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Episulfones. III. Reductive Cleavage of Episulfones by Complex Metal Hydrides

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The reduction of *cis*-stilbene episulfone (I) by such a complex metal hydride as lithium borohydride, sodium borohydride, or lithium aluminum hydride gave dibenzylsulfone (V) selectively as a result of the unusual cleavage of the carbon-carbon single bond. Comparing the difference between lithium aluminum hydride and lithium borohydride or sodium borohydride in various solvent systems, we suggest that particular solvent effects are operating in the present reaction. The reduction of I with lithium aluminum hydride resulted in a low yield (0—10%) of V, while the reduction with lithium borohydride afforded V in a 45% yield. The reduction of styrene episulfone (II) gave no carbon-carbon cleavage product, but it did give a carbon-sulfur fission product, yielding sulfinic acid salt (VIII). The formation of VIII is interesting compared with the reduction of styrene oxide by lithium aluminum hydride. Tetraphenylethylene episulfone (III) produced a carbon-carbon cleavage product, 1, 1, 3, 3-tetraphenyl dimethyl sulfone (XI), in a 68% yield. A reaction mechanism for the reductive cleavage reaction has been proposed on the basis of the above-mentioned results. In addition, we observed that diborane was evolved by the reaction of sulfur dioxide with lithium- or sodium borohydrides.

Much work has been done on the reactivity of heteroatom-containing three-membered ring compounds, for example, epoxides, episulfides, and aziridines. However, the reactions of three-membered rings containing a sulfone group (episulfones) have not yet been studied, except for base-catalyzed reactions.[1,2]

It is very interesting to investigate the physical and chemical behavior of episulfones.

In previous papers[3,4] the present authors have reported the alkaline cleavage of *cis*-stilbene episulfone (I) and the reduction of I by complex metal hydrides. In this paper, we wish to report on the reduction of such episulfones as *cis*-stilbene episulfone (I), styrene episulfone (II), and tetraphenylethylene episulfone (III) by complex metal hydrides. (The episulfones isolated before have been few[1-3,5] because it is difficult to synthesize them because of their unstability.)

Selective Reduction by Complex Metal Hydrides. Reduction of I with complex metal hydrides were carried out under various conditions; the results are summarized in Table 1. The yields of dibenzylsulfone (V) and *cis*-stilbene (VI) obtained totalled almost 100%. No sulfinic acid salt was detected. Therefore, it can be said that the carbon-carbon bond cleavage occurs selectively, without any carbon-sulfur bond fission[6] (Eq. (1)).

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[1] a) N. P. Neureiter, *J. Am. Chem. Soc.*, **88**, 558 (1966); b) L. A. Paquette, *Chem. Commn.*, **1966**, 471.

[2] G. Hesse, E. Reichold and S. Majmudar, *Chem. Ber.*, **90**, 2106 (1957).

[3] Part I: N, Tokura, T. Nagai and S. Matsumura, *J. Org. Chem.*, **31**, 349 (1966).

[4] Part II: S. Matsumura, T. Nagai and N. Tokura, *Tetrahedron Letters*, **1966**, 3929.

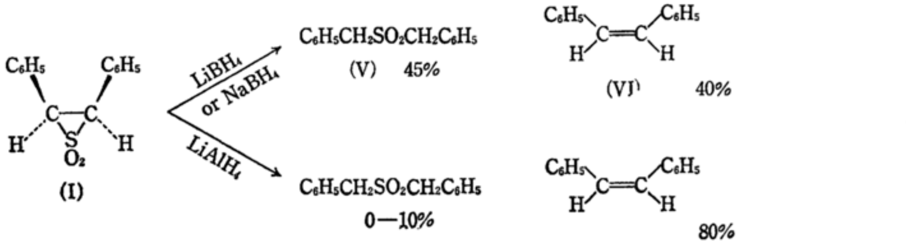
[5] a) H. Staudinger and F. Pfenniger, *Ber.*, **49**, 1941 (1916); b) L. V. Vargha and E. Kovacs, *ibid.*, **75**, 794 (1942); c) G. Opitz and K. Fischer, *Angew. Chem.*, **77**, 41 (1965); d) S. Rossi and S. Mairona, *Tetrahedron Letters*, **1966**, 263; e) L. A. Carpino and R. H. Rynbrandt, *J. Am. Chem. Soc.*, **88**, 5682 (1966).

[6] The stereospecific formation of *cis*-stilbene from I was the result of thermal decomposition.[3] Though I is stable below its dec. pt. (87—88°C) in a pure state without a solvent, it has been found that I decomposes to give *cis*-stilbene in some yield, even at room temperature, if it is dissolved in such solvents as are listed in Table 1. The yield of the olefin from this decomposition in a solvent seems to depend on the solvent used and on the coexistence of a metal cation, though its quantitative relationship is not clear.

TABLE 1. REDUCTION OF *cis*-STILBENE EPISULFONE (I) BY COMPLEX METAL HYDRIDES

Entry	Reducing agent[a]	Solvent	Temp. °C	Products (mol%)	
				Dibenzyl-sulfone (V)	*cis*-Stilbene (VI)
1	$LiAlH_4$	Tetrahydrofuran	15	0	89
2	$LiAlH_4$	Diethyl ether	15	10	65
3	$LiAlH_4$	Diglyme[b]	15	12	77
4	$LiAlH_4$	Tetrahydrofuran	70	4	77
5	$LiBH_4$	Tetrahydrofuran	15	47	40
6	$LiBH_4$	Diethyl ether	15	43	58
7	$LiBH_4$	Diglyme	15	48	28
8	$LiBH_4$	Tetrahydrofuran triethylamine	15	29	65
9	$NaBH_4$	Tetrahydrofuran[c]	15	33	66
10	$NaBH_4$	Diglyme	15	49	50
11	$NaBH_4$	Dimethyl sulfoxide	20	44	61
12	$NaBH_4$	Methanol	15	0	85
13	BH_3[d]	Tetrahydrofuran	15	0	60[f]
14	AlH_3[e]	Tetrahydrofuran	15	0	83
15	H_2AlCl[e] $HAlCl_2$[e]	Tetrahydrofuran	15	0	100
16	LiH	Tetrahydrofuran	15	0	100
17	NaH	Tetrahydrofuran	15	0	100

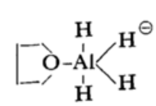
a) A molar ratio of I to the reducing agents of 1 : 2 was used.
b) Diethylene glycol dimethyl ether.
c) Suspension of sodium borohydride in tetrahydrofuran was used.
d) Diborane was generated externally in the reaction flask by adding diglyme saturated with sodium borohydride to boron fluoride etherate. (H. C. Brown and B. C. Subba Rao, *J. Am. Chem. Soc.*, **81**, 6428 (1959).) Excess diborane was used in this reaction.
e) AlH_3, H_2AlCl and $HAlCl_2$ were prepared by the method of Ashby. (E. C. Ashby and J. Prather, *J. Am. Chem. Soc.*, **88**, 749 (1966).) In these reactions, we directly used them prepared from lithium hydride and aluminum chloride in ether.
f) Yield was based on 1,2-diphenyl ethanol obtained.



(1)

Remarkable solvent effects on the reductive cleavage were observed (Table 1). Thus, no dibenzylsulfone (V) was produced when I was treated with lithium aluminum hydride in tetrahydrofuran at room temperature. When diethyl ether or diglyme was used as the solvent, however, V was formed under the same conditions.

This reason might be that tetrahydrofuran forms a complex[7,8] with lithium aluminum hydride (Fig. (A)), thus prohibiting the reactions more or less due to steric reasons. In ether and diglyme, which are weaker bases than tetrahydrofuran, such complexes are dissociated at room temperature, so the yields of V are more in these solvent than in tetrahydrofuran.



(A)

When tetrahydrofuran,[9] diethyl ether, diglyme, and dimethyl sulfoxide (Entries 5-11) were treated

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[7] E. Wiberg and A. Jahn, *Z. Naturforsch.*, **11b**, 489 (1956).

[8] D. Nafstein and C. Vogel, *J. Am. Chem. Soc.*, **88**, 1576 (1966).

[9] The decrease in the yield of V in tetrahydrofuran may be ascribed to the low solubility of sodium borohydride.

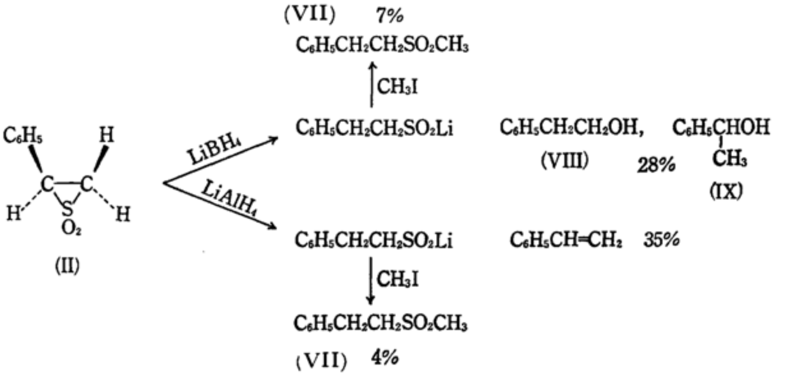
with lithium borohydride or with sodium borohydride, V was produced in very similar yields. Thus, the suggestion has been made that the interactions of lithium borohydride or sodium borohydride with these solvents are diminished.[10] In methyl alcohol, on the contrary, sodium borohydride reacts with the solvent to give[11] sodium tetramethoxyboron, $NaB(OCH_3)_4$ before reduction; thus V is not produced (Entry 12). In the reduction of I in the presence of triethylamine, no marked decrease in the yield of V was observed.

This remarkable difference in reactivity between the aluminum- and boro-hydrides can be explained by the fact that aluminum can expand its octet to form A, while boron cannot.[8]

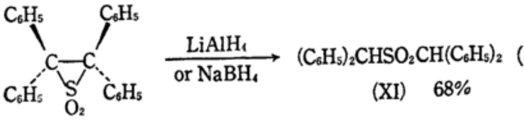
Recently, many workers have discussed the solvent effects on reductions by complex metal hydrides. Eliel *et al.*[12] concluded that sodium borohydride in inert solvents brings about the same steric results as does lithium aluminum hydride in ether, and Dauben[13] postulated that the borohydride species has a greater effective size than the aluminum hydride anion. Wheeler and Huffman[14] claimed that neither borohydride ion nor aluminum hydride ion is solvated.

Contrary to the above suggestions, we have concluded that the marked solvent effect on reduction by alkaline aluminum hydride is due to a complex formation such as A.

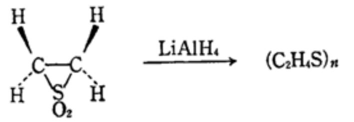
The present authors investigated the reductions of styrene episulfone (II) and tetraphenylethylene episulfone (III), formulated below;



(2)



(III) (3)



(IV) (4)

To clarify the driving force of the carbon-carbon bond cleavage of I, we reduced styrene episulfone (II) by lithium aluminum hydride and lithium borohydride in diethyl ether at 0°C, but the carbon-carbon bond cleavage product was not detected, even after careful alumina-column chromatography. Instead, β-phenylethyl sulfinic acid salt, which was identified as β-phenylethyl methyl sulfone (VII) by the reaction with methyl iodide, was formed, indicating a carbon-sulfur bond cleavage.

It is interesting to note that the normal cleavage product, α-phenylethyl methyl sulfone, was not detected in the reaction mixtures. In the reduction of styrene oxide by lithium aluminum hydride or lithium borohydride, it has been observed[15] that the former gives only α-phenylethyl alcohol, while the latter, on the other hand, gives α- and β-phenylethyl alcohols in a ratio of 74 : 26.[15] This difference may arize from the greater size of the aluminum hydride anion species. In the case of styrene episulfone (II), however, both reducing agents gave abnormal products. The explanation for this unusual reaction is that the carbon-carbon bond length of the episulfone is longer than that of epoxides, thus relaxing the steric prohibition.[16]

During the reaction using lithium borohydride

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[10] Lithium borohydride forms a 1 : 1 complex with diethyl ether, but this complex dissociates at the reaction stage. (E. Wiberg, H. Hoth and R. Uson, *Z. Naturforsch.*, **11b**, 490 (1956).

[11] R. E. Davis and J. A. Gottbrath, *J. Am. Chem. Soc.*, **84**, 895 (1962).

[12] H. Haubenstock and E. L. Eliel, *ibid.*, **84**, 2368 (1962).

[13] W. G. Dauben, G. J. Forken and D. S. Noyce, *ibid.*, **78**, 2579 (1956).

[14] D. M. S. Wheeler and J. W. Huffman, *Experientia*, **16**, 516 (1960).

[15] R. Fuchs and C. A. Van der Werf, *J. Am. Chem. Soc.*, **76**, 1631 (1954); *ibid.*, **78**, 5612 (1956).

[16] We are now studying the physical properties of the episulfone by means of the NMR and UV spectra.

as a reducing agent, we observed that the hydroboration of styrene occurred: α-(IX) and β-phenylethyl alcohol (VIII) were produced in a ratio of about 20 : 80; this ratio was the same as that obtained by the usual hydroboration of styrene.[17a, b]

Such an evolution of diborane is interesting, we first assumed as follows: the produced sulfinic acid salt can not form a complex with diborane, which is different from the behavior of carbanion or oxoanion. Accordingly, the diborane could react with styrene in the case of the present reduction (Eq. (5)):

$$\left.\begin{array}{l} \mathrm{R}^{\ominus}\mathrm{M}^{\oplus} + \mathrm{BH_3} \rightarrow \mathrm{R{-}}\overset{\ominus}{\mathrm{B}}\mathrm{H_3}\,\overset{\oplus}{\mathrm{M}} \\ \mathrm{RO}^{\ominus}\mathrm{M}^{\oplus} + \mathrm{BH_3} \rightarrow \mathrm{R{-}O{-}}\overset{\ominus}{\mathrm{B}}\mathrm{H_3}\,\overset{\oplus}{\mathrm{M}} \\ \mathrm{RSO_2}^{\ominus}\mathrm{M}^{\oplus} + \mathrm{BH_3} \not\rightarrow \mathrm{R{-}SO_2{-}}\overset{\ominus}{\mathrm{B}}\mathrm{H_3}\,\overset{\oplus}{\mathrm{M}} \end{array}\right\} \quad (5)$$

However, as will be described below, we discovered a new route to the formation of diborane by the reaction of lithium borohydride or sodium borohydride with sulfur dioxide. Therefore, this hydroboration must mainly come from the diborane[18] formed by the reaction of the borohydride with sulfur dioxide, which is obtainable from the episulfone. (In the case of lithium aluminum hydride, allane (AlH_3) might be formed, but in our study this reaction did not occur.)

The reduction of tetraphenylethylene episulfone (III) by lithium aluminum hydride or sodium borohydride gave 1, 1, 3, 3-tetraphenyl dimethyl sulfone (XI) in good yields. The formation of XI showed the occurrence of carbon-carbon bond fission, though it was sterically much hindered.

Previously, Hesse *et al.*[2] found that ethylene episulfone (IV) was reduced to give polyethylene sulfide (XII) by lithium aluminum hydride, indicating that no carbon-carbon cleavage of the compound occurred.

To summarize the above results, both *cis*-stilbene episulfone (I) and tetraphenylethylene episulfone (III) gave products formed by selective carbon-carbon-bond fission by complex metal hydrides. On the other hand, neither styrene episulfone (II) nor ethylene episulfone (IV) have the carbon-carbon bonds cleavage products; only the carbon-sulfur bond was cleaved.

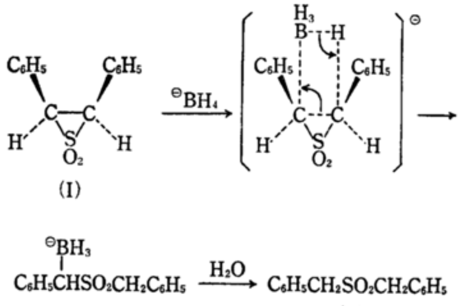
From these results, it seems that at least two phenyl groups are required for the carbon-carbon bond fission.[19] An inductive effect of phenyl groups weakens the carbon-carbon bonds, and a resonance effect of the groups may act to stabilized the resonance forms (B and C) mentioned below. Also, the steric effect by the phenyl groups would make the carbon-carbon bond longer; as a result, the carbon-carbon bond is more vulnerable to attack by nucleophiles.

The driving force for these reactions cannot be the carbanion stabilization of an intermediate or transition state.[20] If this were the case, the carbon-carbon bond of styrene episulfone would be cleaved, giving a carbanion almost identical (formation of benzyl carbanion formed by attack at the α-carbon) to the case of *cis*-stilbene episulfone (I).

The driving force for the reductive cleavage of the carbon-carbon bond should include a relief of the strain.

Thermally, carbon-carbon bond would be stronger than carbon-sulfur bonds, for sulfur dioxide is evolved by the thermal decomposition of episulfones, affording olefins.[6] However, the carbon-carbon bonds have a π-character; in other words, they have a double-bond character according to the Walsh model.[21] Therefore, if carbon-carbon bonds were weakened by such electron-withdrawing substituents as sulfone and phenyl groups in this case, the carbon-carbon bonds would be attacked by nucleophiles.

Let us now discuss the mechanism of these reactions in the case of I. We proposed, in a previous report,[4] a four-centered reaction mechanism for the reduction by lithium borohydride, sodium borohydride, and lithium aluminum hydride (Eq. (6));



(I)

(6)

(V)

The following mechanism would also be attractive:

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[17] a) H. C. Brown and G. Zweifel, *J. Am. Chem. Soc.*, **82**, 4708 (1960). Review: G. Zweifel and H. C. Brown, "Org. Reactions," Vol. 13, John Wiley and Sons, New York (1963), p. 1. b) In the case of the *cis*-stilbene episulfone (I) reduction, 1, 2-diphenylethanol was not formed because of the short reaction time.

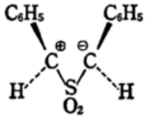
[18] We will report on the reaction in the near future.

[19] G. W. Griffin *et al.* recently reported the photocleavage of phenyl-substituted cyclopropane in ionic fashion to give substituted propanes. This reaction proceeded by a photochemical process, not by heating. On the other hand, in our study, episulfones gave carbon-carbon bond cleavage products more easily, even at room temperature. This difference may be ascribed to the higher energy of the ground state of episulfones. (G. S. Irving, R. C. Petterson, I. Sarkar, H. Kristinsson, C. S. Aaron, G. W. Griffin and G. J. Boudreaux, *J. Am. Chem. Soc.*, **88**, 5675 (1966)).

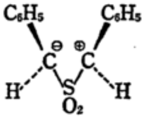
[20] B. Franzus and E. I. Snyder, *ibid.*, **87**, 3423 (1965).

[21] M. Pomerantz *et al.* have reported on the electronic structure and reactivity of bicyclobutanes, showing a π-character in the peripheral and bridgehead bonds (M. Pomerantz and W. Abrahamson, *J. Am. Chem. Soc.*, **88**, 3970 (1966)).

Three-membered rings involving the electron-withdrawing groups, such as tetracyanoethylene oxide,[22] 1, 2-diphenylaziridine,[23] and cyclopropanones,[24] react with olefins, acetylenes, and dienes by 1, 3-dipolar or 1, 3-diradical concerted mechanisms, resulting in carbon-carbon bonds fission. Similarly, the present reaction might occur by a promotion of the episulfone to activated species B and C, which then react with complex metal hydrides by a 1, 3-dipolar-type reaction.

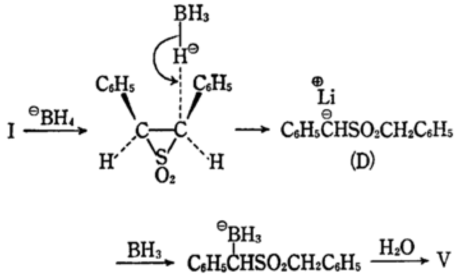


(B)



(C)

There also is another mechanistic route to give V, *i. e.*, the S_N2 type, as shown by epoxide reduction[25] (Eq. (7)):



(7)

There is no clear reason to exclude these mechanisms, since stereochemical and kinetical data are lacking.[26,27] Solvent effects also give no suggestion about the problem. Since the carbanion leading to the formation of V could not be trapped, the fast attack on the carbanion by the liberating hydrogen, as shown in Eq. (8), could not be omitted. The backside-attack mechanism of the reagent due to its complex formation with sulfone group may, however, be ruled out, for borane (BH_3) did not give V at all, though borane would more easily attack the oxygen atom of the sulfone group.

There remains a question of the fate of the liberated sulfur dioxide (liberated by thermal decomposition).

It is noteworthy that sulfur dioxide reacts selectively with lithium borohydride or sodium borohydride to give diborane, without reacting with alkyl lithium (D). To investigate the reductive-cleavage mechanism, the authors added triethylamine to the reaction mixture. The products were V, VI, and, interestingly, triethylamine borane (XIII). If sulfur dioxide did not react with lithium borohydride or sodium borohydride, triethylamine borane would not be formed, since the carbanion (D) would be stronger base than triethylamine, giving no XIII.[28] In addition, the reaction of sulfur dioxide with complex borohydride to give borane was verified (Eq. (8)):

$$4LiBH_4 + SO_2 \xrightarrow{THF} 2BH_3 + Li_2S + 2LiOBH_3 + 2H_2 \qquad (8)$$

The formation of diborane by this method was confirmed by the hydroboration of styrene, and the lithium sulfide liberated was ascertained by a reaction with Pb $(OAc)_2$ to form PbS.[29]

The results of the new route to borane formation and the subsequent use of diborane in sulfur dioxide will be reported elsewhere in detail.

Experimental[30]

Materials. The solvents were purified as follows. Tetrahydrofuran, diethyl ether, dimethyl sulfoxide and triethylamine were obtained from Wako Pure Chemicals. The tetrahydrofuran was purified by refluxing it with sodium for two days. It was then treated with lithium aluminum hydride, and distilled. The diethyl ether was dried over sodium and distilled over lithium aluminum hydride. The dimethyl sulfoxide was refluxed for 10 hr over calcium hydride and distilled at reduced pressure. The triethylamine was distilled over potassium hydroxide pellets. The diglyme (diethylene glycol dimethyl ether) (Aldrich Chemical Co., Inc.) was first distilled over calcium hydride, and then over lithium aluminum hydride.

Lithium borohydride (98%), lithium aluminum hydride, sodium borohydride, lithium hydride, sodium

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[22] W. J. Linn, *J. Am. Chem. Soc.*, **87**, 3665 (1965).

[23] a) A. Padwa and L. Hamilton, *Tetrahedron Letters*, **1965**, 4363; b) A. E. Pohland, R. C. Badger and N. H. Cromwell, *ibid.*, **1965**, 4369; c) R. Huisgen, W. Scheer, G. Szeimies and H. Huber, *ibid.*, **1966**, 397, 405.

[24] a) N. J. Turro, G. W. Byers and P. A. Leermaker, *J. Am. Chem. Soc.*, **86**, 955 (1964); b) P. A. Leermaker, G. Vesley, N. J. Turro and D. C. Neckers, *ibid.*, **86**, 4213 (1964); c) N. J. Turro, P. A. Leermaker, H. R. Wilson, D. C. Neckers, G. W. Byers and G. F. Vesley, *ibid.*, **87**, 2613 (1965).

[25] The borohydride ion, which is more ionic in character than the aluminum hydride ion, yields more V. This suggests that a transition state, such as B or C, may be favored by a more ionic reagent.

[26] R. E. Parker and N. S. Lsaacs, *Chem. Revs.*, 737 (1959).

[27] A few examples of supposed four-centered transition states by sodium borohydride have appeared. CF. F. G. Bordwell and M. L. Douglass, *J. Am. Chem. Soc.*, **88**, 993 (1966); R. E. Dessay and E. Grannen, Jr., *ibid.*, **83**, 3953 (1961).

[28] The carbanion (D) is a stronger base, since α-chlorobenzyl benzyl sulfone treated with triethylamine did not give stilbene.[3]

[29] The reaction of diborane with KOH has recently been reported by Jolly and Schmitt (W. J. Jolly and T. Schmitt, *J. Am. Chem. Soc.*, **88**, 4282 (1966)).

[30] All melting points and boiling points are uncorrected. The infrared absorption spectra were determined on a Hitachi infrared spectrophotometer. The nuclear magnetic resonance spectra were run on a Nihondensi spectrometer at 60 Mc. Tetramethylsilane was used as an internal standard, and chloroform-d was used as the solvent (Chiba Ltd.). V. p. c. analysis was carried out on a Yanagimoto, Model GCS-100, instrument.

hydride, and aluminum chloride were obtained commercially. All these compounds were used without further purification.

Liquid sulfur dioxide was donated by Seitetsu Kagaku and was used after having been dried over phosphorus pentoxide for at least one day.

cis-Stilbene episulfone (I) was synthesized as has been described in a previous report;3) a phenyldiazomethane solution31) (about 0.05 mol in 300 m*l* ether) in a 1-*l* Erlenmeyer flask had a sulfurous acid solution added (6%) over a five-minute period. The solid obtained on cooling was filtered and recrystallized from ether-benzene at about 50°C. Mp 87—88°C (dec.).

Styrene episulfone (II) was obtained by the method of Opitz;5c) in a three-necked, 500 m*l*, round-bottomed flask, equipped with a reflux condenser, a stirrer, and a dropping funnel, there were placed about 0.05 mol of diazomethane and 7.0 g of triethylamine in 100 m*l* of ether. In a dropping funnel there were placed about 11.0 g benzylsulfonyl chloride in 300 m*l* of ether. The solution was then added slowly, over a period of 30 min, to diazomethane triethylamine solution, with the temperature maintained at −30°C (dry ice - triclene bath). After the addition, the solid (triethylammonium chloride) was filtered off and the mother liquor was concentrated by distillation under reduced pressure as fast as possible. The resulting solid (6.5 g (0.039 mol)) was filtered off, washed once with cold ether, and used without further purification; mp 40°C (dec.) (yield 70%). Styrene episulfone was too unstable to be stored it at noom temperature and dried it in a round-bottom flask kept at 0°C (ice bath) by pumping.

Tetraphenylethylene episulfone (III) was synthesized by the method of Staudinger *et al.*5a) Because of its poor stability, III was used as soon as it had been dried for 30 min in a desiccator.

Reduction of *cis*-Stilbene Episulfone (I) by $LiAlH_4$, $LiBH_4$ and $NaBH_4$ (General Procedure). In a three-necked, 200 m*l*, round-bottomed flask, equipped with a reflux condenser and a stirrer, there were placed 0.04 mol of complex metal hydride and 100 m*l* of a solvent. To a well-stirred suspension, there were then added 0.02 mol of *cis*-stilbene episulfone (I) under nitrogen. After 4 hr at room temperature (15° C), the reaction mixture was added to 100 m*l* of ice-water and extracted twice with 150 m*l* of ether. After the combined ether layer had been dried over anhydrous sodium sulfate, the ether was removed under reduced pressure. The white precipitate was washed with ether to give dibenzylsulfone (V).32) V was identified by comparison with an authentic specimen; mp 148—149°C. IR ν_{max}^{KBr} 1302, 1286, 1125, 1113 cm^{-1} (SO_2-stretching). NMR τ=5.9 ppm (methine). The residue (liquid) was *cis*-stilbene, identified as before.3) No product was obtained from the water layer.

Reduction of Styrene Episulfone (II) by $LiBH_4$. In a three-necked flask there was placed 0.764 g (0.035 mol) of lithium borohydride in 150 m*l* of anhydrous ether. To this solution there were then added 2.894 g (0.0172 mol) of styrene episulfone (II). The mixture was stirred at 0°C for 3 hr, and then poured over ice water. It was extracted with ether and dried over Na_2SO_4, after which the ether was evaporated under reduced pressure.

Remaining was a liquid (1.96 g). G. l. c. analysis at 170°C on a PEG 6000 column showed the formation of α- and β-phenylethyl alcohol in the ratio of 20 : 80.33)

The water extract was refluxed with methyl iodide (10 g) for two days, and was then extracted with ether. The evaporation of the solvent gave 0.210 g (0.00114 mol) of white crystals (VII) (mp 87—88°C). β-Phenylethyl methyl sulfone (VII) was identified by comparison with an authentic sample.33)

Reduction of Styrene Episulfone (II) by $LiAlH_4$. Using the technique described above, 0.954 g (0.0261 mol) of lithium aluminum hydride in a 150 m*l* ether solution was added to 3.177 g (0.0189 mol) of styrene episulfone, and the reaction mixture was stirred at 0°C for 3 hr. After having been treated as above, a liquid (0.832 g) remained; it was identified as styrene by g. l. c. analysis (PEG 6000 at 70°C). The water extract was refluxed with methyl iodide (10 g) for two days; it was then extracted with ether to give α-phenylethyl methyl sulfone (0.135 g (0.0011 mol)), which was identical with an authentic sapecimen.

Reduction of Tetraphenylethylene Episulfone (III) by $NaBH_4$ or $LiAlH_4$. To 150 m*l* of a tetrahydrofuran solution containing 0.280 g (0.0074 mol) of sodium borohydride, there was added tetraphenylethylene episulfone (III) (1.127 g (0.00285 mol)) at room temperature (15°C).

The reaction mixture was stirred for 6 hr and then poured into water. The ether extract, after drying, gave 0.59 g of white crystals, which were recrystallized from benzene petroleum ether (30—60°C) to give 1, 1, 3, 3-tetraphenyl dimethyl sulfone (XI) (mp 185—186°C (dec.)).

Found: C, 78.40; H, 5.42%. Calcd for $C_{26}H_{22}O_2S$: C, 78.37; H, 5.57%.

NMR τ=2.5 ppm (phenyl), 4.78 ppm (methine: singlet).

IR ν_{max}^{KBr} 1312, 1130 cm^{-1} (SO_2-stretching).

When treated with lithium aluminum hydride, (III) give a 28% yield of (XI). The residual, tar-like substance was not identified.

Reduction of (I) by $LiBH_4$ or $NaBH_4$ in the Presence of Triethylamine. To a stirred solution of 0.463 g (0.0212 mol) of lithium borohydride and 1.40 g (0.0139 mol) of triethylamine in 100 m*l* of tetrahydrofuran, 2.287 g (0.00937 mol) of *cis*-stilbene episulfone (I) were added, after which the reaction mixture was stirred for 4 hr at room temperature and then decomposed by water. After the residue had been treated as in the above procedure, dibenzylsulfone (V) (0.601 g (0.00244 mol)) and triethylamine-borane (0.580 g (0.00504 mol)) were produced; they were identified by comparison with authentic specimens.34)

IR ν_{B-H} 2300 cm^{-1}, bp 76°C/4 mmHg.

The residual *cis*-stilbene was identified by the coincidence of the IR spectra.

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