BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN VOL. 41 2672—2675 (1968)

Episulfones. IV. The Decomposition Reaction of Episulfones by Bases

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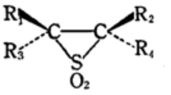
(Received January 25, 1968)

The present paper deals with the decomposition reaction of episulfones in the presence of several bases. The treatment of *cis*-stilbene episulfone (I) with 2 N NaOH gave *trans*-stilbene in a 92% yield, and a hydrogen-deuterium exchange experiment using NaOD showed that 66% of the methine protons of the episulfone were exchanged. On the other hand, the reaction of *n*-butyllithium yielded *cis*-stilbene predominantly, along with *trans*-1,2-diphenylvinyl sulfinate in about a 20% yield. Styrene episulfone (II) gave styrene (80%) and a trace of benzyl methyl sulfone when II was treated with alkali. Tetraphenylethylene episulfone (III) afforded tetraphenylethylene almost quantitatively. The cleavage mechanism by bases is then discussed on the basis of the above results. Ethylene episulfone (IV) is oligomerized by tertiary-amine catalysis.

We have been studying the physical and chemical behavior of episulfones (thiirane 1,1-dioxide) and have previously reported some new reactions.[1a,b] In the present paper, we wish to report on the base-catalyzed decompositions of episulfones and on their mechanisms. The reaction of episulfones with a base to give olefins has been investigated by several workers,[1c,2] but the reaction mechanism has not yet been clarified. In this paper, we will describe the decompositions of several episulfones (I—IV) with various bases and suggest the reaction mechanism.



(I) $R_1=R_2=C_6H_5$ $R_3=R_4=H$
(II) $R_1=C_6H_5$ $R_2=R_3=R_4=H$
(III) $R_1=R_2=R_3=R_4=C_6H_5$
(IV) $R_1=R_2=R_3=R_4=H$
(V)[2] $R_1=R_2=CH_3$ $R_3=R_4=H$

The results of the decomposition of *cis*-stilbene episulfone (I) by various bases are summarized in Table 1.

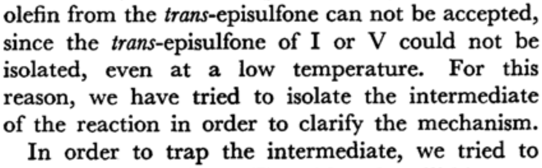
cis-Stilbene episulfone was decomposed to *trans*-stilbene predominantly by the reaction with alkali, while the treatment of I with *n*-butyllithium afforded *cis*-stilbene predominantly. Triethylamine did not cleave the episulfone under the same conditions (0°C, 6 hr).

Recently, Neureiter[2] has proposed a mechanism in which the elimination of α-protons of V by a stronger base is followed by the epimerization to the α-sulfonyl carbanion of the *trans*-form during the process of exchange forming *trans*-olefin by a thermal process; treatment with the *t*-butoxide ion, the strong, hindered base (in *t*-BuOD), resulted in the formation of *trans*-2-butene in a 80% yield, with complete deuteration at the 2 and 3-positions (Scheme 1).

TABLE 1. DECOMPOSITION OF *cis*-STILBENE EPISULFONE (I) BY SEVERAL BASES

Base	Solvent	Temp. (°C)	*cis*-Stilbene	*trans*-Stilbene (%)
2 N NaOH	40%THF-H_2O	0	7	92
2 N LiOH	40%THF-H_2O	0	5	90
2 N KOH	40%THF-H_2O	0	2	89
n-BuLi	THF	0	70	6
$N(Et)_3$	THF	0	No Decomposition	

cis-Butene was favored when V was treated with a weaker base, suggesting that the α-hydrogens were not eliminated in this case.



Scheme I

However, a thermal process to give the *trans*-olefin from the *trans*-episulfone can not be accepted, since the *trans*-episulfone of I or V could not be isolated, even at a low temperature. For this reason, we have tried to isolate the intermediate of the reaction in order to clarify the mechanism.

In order to trap the intermediate, we tried to treat the episulfone (I) with *n*-butyllithium at a low temperature (0°C). We chose the 1,2-diphenyl derivatives because of the ability of the phenyl group to stabilize the system by conjugation.

When I was treated with *n*-butyllithium in

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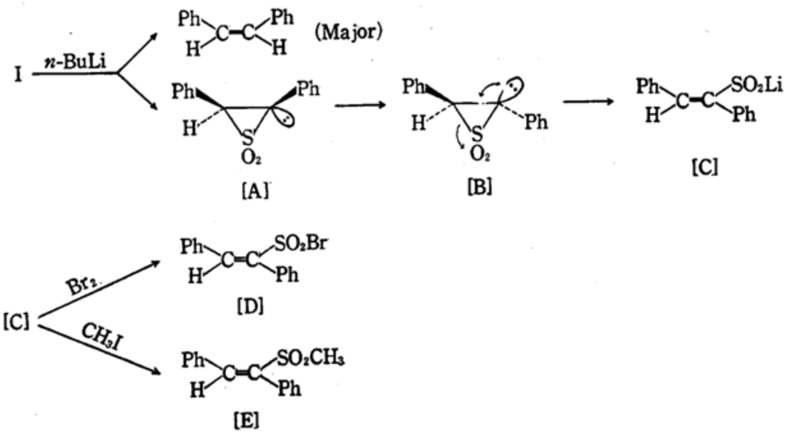
[1] a) S. Matsumura, T. Nagai and N. Tokura, This Bulletin, **41**, 635 (1968). b) *Idem.*, *Tetrahedron Letters*, **1966**, 3929. c) N. Tokura, T. Nagai and S. Matsumura, *J. Org. Chem.*, **31**, 349 (1966).

[2] N. P. Neureiter, *J. Am. Chem. Soc.*, **88**, 558 (1966).

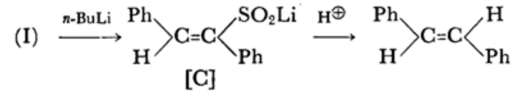


Scheme II

THF, and then with bromine or methyl iodide, *trans*-1,2-diphenylvinylsulfonyl bromide [D] and *trans*-1,2-diphenylvinyl methyl sulfone [E] were formed in 16 and 9% yields respectively, even at 0°C.[3]

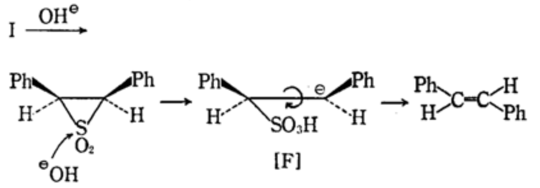
These products were obviously generated through the ring-opening compound, *trans*-1,2-diphenylvinyl sulfinate [C], which was itself formed through [A], and then converted to [B]. The reactions described are outlined in Scheme II.[4]

The above-mentioned results suggest that the formation of *trans*-stilbene or *trans*-2-butene passes through Schemes II and III, if the bases which can eliminate the α-hydrogens but can not attack the sulfur atom of the episulfone, are used.[5] [C] did decompose to *trans*-stilbene when treated with acid.[6]



Scheme III

On the other hand, as there was a 66% hydrogen-deuterium exchange of I in the NaOD-D$_2$O system, the α-hydrogens are certainly eliminated prior to the formation of the [C] intermediate (Scheme III). The [C] intermediate is not unstable at 0°C, so it might be trapped by bromine or methyl iodide if the reaction followed Scheme III. However, our attempts to trap the [C] intermediate were unsuccessful. Therefore, we assumed a mechanism in which the olefinic product (*trans*-stilbene) arose as a result of a nucleophilic attack on the sulfur atom of the episulfone.[7] (Scheme IV).



Scheme IV

The difference between *n*-BuLi and OH⊖ may be ascribed to the fact that *n*-BuLi is rather sterically hindered to attack the sulfur atom. (The H–D exchange reaction might be fast, and the α-sulfonyl carbanion intermediate [A], considerably stable.) Although the [F] intermediate is stable enough to rotate around the C–C single bond, the similar intermediate which arises in the case of V seems to be unstable, giving *cis*-2-butene predominantly before the rotation.

In this connection, it is interesting to note that these results demonstrate that the isomerization of α-sulfonylcarbanion in a three-membered system would also occur.[8]

As may be seen in Table 1, *cis*-stilbene was favored over the *trans*-isomer when *n*-butyllithium was used as the base. This may be interpreted in terms of the finding[1a] that the carbanion formation of I with *n*-butyllithium is slower than the thermal

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[3] The geometrical configurations of these two compounds, [D] and [E], were decided on the basis of a comparison of their mp's with those of an authentic specimen [E]. (M. Ōki and A. Kimura, This Bulletin, **38**, 682 (1965)).

[4] Recently, L. A. Carpino and R. H. Rynbrondt (*J. Am. Chem. Soc.*, **88**, 5682 (1966) have proposed that, in vinylene sulfones, α-hydrogen is eliminated to give acetylene. However, this reaction has no relation to the stereochemical correlation.

[5] Since the isomerization from [A] to [B] would be fast, [A] would not decompose to *cis*-stilbene. However, we cannot completely exclude a mechanism in which *trans*-stilbene is formed through [B], accompanied by the thermal elimination of sulfur dioxide, as has similarly been suggested by Neureiter.[2]

[6] W. E. Truce and J. R. Norell, *J. Am. Chem. Soc.*, **85**, 3036 (1963).

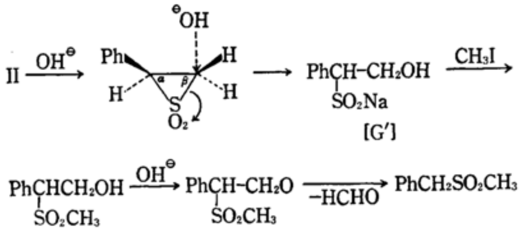
[7] A similar mechanism was recently presented by L. A. Paquette and L. S. Wittenbrook, *ibid.*, **89**, 4483 (1967).

[8] E. J. Corey, H. Konig and T. H. Lowy, *Tetrahedron Letters*, **1962**, 515.

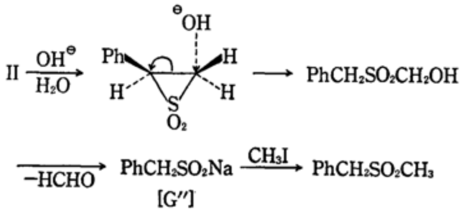
decomposition[1c] of I. *trans*-2-Butene was formed predominantly when V was treated with *t*-butoxide ion, because the carbanion formation was faster than the thermal elimination of sulfur dioxide (Scheme I).[2]

When styrene episulfone (II) was treated with alkali (2 N NaOH), styrene (80%), and a trace of the sulfinate, [G′] or [G″] (identified as benzyl methyl sulfone (0.4%)) was produced. The process of the formation of styrene may be analogous to the mechanistic route described in Scheme IV, and the benzyl sulfone may be formed according to either Scheme V or VI.[9]

Scheme V shows a C–S bond fission, and Scheme VI involves an interesting C–C bond cleavage.[1a,b] It is not yet clear which of the two schemes is correct.

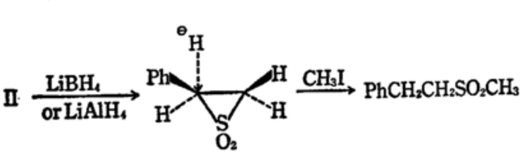


Scheme V



Scheme VI

The hydroxide-ion attack on the β-carbon of II essentially resembles the reaction of styrene oxide. It is interesting to compare with findings previously reported;[1a] the α-carbon of II was selectively attacked by the hydride ion ($LiBH_4$ or $LiAlH_4$) (Scheme VII). The sterically larger molecule, OH⊖, should attack a less hindered site.



Scheme VII

Recently, Desiderate and Sass[10] reported on the crystal structure of *cis*-2-butene episulfone V and showed that the C–C bond length is, surprisingly, 1.60 Å (which is much longer than those of epoxide (1.47 Å) and episulfide (1.49 Å)). Our previous proposal[1a] concerning this abnormal bond length is thus confirmed; however, we are now studying this point in detail.

Tetraphenylethylene episulfone (III) gave tetraphenylethylene exclusively (92%) when III was treated with 2 N NaOH, probably by attacking the sulfur atom as is described in Scheme IV.

These results suggest that the sulfur atoms of episulfones are attacked by OH⊖, giving olefins.

Ethylene episulfone (IV) was first synthesized by Hesse *et al.*, and several reactions toward the episulfone have been reported on; for example, when IV was treated with NaOH, unidentified products were produced. We used *t*-amines, such as pyridine, triethylamine, and 2,6-lutidine, and found that an oligomerization occurs. The elemental analyses of these products are summarized in Table 2. The products were insoluble in almost all solvents except for an alkali solution, while there was an accompanying decomposition. (The oligomers did not dissolve in concentrated H_2SO_4.)

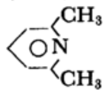
It is well known that the olefins containing strong electron-withdrawing groups are polymerized even by *t*-amines such as triethylamine. Compared with other heterocyclic three-membered rings, episulfones are easily attacked by nucleophilic reagents because of having a strong electron-withdrawing sulfone group.

The structure of the oligomers would seem to be:

$$-(-CH_2CH_2-SO_2-)_{\overline{n}}$$

However, these products were all insoluble in the solvents, and only the IR spectra and elemental analysis gave any information, however little, about the structures. Because of the insolubility, the molecular weights could not be measured, but if the terminals are *t*-amines, the degrees of polymerization can not be very high.

TABLE 2. ELEMENTAL ANALYSES, DECOMPOSITION POINTS, AND YIELDS OF THE POLYMER (25°C, Base/IV=1/4).

Base	C	H	N	S	D.P.	Yield (%)
	27.44	4.32	2.00	23.48	270	57
$(C_2H_5)_3N$	28.54	4.98	1.29	25.92	270	21
	29.06	4.40	1.22	28.13	270	12

Experimental

Materials. The *cis*-stilbene episulfone (I), styrene episulfone (II), tetraphenylethylene episulfone (III), and ethylene episulfone (IV) were synthesized as has described in a previous paper.[1a]

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[9] D. C. Dittmer and M. E. Christy, *J. Am. Chem. Soc.*, **84**, 399 (1962).

[10] R. Desiderate and R. L. Sass, *Acta Cryst.*, **23**, 430 (1967).

The sodium deuteroxide and deuterium oxide were obtained from Ciba Ltd.

The tetrahydrofuran was purified by refluxing it with sodium for two days, followed by distillation in the presence of lithium aluminum hydride.

All the melting points and boiling points are uncorrected. The infrared absorption spectra were determined on a Hitachi Infrared Spectrophotometer. The NMR Spectra were run on a Nihondenshi Spectrometer at 60 Mc. Tetramethylsilane was used as an internal standard, and *d*-chloroform was used as the solvent (Ciba Ltd.). Vpc analysis was carried out on a Yanagimoto Model GCS-100 Instrument.

Reaction of Episulfones with Alkali (General Procedure). A mixture of an episulfone (about 0.002 mol) and aqueous 2 N alkali (40%) in a THF-solution (50 m*l*) was stirred for 20 min at 0°C. The reaction mixture was then added to ice water (50 m*l*) and extracted twice with 50 m*l* of ether. After the combined ether layer had been dried over sodium sulfate (anhydrous), the ether was removed under reduced pressure. The products were identified as follows. The *cis*- and *trans*-stilbene were separated by fractional crystallization. (The *cis*-stilbene was identified as has been described in a previous paper,[1c] while the *trans*-form was a solid material which melted at 124°C.) The styrene was determined by Vpc. The benzyl methyl sulfone and tetraphenylethylene were identified by comparison with authentic specimens (mp 123°C and 222°C respectively).

A deuterium exchange experiment was carried out under nitrogen; the procedure was similar to that described above. The *d*-*trans*-stilbene was analysed by means of the NMR spectra. The ratio of the area of the peak due to phenyl protons to that area due to olefin protons was 15 : 1, showing that 70% of the olefin protons were deuterated (τ(phenyl) 2.6, (olefin 2.85)).

Reaction of *cis*-Stilbene Episulfone (I) with *n*-Butyllithium. *n*-Butyllithium (about 0.002 mol) was prepared in dry THF, and to this solution *cis*-stilbene episulfone (1.0 g; 0.004 mol) in THF (10 m*l*) was added slowly at 0°C. After the reaction mixture had then been stirred for 30 min, bromine (3.0 g) or methyl iodide (3.0 g) was added, drop by drop; the solvents were then evaporated under reduced pressure. The products were separated on the basis of their solubility; that is, *trans*-1,2-diphenylvinylsulfonyl bromide was soluble in petroleum ether, while the residue (dibromostilbene) was sparingly soluble in petroleum ether. *trans*-1,2-Diphenylvinyl methyl sulfone was also separated and recrystallized from ether-petroleum ether.

The product [D], *trans*-1,2-diphenylvinylsulfonyl bromide, was identified on the basis of the following data: mp 122—124°C, NMR (in $CDCl_3$) $\tau=2.88$ (5H, multiplet, aromatic) 2.53 (5H, singlet, aromatic) 2.21 (1H, singlet, olefinic porton), IR ν_{max}^{KBr} 1620, 818 (tri-substituted olefin) 1350, 1148 cm^{-1} (ν_{SO_2}), UV $\lambda_{max}^{95\%EtOH}$ 287 (14700), 270 (14800), 216 mμ (ε 20300). Found: C, 51.94; H, 3.23%. Calcd for $C_{14}H_{11}BrO_2S$: C, 52.02; H, 3.43%.

trans-1,2-Diphenylvinyl methyl sulfone [E] was identified on the basis of the following data: mp 118—119°C, NMR (in $CDCl_3$) $\tau=7.21$ (3H, singlet, CH_3), 2.84 (5H, multiplet, aromatic), 2.56 (5H, singlet, aromatic), 2.17 (1H, singelt, olefinic proton), IR ν_{max}^{KBr} 1645, 825 (tri-substituted olefin) 1308, 1315, 1132 cm^{-1} (ν_{SO_2}). UV $^{95\%EtOH}_{max}$ 267 (17400), 217 mμ (ε 23000).

Found: C, 69.81; H, 5.61%. Calcd for $C_{15}H_{14}O_2S$: C, 69.74; H, 5.46%.

Reaction of Ethylene Episulfone (IV) with *t*-Amines (General Procedure). A mixture of ethylene episulfone (0.023 mol) and *t*-amines (0.005 mol) in THF (20 m*l*) was allowed to stand for two days at room temperature. The resulting precipitates were washed three times with 95% ethanol, and then three times with water, and dried in a desiccator.