratio of 10^4. Using the $k^{(4)}{}_{\mathrm{obsd}}/k^{(5)}{}_{\mathrm{obsd}}$ ratio of 650 reported in Table I (reactions in 40% dioxane at 25°) gives a $k_2^{(4)}/k_2^{(5)}$ value of 1/15. This indicates that intramolecular displacement of bromine by the carbanion in PhCHBrSO$_2$CH$_2^-$ is *ca.* 15 times as rapid as in Ph$\bar{\mathrm{C}}$HSO$_2$CH$_2$Br. The difference is probably due to a combination of a greater nucleophilicity of the carbanion in PhCHBrSO$_2$CH$_2^-$ and a greater susceptibility of the C-Br bond in this series to cleavage (phenyl activation; phenyl activation is well established for intermolecular nucleophilic displacements).

According to mechanism 1 the ρ values in Table I are a composite of K_{eq} for step 1 and ρ_{k_2} for step 2, *i.e.*

$$\rho_{\mathrm{obsd}} = \rho_{K_{\mathrm{eq}}} + \rho_{k_2}$$

Judging from the ρ value for the equilibrium constant of ArCH$_2$SO$_2$CH$_3$ in DMSO (ρ = 5.0[19]) $\rho_{K\mathrm{eq}}$ for ArCH$_2$SO$_2$CH$_2$Br in MeOH will be *ca.* 4. Using this value and ρ_{obsd} of 1.47 (Table I) gives $\rho_{k_2} \cong -2.5$ in 40% dioxane or methanol. In other words, electron-releasing groups strongly accelerate step 2 (*i.e.*, increase k_2). This is understandable for mechanism 1 on the basis of increased nucleophilicity of the carbanion, or for mechanism 2 on the basis of enhancement of the rate of ionization through an electrostatic effect. A similar analysis of ρ_{obsd} for ArCHBrSO$_2$CH$_3$ (1.29), ArCHBrSO$_2$CH$_2$Ph (1.51), and ArCHClSO$_2$CH$_2$Ph (1.64) systems favors interpretation by mechanism 1. In these systems the Ar group is separated from the acidic hydrogen atom by two additional atoms. Judging from the equilibrium ρ values in water of 1.00 for ArCO$_2$H, 0.562 for ArCH$_2$CO$_2$H, and 0.237 for ArCH$_2$CH$_2$CO$_2$H,[20a] and ρ = 0.253 for ArSO$_2$CH$_2$CO$_2$H,[20b] the ρ value for ArCH$_2$SO$_2$CH$_3$ (or 5) should be about one-fourth that observed for ArCH$_2$SO$_2$CH$_3$ or *ca.* 1.0. The ρ values for the other two systems (6) should be somewhat smaller. This analysis then makes ρ_{k_2} for the ArCHBrSO$_2$CH$_3$, ArCHBrSO$_2$CH$_2$Ph, and ArCHClSO$_2$CH$_2$Ph systems small and positive. A positive ρ value for k_2 is of course inconsistent with mechanism 2, since one would expect a negative ρ for the step

$$\mathrm{ArCHBrSO_2CH_2}^- \longrightarrow \mathrm{Br}^- + \mathrm{Ar}\overset{+}{\mathrm{C}}\mathrm{HSO_2CH_2}^-$$

On the other hand, a small positive ρ for an intramolecular nucleophilic displacement of a benzylic halide seems reasonable, since intermolecular nucleophilic displacements with benzylic halides often have small positive ρ values.[21]

The smaller negative ρ (*ca.* -1.7) calculated (as above) for ArCH$_2$SO$_2$CHBrPh, as compared to ArCH$_2$SO$_2$CH$_2$Br, is consistent with the reaction becoming less sensitive to the nucleophilicity of the carbanion as cleavage of the C-Br bond becomes more facile (owing to phenyl activation).

It is amusing to compare the results with the ArCH$_2$SO$_2$CH$_2$Br system with those of the ArCH$_2$COCH$_2$Cl system, where ρ for loss of chloride ion is *ca.* -5.[22] The large negative ρ for the chloro ketone system has been interpreted as indicating ionization to form a dipolar ion.[22] The formation of dipolar ion intermediates in such Favorskii rearrangements is supported by the marked rate acceleration of halide loss observed with methyl substitution (ArCH$_2$COCHClCH$_3$) system,[6a] the formation in some systems of unusual cyclization products,[6b] and the changes in stereochemistry observed with changing conditions.[6c,23] As will be brought out below, the effect of methyl substitution in the ArCH$_2$SO$_2$CH$_2$Br system argues *against* the dipolar intermediate; the observation of a high degree of stereoselectivity in the Ramberg-Bäcklund reaction provides additional evidence against the dipolar mechanism.[24]

Effect of Methyl Substitution. The effect of methyl substitution at the α or the α' positions of ArCH$_2$SO$_2$CH$_2$X (4) and ArCHXSO$_2$CH$_3$ (5) systems are summarized in Table II.

Examination of Table II shows that substitution of one or two methyl groups α to the halogen atom in 4 has surprisingly little effect on the rate of activation parameters. (Note the comparisons for the first five items in Table II.)

Table II
Effects of Methyl Substitution on the Rates of Reaction of $PhCH_2SO_2CH_2X$ (4) and $PhCHXSO_2CH_3$ (5) in 40% (v/v) Dioxane–Water

Registry no.	Halo sulfone	Temp, °C	k, M^{-1} sec^{-1}	k_{rel}	E_a, kcal/mol	ΔS^* (25°), eu
5335-44-4	$PhCH_2SO_2CH_2Cl$	35.0	$1.58 \pm 0.05 \times 10^{-3}$	(1.00)		
		49.57	$1.04 \pm 0.04 \times 10^{-2}$			
		25.0	3.90×10^{-4} (calcd)		25.6	+9.6
51392-35-9	$PhCH_2SO_2CHClMe$	35.0	$1.74 \pm 0.02 \times 10^{-3}$	1.10		
		49.95	$1.17 \pm 0.02 \times 10^{-2}$			
		25.0	4.37×10^{-2} (calcd)		25.2	+8.7
51392-36-0	$PhCH_2SO_2CClMe_2$	35.0	$1.80 \pm 0.04 \times 10^{-3}$	1.14		
		49.65	$1.15 \pm 0.05 \times 10^{-2}$			
		25.0	4.54×10^{-4} (calcd)		25.1	+8.5
19217-58-4	$PhCH_2SO_2CH_2Br$	25.04	$8.08 \pm 0.04 \times 10^{-2}$	(1.00)		
		49.60	1.18 ± 0.05		20.9	+4.5
51392-37-1	$PhCH_2SO_2CHBrMe$	25.07	$1.08 \pm 0.003 \times 10^{-1}$	1.34		
		49.60	1.63 ± 0.07		21.2	+6.0
23211-69-0	$PhCHBrSO_2CH_3$	34.97	$4.39 \pm 0.14 \times 10^{-4}$			
		49.96	$2.54 \pm 0.05 \times 10^{-3}$			
		25.00	1.24×10^{-4} (calcd)	(1.00)	23.2	−0.7
35501-00-9	$PhCHBrSO_2CH_2Me$	34.96	$1.18 \pm 0.07 \times 10^{-3}$			
		49.91	$6.93 \pm 0.07 \times 10^{-3}$			
		25.00	3.29×10^{-4} (calcd)	2.65	23.4	+2.1
35500-99-3	$PhCHBrSO_2CHMe_2$	38.69	$1.15 \pm 0.04 \times 10^{-3}$			
		50.00	$4.04 \pm 0.23 \times 10^{-3}$			
		25.00	2.21×10^{-4} (calcd)	1.78	22.3	−2.6
38009-86-8	$PhCHClSO_2CH_3$	50.0	(1.4×10^{-5})[a]	(1.00)		
51392-16-6	$PhCHClSO_2CHMe_2$	50.0	4.60×10^{-5}	3.3		
	$PhCH_2SO_2CHBrMe$	49.60	1.63 ± 0.07			
	$PhCH_2SO_2CHBrMe$	25.07	$1.08 \pm 0.03 \times 10^{-1}$	21.8	21.2	+6.0
51392-38-2	$PhCHMeSO_2CHBrMe$	25.04	$4.95 \pm 0.07 \times 10^{-3}$	(1.00)		

[a] F. G. Bordwell and G. D. Cooper, *J. Amer. Chem. Soc.*, **73**, 5187 (1951).

This is in sharp contrast to the $PhCH_2COCH_2X$ system, where α-methyl substitution brings about a minimum rate acceleration of 220-fold. (The actual rate enhancement could be much greater.)[6a] The results with 4 also differ from those observed in base-promoted epoxide formation from 2-chloroalkanols, where methyl substitution in the series $HOCH_2CH_2Cl$, $HOCH_2CH(Me)Cl$, $HOCH_2C(Me)_2Cl$ leads to relative rates of (1.0):5.5:250.[25] These rate accelerations find a logical explanation in that α-methyl groups are known to strongly stabilize carbonium ions.[6a,7,26] Evidently the amount of ionic character for the C–X bond developed in the transition state for the reactions of $PhCH_2SO_2CH(Me)Br$ and $PhCH_2SO_2C(Me)_2Br$ are far less than in epoxide formation from $^-OCH_2C(Me)_2Cl$ or in the Favorskii rearrangement of $Ph\bar{C}HCOCH(Me)Cl$. In other words, for reactions of 4 and its α-methyl derivatives there is no evidence for either a dipolar ion transition state or a dipolar ion intermediate.

Examination of Table II shows that methyl substitution at the α′ position in $ArCHBrSO_2CH_3$ (5) (items 6-10) also has very little effect on the rate. This again contrasts with epoxide formation, where the relative rates in the series $HOCH_2CH_2Cl$, $HOCH(Me)CH_2Cl$, $HOC(Me)_2CH_2Cl$ are (1.0):21:250.[25] Accelerations by β-methyl groups in such instances have been explained by assuming the development of positive charge at the β-carbon atom in the transition state,[7] and by an entropy effect wherein methyl substitution lowers the ground-state entropy, making entropy loss less for more crowded systems in going from ground state to transition state.[28] Only the latter effect would be expected to apply in the present instance. Evidently, it is counteracted by some other factor or factors. One such could be decreased equilibrium concentrations of carbanions with successive methyl substitution.[19] This effect will be at least partially counteracted by increased carbanion nucleophilicity.

The large k^{Br}/k^{Cl} leaving group effects in the Ramberg–Bäcklund reaction found earlier in methanol have been substantiated and augmented in the present study (Table III). It should be noted that the k^{Br}/k^{Cl} rate ratios decrease rather markedly with increasing temperature because the activation energies for chloro sulfones are *ca.* 4 kcal/mol higher than those of bromo sulfones (Table II).

Table III
Relative Rate Ratio for α-Bromo and α-Chloro Sulfones in the Ramberg–Bäcklund Reaction in 40% Dioxane–Water at 25°

α-Halo sulfone	k^{Br}/k^{Cl}
$PhCH_2SO_2CH_2X$	207[a]
$PhCH_2SO_2CH(Me)X$	247
$PhCH_2SO_2CH(Ph)X$	169[b]
$CH_3SO_2CH(Ph)X$	181[c]
$Me_2CHSO_2CH(Ph)X$	88[c]

[a] At 50° the ratio is 133; in MeOH at 50° it is 128. [b] At 25° in MeOH the ratio is 280. [c] At 50°.

Experimental Section

Substituted α-Chlorobenzyl Benzyl Sulfones. The corresponding meta- or para-substituted benzyl sulfides were chlorinated and the resulting chloro sulfides were oxidized *in situ*, as in the following procedure.[11] A solution of 8.47 g (0.0628 mol) of sulfuryl chloride in 60 ml of dry CCl_4 was added dropwise over 100 min to a stirred solution (under nitrogen) of 15.1 g (0.0621 mol) of bis(4-methylbenzyl) sulfide dissolved in 80 ml of dry CCl_4 kept at reflux. After an additional 1 hr of reflux the solution was cooled to 0° and treated with a solution of 28.6 g (0.166 mol) of 80% *m*-chloroperoxybenzoic acid in 250 ml of dry CH_2Cl_2. After allowing it to warm to room temperature over a 4-hr period the reaction mixture was diluted with 100 ml of $CHCl_3$ and washed successively with aqueous $NaHSO_3$, saturated $NaHCO_3$, and water. After drying ($MgSO_4$) the solvent was evaporated and the chloro sulfone was crystallized from 95% ethanol, mp 160.8–161.7°. The yields in these preparations averaged 70%. Nmr: 7.3–7.7 (m, 8 H), 5.49 (s, 1 H), AB quartet, $\nu_A = 4.73$, $\nu_B = 4.34$ ($J_{AB} = 14.7$ Hz, 2 H), 2.43 (s, 3 H), 3.40 ppm (s, H).

The other chloro sulfones had similar nmr spectra. Analytical data are summarized in Table IV.

Table IV
Melting Points and Analytical Data[a] for α-Chlorobenzyl Benzyl Sulfones, $ArCHClSO_2CH_2Ar$

Registry no.	Substituent	Mp, °C[b]	Molecular formula	Calcd, %		Found, %	
				C	H	C	H
51392-39-3	4-Methyl	160.8–161.7	$C_{16}H_{17}ClO_2S$	62.23	5.55	62.31	5.35
51392-40-6	3-Methyl	75.2–77	$C_{16}H_{17}ClO_2S$	62.23	5.55	62.23	5.60
51392-41-7	4-Nitro	190–191	$C_{14}H_{11}ClN_2O_6S$	45.34	2.99	45.22	3.09
51392-42-8	3-Nitro	160.5–162.8	$C_{14}H_{11}ClN_2O_6S$	45.34	2.99	45.61	3.05
51392-43-9	3-Fluoro	95–96.5	$C_{14}H_{11}ClF_2O_2S$	53.09	3.50	53.15	3.47
51392-44-0	4-Methoxy[c]	145.5–146.5	$C_{16}H_{17}ClO_4S$	56.39	5.03	56.16	5.06

[a] Micro-Tech, Skokie, Ill. [b] Uncorrected. [c] Prepared using *N*-chlorosuccinimide.

Table V
Melting Points and Analytical Data[a] for α-Bromobenzyl Methyl Sulfones, $ArCHBrSO_2CH_3$

Registry no.	Substituent	Mp, °C[b]	Molecular formula	Calcd, %		Found, %	
				C	H	C	H
51392-45-1	4-Methyl	104–105	$C_9H_{11}BrO_2S$	41.08	4.21	40.91	4.18
51464-53-0	3-Methyl	64.4–67	$C_9H_{11}BrO_2S$	41.08	4.21	41.02	4.15
51392-46-2	4-Nitro[c]	160–160.7	$C_8H_8BrNO_4S$	32.67	2.74	32.99	2.90
51392-47-3	3-Nitro	159–160	$C_8H_8BrNO_4S$	32.67	2.74	32.9;	2.92
51392-48-4	3-Fluoro	63–64	$C_8H_8BrFO_2S$	35.97	3.02	35.79	3.09
51392-49-5	4-Chloro	119–119.9	$C_8H_8BrClO_2S$	33.88	2.84	34.09	2.90

[a] Micro-Tech, Skokie, Ill. [b] Uncorrected. [c] Bromine was used as the brominating agent.

α-Bromobenzyl Methyl Sulfones. These bromo sulfones (Table V) were prepared from the corresponding sulfides by a method similar to that described above using *N*-bromosuccinimide as the brominating agent. Chromatography over silica gel was required to obtain pure samples of all but the 3-nitro derivative.[11]

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Registry No.—Bis(4-methylbenzyl) sulfide, 13250-88-9; bis(3-methylbenzyl) sulfide, 25033-32-3; bis(4-nitrobenzyl) sulfide, 1835-71-8; bis(3-nitrobenzyl) sulfide, 51392-50-8; bis(3-fluorobenzyl) sulfide, 51392-51-9; bis(4-methoxybenzyl) sulfide, 34106-64-4; methyl 4-methylbenzyl sulfide, 5925-57-5; methyl 3-methylbenzyl sulfide, 51392-52-0; methyl 4-nitrobenzyl sulfide, 51392-53-1; methyl 3-nitrobenzyl sulfide, 51392-54-2; 3-fluorobenzyl methyl sulfide, 50396-78-6; 4-chlorobenzyl methyl sulfide, 5925-82-6.

References and Notes

(1) Abstracted in part from the Ph.D. Dissertation of M. D. Wolfinger, Northwestern University, June 1968.

(2) Concerted 1,3-eliminations are also possible but, for reasons given elsewhere,[3] we believe these to be rare if they exist at all.

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(17) In the parent sulfone, $PhCH_2SO_2CH_3$, the rate of deuterium exchange in MeOD catalyzed by MeONa is *ca.* 2 × 10^4 greater at 25° in the benzylic than in the methyl position.[18]

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(21) For S_N2 reactions of $ArCH_2Cl$ with iodide ion in acetone $\rho = 0.81$; with trimethylamine in benzene $\rho = 0.37$; with hydroxide ion in water $\rho = -0.33$.[20a] Benzyl fluorides with lyate ion in 95% ethanol have $\rho = 0.45$.[20a]

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