−10°. The temperature of decomposition, the strong hydroperoxide test before decomposition (and weak test after the exothermic reaction), and the fact that no hydroperoxide is present in the nmr spectra of several of the ethers studied would suggest that this intermediate is the hydrotrioxide, I.

The exothermic decomposition at −10° found for this system checks qualitatively with Bartlett and Guaraldi's observation[10] of a sharp irreversible decrease in the esr signal from di-*t*-butyl trioxide at about −12°.

Even if I is this thermally unstable intermediate, the amount formed directly by reaction 1 *vs.* the amount formed in reaction 9 cannot be ascertained by the data presented in this paper. It is certain that reaction 1 cannot be the only one operating, even at −78°, since product ratios, relative rates, etc., vary with oxygen *vs.* nitrogen as the ozone carrier.[31]

(31) Although this investigation leaves many questions unanswered as to the exact mechanism of the ozonation of ethers, isotope effect measurements and relative rate determinations appear to be of limited

In summary, the mechanism of the ozonation of ethers is a complicated one involving a free radical chain process and an unstable intermediate tentatively assigned structure I. Varying conditions (solvent polarity, temperature, and ozone carrier gas) could lead to more synthetic utility for the ozonation of ethers.

further usefulness. The identity of the temperature-sensitive intermediate and the exact product distribution are amenable to study by low-temperature nmr spectroscopy, and we have begun such a study. It has been suggested by a referee that since an unstable intermediate (presumably I) is present, a reaction sequence 1, 3, 5, 6, 7 and termination reactions 11–14 can account for the reaction mechanism more simply than the sequence outlined. Analogy and thermochemical reasoning led us to consider reactions such as (4) and (8) to go along with reaction 1 as ozone-consuming reactions. Until both the amount (we believe it to be present in small yield) and the exact structure of the unknown intermediate are established, we prefer the mechanism hypothesized here.

α-Halo Sulfones. X. Kinetics and Mechanism of the Rearrangement of Acyclic α-Halo Sulfones with Hydroxide Ion[1]

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Abstract: Kinetic and product studies of the reactions of $CH_3CH_2SO_2CHClR$ and $CH_3CHClSO_2CH_2R$ with hydroxide ion in aqueous dioxane have been performed. As the size of the R group increases from methyl to isopropyl, the proportion of *cis* olefin in the product mixture is seen to decrease. Parallel results were obtained when these α-chloro sulfones were rearranged with phenyllithium in xylene. The *cis* isomer did predominate in all cases and was seen to be formed consistently in greater relative yield when the leaving group was attached to the more bulky of the alkyl groups within a given isomeric pair. Although the rates of rearrangement did not vary excessively within the series examined, slightly faster displacements of chloride ion were noted when the halogen was attached to the less bulky alkyl substituent. A mechanistic interpretation is advanced to reconcile the available data.

The reaction by which α-halo sulfones (**1**) are converted to olefins upon treatment with base has developed into a transformation of considerable theoretical interest.[2] Because the double bond in the product (**2**) cleanly and unequivocally supplants the sulfonyl group of the starting halo sulfone, the rearrangement has also proven synthetically useful.[3] However utilitarian the process may be, it is the mecha-

$$RCH_2SO_2CHR' \xrightarrow{\text{base}} RCH=CHR'$$

$$\underset{\displaystyle Cl}{\big|}$$

1   **2**
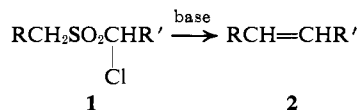
(1) For previous paper in this series, see L. A. Paquette, L. S. Wittenbrook, and K. Schreiber, *J. Org. Chem.*, **33**, 1080 (1968).

(2) For recent reviews of this subject, see (a) L. A. Paquette, *Accounts Chem. Res.*, **1**, 209 (1968); (b) L. A. Paquette in "Mechanisms of Molecular Migrations," Vol. I, B. S. Thyagarajan, Ed., Interscience Publishers, New York, N. Y., 1968, in press; (c) F. G. Bordwell, *Organosulfur Chem., Org. Sulfur Symp., 2nd Groningen, Neth.*, 311 (1966).

(3) (a) L. A. Paquette, *J. Am. Chem. Soc.*, **86**, 4383 (1964); (b) N. P. Neureiter, *J. Org. Chem.*, **30**, 1313 (1965); (c) L. A. Paquette and J. C. Philips, *Tetrahedron Letters*, 4645 (1967).

nistic detail of this rearrangement which continues to be the prime concern of several research groups principally because the Ramberg–Bäcklund reaction has supplied a number of uniquely varied and subtle problems which appear to be resolvable by physical-organic techniques.

At the present time, the gross mechanistic features of the title reaction are quite well understood.[2] Thus, evidence from a number of sources clearly indicates the existence of a rapid preequilibrium between the α-halo sulfone and all of its possible carbanions. Further, the rate of release of halide ion in aqueous base has been shown to be first order in halo sulfone and first order in hydroxide ion. Although the alkaline conditions required for rearrangement are sufficiently strenuous to preclude isolation of intermediate episulfones, the availability of both symmetrical and unsymmetrical episulfones by alternate syntheses has made it possible to establish that the decomposition of these three-membered sulfones under customary rearrangement conditions is markedly stereospecific.[4] There-

fore, the configuration of the olefinic product is clearly determined in the second step of the rearrangement (eq 2). This consideration brings us to perhaps the most puzzling aspect of the α-halo sulfone rearrangement: why does the cyclization of eq 2 (Scheme I)
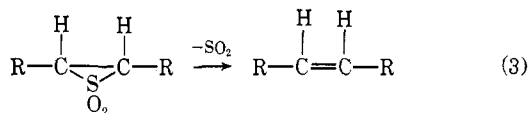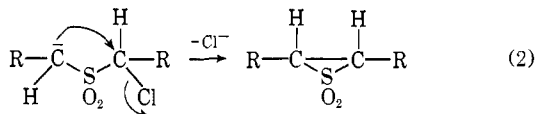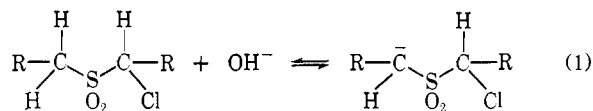
Scheme I

exhibit a strong preference for formation of the *cis* isomer? It is precisely to this question of mechanistic detail that the present study is directed.

The suggestion has been made that the enhanced rate of cyclization leading to *cis*-2,3-dialkyl episulfones is primarily the result of intervening London forces.[5] That is to say, at some critical distance prior to C–C bond formation, there is a net force of attraction (F_A) predominating over repulsion (F_R) between the two alkyl groups which effectively lowers the energy of the *cis* transition state relative to that of the *trans* isomer. The point at which $F_A - F_R$ is a maximum has been estimated for the α-chloroethyl ethyl sulfone–*cis*-2-butene system to be 3.5 Å.[5b] Because this distance lies well outside the range of normal covalent bond distances, serious doubts are raised with regard to whether a transition-state energy can be influenced so early in a bonding process. Furthermore, since attractive forces vary approximately as the reciprocal sixth power of the distance[6] whereas repulsive forces vary as the reciprocal of the twelfth power,[7] it follows logically that repulsive forces will exceed attractive forces at the point of bond formation.

A second rationalization has been advanced which proposes that maximum solvation of the transition state in which alkyl groups are *cis* effectively lowers the *cis* transition state energy.[8] While this postulate based on steric inhibition to solvation is interesting, product compositions are seen to be remarkably constant over a wide range of bases and solvents.[5,9] Consequently, solvent effects appear to play no major role in the over-all stereochemical result.

(4) Exceptions to this stereochemical behavior have been noted when very strong bases such as *t*-butoxide were employed or when an acidifying substituent such as phenyl was present. Because these results are very likely due to epimerization of the episulfone intermediates prior to elimination of sulfur dioxide, they will prove not to be pertinent to the subject matter of this paper.

(5) (a) N. P. Neureiter and F. G. Bordwell, *Tetrahedron Letters.*, 85, 1209 (1963); (b) N. P. Neureiter, *ibid.*, 88, 558 (1966).

(6) K. S. Pitzer and E. Catalano, *J. Am. Chem. Soc.*, 78, 4844 (1956).

(7) J. O. Hirschfelder, C. F. Curtis, and R. B. Bird, "Molecular Theory of Gases and Liquids," John Wiley & Sons, Inc., New York, N. Y., 1954, pp 1070–1075.

(8) D. J. Cram, "Fundamentals of Carbanion Chemistry," Academic Press, New York, N. Y., 1965, pp 253–255.

(9) Present work.

In spite of considerable theoretical discussion concerning this interesting stereochemical question, rearrangements of a relatively small number of acyclic α-halo sulfones have been studied in detail. We felt that before an answer to the stereochemical question could be provided, a systematic study of a more diversified selection of α-halo sulfones was required. Accordingly, we have accumulated product and rate data for a series of such molecules in which the steric nature of the substituent group is gradually altered and electronic factors are maintained as constant as possible.[10]

Rate Studies

The rearrangements of **3–7** were performed in dioxane–water (30:70, v/v), 1.26 N in hydroxide ion, under pseudo-first-order conditions at 50°. The preparation of the starting materials is described in the Experimental Section. Reaction rates were followed by potentiometric titration of released chloride ion with standard silver nitrate solution, and the reactions were carried through approximately two half-lives. In those examples which rearranged slowly, dissolution of the glass gradually occurred during the extensive reaction times required, and this effect of the alkali became apparent beyond this period. Table I lists

Table I. Rate Constants and Relative Rates for the Rearrangement of α-Chloro Sulfones in Dioxane–Water 30:70, v/v, 1.26 N in Hydroxide Ion at 50.28 ± 0.03°

Sulfone	Rate constant, $10^7 k_1$, sec^{-1}	Rel rate
$CH_3CH_2SO_2CH(Cl)CH_3$ (**3**)	16.85 ± 0.06	1.0
$CH_3CH_2SO_2CH(Cl)(CH_2)_2CH_3$ (**4**)	8.00 ± 0.06	0.47
$CH_3CH(Cl)SO_2(CH_2)_3CH_3$ (**5**)	20.47 ± 0.07	1.2
$CH_3CH_2SO_2CH(Cl)CH(CH_3)_2$ (**6**)	3^a	0.18
$CH_3CH(Cl)SO_2CH_2CH(CH_3)_2$ (**7**)	16.00 ± 0.16	0.94

^{a} Corrected for concomitant production of acetone (see text).

the rate constants which represent the average of two or more runs. Examination of Table I reveals that the release of chloride ion under pseudo-first-order conditions is not subject to marked change over a fairly substantial range of alkyl substitution. Within this rather small range, however, the rate data do reveal that chloride ion is released more rapidly when attached to the less bulky alkyl residue (compare **4** *vs.* **5** and **6** *vs.* **7**).

Thermodynamic parameters were experimentally determined for the rearrangement of **3** (Table II). In our initial experiments to obtain similar data on the remaining α-halo sulfones, an inverse solubility effect in the aqueous dioxane medium with increasing temperature, not observed with **3**, was noted (also seen in related aqueous organic systems); accordingly, these studies were not pursued. Inspection of Table II discloses the existence of a large activation energy and a slightly negative entropy for this reaction.

Product Studies

Conversion of **3–7** to olefinic products was carefully effected by heating the appropriate α-chloro sulfone in

(10) In order to guarantee that the rates and product ratios should reflect only steric factors, substituent groups (such as phenyl) that would make the intermediate episulfone subject to epimerization or render the leaving group more labile have been avoided.

Table II. Activation Parameters for the Rearrangement of α-Chloroethyl Ethyl Sulfone (3) in Dioxane-Water 30:70, v/v, 1.26 N in Hydroxide Ion

Temp, °C	k_1, sec^{-1}	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
50.28 ± 0.03	16.93 ± 0.02 × 10^{-7}		
63.07 ± 0.03	91.06 ± 0.12 × 10^{-7}		
75.98 ± 0.04	425.9 ± 5.1 × 10^{-7}	27.4 ± 0.2[a]	−0.8 ± 0.4[a]

[a] Derived from second-order rate constants calculated on the basis of the relationship $k_2 = k_1/[\text{OH}^-]$.

aqueous 2 N sodium hydroxide solution at 95–100°. Volatile products were carried over by a nitrogen stream and were condensed at −78°; the contents of the trap were periodically weighed and checked for content and composition by appropriate vpc techniques (see Experimental Section). An organic co-solvent was not employed in the product studies in order to simplify the analyses. In all cases, the anticipated *cis* and *trans* olefins were formed (Table III), and their identities were verified by comparison of

**Table III.** Reaction of α-Chloro Sulfones with 2 N Sodium Hydroxide[a]

α-Chloro sulfone	Product	Yield, %	% cis	% trans
α-Chloroethyl ethyl (3)	2-Butene	76	78.8	21.2
α-Chloropropyl ethyl (8)[b]	2-Pentene	57	71.3	28.7
α-Chloroethyl propyl (9)[b]	2-Pentene	74	65.8	34.2
α-Chlorobutyl ethyl (4)	2-Hexene	63	69.4	30.6
α-Chloroethyl butyl (5)	2-Hexene	76	66.2	33.8
α-Chloroisobutyl ethyl (6)	4-Methyl-2-pentene	41[c]	59.4	40.6
α-Chloroethyl isobutyl (7)	4-Methyl-2-pentene	70	51.0	49.0

[a] The total of *cis* and *trans* olefins in each case is normalized to 100%. [b] Taken from the report of Neureiter (ref 5b). [c] The low yield is caused by a competing reaction (see text).

vpc retention times and spectral data with those of authentic materials. Care was taken to ensure the reproducibility of the results; in actual fact, the yield precision is ±2% and the isomer content is accurate to ±0.5%. Thus the 3.2% difference in *cis*-2-hexene from **4** and **5**, as well as the 8.4% difference in *cis*-4-methyl-2-pentene from **6** and **7**, are well beyond the limits of experimental error. Neureiter[5b] had established earlier that the 5.5% difference in *cis*-2-pentene from **8** and **9** was reproducible to ±0.3%. Although *cis*-alkenes predominate in all the examples studied, the particular *cis* isomer is consistently seen to be formed in significantly greater relative yield when the leaving group is attached to the more bulky of the two alkyl groups within a given isomeric pair. Such differences show that the isomeric sulfone pairs do not cyclize to the same mixture of intermediate episulfones. Such data point to differing steric requirements of the alkyl groups attached to the nucleophilic carbon and the carbon which is the seat of displacement.

In the examples studied, no other volatile products were detected, except in the case of α-chloroisobutyl ethyl sulfone (6). In this instance, the formation of acetone (24%) was also observed. A plausible mechanism for the production of this ketone is outlined in Scheme II. To our knowledge, no precedent for the over-all transformation exists, although the steps taken individually are well known; in particular, the

final step involving cleavage of the β-hydroxy sulfone has been put to ingenious use by Corey and Lowry.[11] As indicated, the mechanistic sequence also requires the formation of ethyl methyl sulfone (10). Indeed, extraction of the spent reaction mixture from **6** did yield quantities of **10**. With regard to the elimination step, it is particularly noteworthy that 1,3 elimination proceeds so slowly that 3,4 elimination involving removal of one of the least acidic protons in the system can compete effectively.

Scheme II
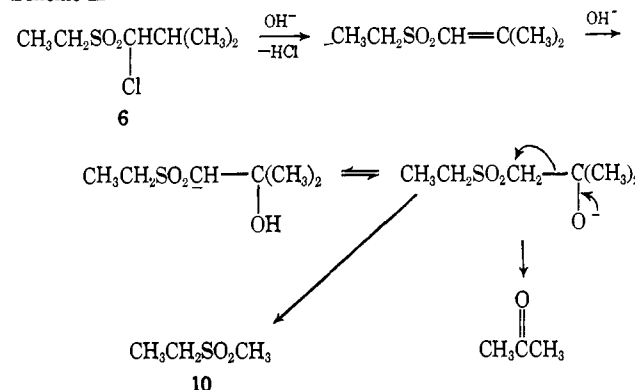
In another series of experiments designed to evaluate the function of solvent and basic reagent on the stereochemistry of the rearrangement, α-halo sulfones **3–7** were treated with phenyllithium in a solvent system consisting primarily of xylene. In a typical experiment, a 2.11 M solution of phenyllithium in benzene–ether (70:30) was added to a solution of the appropriate sulfone in xylene previously heated to 100°. Volatile products were collected, weighed, and analyzed for isomer composition much in the same manner described above. The results are summarized in Table IV. Comparison of the various isomer ratios with

Table IV. Reaction of α-Chloro Sulfones with Phenyllithium[a]

α-Chloro sulfone	Product	Yield, %[b]	% cis[c]	% trans[c]
3	2-Butene	80[d]	73.3[d]	26.7[d]
4	2-Hexene	30	68.0	32.0
5	2-Hexene	30	63.8	36.2
6	4-Methyl-2-pentene	59	59.0	41.0
7	4-Methyl-2-pentene	56	51.7	48.3

[a] The total of *cis* and *trans* olefins in each case is normalized to 100%. [b] Yields are normalized (see Experimental Section). [c] Isomer ratios accurate to ±0.5%. [d] Sulfone added to refluxing phenyllithium solution (0.75 M) in benzene (data of ref 5b).

those obtained in aqueous sodium hydroxide solution (Table III) indicates very little change in stereochemi-

(11) E. J. Corey and T. H. Lowry, *Tetrahedron Letters*, 793 (1963).

Table V. Exchange–Racemization Ratios and Activation Parameters for Sulfones **11–13** (2:1 Ethanol–Water; 72°)[a]

Compd no.	Sulfone	k_{ex}/k_{rac}	Exchange		Racemization	
			$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu	$\Delta H^{\ddagger}$, kcal/mol	$\Delta S^{\ddagger}$, eu
11	$(CH_3)_3CSO_2CH$—CH_3 | C_6H_{13}-n	107	15	−33	29	−1.7
12	$C_6H_5SO_2CH$—CH_3 | $C(CH_3)_3$	58	14	−36	25	−14
13	$C_6H_5SO_2CH$—CH_3 | C_6H_5	44	16	−5.4	23	+0.1

[a] Data taken entirely from ref 19.

cal composition. In contrast to the results of Cram and coworkers[12] in which the configurational stabilities of α-sulfonyl carbanions have been shown to be a function of the solvent, medium effects appear to be relatively unimportant in the α-halo sulfone rearrangement. Certainly more extensive work is needed before this conclusion becomes unequivocally established; suffice it to say, however, that in the present instance a change of the solvent dielectric constant from approximately 64 in the case of H_2O–dioxane to approximately 2 in the xylene experiments results in remarkably little alteration in product distribution.

Discussion

A substantial amount of previous work has shown that the rate of base-catalyzed hydrogen–deuterium exchange at an asymmetric carbon adjacent to a sulfonyl group is greater than the rate of racemization at that center.[12] Two possible reasons for the inhibition of inversion have been suggested. The first proposal is that the asymmetry of α-sulfonyl carbanions is due to a pyramidal α carbon in which rotation about the C_α–S bond is restricted and in which constraint to maintain geometry is caused by electrostatic inhibition to inversion.[13] The alternative viewpoint pictures such anions as effectively planar[14] with racemization occurring relatively slowly because of a barrier to rotation. In order to explain the exchange–racemization data in terms of the effectively planar ion, however, removal of a proton so as to produce a carbanion in an asymmetric conformation is required; the proton must then be returned to the same side of the molecule in order to account for retention of configuration. According to this view, racemization occurs either through rotation about the C_α–S bond in the ion or by nonstereospecific reprotonation. Recently, Corey and Lowry[11] have provided evidence establishing that α-sulfonyl carbanions are protonated from the direction *syn* to the sulfonyl oxygens. For reasons of microscopic reversibility, therefore, it must be concluded that α-sulfonyl protons are abstracted preferentially by base when they are situated between the oxygen atoms of the sulfonyl group.[15]

(12) For a review of the work in this area, see ref 8.
(13) D. J. Cram and T. A. Whitney, *J. Am. Chem. Soc.*, **89**, 4651 (1967), and earlier papers of this series.
(14) It should be pointed out that, at the present time, a distinction between a purely sp^2-hybridized anion or an sp^3-hybridized ion which inverts rapidly as compared to protonation rates has not been made experimentally. The term "effectively planar" is employed herein to denote this indistinguishable carbanion type.
(15) In this regard, A. Rauk, E. Buncel, R. F. Moir, and S. Wolfe [*J. Am. Chem. Soc.*, **87**, 5498 (1965)] have provided a striking example of a reaction which proceeds *via* an asymmetric carbanion attached

In the present analysis of the available stereochemical data on α-halo sulfone rearrangements, we have relied on the concept that α-sulfonyl carbanions are effectively planar with a barrier to rotation.[11,16] Supporting evidence for this carbanion model has recently been advanced by Bordwell and coworkers.[17] The magnitude of the energy barrier for α-sulfonyl carbanion racemization caused by C_α–S rotation now becomes an important consideration. Initially, estimates were made that the rotational barrier in question need not be very large to account for the stereospecific effects exhibited by α-sulfonyl anions.[11,18] More recently, however, Lowry[19] has measured exchange–racemization ratios and activation parameters for sulfones **11–13** in 2:1 ethanol–water and observed that the $\Delta H^{\ddagger}$ for racemization varied between 23 and 29 kcal/mol (Table V). An nmr spectral study by Ratajczak, Anet, and Cram[20] of various alkali metal salts of 2,2-dimethylcyclopropyl phenyl sulfone (**14**) in mixtures of dimethyl-d_6 sulfoxide and tetrahydrofuran-d_8 has revealed that the free energies of activation $(\Delta F^{\ddagger})$ for enantiomer interconversion (**14a** ⇌ **14b**) were of the order of 16.5–18 kcal/mol. If the plausible assumption is made that entropies of activation for these inversion

14a **14b**
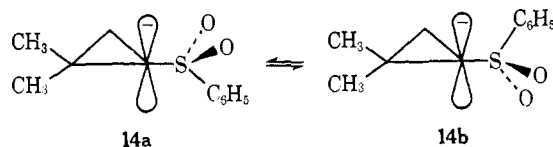
processes are negligible, then the $\Delta H^{\ddagger}$ values for the rotation in the various salts are again sizeable.

Scheme III illustrates the major factors which are at play in the conversion of a typical dialkyl-substituted α-chloro sulfone to a mixture of alkenes. In constructing modified Newman projections **15** and **16**[21] of such an α-chloro sulfone, we have adopted the entirely

to a sulfoxide group [see also S. Wolfe and A. Rauk, *Chem. Commun.*, 778 (1966)].
(16) (a) E. J. Corey and E. T. Kaiser, *J. Am. Chem. Soc.*, **83**, 490 (1961); (b) E. J. Corey, H. König, and T. H. Lowry, *Tetrahedron Letters*, 515 (1962); (c) E. J. Corey and T. H. Lowry, *ibid.*, 803 (1965).
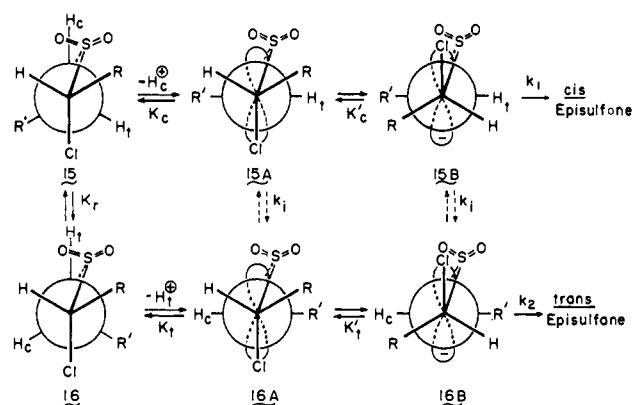(17) F. G. Bordwell, D. D. Philips, and J. M. Williams, *J. Am. Chem. Soc.*, **90**, 426 (1968).
(18) D. J. Cram and A. S. Wingrove, *ibid.*, **85**, 1100 (1963); **84**, 1496 (1962).
(19) T. H. Lowry, Ph.D. Thesis, Harvard University, 1965, p 30.
(20) A. Ratajczak, F. A. L. Anet, and D. J. Cram, *J. Am. Chem. Soc.*, **89**, 2072 (1967).
(21) Such projections are employed in order to emphasize the steric interplay which exists between R and R′ in both ground and transition states. Only one enantiomer is pictured for reasons of conciseness. Structures **15** and **16** are constructed so as to minimize Cl–SO_2 dipole-dipole interactions. It is recognized that such dipole effects will be maximized in purely hydrocarbon media such as benzene and less important in solvents of high dielectric constant such as water.

Scheme III

H$_c$
O$\sim$S$\neq$O

15 15A 15B

K$_r$ k$_i$ k$_i$

16 16A 16B

$$\xrightarrow{k_1} \text{cis} \atop \text{Episulfone}$$

$$\xrightarrow{k_2} \text{trans} \atop \text{Episulfone}$$

reasonable assumptions that the most stable ground-state conformations will be characterized by minimal alkyl–alkyl interactions and that the C–S bonds exhibit "free" rotation. Projections **15B** and **16B** depict semi-W transition states[22] which are produced by selective α'-proton abstraction along the bisector of the oxygen–sulfur–oxygen bond angle (see **15A** and **16A**) and rotation about the C–S bond of the halogenated carbon (rotation about the carbanion–sulfur bond is restricted as discussed above). In **15B** and **16B** the orientation of the carbanion bonding orbital sphere is ideal for intramolecular 1,3 displacement of chloride ion. These stereochemical and conformational considerations are in substantial agreement with the previously indicated conformational requirement for the Ramberg–Bäcklund reaction[3c,23] and with recent data concerning the cyclization of γ-halo sulfones in base.[24] The illustrated conversion of **15** to cis-episulfone and **16** to trans-episulfone (Scheme III) thus constitutes an example of double inversion.[24d]

In view of the fact that proton abstraction (H$_c$) from **15** and concomitant rehybridization of the α'-sulfonyl carbanion atom does not result in an enhancement of steric compression such as that seen in loss of H$_t$ from **16**, the steady-state concentration of **15A** can be expected to exceed that of **16A**. Since proton removal is known to be rapid and reversible in alkaline aqueous media,[5,23] this ratio will be held constant by the reprotonation steps. Under conditions of irreversible proton abstraction (e.g., phenyllithium in xylene), the ease of interconvertibility of **15A** and **16A** will be substantially decreased and will depend in great part on the barrier to rotation separating the two isomeric, asymmetric carbanions.

Rotation of the proximate carbon in **15A** needed to attain the semi-W conformation necessitates that the R substituent pass across the face of H$_t$ (lowest energy pathway) while in **16A** the same substituent must rotate by R' (or alternatively by the SO$_2$ group). Thus the rate of formation of **15B** can be expected to be faster than that of **16B**. Since the rate constants associated with K_c and K_c' have already been considered to be of

(22) For the definition of this term, see A. Nickon and N. H. Werstiuk, *J. Am. Chem. Soc.*, **89**, 3914 (1967).

(23) L. A. Paquette, *ibid.*, **86**, 4085 (1964).

(24) (a) S. J. Cristol, J. K. Harrington, and M. S. Singer, *ibid.*, **88**, 1529 (1966); (b) S. J. Cristol and B. B. Jarvis, *ibid.*, **88**, 3095 (1966); (c) S. J. Cristol and B. B. Jarvis, *ibid.*, **89**, 401 (1967).

(24d) NOTE ADDED IN PROOF. A similiar rationalization has been advanced recently: F. G. Bordwell, B. B. Jarvis, and P. W. R. Corfield, *ibid.*, **90**, 5298 (1968).

greater magnitude than those in the t series, it now follows that, even should k_2 exceed k_1 (anticipated) by some arbitrary but not excessively large factor, the over-all rate of formation of cis-episulfone will remain faster than that of the trans isomer because of favorable relative rate constants of the preequilibria.

In the particular case of α-chloroethyl ethyl sulfone (**3**), the ratio of cis- to trans-2-butene produced at 100° (Table III) denotes that the difference in energy of the two transition states at this temperature is 0.97 kcal/mol.[25] When this value is compared to the measured enthalpy of the rearrangement process (27.4 kcal/mol, Table II), it follows that the observed product composition reflects a small difference in energy. Similar calculations for the remaining isomeric olefin ratios listed in Table III reveal that the differences in free energies of activation of the competing reactions which lead to the respective cis- and trans-episulfones differ by 0.10–0.72 kcal/mol. Therefore, the magnitude of the "cis effect"[5b] is not great.

Comparison of the rates of rearrangement of isomeric pairs **4:5** and **6:7** (Table I) has shown that chloride ion is released more rapidly when attached to the less bulky alkyl chain. These results correlated well with the above carbanion model in which the larger group is seen to be less subject to nonbonded interactions when attached to sp^2-hybridized carbon. This lesser steric compression will become most significant as the transition states leading from **15B** and **16B** are approached, with less steric strain resulting when R' > R as compared to when R > R'. Also, in those examples wherein the more bulky alkyl substituent is situated on the halogen-bearing carbon, a proportionate decrease in the ease of chloride displacement can be expected.

The present results also show that a higher percentage of the cis olefin is formed consistently when the halogen is attached to the larger alkyl residue of an isomeric α-halo sulfone pair (Table III). These data are consistent with the concept that the greater nonbonded interactions operating when R > R' will increase the rotational barrier involved in proceeding from **16A** to semi-W transition state **16B**, the precursor to the trans olefins. Since a similar effect will not be experienced in the C$_\alpha$–S bond rotation connecting **15A** and **15B**, an increase in the amount of cis olefin is not unexpected.

Finally, the percentage of cis olefin is seen to diminish as the size of the substituent groups increase. This decrease in the cis:trans ratio can be construed as a reflection of the increase in resistance to formation of cis episulfone as the effective bulk of R and R' is increased with the result that k_2 is able to compete more effectively with k_1. The trans olefin does not yet predominate in the case of 7 (R = CH$_3$; R' = CH(CH$_3$)$_2$) presumably because the unfavorable rate constant associated with the **16A:16B** interconversion serves to retard also the production of trans episulfone.

Experimental Section

Physical Data. Melting points are corrected and boiling points are uncorrected. The microanalyses were performed by the Scan-

(25) Determined from the equation $\Delta\Delta F^{\ddagger} = -2.3\ RT \log (k_{cis}/k_{trans})$ [E. L. Eliel, "Stereochemistry of Carbon Compounds," McGraw-Hill Book Co., Inc., New York, N. Y., 1962, pp 238–239]. Since the yields of each olefin are proportional to the rates of their formation, k_{cis}/k_{trans} = % cis/% trans.

dinavian Microanalytical Laboratory, Herlev, Denmark. Infrared spectra were determined with a Perkin-Elmer Model 237 spectrometer fitted with sodium chloride prisms. Ultraviolet spectra were recorded with a Cary Model 14 spectrometer. The nmr spectra were determined with a Varian A-60 spectrometer purchased with funds made available through the National Science Foundation. Percentage compositions from vpc analyses refer to calibrated relative areas observed for the different components.

General Procedure for the Preparation of α-Chloro Sulfones. The requisite α-chloro sulfides were prepared by condensation of the appropriate mercaptans and aldehydes in the presence of hydrogen chloride. The procedure used has been adequately described by Neureiter[3b] and by Böhme.[26] The crude α-chloro sulfides were not purified, but were immediately oxidized to the corresponding sulfones. This conversion was achieved by dropwise addition of an ethereal solution of the α-chloro sulfide to a stirred solution of 2.5 molar equiv of monoperphthalic acid in ether at 0°. After the addition was complete, the reaction mixture was allowed to stir overnight at ambient temperature. Filtration of the insoluble phthalic acid gave the crude sulfone in ethereal solution. To remove dissolved phthalic acid, this solution was washed first with a saturated sodium bicarbonate solution and then with water. The ethereal layer was separated, dried, and evaporated *in vacuo* to give the crude α-chloro sulfones as colorless liquids. Fractional distillation of the crude product and recrystallization of the distillate from ether–pentane at −78° afforded pure sulfones. These were distilled one or two more times to ensure the absence of solvent. In all cases the compounds were obtained in a purity greater than 99% as determined by vpc.

α-Chloroethyl Ethyl Sulfone (3). From 9.7 g (0.20 mol) of paraformaldehyde and 12.4 g (0.20 mol) of ethyl mercaptan, followed by oxidation of the crude α-chloro sulfide with 0.5 mol of monoperphthalic acid, there was obtained 11.0 g (35%) of **3** after one fractional distillation, bp 68–72° (0.45 mm). Pure **3** was obtained as a colorless oil: bp 75° (1.0 mm); n^{20}D 1.4724 (lit.[3b] bp 64–65° (0.5 mm); n^{20}D 1.4723); λ_{max}^{neat} 7.60 and 8.80 μ (−SO₂−); $\delta_{TMS}^{CDCl_3}$ 1.40 (3 H, triplet, J = 7.5 Hz, −CH₂CH_3), 1.92 (3 H, doublet, J = 7.0 Hz, −CHClCH_3), 3.26 (2 H, quartet, J = 7.5 Hz, −SO₂CH_2−), and 4.98 (1 H, quartet, J = 7.0 Hz, −SO₂CHCl−).

α-Chlorobutyl Ethyl Sulfone (4). From 15.9 g (0.22 mol) of *n*-butyraldehyde and 12.4 g (0.20 mol) of ethyl mercaptan, there was obtained 15.0 g (41%) of pure **4**; bp 85–85.5° (0.45 mm); n^{26}D 1.4682; λ_{max}^{neat} 7.58 and 8.77 μ (−SO₂−); $\delta_{TMS}^{CDCl_3}$ 0.8–2.5 (10 H, triplet, J = 7.2 Hz, overlapping multiplet), 3.27 (2 H, quartet, J = 7.2 Hz, −SO₂CH_2−), 4.6–4.9 (1 H, multiplet, −SO₂CHCl−).

Anal. Calcd for C₆H₁₃ClO₂S: C, 39.02; H, 7.13; Cl, 19.20. Found: C, 38.85; H, 7.01; Cl, 19.45.

n-Butyl α-Chloroethyl Sulfone (5). Reaction of 9.7 g (0.22 mol) of paraldehyde and 18.0 g (0.20 mol) of *n*-butyl mercaptan in the predescribed manner afforded 22.7 g (62%) of **5** as a colorless liquid; bp 74–75° (0.15 mm); n^{26}D 1.4669; λ_{max}^{neat} 7.57 and 8.80 μ (−SO₂−); $\delta_{TMS}^{CDCl_3}$ 0.8–2.1 (10 H, complex pattern), 3.2 (2 H, triplet, J = 7.5 Hz, −SO₂CH_2−), and 4.86 (1 H, quartet, J = 7.1 Hz, −SO₂CHCl−).

Anal. Calcd for C₆H₁₃ClO₂S: C, 39.02; H, 7.13; Cl, 19.20. Found: C, 39.16; H, 6.91; Cl, 19.24.

α-Chloroisobutyl Ethyl Sulfone (6). Reaction of 12.4 g (0.20 mol) of ethyl mercaptan and 15.9 g (0.22 mol) of isobutyraldehyde afforded 18.0 g (49%) of **6** as a colorless oil: bp 79–80° (0.5 mm); n^{26}D 1.4709; λ_{max}^{neat} 7.58 and 8.75 μ (−SO₂−); $\delta_{TMS}^{CDCl_3}$ 1.17 (6 H, doublet, J = 7.0 Hz, (CH_3)₂CH−), 1.38 (3 H, triplet, J = 7.5 Hz, CH_3−CH₂−), 2.5–3.1 (1 H, multiplet, (CH₃)₂CH−), 3.21 (2 H, quartet, J = 7.5 Hz, −SO₂CH_2CH₃), and 4.69 (1 H, doublet, J = 3.4 Hz, −CHClSO₂−).

Anal. Calcd for C₆H₁₃ClO₂S: C, 39.02; H, 7.13; Cl, 19.20. Found: C, 38.99; H, 7.05; Cl, 19.38.

α-Chloroethyl Isobutyl Sulfone (7). From 5.3 g (0.12 mol) of paraldehyde and 9.0 g (0.10 mol) of isobutyl mercaptan, there was obtained 12.3 g (67%) of **7** as a colorless oil; bp 83–84° (0.6 mm); n^{25}D 1.4653; λ_{max}^{neat} 7.63 and 8.78 μ (−SO₂−); $\delta_{TMS}^{CDCl_3}$ 1.08 (6 H, doublet, J = 7.1 Hz, (CH_3)₂CH−), 1.81 (3 H, doublet, J = 7.0 Hz, −CHClCH_3), 1.9–2.7 (1 H, multiplet, (CH₃)₂CH−), 3.09 (2 H, doublet, J = 6.5 Hz, −SO₂CH_2−), and 4.80 (1 H, quartet, J = 7.0 Hz, −CHClCH₃).

Anal. Calcd for C₆H₁₃ClO₂S: C, 39.02; H, 7.13; Cl, 19.20. Found: C, 39.04; H, 7.06; Cl, 19.55.

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(26) (a) H. Böhme, H. Fischer, and R. Frank, *Ann.*, **563**, 54 (1949); (b) H. Böhme and H.-J. Cran, *ibid.*, **581**, 133 (1963); (c) H. Böhme, *Ber.*, **69B**, 1610 (1936).

Rate Studies

Reagents. Pure dioxane was prepared by refluxing commercial reagent grade dioxane over sodium metal for 24 hr followed by fractional distillation at atmospheric pressure. A stock solution of 1.26 N aqueous sodium hydroxide, 30% dioxane by volume, was prepared as follows. Reagent grade sodium hydroxide, 51 g, was dissolved in 600 ml of double-distilled water.[27] This solution was quantitatively transferred to a 1-l. volumetric flask, 300 ml of purified dioxane added, and the solution diluted to the mark with water (after cooling to 20°). The alkaline stock solution was stored in a tightly stoppered plastic bottle. Before each kinetic run this solution was restandardized to ensure reproducibility by titration of a 1.997-ml aliquot with standard 0.01 N hydrochloric acid solution. Over all kinetic runs the aliquot consumed 25.10 ± 0.04 ml of 0.1004 N hydrochloric acid solution. A 1.3 M nitric acid solution was prepared by appropriate dilution of commercial reagent grade concentrated nitric acid.

Equipment and Glassware. All reactions were carried out in a well-stirred thermostated bath held at the desired temperature. Titrations were carried out with a calibrated (water) 10-ml (tolerance ± 0.01 ml) gravity-filling buret. Aliquots were taken with calibrated (water) pipets.

Kinetic Procedure. An approximately 0.03 M solution of each sulfone (accurately weighed) in the 1.26 N aqueous sodium hydroxide–30% dioxane (v/v) solution was prepared in a 50-ml volumetric flask. Analytically pure sulfones were used throughout the experiments (product studies included). Aliquots of this solution slightly in excess of 2.5 ml were removed with a syringe and introduced into glass ampoules. The ampoules were sealed and placed in the kinetic bath. After thermal equilibrium was attained (10–15 min), two ampoules were withdrawn for the zero point, quenched in ice water, and then placed in a beaker of water adjusted to the temperature at which a pipet was calibrated (±0.5). Each ampoule was broken open, and exactly 1.997 ml of solution was removed. The aliquot was run into a 50-ml beaker which contained 5 ml of water, *ca.* 1.5 ml of 1.3 M nitric acid solution, and two drops of 1% phenolphthalein. To effect an end point (colorless), additional 1.3 M nitric acid solution was added dropwise (pH 6–7). Enough water was then added to bring the total volume to 10 ml. The chloride ion content of this solution was measured by a potentiometric titration with standard silver nitrate solution as follows. Addition of silver nitrate solution from a 10-ml gravity-filling buret was done in a dropwise manner to the stirred solution. The end point was detected with a Model 94-17 chloride ion electrode (Orion Research, Inc., Cambridge, Mass.) immersed in the sample solution and connected to a standard calomel reference electrode by a 0.3 M potassium sulfate–4% agar salt bridge. One side of the bridge was immersed in the sample solution and the other in a 0.3 M potassium sulfate solution. The reference electrode was also immersed in the 0.3 M potassium sulfate solution to complete the circuit. The end point was determined by observation of the

(27) Whenever "water" is referred to subsequently in this section, double-distilled water is to be assumed.

change in millivolts (ΔE) on a Beckman Model G pH meter (set up for a millivolt scale) with the change in volume of silver nitrate solution added (ΔV). A plot of $\Delta E/\Delta V$ vs. milliliters of solution added yielded the stoichiometric point where chloride ion concentration was nil. The remaining ampoules were removed at appropriately timed intervals, immediately quenched in ice water, and titrated as previously described. All titrations were corrected according to a calibration curve prepared in the same manner as sample solutions, but with known amounts of chloride ion present. Rates were followed up to two half-lives (eight to ten points per run). All rates are determined from calculated infinity points because infinity titers were found to be unreliable for reasons discussed in the text. The data in Tables II and III reflect least-squares solutions of the data.

Product Studies

General Procedure for Product Studies in Aqueous Sodium Hydroxide Solution. In a typical experiment n-butyl α-chloroethyl sulfone (5), 1.85 g (10 mmol), was placed in a 100-ml reaction flask fitted with a magnetic stirrer, nitrogen gas inlet tube, and 3-in. Vigreux column atop of which was a Bantamware distillation head. To the sulfone was added in one portion 60 ml of 2 N sodium hydroxide solution (120 mmol). The reaction mixture was slowly warmed to a gentle reflux (vigorous stirring), and the volatile product was carried over by a slow (one to three bubbles per sec) nitrogen stream into a pear-shaped flask (surrounded by a Dry Ice–acetone bath) attached to the distillation head. After 2.5 hr the contents of the receiver were removed, accurately weighed (0.48 g), and checked by vpc[28] at ambient temperature. Again at 4.5 (0.15 g) and 6.0 hr (<0.01 g) the volatile product was removed, weighed, and checked by vpc. Reactions were generally allowed to proceed 0.5–1 hr beyond the point where no additional product was observed. The total weight of olefin in this case was 0.62 g or 74% yield. Only the isomeric cis- and trans-2-hexenes were produced. The olefins were readily identified by comparison of retention times with authentic samples[29] and by peak enhancement. Infrared and nmr spectra of isolated samples confirmed the structural assignments.

The other sulfones were rearranged in identical fashion. Analysis of the isomeric 4-methyl-2-pentene mixture was accomplished with a 100 ft × 0.020 in. stainless steel coated open tubular column prepared with squalene liquid phase.[30] All of the product

studies were performed in duplicate and yields and product ratios are the average of at least two runs.

In the case of **6**, ether extraction of the neutralized spent reaction mixture gave 260 mg (24%) of the known methyl ethyl sulfone (**10**) as colorless needles, mp 34–36°.

General Procedure for Product Studies in Xylene–Phenyllithium. In a typical experiment α-chlorobutyl ethyl sulfone (**4**), 1.85 g (10 mmol), was transferred into a 100-ml reaction flask fitted with magnetic stirrer, syringe cap, nitrogen gas inlet tube, and 3-in. Vigreux column atop of which was a Bantamware distillation head. To the reaction vessel was added 25 ml of dry, purified xylene, and the solution which resulted was warmed to 100°. A total of 10.5 ml (22 mmol) of a 2.11 M solution of phenyllithium (in benzene–ether (70: 30%)) was added dropwise from a syringe with vigorous stirring. The immediate formation of a white precipitate was noted. Upon completion of the addition (20 min), the reaction mixture was warmed to 120°, and the volatile products were carried over by a slow nitrogen stream into a pear-shaped flask (surrounded by a Dry Ice–acetone bath) attached to the distillation head. After 20 min ($t = 0$ at completion of addition) the contents of the receiver were removed, accurately weighed (1.90 g), and checked by vpc.[28] Again at 45 (0.40 g) and 75 min (0.1 g) the volatile product was removed, weighed, and checked by vpc. Reactions were generally allowed to proceed 0.5–1 hr beyond the point where no additional olefin product was observed. Benzene contaminated these later fractions, but was no problem as long as the more volatile products were present. Because of the presence of ether in the distillates, yields were estimated from knowledge of ether to olefin ratios and the respective total weights. Olefin compositions were determined in the same manner as described above. No other products were detected in any case, either in the distillates or in the spent reaction mixtures. All of the product studies were done in at least duplicate.

To test the solubility of the olefins under the reaction conditions, a known mixture of cis- and trans-2-hexene was slowly added below the surface of a stirred solution of xylene heated to 120° under comparable conditions. A 75% recovery of the olefin mixture (same ratio as introduced) was realized. These results could be duplicated, and yields in Table IV have been increased by 25% to reflect the loss. Since the base was never present in excess, the olefins were not checked for possible isomerization by phenyllithium under the reaction conditions.

(28) A 22 ft × 0.25 in. aluminum column packed with 15% β,β'-oxidipropionitrile on Chromosorb P was employed in conjunction with an Aerograph A90-P3 gas chromatographic unit.

(29) We are indebted to Dr. Kenneth Grennlee for generous samples of these isomerically pure hydrocarbons.

(30) We thank Dr. D. Slater for the use of his Perkin-Elmer F-11 flame ionization gas chromatograph and attendant hardware.