Stereochemistry and Mechanism of the Ramberg–Bäcklund Reaction. Reaction of Diastereomeric α-Halo Sulfones with Base[1]

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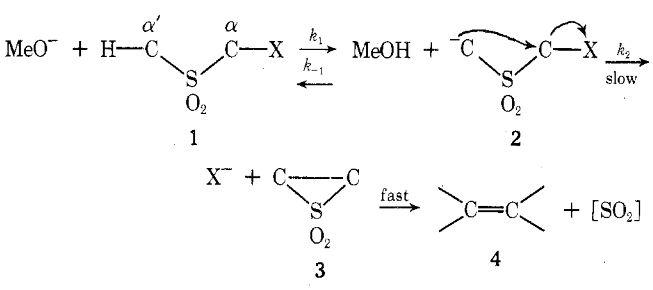
Bromination with *N*-bromosuccinimide of either *meso*- or *dl*-$PhCH(Me)SO_2CH(Me)Ph$ gave a nearly equimolar quantity of diastereomers, $PhCH(Me)SO_2CBr(Me)Ph$. Treatment of the higher melting erythro isomer (**5a**) with NaOMe in MeOH gave *cis*- and *trans*-α,α′-dimethylstilbene in a 93:7 ratio, whereas the threo isomer (**5b**) gave over 95% of *trans*-α,α′-dimethylstilbene. In reactions with **5a** and **5b** run to 10% or less conversion in MeOH the ratio of exchange to epimerization was *ca.* 50–100:1.0. The kinetics with **5a** were second order, but with **5b** they were independent of methoxide ion concentration when the base concentration was above 0.05 *M*. The latter behavior indicated that thermal decomposition of *trans*-2,3-dimethyl-2,3-diphenylthiirane 1,1-dioxide was rate limiting, and this was supported by independent spectroscopic evidence. Reaction of the diastereomers of $PhCH(Me)SO_2CH(Br)CH_3$ with NaOMe–MeOH was also stereoselective, one isomer (presumably threo) giving *cis*- and *trans*-2-phenyl-2-butene in a ratio of *ca.* 70:30 and the other isomer (presumably erythro) giving the opposite ratio. Recovery and nmr analysis of starting materials from incomplete reactions showed that extensive epimerization was accompanying these reactions. Reaction of $PhCBr(Me)SO_2CH_2CH_3$ gave *cis*- and *trans*-2-phenyl-2-butene in a ratio of *ca.* 53:47, which differs appreciably from the equilibrium ratio for these alkenes (83:17). It is suggested that the stereochemistry in such instances is dictated to an appreciable extent by the formation of one of two possible diastereomeric carbanions in a higher equilibrium concentration.

Earlier studies of the Ramberg–Bäcklund reaction in a variety of systems support the stepwise mechanism shown in Scheme I.

Scheme I

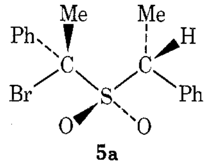


Establishment of an equilibrium between **1** and **2** has been demonstrated for α-halo sulfones of widely differing structures by deuterium exchange studies.[2] Step 2 (thiirane 1,1-dioxide formation), rather than step 3 (alkene formation), has been shown to be rate limiting in these systems by comparisons of titrimetric and spectrophotometric rates,[2] and by studies with thiirane 1,1-dioxides, which show that their rate of decomposition is usually such as to preclude their isolation under the reaction conditions.[3] It is not surprising, then, that prior to the present work[1] there has been no direct evidence for the formation of a thiirane 1,1-dioxide intermediate in these systems. Good indirect evidence was provided, however, from studies of the dehydrobromination of $PhCHBrSO_2CHBrPh$. Here the presence of 2,3-diphenylthiirene 1,1-dioxide as a transient intermediate was detected spectrophotometrically.[4] This intermediate must arise from dehydrobromination of 2-bromo-2,3-diphenylthiirane 1,1-dioxide, and, indeed, the thermal decomposition products, *cis*- and *trans*-2-bromostilbene, from this thiirane 1,1-dioxide are observed as by-products,[4] or, under other conditions, as principal products.[5]

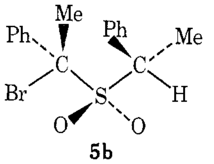
The dehydrobromination and debromination of *dl*- and *meso*-$PhCHBrSO_2CHBrPh$ have been shown to occur stereoselectively with inversion of configuration at each chiral center.[5] The stereoselective dehydrobromination of *erythro*- and *threo*-$PhCBr(Me)SO_2CH(Me)Ph$ (**5a** and **5b**, respectively), which also occurs by a double inversion mechanism, is the principal subject of the present paper.[1] Another aspect of the stereochemistry that has been examined is the preferential formation of cis alkenes from the reaction of α-halo sulfones of the type $RCHXSO_2CHR$.

Results

Treatment of either *meso*- or *dl*-bis-α-methylbenzyl sulfone with *N*-bromosuccinimide in the presence of benzoyl peroxide in refluxing carbon tetrachloride yielded a nearly equimolar mixture of diastereomeric α-bromo-α-methylbenzyl α-methylbenzyl sulfones (**5**). The diastereomers were separated by column chromatography on acidic alumina into monobromides melting at 76 and 112°. Single-crystal X-ray analysis of the 112° isomer identified it as the *dl*-erythro bromo sulfone (**5a**).[6] This requires the 76° isomer to have the *dl*-threo configuration (**5b**). The gross structures of **5a** and **5b** are supported by their ir and nmr spectra and by elemental analysis.



5a



5b

Reaction of **5a** or **5b** with sodium methoxide in methanol yielded α,α′-dimethylstilbenes (**8**) quantitatively and stereoselectively. Thus the *dl*-erythro bromide **5a** gave *cis*- and *trans*-α,α′-dimethylstilbene (**8a** and **8b**) in a 93:7 ratio at 25°, and the *dl*-threo isomer **5b** gave the *trans*-stilbene (**8b**) in excess of 95%. Several experiments were performed in methanol-*O-d* at 0° from which the starting material was recovered after partial conversion to alkenes. The recovered mixture from a reaction of **5a** with excess methoxide ion after 62% conversion contained **8a** and **8b** in a *ca.* 9:1 ratio and 38% of the deuterium-exchanged bromo sulfone (**5a**-d_1). When a similar reaction of **5a** was quenched after 10% conversion, exchange was incomplete, however, and the following composition was indicated by nmr analysis of the mixture: *ca.* 10% α,α′-dimethylstilbene (**8a** and **8b**), *ca.* 40% **5a**, and *ca.* 50% **5a**-d_1. These data indicate that the ratio of exchange to epimerization for **5a** is about 50:1 at 0°.[7] A reaction of **5b** which was in-

Table I
Rate Data for the Reaction of *erythro*-PhCBr(Me)SO$_2$CH(Me)Ph (5a) with Sodium Methoxide in Methanol[a,b]

Temp, °C	[MeO$^-$]	$10^2 k$, M^{-1} sec^{-1}
25.0	0.0173	2.0
25.0	0.0518	2.0
25.2	0.0590	2.1[c]
25.2	0.0787	2.2[c]
25.0	0.0944	1.8
25.0	0.0944	1.5[d]
25.0	0.0994	1.3[e]
34.9	0.0118	5.9
34.6	0.0236	6.3
44.8	0.0118	18
44.8	0.0236	19
44.7	0.1180	14
44.7	0.2361	9.2

[a] Unless otherwise indicated the second-order rate constants were determined spectrophotometrically under pseudo-first-order conditions. Runs were usually in triplicate and were reproducible to ±5%. [b] From a plot (r = 0.998) of log k *vs.* $1/T$ at three temperatures, E_a = 21.2 kcal mol^{-1} and ΔS^* = 3 eu (at 25°). [c] Titrimetric rate [d] 0.026 M LiClO added. [e] 0.198 M LiClO$_4$ added.

Table II
Kinetic Data for the Reaction of *threo*-PhCBr(Me)SO$_2$CH(Me)Ph (5b) with Sodium Methoxide in Methanol[a,b]

Temp, °C	[MeO$^-$]	$10^4 k$, sec^{-1}
25.0	0.0518	7.4
25.0	0.0944	7.2
25.0	0.0944	7.2[c]
25.0	0.0944	7.2[d]
34.7	0.1180	23
34.7	0.2361	22
44.7	0.1180	73
44.7	0.2361	73

[a] Spectrophotometric rates run at least in triplicate (reproducible to within ±5%). [b] From a plot of log k *vs.* $1/T$ (r = 0.9995), E_a = 22.0 kcal mol^{-1} and ΔS = 1.0 eu. [c] 0.026 M LiClO$_4$ added. [d] 0.198 M LiClO$_4$ added.

Table III
Rate Data for the Reaction of PhCH$_2$SO$_2$CHBrPh (5) and Its Derivatives with Sodium Methoxide in Methanol at 25°

α-Bromo sulfone	$10^2 k$,[a] M^{-1} sec^{-1}	k (relative)
PhCH$_2$SO$_2$CHBrPh (1)	7.5[b]	1.0
PhCH$_2$SO$_2$C(Me)BrPh	11.5	1.5
PhCH(Me)SO$_2$CHBrPh	1.5	0.20
PhCH(Me)SO$_2$C(Me)BrPh (5a)	2.0	0.27
PhCH(Me)SO$_2$CHBrCH$_3$ (9)	0.025	0.0033

[a] Spectrophotometric rates determined under pseudo-first-order conditions. [b] Reference 2a.

terrupted after only *ca.* 6% conversion to stilbenes led to the recovery of *ca.* 67% **5b** and 27% sulfone **5b**-d_1 and an exchange to epimerization ratio of *ca.* 90:1. A reaction of **5b** with excess methoxide ion in MeOD which was interrupted after *ca.* 10% conversion to α,α′-dimethystilbenes led to the recovery of *ca.* 30% unreacted **5b** and *ca.* 60% **5b**-d_1 with an exchange to epimerization ratio of *ca.* 120:1. When the reaction with **5b** was allowed to go to 45% conversion the recovered bromo sulfone had undergone complete exchange. The results show that protonation of the carbanions derived from **5a** or **5b** with methanol occurs about five times as rapidly as does the intramolecular displacement to form the thiirane 1,1-dioxide under these conditions.

The kinetics of the reaction of **5a** with methoxide ion in methanol were found to be first order in methoxide ion over a wide range of concentrations and overall second order (Table I). The second-order rate constants showed a slight decrease with increasing base concentration or upon addition of lithium perchlorate (small negative salt effect). The rate of bromide ion release (titrimetric rate) was found to be equal to the rate of stilbene formation (spectrophotometric rate) within experimental error.

The kinetic behavior of *dl-threo*-PhCH(Me)SO$_2$CBr(Me)Ph (**5b**) with NaOMe–MeOH was dramatically different from that of the *dl*-erythro isomer **5a.** At base concentrations below *ca.* 0.05 M the pseudo-first-order spectrophotometric rate constants increased with increasing base concentration, but at higher concentrations the rate of α,α′-dimethylstilbene formation became *independent* of base concentration (Table II). On the other hand, the titrimetric rate constants (for bromide ion release) were found to be first order in methoxide ion (k = 2.6 × 10^{-2} M^{-1} sec^{-1} at 25° with methoxide ion concentrations of either 0.0295 or 0.0590 M). With excess base of 0.1 M concentration the rate of pseudo-first-order bromide ion release was *ca.* 3.5 times as fast as the rate of α,α′-dimethylstilbene formation.

The kinetic results with **5b** indicate that in this instance decomposition of the intermediate thiirane 1,1-dioxide is the rate-limiting step. This would require a buildup of the intermediate and, indeed, evidence for such a buildup was obtained by an examination of the absorbancy *vs.* time curve. With methoxide concentrations in the range 0.05–0.118 M the absorbance in the 240–250-nm region due to **5b** was observed to decrease with time. This decrease was followed by an increase in absorbance as *trans*-α,α′-dimethylstilbene (**8b**) began to appear.[8] Excellent first-order plots were obtained from the latter portion of the absorbance *vs.* time curve. An absorbance *vs.* time curve was calculated from the experimentally determined spectrophotometric rate constant (first-order rate constant for thiirane 1,1-dioxide decomposition) and the titrimetric rate constant (second-order rate constant for bromide release) using the following initial conditions: the concentration of **5b** being 1.0 × 10^{-4} M and the methoxide ion concentration being 5.18 × 10^{-2} M at 25°. The plot of concentration *vs.* time for these consecutive reactions showed a maximum buildup of thiirane 1,1-dioxide (**7b**) equaling approximately 50% of the initial concentration of **5b.** Using experimentally determined values for molar absorptivities of **5b** and **8b**, an absorbance *vs.* time curve was also calculated. (The absorbance of **7b** was assumed to be negligible.) This curve was in excellent agreement with the experimental curve for a reaction of **5b** under comparable conditions.

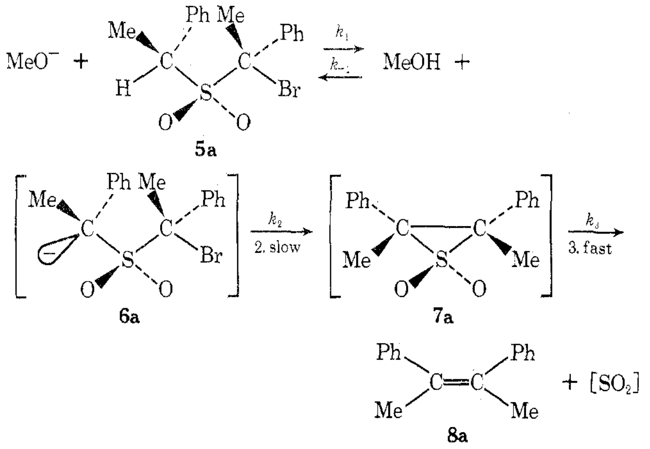
Stereoselectivity was also observed for the Ramberg–Bäcklund reactions of diastereomeric α-methylbenzyl α-bromoethyl sulfones, PhCH(Me)SO$_2$CH(Br)CH$_3$ (**9**), with sodium methoxide in methanol. One diastereomer gave a mixture of 2-phenyl-*cis*- and *trans*-2-butene in a 30:70 ratio, whereas with the other diastereomer the ratio was 77:23. Nmr analysis of incomplete reactions of the diastereomer giving mainly cis alkene indicated that epimerization was occurring during the reaction, which is not surprising in view of the presence of two epimerizable reaction sites and a rate of reaction *ca.* 100 times slower than for system **5** (Table III). When *ca.* 17% of unreacted material remained it had been epimerized to the extent of 15%, 85% of the original diastereomer remaining. A comparable experiment with the other isomer showed 31% epimerization.

Reaction of $PhCBr(Me)SO_2CH_2CH_3$ (**10**), a structural isomer of **9**, with 0.62 *M* sodium methoxide in methanol at reflux for 24 hr gave a 57:43 ratio of 2-phenyl-*cis*- and *trans*-2-butene. (Equilibration studies in acetic acid have shown the cis isomer to be favored at equilibrium by a 83:17 ratio.[9]) Recovery of **10** (70%) from a comparable reaction at room temperature showed complete exchange of the α'-hydrogen atoms by deuterium.

The rate studies described above allow an evaluation of the effect of methyl substitution on the rate of thiirane 1,1-dioxide formation (Table III).

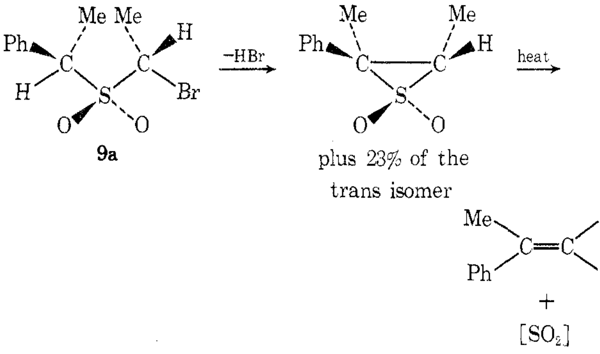
Discussion

Mechanism for the Reaction with 5a, 9a, and 9b. The results indicate that the mechanism for the reaction of the erythro bromo sulfone **5a** is essentially that outlined in Scheme I, except that deuterium exchange experiments show that equilibrium involving the carbanion **6a** is not complete. Evidently the intramolecular nucleophilic displacement (governed by k_2) competes favorably with solvent exchange with the initially formed "singly" solvated carbanion, which is presumably the rate-limiting step for the exchange reaction.[10]



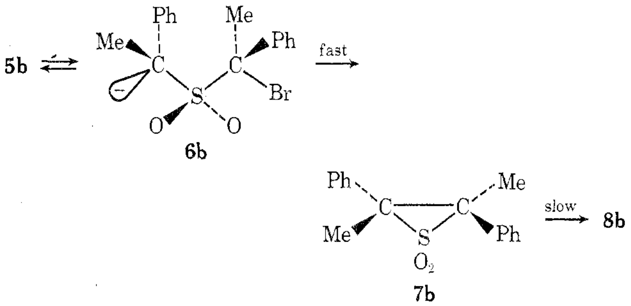
The deuterium exchange experiments show that the rate of the exchange reaction is *ca.* 5 times k_2. Exchange occurs with retention of configuration. [The exchange to epimerization rate ratios in MeOH at 0° of *ca.* 50–100:(1.0) for **5a** and **5b** are of the same order of magnitude as was found previously for $PhCH(Me)SO_2CH(Me)Ph$ (*ca.* 200:1) under comparable conditions.[11]] Reaction of **5a** with methoxide ion involves stereoselective removal of the proton from a conformation wherein it is cis to and flanked by the two sulfonyl oxygen atoms.[11,12] In step 2 inversion occurs at the carbanion carbon and also at the carbon atom holding the bromine atom[1,5] to give *cis*-2,3-dimethyl-2,3-diphenylthiirane 1,1-dioxide (**7a**). The latter cannot epimerize by deprotonation–protonation, as does *cis*-2,3-diphenylthiirane 1,1-dioxide,[2a] because it lacks the necessary α-hydrogen atoms. Stereoselective decomposition of **7a** then occurs to give *cis*-α,α'-dimethylstilbene (**8a**). The experimental results do not exclude double-retention stereochemistry, but we believe this pathway to be unlikely for reasons given earlier.[5] The present results provide further evidence against a dipolar ion mechanism,[2b,13] since one would hardly expect a dipolar ion of the type $^-PhC(Me)SO_2C(Me)Ph^+$ (derived from **5a** or **5b**) to maintain chirality at both the carbanion and carbonium ion centers.

The mechanism for the reactions of the diastereomers of $PhCH(Me)SO_2CH(Br)CH_3$ (**9**) is no doubt similar to that for **5a**. The rate of alkene formation from **9** is about 100 times slower than from **5a**. Since the carbon atoms from which the carbanions are derived are structurally similar for **5a** and **9**, the slower rate must be due primarily to a slower displacement step in **9**.[14] More extensive epimerization of **9a** or **9b** would be expected for this reason, and also because of the presence of a proton on the carbon atom holding the bromine atom.[15] Assuming that double-inversion stereochemistry is being followed, as seems likely, the diastereomer giving mainly 2-phenyl-*cis*-2-butene must be the threo isomer (**9a**), and that giving mainly 2-phenyl-*trans*-2-butene must be the erythro isomer (**9b**).



Effect of Methyl Substitution. Examination of Table III shows that substitution of a methyl group at the α position of **1** causes a 1.5-fold rate acceleration, whereas methyl substitution at the α' position causes a fivefold rate retardation. The effect of α,α'-dimethyl substitution is intermediate. These small methyl effects are comparable to those observed in related systems.[2c] Since a large rate acceleration would be expected for reaction by a dipolar mechanism,[2c] the present results provide additional evidence against this mechanism.

Mechanism for the Reaction with 5b. The nonidentity of the titrimetric and spectrophotometric rates for **5b**, the lack of dependence of the rate of alkene formation on methoxide ion concentration,[17] and the spectrophotometric evidence for a buildup of a thiirane 1,1-dioxide intermediate are all consistent with a change in mechanism from that shown in Scheme I to one where thermal decomposition of *trans*-2,3-diphenyl-2,3-dimethylthiirane 1,1-dioxide (**7b**) has become rate limiting.



This change in mechanism must be caused by a considerably slower rate of decomposition for **7b** than for the corresponding cis isomer **7a**. This conclusion is supported both by the small differences in the rate of formation of **7a** from **5a**, as compared to the rates for comparable substrates wherein thiirane 1,1-dioxide formation is rate limiting (Table III), and by the fact that the rate of first-order decomposition for **7b** in MeOH at 25° is *ca.* 33 times slower than that reported for *trans*-2,3-diphenylthiirane 1,1-dioxide under comparable conditions.[3]

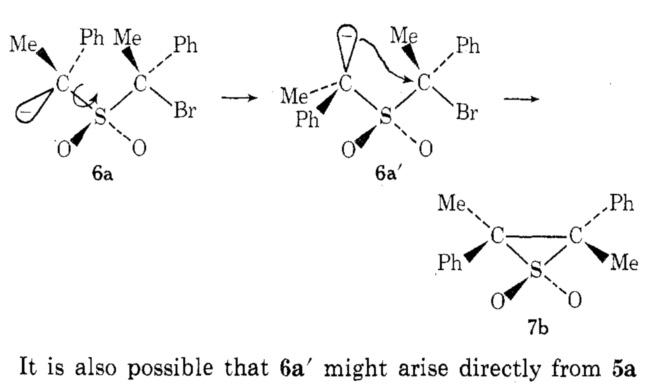
It is noteworthy that the rates of thermal decomposition of thiirane 1,1-dioxides follow the order *trans*-2,3-diphenyl[3] and *cis*-2,3-dimethyl-2,3-diphenyl > *trans*-2,3-dimethyl-2,3-diphenyl > *cis*-2,3-diphenyl[3] > *cis*-2,3-dimethyl,[13] and that the overall difference in rates does not appear to be greater than about two orders of magnitude. The faster rate of decomposition of *trans*-2,3-diphenylthiirane 1,1-dioxide than either its cis isomer or *trans*-2,3-dimethyl-2,3-diphenylthiirane 1,1-dioxide indicates that the stability of the incipient product alkene, rather than steric repulsions in the thiirane 1,1-dioxides, is the more important rate-controlling factor. On the other hand, the opposite conclusion is reached by comparing the rates for **7a** and **7b**. Evidently neither of these factors is very large or is particularly dominant.

Relative Rates of Protonation, Epimerization, and Bromide Ion Expulsion of α-Sulfonyl Carbanions. The rate of deuteration (k_{-1} [MeOD]) of carbanion **6a** and the rate of intramolecular displacement (k_2) of bromide ion by the carbanion are competitive. The experimental data indicate that the rate of formation of deuterated sulfone **5a**-d_1 is *ca.* 5 times as fast as the rate of formation of *cis*-α,α′-dimethylstilbene (**8a**). Assuming a steady-state concentration of **6a** and the mechanistic scheme shown

$$k_{\mathrm{obsd}} = \frac{k_1k_2}{k_{-1}[\mathrm{MeOD}] + k_2} = \frac{k_1k_2}{5k_2 + k_2} = \frac{k_1}{6}$$

From this relationship we find that $k_1 = 6k_{\mathrm{obsd}} \cong 1.2 \times 10^{-1}\ M^{-1}\ \mathrm{sec}^{-1}$ at 25° for PhCH(Me)SO$_2$CBr(Me)Ph (**5a**). This is *ca.* 100 times the rate of exchange observed for PhCD(Me)SO$_2$CD(Me)Ph catalyzed by NaOMe in MeOH.[18] Acceleration of the rate of exchange by the γ-bromine atom is, therefore, remarkably large. A similar effect has been observed and commented on elsewhere.[10]

Formation of *ca.* 7% of *trans*-α,α′-dimethylstilbene (**8b**) from **5a** is presumably caused by epimerization of **5a** to some **5b** prior to reaction, rather than by a nonstereoselective decomposition of *cis*-2,3-dimethyl-2,3-diphenylthiirane 1,1-dioxide (**7a**). This view is supported by the similarity of the $k_{\mathrm{ex}}/k_{\mathrm{ep}}$ ratio calculated on the basis of this assumption with that found under comparable conditions with PhCH(Me)SO$_2$CH(Me)Ph isomers.[19] Alternatively, **8b** might arise from carbanion **6a′**, a rotamer of **6a**. One can imagine that *ca.* 7% of the **6a** carbanions overcome the rotational barrier to give **6a′** (the inverted form of carbanion **6b**). Ring closure will then give thiirane 1,1-dioxide **7b**, which decomposes to **8b**.



It is also possible that **6a′** might arise directly from **5a** by deprotonation of a conformation in which the H–C bond is anti to the oxygen atoms of the sulfone group.[10,12]

Stereochemistry of the Reaction of RCHXSO$_2$CH$_2$R Type Sulfones. In base-initiated 1,3-elimination reaction with RCHXSO$_2$CH$_2$R, where R is an alkyl group, cis alkenes are formed in considerably greater concentrations than expected from thermodynamic control. Thus, the per cent of *cis*-RCH=CHR is 78% for R = Me, 56% for R = Et, and 52% for R = Pr.[13] At least four explanations have been offered to account for these unusual results: (1) attraction between the methyl groups in the transition state in the nucleophilic displacement step,[13] (a) lesser steric inhibition of solvation in this step,[20] (3) a higher concentration of the carbanion precursor of the cis thiirane 1,1-dioxide caused by a difference in rotational barriers,[21] and (4) preferential formation of a higher equilibrium concentration of the diastereomeric carbanion precursor of the cis thiirane 1,1-dioxide.[22]

Recently it was shown that kinetic control of the stereochemistry is operative even when R = Ph, since as much as 32% of *cis*-stilbene is formed from PhCHBrSO$_2$CH$_2$Ph when the base used to initiate the 1,3-elimination is dimethylformamide (DMF).[5] Kinetic control must also be operative in the stereoselective debrominations and dehydrobrominations of *dl*- and *meso*-PhCHBrSO$_2$CHBrPh by triphenylphosphine and DMF, respectively.[5] The stereoselective dehydrobrominations of the diastereomeric α-bromo sulfones PhCBr(Me)SO$_2$CH(Me)Ph (**5a** and **5b**) and PhCH(Me)SO$_2$CHBrMe (**9a** and **9b**) in the present study also appear to be under kinetic control, as does the dehydrobromination of PhCBr(Me)SO$_2$CH$_2$CH$_3$ [*ca.* 43% of *trans*-PhC(Me)=CHCH$_3$ formed as compared to *ca.* 17% expected on the basis of thermodynamic control[23]].

The evidence indicating that in some instances there is a preference for two phenyl groups to become cis rather than trans in the thiirane 1,1-dioxide (*e.g.*, the preferential formation of *cis*-2,3-dimethylstilbene from **5a**[23]) and for the preferential formation of a thiirane 1,1-dioxide where a phenyl and a methyl group, rather than two methyl groups, are cis (*e.g.*, the preferential formation of *trans*-α-methylstilbene from one diastereomer of **9**) argues against control of stereochemistry by attractive forces between R groups in the step wherein the thiirane 1,1-dioxide is formed.[13] The evidence points, then, to the carbanion-forming step as that controlling the stereochemistry.

A scheme for stereochemical control through preferential formation of one of two possible diastereomeric carbanions[22] can be illustrated with the reaction of MeCH$_2$SO$_2$CBr(Me)Ph (**10**). Deprotonation of **10** by methoxide ion can give either carbanion **10a** or **10a′**, each of which would be expected to maintain its asymmetry for some

Table IV
Summary of Bromination of α-Methylbenzyl Sulfones

Reactant	Mmol	CCl$_4$, ml	Reaction time, hr	Product	Yield, %
PhCH(CH$_3$)SO$_2$C$_2$H$_5$	50	100	48	**10**	70 (48)[a]
[PhCH(CH$_3$)]$_2$SO$_2$	50	100	32	**5**	80 (37)
PhCH(CH$_3$)SO$_2$CH$_2$Ph	10	50	18	**11**[b]	75 (41)

[a] Isolated yield is enclosed in parentheses; the other figure represents per cent as determined by nmr analysis. [b] Compound **11** is PhCH$_2$SO$_2$CBr(CH$_3$)Ph.[25]

Table V
Physical Data of Bromo Sulfones[a,b]

Compd	Mp, °C	Nmr spectra[c]		
5a	112	1.67	2.13	4.13
5b	76	1.53	2.20	4.80
9a[d]		1.77	1.84	4.24 4.80
10	67	1.23	2.62	2.94
11	138	2.48	4.20	

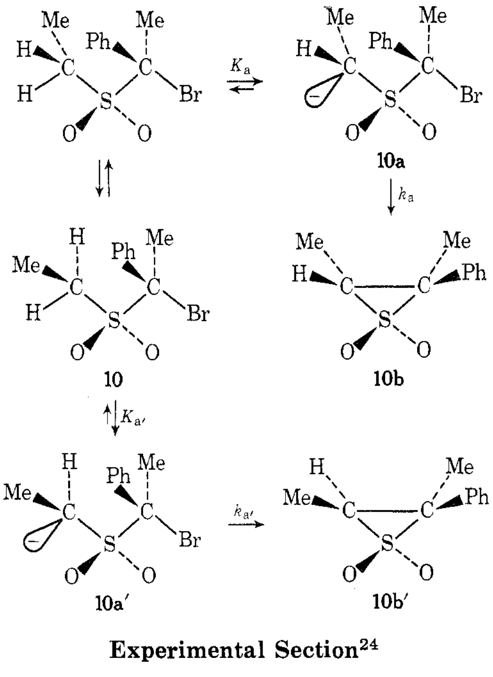
[a] Satisfactory analytical data (±0.4% for C and H) were reported for all new compounds listed in the table: Ed. [b] The sulfones had maxima at *ca.* 7.7 and 7.9 μ. [c] Chemical shifts are reported in δ units relative to TMS as internal standard in dilute chloroform-*d* solution. [d] Recovered as an oil by chromatographing the filtrate obtained from the crystalline isomer **9b**.[27]

Table VI
Methoxide Ion Induced 1,3-Elimination and Deuterium Exchange of 5, 9, and 10

Bromo sulfone	Mmol	[MeO$^-$][a]	Solvent	Reaction time, hr	Product(s), (yield, %)[b]
5a	0.39	0.063	MeOD	0.35[c]	**5a** (40), **5a**-d_1 (50), **9a** and **8b** (*ca.* 10)
5a	0.57	0.13	MeOD	1.0[c]	**5a**-d_1 (38), **8a** (56), **8b** (*ca.* 6)
5a	0.39	0.19	MeOH	16[d]	**8a** (93), **8b** (7)
5b	0.28	0.090	MeOD	0.05[c]	**5b** (67), **5b**-d_1 (27), **8b** (*ca.* 6)
5b	0.28	0.065	MeOD	0.10[c]	**5b** (30), **5b**-d_1 (60), **8b** (*ca.* 10)
5b	0.38	0.065	MeOD	0.28[c]	**5b**-d_1 (55), **8b** (45)
5b	0.31	0.13	MeOH	12[d]	**8b** (*ca.* 100)
9a	0.74	0.18	MeOH	4[d]	**9a** (59), **9b** (31)[f]
9a	1.1	0.57	MeOH	24[e]	*trans*-PhBu (70), *cis*-PhBu (30)
9b	2.7	0.85	MeOD	4[d]	**9b** (85), **9a** (15)[f]
9b	1.1	0.93	MeOD	24[e]	*trans*-PhBu-d_1 (23), *cis*-PhBu-d_1 (77)
10	1.5	0.18	MeOD	24[d]	**10**-d_2 (70)[g]
10	0.87	0.52	MeOD	24[e]	*trans*-PhBu-d_1 (43), *cis*-PhBu-d_1 (57)

[a] In each experiment excess sodium methoxide was used. Millimoles of methoxide ion may be calculated by multiplying the given concentration by volume used (20 ml in each case). [b] Product ratios were determined by nmr and were checked by vpc for products derived from **9** and **10**. The deuterated bromo sulfones (**5a**-d_1, **5b**-d_1, and **10**-d_2) were isolated and identified by ir and melting point. [c] At 0°. [d] Room temperature. [e] Reflux temperature. [f] Also contained *ca.* 85% 2-phenyl-*cis*- and *trans*-2-butene (*cis*-PhBu and *trans*-PhBu, respectively). [g] Isolated sulfone.

time in methanol solution. Carbanion **10a** will react by double inversion to form thiirane 1,1-dioxide **10b**, which gives rise to the more stable alkene, *cis*-2-phenyl-2-butene; similarly **10a′** forms **10b′** and *trans*-2-phenyl-2-butene. The rates of formation of the cis and trans alkenes, assuming rate-limiting thiirane 1,1-dioxide formation, will be $k_{\text{cis}} = K_ak_a$ and $k_{\text{trans}} = K_{a'}k_{a'}$. Presumably the rate constant k_a will be larger than $k_{a'}$, but this factor favoring formation of **10b** over **10b′** can be counteracted, or even overshadowed if K_a is substantially larger than $K_{a'}$. In this particular example the two factors approximately balance one another, since the cis:trans alkene ratio is *ca.* 53:47. (In other instances the relative size of the equilibrium constants appears to play the dominant role.) Unfortunately at present we have little insight as to the reason why the equilibrium constant K_a is larger than $K_{a'}$. Presumably **10a** is more stable than **10a′** because of differences in solvation.



Experimental Section[24]

Bromination of α-Methylbenzyl Sulfones. The parent sulfone, *N*-bromosuccinimide (between 1 and 2 equiv) and a catalytic amount of benzoyl peroxide were heated at reflux temperature for the indicated periods (Table IV).

Product Studies. The α-bromo sulfones (Table V) were allowed to react with excess sodium methoxide in methanol (or methanol-d_1). The reaction mixture was either quenched with nitric acid and/or diluted with water and extracted with dichloromethane or pentane. The organic layer was dried ($MgSO_4$), the solvent was removed under reduced pressure, and the products were analyzed (Table VI).

Kinetic Method. The spectrophotometric and titrimetric rates were determined by previously reported methods.[2,3]

Acknowledgment. We are grateful to the National Science Foundation (GP-29539X) for support of this work.

Registry No.—**1**, 19217-59-5; **5a**, 51380-66-6; **5b**, 51380-67-7; **9a**, 51392-55-3; **9b**, 51392-56-4; **10**, 51392-57-5; **11**, 51392-58-6; PhCH(Me)SO_2CHBrPh, 51392-59-7; PhCH(CH_3)$SO_2C_2H_5$, 51392-60-0; [PhCH(CH_3)]$_2SO_2$, 16907-49-6; PhCH(CH_3)SO_2CH_2Ph, 36611-88-8.

References and Notes

(1) For a preliminary account of this work, see F. G. Bordwell, E. Doomes, and P. W. R. Corfield, *J. Amer. Chem. Soc.*, **92**, 2591 (1970).

(2) (a) F. G. Bordwell and J. M. Williams, Jr., *J. Amer. Chem. Soc.*, **90**, 435 (1968); (b) F. G. Bordwell and J. B. O'Dwyer, *J. Org. Chem.*, **39**, 2519 (1974); (c) F. G. Bordwell and M. D. Wolfinger, *ibid.*, **39**, 2521 (1974).

(3) F. G. Bordwell, J. M. Williams, Jr., E. B. Hoyt, Jr., and B. B. Jarvis, *J. Amer. Chem. Soc.*, **90**, 429 (1968).

(4) F. G. Bordwell, J. M. Williams, Jr., and B. B. Jarvis, *J. Org. Chem.*, **33**, 2026 (1968).

(5) F. G. Bordwell and B. B. Jarvis, *J. Amer. Chem. Soc.*, **95**, 3585 (1973).

(6) P. W. R. Corfield, unpublished results. The conformation shown for **5a** is that found in the crystal.

(7) The exchange to epimerization ratio was calculated from the expression k_{ex}/k_{ep} = % exchange/[(% conversion)(fraction epimerized)] = 50/[(10)(10/90)] = 55. An average of three runs gave an average k_{ex}/k_{ep} = 50.

(8) The length of the induction period and the magnitude of the decrease in absorption depended on the initial concentration of methoxide ion. With 2 *M* NaOMe the disappearance of adsorption due to **5b** was immediate.

(9) D. J. Cram and M. R. V. Sahyun, *J. Amer. Chem. Soc.*, **85**, 1257 (1963).

(10) See the discussion in ref 2b.

(11) F. G. Bordwell, D. D. Phillips, and J. M. Williams, Jr., *J. Amer. Chem. Soc.*, **90**, 426 (1968).

(12) (a) E. J. Corey and T. H. Lowry, *Tetrahedron Lett.*, 803 (1965); (b) S. Wolfe, *Accounts Chem. Res.*, **5**, 102 (1972).

(13) N. P. Neureiter, *J. Amer. Chem. Soc.*, **88**, 558 (1966).

(14) Evidence for acceleration of the displacement step by phenyl has been noted previously (see ref 2b and references cited therein).

(15) An α-bromine atom in a sulfone has been shown to accelerate ex-

change at the α position by a factor of ca. 10^3.[16] Epimerization of *cis*- or *trans*-2,3-dimethyl-2-phenylthiirane 1,1-dioxide is unlikely, since *cis*-2,3-dimethylthiirane 1,1-dioxide, which has an acidic proton of a comparable type, does not epimerize under these conditions.[13]

(16) D. A. Schexnayder, Ph.D. Dissertation, Northwestern University, June 1968.

(17) This result is more definitive than the rough kinetic studies of the decomposition of the unstable thiirane 1,1-dioxides themselves.[3] Furthermore, reexamination of the earlier data[3] makes us doubtful as to the reality of the small accelerations in rates observed with increasing methoxide concentration. Our present view is that the decomposition of thiirane 1,1-dioxides is *not* accelerated by low concentrations of bases.

(18) The rate constant k_{-1} probably refers in actual practice to solvent exchange rather than protonation, since the rate-limiting step in these exchanges is probably solvent exchange.[10] Corrections for statistical factors and isotope effects need also to be made, but the 100-fold figure should be of the right order of magnitude.

(19) F. G. Bordwell, D. D. Phillips, and J. M. Williams, Jr., *J. Amer. Chem. Soc.*, **90**, 426 (1968).

(20) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, pp 254–255.

(21) L. A. Paquette, *Accounts Chem. Res.*, **1**, 209 (1968). It is true that this carbanion (labeled **24** in the paper) may be formed faster than that leading to the trans thiirane 1,1-dioxide (**25**) because of a lower rotational barrier, but it is also true that **24** will revert faster to its rotamer (I). There is no reason to believe, then, that the equilibrium concentration of **24** will be higher than that of **25** for this reason, as was assumed.

(22) F. G. Bordwell, B. B. Jarvis, and P. W. R. Corfield, *J. Amer. Chem. Soc.*, **90**, 5298 (1968).

(23) It is assumed that the relative equilibrium concentrations of cis and trans 2,3-, 2,2,3-, and 2,2,3,3-substituted thiirane 1,1-dioxides will not differ greatly from those of the corresponding cis and trans alkenes. This assumption is supported by the formation of a near-equilibrium concentration of *cis*- and *trans*-2-butene from *cis*-2,3-dimethylthiirane 1,1-dioxide when equilibration is effected with *t*-BuOK-*t*-BuOH,[13] and by the formation of only *trans*-stilbene from *cis*-2,3-diphenylthiirane 1,1-dioxide when equilibration is effected with NaOMe-MeOH.[3]

(24) Nmr spectra were determined on a Varian A-60 spectrometer (60 MHz). Infrared spectra were run on a Beckman IR-5 spectrophotometer in KBr disks. Analyses were performed by Micro-Tech Laboratories, Skokie, Ill.

(25) Compound **11** was formed to the exclusion of $PhCHBrSO_2CH(CH_3)Ph$. Data obtained in these experiments indicate that free-radical brominations α to the sulfone group are effective when the hydrogen atom being replaced is both benzylic and tertiary. In fact, it was found previously that simple benzyl and allyl sulfones do not undergo free-radical bromination under comparable conditions.[26]

(26) See H. J. Baker, W. Steven, and N. Dost, *Recl. Trav. Chim. Pays-Bas*, **67**, 451 (1948); *Chem. Abstr.*, **43**, 559 (1949).

(27) M. D. Wolfinger, Ph.D. Dissertation, Northwestern University, June 1968, p 240.

Concerning Driving Forces for 1,3-Elimination Reactions. Dehydrohalogenation of 1-Halo-2-thia-2,3-dihydrophenalene 2,2-Dioxides in a Ramberg-Bäcklund Reaction

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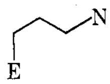
Data obtained for the reaction of 1-bromo-2-thia-2,3-dihydrophenalene 2,2-dioxide (8) with NaOMe and MeOH, including deuterium exchange, kinetic order, kinetic salt effects, and kinetic activation parameters, are shown to be remarkably similar to data obtained under similar conditions in a study of an open-chain analog, $PhCHBrSO_2CH_2Ph$ (9). The evidence points to a two-stage (carbanion) mechanism for 8, despite the presence of a geometry that would appear to favor a one-stage (concerted) mechanism. It is concluded that the concerted mechanism for 1,3-elimination has relatively little driving force.

The stereochemistry of two-stage 1,3-elimination reactions involving carbanion intermediates is dictated primarily by the necessity of inversion at the nucleofugal center (N).[1] In acyclic systems this requires removal of the electrofugal atom or group (E) from either conformation 1 (exo-sickle) or conformation 2 (W). Concerted 1,3-elimination reactions could also presumably utilize transition states with geometries corresponding to 1, 2, or one of three other possibilities (endo-S, apo-S, or U).[2]



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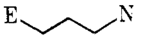
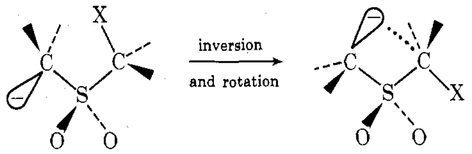


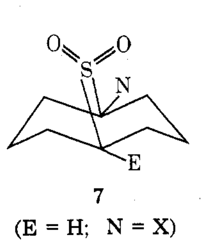
2

1,3-Dehydrobromination of $PhCH(Me)SO_2CBr(Me)Ph$ (3)[3] and 1,3-debromination of $PhCHBrSO_2CHBrPh$ (4)[1] have been found to involve carbanion intermediates and to prefer overall W geometry (2). Here the preference of W over exo-S geometry is believed to be dictated by preferred deprotonation (of 3) or removal of Br^+ (from 4) from a conformation in which these electrofugal atoms are flanked by the two oxygen atoms of the sulfonyl group.[1,3] The resulting carbanion (*e.g.*, 5) is prevented for steric reasons from effecting ring closure. The transition state required for ring closure is 6 wherein carbanion 5 has inverted its configuration and rotation has occurred around the O_2S–CX bond so as to permit inversion of configuration when the nucleofugal group X departs.[1] (Rotation around O_2S–C^- would give the wrong stereochemical result: a barrier to this rotation is assumed.)



5 **6**

If this representation of the reaction is correct, one would expect 1,3-eliminations of this type to be particularly facile in cyclic analogs such as 1-halo-9-thiabicyclo-[3.3.1]nonane 1,1-dioxides (7), where the E and N atoms are fixed in the W configuration and the E atom is flanked by the oxygen atoms of the sulfonyl group, or 1-



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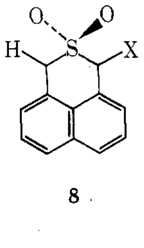
(E = H; N = X)



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