but there is no experimental evidence for this mechanism. In contrast the analogous reactions which lead to MnO_3F and CrO_2F_2 are very rapid at room temperature and strongly exothermic.

Occasionally the fluorosulfate is stable enough to distil from the reaction mixture without decomposition. Thus in the reaction of As_2O_5 with HSO_3F, in addition to AsF_5, and probably also $AsOF_3$, varying amounts of $AsF_2(SO_3F)_3$ and $AsF_3(SO_3F)_2$ are obtained.[37] From BaH_4TeO_6 the fluorosulfate F_5TeOSO_2F is obtained in very good yield.[38] Alkali and alkaline earth chlorides and fluorides are converted to the corresponding fluorosulfates when dissolved in fluorosulfuric acid, and the pure salts can be obtained by removal of HCl or HF and excess HSO_3F.[39,40] Dinitrogen trioxide and dinitrogen pentoxide yield nitronium fluorosulfate and nitrosyl fluorosulfate, respectively, on reaction with fluorosulfuric acid.[41,42] Nitrosyl fluorosulfate has also been prepared by allowing fluorosulfuric acid to react with nitrosyl chloride.[43]

(37) E. Hayek, A. Aigensberger, and A. Engelbrecht, *Monatsh. Chem.*, **86**, 735 (1955).
(38) A. Engelbrecht and F. Sladky, *ibid.*, **96**, 159 (1965).
(39) O. Ruff, *Ber.*, **47**, 656 (1914).
(40) W. Traube, J. Hoerenz, and F. Wunderlich, *ibid.*, **52B**, 1272 (1919).
(41) W. Lange, *ibid.*, **60B**, 967 (1927).
(42) D. R. Goddard, E. D. Hughes, and C. K. Ingold, *J. Chem. Soc.*, 2559 (1950).
(43) A. A. Woolf, *J. Chem. Soc.*, 1053 (1950).

The Base-Induced Rearrangement of α-Halo Sulfones

LEO A. PAQUETTE

Department of Chemistry, The Ohio State University, Columbus, Ohio

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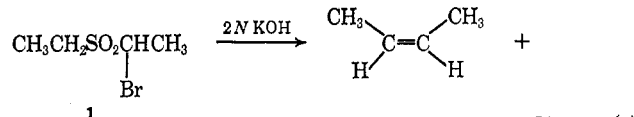
The hydroxide ion promoted rearrangements of α-chloro, α,α-dichloro, and α,α,α-trichloro sulfones are discussed. The reactions are shown to proceed by means of initial α′-sulfonyl carbanion formation and 1,3 elimination of chloride ion, most probably *via* semi-W transition states. The mechanism by which α-chloro sulfones are converted predominantly to the less stable *cis*-alkenes is discussed in some detail. Episulfones are formed in each instance, and such three-membered heterocycles (whether of *cis* or *trans* stereochemistry) decompose stereospecifically to olefins under the customary reaction conditions unless endowed with particularly acidic protons; the rates of formation of the isomeric episulfones are considered to be controlled by the relative rates of various preequilibria as well as by those of intramolecular displacement. The rearrangement of related dichloro sulfones proceeds to a substantial extent by way of thiirene dioxide intermediates, unless structural considerations disallow elimination of a second molecule of HCl. α,α,α-Trichloro sulfones behave similarly and give rise in certain instances to chlorothiirene dioxide derivatives. Such strained and reactive tetravalent sulfur-containing molecules are not stable to the reaction conditions and yield a variety of products. Application of the electrocyclic selection rules to the decomposition of episulfones and thiirene dioxides predicts a nonconcerted thermal expulsion of SO_2. A tentative explanation is advanced to reconcile such apparent nonconcertedness with the specificity of alkene formation from episulfones.

The marked resistance of α-halo sulfones to *intermolecular* nucleophilic substitution reactions has been well documented over the years[1] and has been the subject of considerable speculation. In 1940, however, Ramberg and Bäcklund[2a] reported on their discovery that α-bromoethyl ethyl sulfone (**1**) and several related α-halo sulfones readily released halide ion when treated with 2 *N* KOH and were converted in good yield to alkenes, the *cis* isomers of which predominated.

(1) (a) F. Raschig and W. Prahl, *Ann.*, **448**, 307 (1926); (b) T. Thomson and T. S. Stevens, *J. Chem. Soc.*, 69 (1932); (c) W. M. Ziegler and R. Connor, *J. Am. Chem. Soc.*, **62**, 2596 (1940); (d) T. B. Johnson and I. B. Douglass, *ibid.*, **63**, 1571 (1941); (e) F. G. Bordwell and G. D. Cooper, *ibid.*, **73**, 5184 (1951); (f) note however, the recent report of F. G. Bordwell and B. B. Jarvis, *J. Org. Chem.*, **33**, 1182 (1968).
(2) (a) L. Ramberg and B. Bäcklund, *Arkiv. Kemi Mineral. Geol.*, **13A**, No. 27 (1940); *Chem. Abstr.*, **34**, 4725 (1940); (b) F. G. Bordwell and G. D. Cooper, *J. Am. Chem. Soc.*, **73**, 5187 (1951).

Although such contrasting facile displacements of halide ion are of obvious mechanistic interest, further work

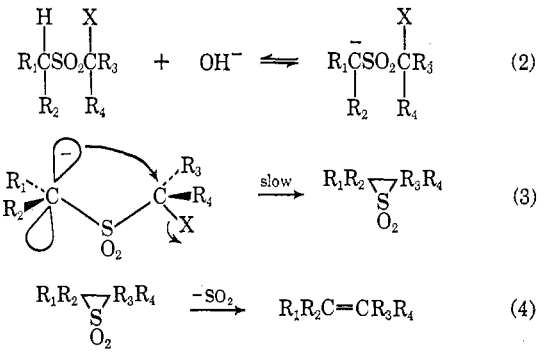


1

$$KBr + K_2SO_3 \quad (1)$$

on this rearrangement did not appear again until 1951. At this time, Bordwell and Cooper[2b] set forth data that permitted them to propose a mechanism for alkene formation. On the basis of the fact that the rate of release of halide ion from an α-halo sulfone is first order in both hydroxide ion and sulfone, these workers proposed the reaction scheme given by eq 2–4.

Albeit this mechanism did explain in a qualitative



(2)

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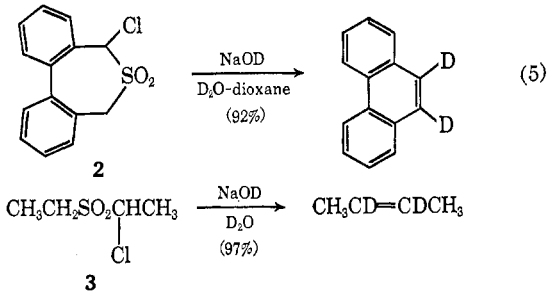
(4)

way the manner of C=C formation and SO_2 expulsion, a great many questions remained to be answered, and in 1962 we set out to enrich our understanding of this intriguing molecular reorganization, to determine the scope of the α-halo sulfone rearrangement, and to examine possible synthetic applications of the reaction. In the intervening years since our initial investigations began, independent work has been published by several research groups. It shall be my purpose in this account to include also the relevant results of my colleagues in order that proper perspective of the progress to date be made available to the reader.

Evidence for Reversible Carbanion Formation. Evidence from a number of sources supports the rapid preequilibrium of the α-halo sulfone with all of its possible carbanions (eq 2). For example, reaction of **2** or **3** with NaOD in D_2O was found to give olefins which were essentially completely deuterated at the vinyl positions.[3,4] The possibility that exchange was taking place at a later stage of the reaction, for example, with

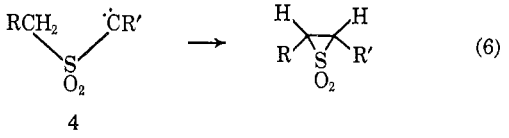


(5)

the thiirane 1,1-dioxide (episulfone) intermediate (see below), was ruled out by treating α-bromobenzyl benzyl sulfone with $NaOCH_3$ in CH_3OD and allowing the reaction to proceed for one half-life. The recovered α-bromo sulfone showed complete deuterium exchange at the α and α' positions.[5]

Establishment of the intervention of carbanions in a preequilibrium does not, however, conclusively establish that a carbanion is necessarily on the reaction pathway leading to the observed olefins.[6] Three alternative reasonable mechanisms can be advanced in explanation of the cyclization step (eq 3).[3] The first of these would involve concerted proton removal and halide ion loss in the transition state leading to the episulfone intermediate. However, the unusually large leaving group effect observed, for example, with $C_6H_5CH_2SO_2CHXC_6H_5$ (Br:Cl rate ratio = 620 at 0°)[5] can be better rationalized in terms of a carbanion mechanism. The Br:Cl rate ratio in concerted 1,2 eliminations lies in the range of (40–80):1.

The second possible alternative involves the generation of an α-sulfonyl carbene (**4**) which goes over to the episulfone intermediate by insertion into the C–H



(6)

4

bond of the α'-methylene group. However, such a mechanistic sequence can be ruled out because (a) α,α-dichloro and α,α,α-trichloro sulfones, systems which are incapable of forming carbenes, readily undergo base-induced rearrangements (see below),[7–11] (b) α-

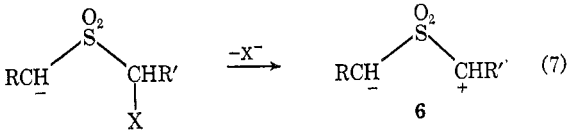
$ClCH_2SO_2R$

5a, R = C_6H_5

b, R = $C(CH_3)_3$

chloro sulfones such as **5a** and **5b** which are capable of α elimination but not of 1,3 elimination give no adducts derivable from carbenoid intermediates and, in fact, lose chloride ion only very slowly,[3,5] and (c) substitution of an α-phenyl group causes rate acceleration[2b] whereas its inductive effect should retard the rate of α elimination.

A third possible mechanism involves zwitterions such as **6**. However, the formation of such dipolar



(7)

6

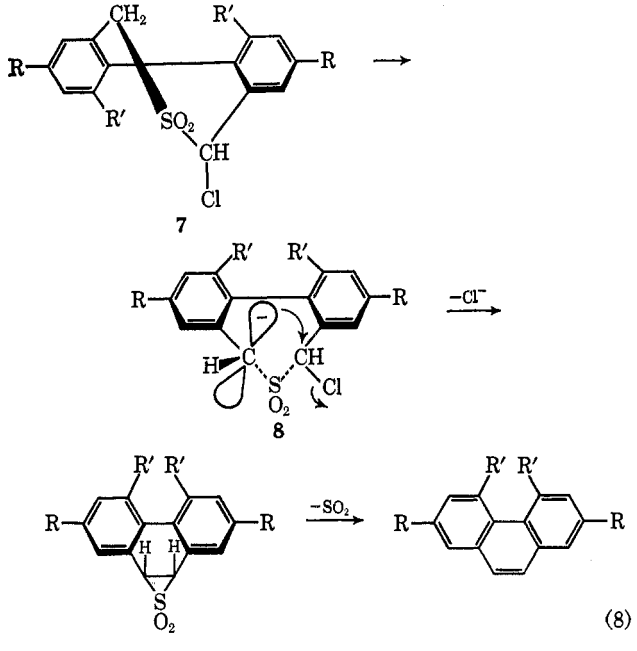
intermediates can be anticipated to be very energetically unfavorable due to the strong electrostatic repulsion associated with the proximity of positive centers. The free energies of activation in such cases are predicted to be too high for bond heterolysis to occur readily.

Therefore, the existing data are best in accord with the view that discrete carbanions are involved in the cyclization step.

Steric Requirements of the 1,3-Elimination Reaction. From the outset of our investigations, we were particularly struck by the fact that, despite the success of the rearrangement in the acyclic systems examined to that time, this reaction had given poor results when applied

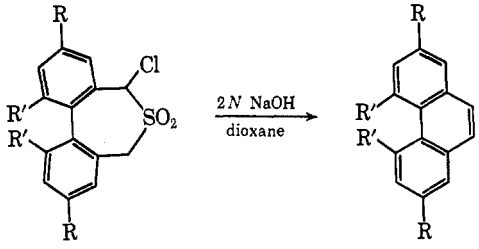
(3) L. A. Paquette, *J. Am. Chem. Soc.*, **86**, 4085 (1964).
(4) N. P. Neureiter and F. G. Bordwell, *ibid.*, **85**, 1209 (1963); N. P. Neureiter, *ibid.*, **88**, 558 (1966).
(5) F. G. Bordwell and J. M. Williams, Jr., *ibid.*, **90**, 435 (1968).
(6) R. Breslow, *Tetrahedron Letters*, 399 (1964).
(7) L. A. Paquette, *J. Am. Chem. Soc.*, **86**, 4089 (1964).
(8) L. A. Paquette and L. S. Wittenbrook, *Chem. Commun.*, 471 (1966).
(9) L. A. Paquette and L. S. Wittenbrook, *J. Am. Chem. Soc.*, **89**, 4483 (1967).
(10) L. A. Paquette, L. S. Wittenbrook, and V. V. Kane, *ibid.*, **89**, 4487 (1967).
(11) L. A. Paquette and L. S. Wittenbrook, unpublished observations.

to two cyclic α-halo sulfones.[12,13] We reasoned that the highly favorable geometry for SN2 displacement of halide ion available to aliphatic sulfones because of rotational freedom might perhaps be more difficult to achieve in the more conformationally fixed cyclic sulfones. In other words, the α′-sulfonyl carbanion of eq 3 was believed to exhibit a conformational requirement. To derive information on this point, the 2-chloro-2,7-dihydro-3,4:5,6-dibenzothiepin 1,1-dioxide system (**7**) was selected for study because of its inherently suitable geometry for facile intramolecular 1,3 elimination.[3] While the most strain-free conformation of this molecule is one in which the biphenyl moiety is considerably distorted from planarity, *viz.*, **7**, a quasi-stable conformation (**8**) is attainable in which all six carbon atoms of the heterocyclic seven-membered ring are mutually coplanar and the sulfone group is bent below (or above) this plane. In **8**, the conformation of the carbanion bonding-orbital sphere is ideally oriented for the intramolecular 1,3 displacement of chloride *via* a semi-W[14] transition state. Furthermore,



(8)

the large negative field of the sulfonyl oxygens[15] is adequately removed from the site of displacement because of the strict steric requirement which forces the sulfone group to the underside of the molecule. Evidently, formation of an episulfone intermediate at any stage of the rearrangement of **7** necessitates for conformational reasons that the two benzene rings become coplanar. Placement of methyl groups at the R′ positions in **7** should effectively prohibit the attainment of coplanarity in the molecule because of the resulting large degree of steric crowding; the α′-sulfonyl carbanion in such a situation will not be capable of adopting the requisite semi-W conformation, and episulfone formation should be disallowed. The successful conversion of **9a** and **9b** to the respective phenanthrenes and the failure of **9c** to rearrange even after prolonged (5 days) heating (**9c** was recovered intact) are entirely consistent with the concepts of a conformational requirement and the intermediacy of episulfone intermediates.[3,16]



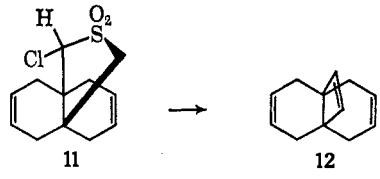
(9)

9a, R = R′ = H
b, R = CH_3; R′ = H
c, R = H; R′ = CH_3

10a, R = R′ = H (96%)
b, R = CH_3; R′ = H (92%)

More recently, Cristol and coworkers have shown convincingly that the formation of cyclopropyl sulfones by cyclization of γ-halo sulfones in base can occur only when the semi-W transition state is attainable.[17] It seems clear, then, that alkali-induced 1,3 eliminations involving sulfonyl groups proceed stepwise and result in displacement of the leaving group with inversion.

A later objective was to examine the effect of solvation on the ease of cyclization, and chloro sulfone **11** has been examined briefly in this regard.[18] Treatment of **11** with 2 *N* NaOH in aqueous dioxane at reflux for 4 days led to the almost complete recovery of starting



(10)

material. The formation of α-sulfonyl carbanions under these conditions was established by employing D_2O and isolating the trideuterated congener of **11** in high yield. By contrast, when **11** was treated with powdered potassium *t*-butoxide in dry tetrahydrofuran at 0° for 5 hr, the derived cyclobutene **12** was produced in 54% yield. The failure of the α-halo sulfone rearrangement in aqueous dioxane may be caused by strong hydrogen bonding to the carbanionic centers under these conditions which prevents attainment of the requisite geometry for intramolecular SN2 displacement. Not unsurprisingly, therefore, both base

(12) T. Bacchetti and A. G. Arnaboldi, *Atti Accad. Nazl. Lincei Mem Rend. Classe Sci. Fis. Mat. Nat.*, **15**, 75 (1953); *Chem. Abstr.*, **49**, 2301 (1955).

(13) I. Mischon, Ph.D. Thesis, Technische Hochschule zu Karlsruhe, Germany, 1955.

(14) A. Nickon and N. H. Werstiuk, *J. Am. Chem. Soc.*, **89**, 3914 (1967).

(15) C. Y. Meyers, *Tetrahedron Letters*, 1125 (1962).

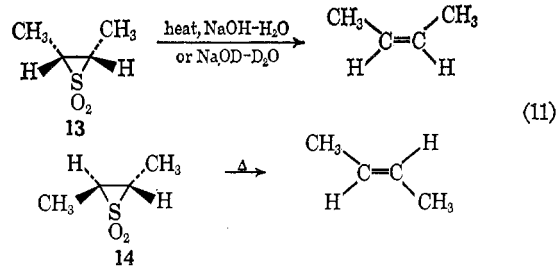
(16) A 1,6 elimination to give a 3,4:5,6-dibenzothiepin 1,1-dioxide intermediate would also require eclipsing of the R′ groups and therefore may be considered plausible. However, such a pathway requires rupture of the aromatic sextet in both benzene rings and thus must be associated with a very high activation energy. For this reason, we have dismissed the likelihood of its intervention in the rearrangements of **9a** and **9b**.

(17) (a) S. J. Cristol, J. K. Harrington, and M. S. Singer, *J. Am. Chem. Soc.*, **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).

(18) L. A. Paquette and J. C. Philips, *Tetrahedron Letters*, 4645 (1967).

and solvent play central positions in the practical applications of this rearrangement.

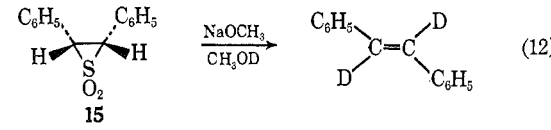
Stereochemical Factors Involved in Episulfone Formation and Decomposition. If a step subsequent to carbanion formation is in fact rate determining (eq 3), a halogen element effect is to be expected, and such has been observed.[4,5] Unfortunately, however, the alkaline conditions needed for rearrangement are sufficiently strenuous that decomposition of intermediate episulfones occurs concomitantly. Although the preparation of such three-membered heterocycles by this method is precluded, methods have been developed for the synthesis of both symmetrical and unsymmetrical thiirane 1,1-dioxides. The opportunity to examine the stereochemical consequences of eq 4 is therefore available. Episulfones decompose near room temperature to eliminate SO_2 and produce isomerically pure alkenes in stereospecific fashion (eq 11). The rate of decomposition is apparently accelerated by base. When pure **13** was heated either neat, dissolved in an organic



13 **14** (11)

solvent, or with 2 *N* NaOH solution, for example, *cis*-2-butene contaminated with less than 0.5% of the *trans* isomer was the only organic product. Decomposition of **13** in D_2O solvent with NaOD as base again gave *cis*-2-butene with only 5% of the two vinyl protons replaced by deuterium.[4] The resistance of **13** to carbanion formation under these conditions is perhaps a function of the geometry and hybridization imposed on the external C–H bonds by the three-membered ring[19] and is to be compared with the ease of α-sulfonyl carbanion formation in **3** (eq 5). When the decomposition of **13** was performed with *t*-BuO$^-$K$^+$–*t*-BuOD, the 2-butene was predominantly the *trans* isomer and was essentially completely deuterated at the 2 and 3 positions. It appears therefore that, in the presence of strong base, episulfone **13** exchanges its α hydrogens more rapidly than it loses SO_2 and that, in the process of exchange, epimerization to an equilibrium mixture of *cis*- and *trans*-episulfones takes place. However, the stereochemical results do not conclusively establish that the *trans*-episulfone dominates the equilibrium because the position of such an equilibrium is completely irrelevant to the fate of either isomer. Rather, the amounts of *cis*- and *trans*-2-butenes formed in the subsequent step(s) are determined solely by the relative differences in stability of the transition states leading to olefins, assuming no equilibration of intermediate species later in the mechanistic sequence (control experiments established that simple olefins do not isomerize under the reaction conditions).

The behavior of episulfones in which the acidity of the α-sulfonyl protons is enhanced, as by phenyl substitution, *viz.* **15**, is similar, except that weaker base–



15 (12)

solvent systems can cause epimerization and deuterium exchange (eq 12).[20,21]

Clearly, therefore, since *cis*- and *trans*-episulfones are not interconverted under the usual reaction conditions, except perhaps in those few examples which possess unusually acidic α-sulfonyl protons, the stereochemical configuration of the olefinic product is determined in the second step of the rearrangement. This consideration brings us to one of the most intriguing aspects of the α-halo sulfone rearrangement: why does the cyclization exhibit a strong preference for formation of the *cis* isomer?

Evidently, the rate of release of chloride ion from a variety of α-chloro sulfones under pseudo-first-order conditions is not subject to dramatic change over a relatively wide range of alkyl substitution (Table I).[22] Although the *cis*-alkene predominates in all examples studied, this 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, a conclusion which is also borne out by the 2–4-fold rate variations. 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 our analysis of the available stereochemical data, we have relied on the concept that α-sulfonyl carbanions are effectively planar with a barrier to rotation.[23] Corey's experiments have also provided evidence establishing that α-sulfonyl carbanions are protonated from the direction *syn* to the sulfonyl oxygens.[23] For reasons of microscopic reversibility, therefore, it must be concluded that α-sulfonyl protons are preferentially abstracted by base when they are situated between the oxygen atoms of the sulfonyl group. In construct-

(19) Another possibility is that the rate of decomposition is faster than the rate of deuterium exchange under these conditions. Evidence to this effect has recently been obtained by Bordwell and his coworkers[5] with phenyl-substituted episulfones.

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

(21) N. Tokura, T. Nagai, and S. Matsumura, *J. Org. Chem.*, **31**, 349 (1966).

(22) L. A. Paquette and L. S. Wittenbrook, work in progress.

(23) (a) E. J. Corey, H. Konig, and T. H. Lowry, *Tetrahedron Letters*, 515 (1962); (a) E. J. Corey and T. H. Lowry, *ibid.*, 593 (1965); (c) E. J. Corey and T. H. Lowry, *ibid.*, 803 (1965); (d) for more recent supporting evidence, see F. G. Bordwell, D. D. Phillips, and J. M. Williams, Jr., *J. Am. Chem. Soc.*, **90**, 426 (1968).

Table I

Reaction of Various Sulfones with Hydroxide Ion.

Sulfone	k, sec^{-1} [a]	Product	% yield[b]	% *cis*	% *trans*
$CH_3CH_2SO_2CH(Cl)CH_3$ (**3**)	16.8×10^{-7}	2-Butene	75	78.8	21.2
$CH_3CH_2SO_2CH(Cl)CH_2CH_3$[c] (**16**)		2-Pentene	57	71.3	28.7
$CH_3CH(Cl)SO_2CH_2CH_2CH_3$[c] (**17**)		2-Pentene	74	65.8	34.2
$CH_3CH_2SO_2CH(Cl)(CH_2)_2CH_3$ (**18**)	8.0×10^{-7}	2-Hexene	61	69.4	30.6
$CH_3CH(Cl)SO_2(CH_2)_3CH_3$ (**19**)	20.5×10^{-7}	2-Hexene	76	66.2	33.8
$CH_3CH_2SO_2CH(Cl)CH(CH_3)_2$ (**20**)	3×10^{-7}	4-Methyl-2-pentene	61	59.4	40.6
$CH_3CH(Cl)SO_2CH_2CH(CH_3)_2$ (**21**)	16.0×10^{-7}	4-Methyl-2-pentene	70	51.0	49.0

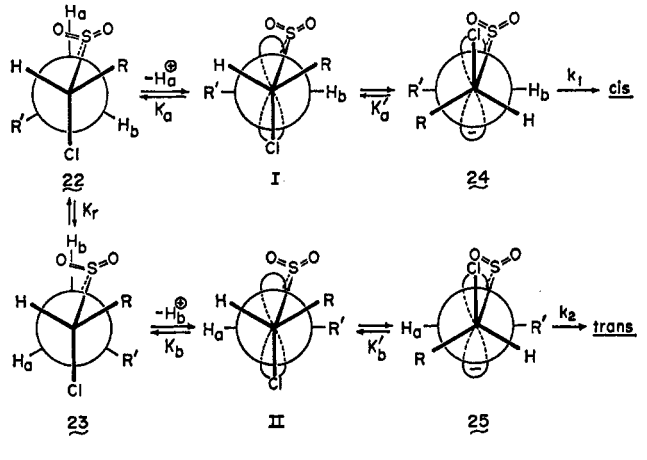
[a] In 30% dioxane–70% H_2O (v/v), 1.26 N in hydroxide ion at 50°.[22] [b] 2 N NaOH at 95–100°.[22] [c] Reference 4.

ing modified Newman projections (**22** and **23**[24]) of a typical α-chloro sulfone, we have adopted the entirely reasonable assumptions that the most stable conformations will be characterized by minimal alkyl–SO_2 and alkyl–alkyl interactions and that the C–S bonds exhibit "free" rotation. Projections **24** and **25** depict semi-W transition states which result from selective α′-proton abstraction and rotation around the C–S bond of the halogenated carbon (rotation around the carbanion–sulfur bond is known to be restricted).

Previously, preferential formation of *cis*-2,3-dialkyl episulfones has been explained on the basis of London attractive forces between R and R′ in the transition state;[4] alternatively, less steric inhibition to solvation in the *cis* transition state has been implicated.[25] Although these concepts are interesting, they do not satisfactorily explain all the data. We prefer the following interpretation.

Scheme I illustrates the major factors which are at

Scheme I



play in the conversion of a typical α-chloro sulfone to a mixture of alkenes.[22] Given that **22** is more stable than **23** because of the obvious difference in strain energies, it follows that this chemical entity will be of lower energy. In view of the fact that proton abstraction (H_a) from **22** and concomitant rehybridization of the α′-sulfonyl carbon atom does not result in an enhancement in steric compression of the type observed in the loss of H_b from **23**, some degree of steric rate retardation can be expected in the latter instance. Further, rotation of the proximate carbon in I needed to attain the semi-W conformation necessitates that the R substituent pass across the face of H_b (lowest energy pathway) while in II the same substituent must rotate by R′ (or alternatively by the SO_2 group); thus, the rate of formation of **24** can be expected to be faster than that of **25**. The over-all rates of formation of the isomeric episulfones may be derived as shown in eq 13,

$$k_{cis} = [\mathbf{22}]K_aK_a'k_1 \qquad k_{trans} = [\mathbf{23}]K_bK_b'k_2 \tag{13}$$

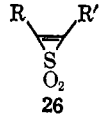
and it follows that the *cis*:*trans* rate ratio may be expressed as in eq 14. Since the rates associated with

$$\frac{d[cis]/dt}{d[trans]/dt} = \frac{K_rK_aK_a'k_1}{K_bK_b'k_2} = \mathbf{K}\frac{k_1}{k_2} \tag{14}$$

K_a and K_a' have already been considered to be of greater magnitude than those in the b series, it is now apparent that, even should k_2 exceed k_1 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 rates of the preequilibria.

The Curtin–Hammett principle which is based on transition-state theory points out that *product composition* is dependent not on the relative energies of the ground-state conformers but only on the relative energies of the respective transition states. The lower energy of the *cis*-episulfone transition state in reality reflects the easier path available to **22** for the reasons discussed above.

Rearrangements of α,α- and α,α′-Dihalo Sulfones. A study of the rearrangement of α,α-dichloro sulfones was initiated almost simultaneously in our laboratories. The early impetus for this work was the desire to develop an entry into the thiirene 1,1-dioxide system, *e.g.*, **26**, and to rule out the intervention of carbenoid



26

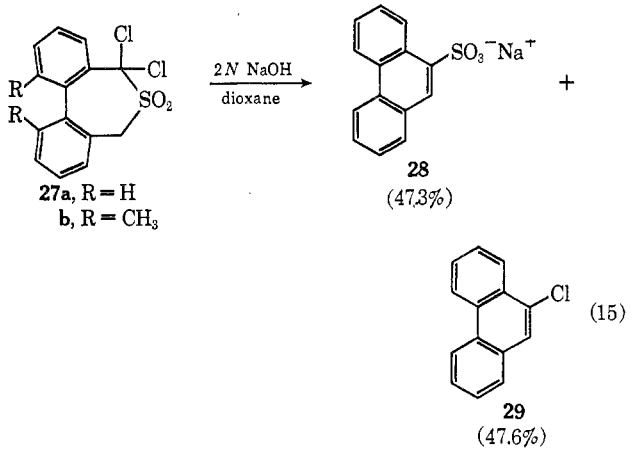
intermediates (see above). We were hopeful that such unsaturated three-membered-ring sulfones would be more stable than their saturated counterparts and per-

(24) 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 clarity. Structures **22** and **23** are constructed so as to minimize Cl–SO_2 dipole–dipole interactions.

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

haps be capable of isolation under the customary rearrangement conditions (not realized, as we shall see).

Initially, recourse was again made to the dibenzothiepin ring system.[7] Treatment of α,α-dichloro sulfone **27a** with 2 *N* NaOH in dioxane resulted in facile rearrangement to **28** and **29**. The identical result was observed starting with the α,α'-dichloro congener.[26] In contrast, **27b** was not rearranged even



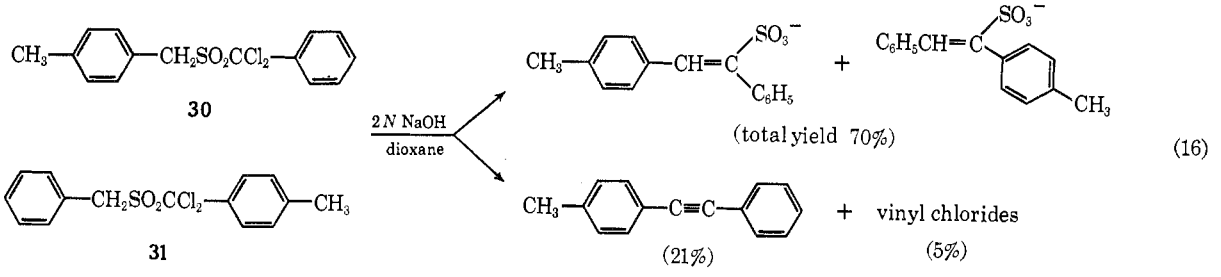
27a, R = H
b, R = CH_3

28 (47.3%)

29 (47.6%) (15)

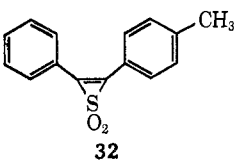
after prolonged exposure and could be recovered intact. Extrapolation of earlier argumentation[3] to these results led to the conclusion that such rearrangements proceed initially through chloro episulfone intermediates.[7]

Evidence which established that chloro episulfones



(16)

do undergo significant 1,2 elimination of HCl was derived from two sources. First, when dichloro sulfones **30** and **31** were rearranged with aqueous hydroxide ion, there resulted an identical mixture of products except, of course, for the isomeric vinyl halides.[9] The identity of the sulfonic acid composition and the product ratios in these examples virtually require that thiirene dioxide **32** be the common precursor formed during the rearrangement. Secondly, we have pre-



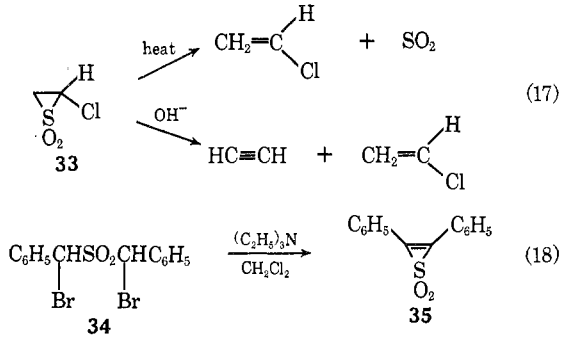
32

pared 2-chlorothiirane 1,1-dioxide (**33**), the parent chloro episulfone, and have observed that this substance is readily decomposed into SO_2 and vinyl chloride when heated.[10] When **33** was treated with aqueous hydroxide, vigorous evolution of acetylene and vinyl chloride resulted.[10] Since vinyl chloride was stable to such treatment, acetylene formation testifies to the likely intervention of thiirene dioxide.

Seemingly, therefore, the initial chloro episulfone intermediate may suffer either expulsion of SO_2 to give vinyl chlorides (stable under the reaction conditions) or base-induced loss of HCl. In the latter event, the resulting thiirene dioxides are subject either to loss of SO_2 (acetylenes result) or to conversion to vinylsulfonic acids. Alternative mechanisms for sulfonic acid formation have been eliminated from consideration.[10,27]

As with episulfone intermediates, it has not yet proven possible to isolate thiirene dioxides from rearrangements of the above type. However, Carpino and McAdams[28] have recently shown that α,α'-dibromodibenzyl sulfone (**34**) can be converted under "modified conditions" to the stable crystalline sulfone **35**. The isolation of **35** as well as its smooth thermal conversion into diphenylacetylene and transformation in the presence of hydroxide ion into 1,2-diphenylethylenesulfonic acid serve to confirm further the intermediacy of thiirene dioxides.

Given that chloro episulfones such as **36** and **37** also decompose stereospecifically to chloro olefins, then the stereochemistry of these vinyl halides is determined in the cyclization. However, the observed *cis*:*trans*



(17)

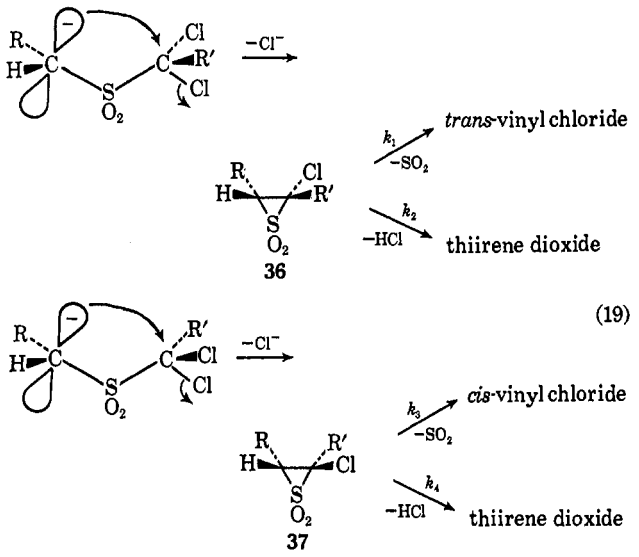
(18)

ratio of isolated vinyl chlorides should not be used to evaluate the relative importance of the two possible transition states in these instances because relative rates of sulfur dioxide expulsion and elimination of

(26) L. A. Paquette and R. Fraley, unpublished observations.

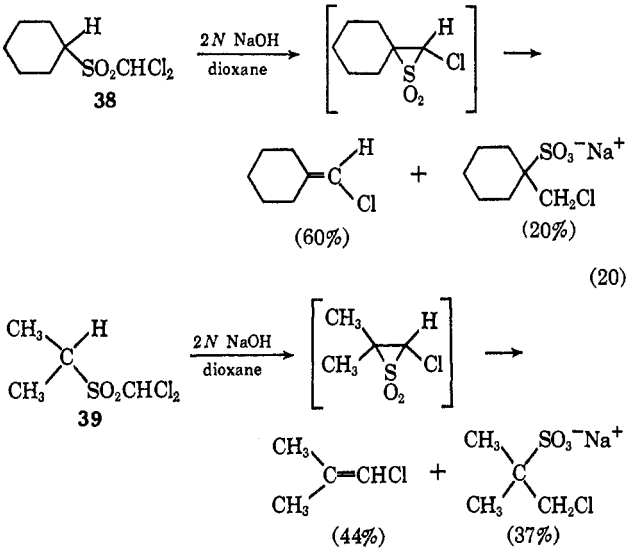
(27) L. A. Paquette, "Mechanisms of Molecular Migrations," Vol. I, B. S. Thyagarajan, Ed., Interscience Publishers, Inc., New York, N. Y., 1968, in press; Professor F. G. Bordwell has recently informed the author that additional confirmatory evidence for thiirene dioxide intermediates has been obtained in his laboratory.

(28) L. A. Carpino and L. V. McAdams, *J. Am. Chem. Soc.*, **87**, 5804 (1965).



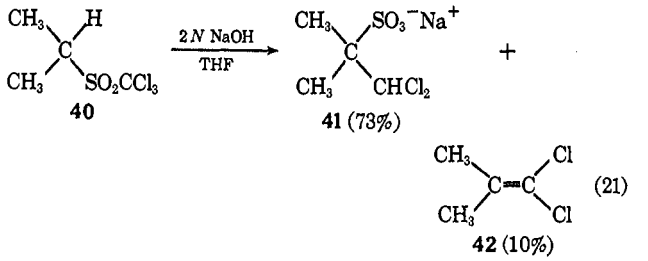
hydrogen chloride from **36** and **37** can be expected to differ, and stereochemical significance is lost upon thiirene dioxide production.[9]

Base-promoted rearrangements of a selected number of dichloromethyl sulfones have been studied to provide evidence on the generation and fate of monosubstituted thiirene dioxides and the factors which control the yield variations of the acetylenes, vinyl chlorides, and vinylsulfonic acids.[10] With regard to the last point, exposure of **38** and **39** to aqueous NaOH solution resulted in good conversion to vinyl chlorides and sulfonic acids containing chloromethyl groups. In these examples, further dehydrohalogenation of the intermediate chloro episulfones is not possible, and the products therefore reflect the true reactivity of such strained rings in the absence of competing loss of hydrogen chloride.[10]

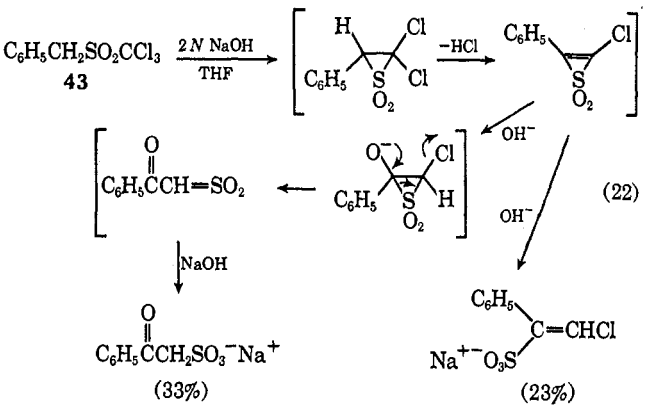


Rearrangements of α,α,α-Trichloro Sulfones. The demonstrated intervention of thiirene dioxide intermediates prompted a study of related trichloro sulfones to ascertain if such systems were subject to ready rearrangement and to analyze the role played by chlorothiirene dioxide intermediates should they be formed.

Marked susceptibility to rearrangement was noted when **40** was observed to be transformed readily in base to **41** and **42**.[29] The structures of **41** and **42**

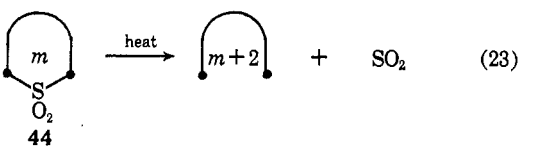


denote unequivocally the occurrence of a 1,3 elimination and the intervention of reactive 2,2-dichloro episulfones. In the case of **43** and similar trichloro sulfones,[24] the results presently available can best be interpreted in terms of chlorothiirene dioxide intermediates (eq 22). Thus, it may be concluded that α-halo sulfones dis-



play a propensity for 1,3 elimination and formation of episulfones (and their transformation products) irrespective of the degree of halogen substitution.

Concerning the Mechanism of Sulfur Dioxide Expulsion from Episulfones and Thiirene Dioxides. The extrusion of SO_2 from a cyclic sulfone such as **44** is an electrocyclic process for which the selection rules[30] predict concerted symmetry-allowed disrotatory motion in those cases where $m = 4q + 2$ and conrotatory



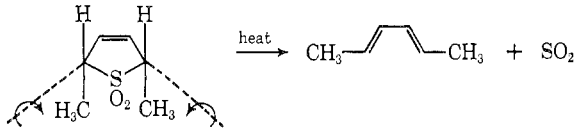
motion when $m = 4q$ (m is the number of π electrons undergoing bond alternation and q is any integer 0, 1, 2...). The alternative pathways would be multistep mechanisms involving dipolar or diradical intermediates.

In this regard the thermally induced decompositions

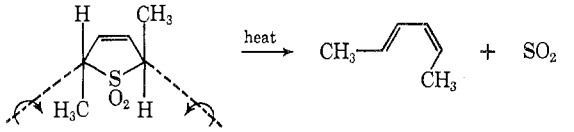
(29) L. A. Paquette and L. S. Wittenbook, manuscript in preparation.

(30) (a) R. B. Woodward and R. Hoffmann, *J. Am. Chem. Soc.*, **87**, 395 (1965); (b) R. Hoffmann and R. B. Woodward, *ibid.*, **87**, 2046 (1965).

of 2,5-dihydrothiophene 1,1-dioxides such as **45** and **46** have been shown to be completely stereospecific and to afford *trans,trans*- and *cis,trans*-2,4-hexadienes, respectively.[31] Thus, these sulfolenes ($m = 2$) are converted to their components in the concerted disrotatory manner predicted by the selection rules.

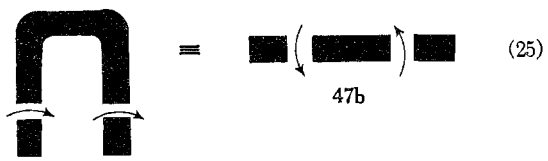


45 (24)



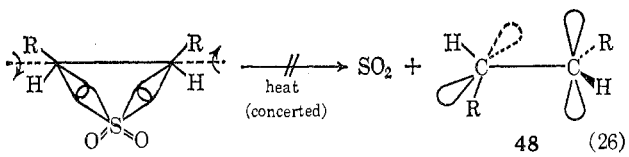
46

In the case of *cis*- or *trans*-episulfones ($m = 0$), however, concerted thermal decomposition is symmetry forbidden. This conclusion is derivable in the following manner. For the special case of ethylene formation, the usual shorthand depiction of electrocyclic transformations (*viz.*, **47a**)[30a] must first be transformed into the linear form **47b**. Application of the conrotation process to such three-membered rings now requires the



47a **47b** (25)

formation of a twisted ethylene unit (**48**). Equation 26 depicts the decomposition of a *cis*-episulfone in this

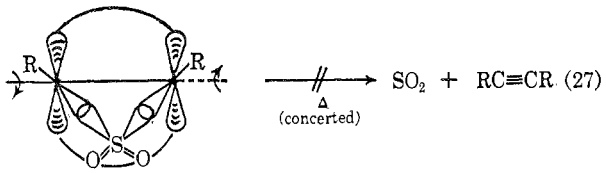


48 (26)

manner. In this illustration, bond termini have been rotated by 45°; when bond rotation has proceeded approximately to this extent, the SO_2 molecule can be expected to be sufficiently well freed from its prior bonding commitment to be considered expelled.

Because of the symmetry inherent in such a high-energy intermediate (**48**) (*i.e.*, because of the almost equal likelihood for rotation in both possible directions to arrive at the π-bonded ethylene derivative), the capability of the system to sustain stereospecificity during the decomposition must be considered highly unlikely. Yet the thermal episulfone-to-olefin conversion is known to be highly stereospecific in the case of alkyl and aryl derivatives (see above).

Concerted SO_2 expulsion from thiirene dioxides must also be considered symmetry forbidden (eq 27). Theoretically, this group of heterocycles again represents a case with $m = 0$ since the double bond remains essentially unchanged (*i.e.*, bond alternation does not occur) in proceeding to acetylenes.



It is apparent therefore that an alternative explanation is necessary to reconcile not only the nonconcertedness but also the stereospecificity of episulfone decomposition.[32] Recent evidence[20] suggests that such SO_2 expulsions from episulfones proceed by way of 1,3-diradical intermediates which possess significant rotational barriers.[33] The acceleration of episulfone decomposition in base has been interpreted in terms of a diradical anion intermediate arising from initial addition of methoxide ion to the sulfone group.[20] Further work on this subject can be expected; suffice it to say at the present time that hydroxide ion attack at tetravalent sulfur is obviously required in the conversion of thiirene dioxides into vinylsulfonic acids, although the exact moment of S–O bond formation (*i.e.*, prior to, or after, ring rupture) remains unknown.

I wish to express my appreciation to Dr. Lawrence S. Wittenbrook, my collaborator, who deserves the major credit for the work from my laboratory that is described in this paper. I wish also to express my thanks to the National Science Foundation, the U. S. Public Health Service, and the Alfred P. Sloan Foundation for support of this research.

(31) (a) W. L. Mock, *J. Am. Chem. Soc.*, **88**, 2857 (1966); (b) S. M. McGregor and D. M. Lemal, *ibid.*, **88**, 2858 (1966).

(32) The applicability of the selection rules to three-membered rings has recently been questioned [J. P. Freeman and W. H. Graham, *J. Am. Chem. Soc.*, **89**, 1761 (1967)]. However, a number of lines of evidence make a concerted decomposition unlikely; these points have been summarized by Bordwell, *et al.*[20]

(33) R. Hoffmann and R. B. Woodward, *Accounts Chem. Res.*, **1**, 17 (1968); we thank Professor Hoffmann for a preprint of his full paper on this subject.