ml.) a 15% solution of butyllithium in hexane (20.5 ml.) was added; after 15 min. a solution of keto compound IIIa (3 g.) in 50 ml. of ether was slowly added and the mixture was refluxed overnight. The reaction mixture was poured into water, the organic layer was extracted with hot hexane, the solvent was evaporated, and a clear oil (2.8 g.) was obtained. Distillation gave a fraction (1.85 g.): b.p. 85°(0.5 mm.); d^{22} 0.850; $n^{22}\text{D}$ 1.4923; trihydrochloride m.p. 79–80°; ν_{max} 2925, 1650, 1375, 883 cm.$^{-1}$; n.m.r. 1.65, 1.03, 4.7, 5.05, 5.35. Physical properties reported[5] for β-bisabolene are b.p. 110–111° (3 mm.), d^{20} 0.8606, $n^{20}\text{D}$ 1.48598, trihydrochloride m.p. 79.5–80°.

Direct comparison with β-bisabolene obtained from lanceol[5,15] showed identical infrared and n.m.r. spectra and retention times on v.p.c., using a silicone SE-30 column at 200°.

2-Methyl-6-keto-6-(p-tolyl)-Δ^2-hexene (Va).—The bromo compound II (17 g.) was slowly added at room temp. with stirring to Mg turnings (2.6 g.) in anhydrous ether (100 ml.). When the reaction was completed (45 min.) the organomagnesium compound was slowly added to a mixture of p-toluic acid chloride, (17.9 g.), cuprous chloride (200 mg.) in anhydrous ether (100 ml.). The reaction mixture was treated as above yielding 16 g. of an oily product. Fractional distillation afforded a fraction (13 g.), b.p. 93° (0.1 mm.), which crystallized on standing. Recrystallization from hexane gave the analytical sample: m.p. 47.5–48.5°; ν_{max} 2925, 1693, 1610, 1375 cm.$^{-1}$; n.m.r. 2.6, 2.3, 5.15 (triplet), 7.2 (doublet), 7.85 (doublet).

Anal. Calcd. for $C_{14}H_{18}O$: C, 83.12; H, 8.97; O, 7.91. Found: C, 83.09; H, 8.84; O, 8.11.

2-p-Tolyl-6-methylhepta-1,5-diene (Vb).—A suspension of triphenylphosphonium bromide (15.4 g.) in ether (150 ml.) was treated with a 15% solution of butyllithium in hexane (40.6 ml.); after 15 min., keto compound Va (6 g.) in ether (50 ml.) was added. The reaction mixture was processed as in the preparation of IIIc, yielding an oil (5.3 g.) which, after fractional distillation, afforded a fraction (4.5 g.), b.p. 98–100 (0.75 mm.). Purification by preparative thin layer chromatography in silica gel, using a 95:5 hexane–ethyl acetate mixture as developer, gave the analytical sample: d^{22} 0.9550; $n^{22}\text{D}$ 1.5280; ν_{max} 2915, 1625, 1375, 885 cm.$^{-1}$; n.m.r. 1.55, 1.65, 2.33, 4.95, 5.20, 7.2 (doublet), 7.4 (doublet).

Anal. Calcd. for $C_{15}H_{20}$: C, 89.94; H, 10.06. Found: C, 90.02; H, 9.94.

Dehydration of 2-p-Tolyl-6-methylhept-5-en-2-ol (VI).—A suspension of VI (15 g.) in a 10% aqueous solution of oxalic acid (150 ml.) was refluxed for 4 hr. After the usual extraction procedure, an oily product was obtained. Preparative thin layer or vapor phase chromatography afforded two main products. The major one (60%) was identified, by comparison of its infrared and n.m.r. spectra, as Vb. The other one (20%), was starting material (VI).

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[15] We are indebted to Dr. Y. R. Navès for a sample of l-lanceol.

The Stereospecific Formation and Decomposition of a *cis*-Episulfone from Phenyldiazomethane and Sulfur Dioxide

Niichiro Tokura, Toshikazu Nagai,
and Shoichi Matsumura

*Department of Applied Chemistry, Faculty of Engineering,
Osaka University, Higashinoda, Osaka, Japan*

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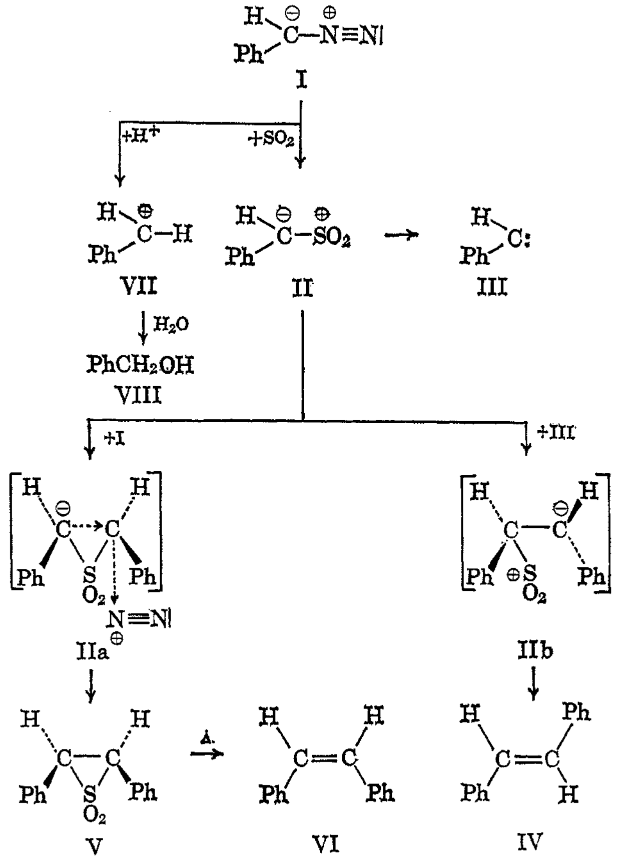
It has long been recognized that by the reaction between a diazomethane derivative and liquid or gaseous sulfur dioxide an alkene is produced, presumably *via* an ethylene sulfone. Tetraphenylethylene sulfone and ethylene sulfone, respectively, have been isolated from diphenyldiazomethane by Staudinger and Pfenninger,[1] and from diazomethane by Hesse, *et al.*,[2] but in these symmetrical ethylene derivatives, the stereospecificity of the reactions is obscure.

Scheme I



The present note deals with a synthesis of *cis*-stilbene *via* *cis*-1,2-diphenylethylene episulfone which has been obtained by the reaction of phenyldiazomethane with sulfur dioxide or an aqueous solution of sulfur dioxide.[3,4]

When a solution of phenyldiazomethane (I) in a solvent such as n-hexane, cyclohexane, benzene, or ether was treated with sulfur dioxide or with an aqueous solution of sulfur dioxide, there was obtained, in addition to *trans*-stilbene (IV), *cis*-stilbene (VI), benzaldehyde (IX), benzal azine, benzyl alcohol (VIII), and *cis*-1,2-diphenylethylene episulfone (V) in good yield. On heating at the melting point (85–86°), this sulfone was converted stereospecifically and quantitatively to *cis*-stilbene, whereas treatment with 0.2 N alkali at 50° gave 61% *trans*- and 39% *cis*-stilbene. The results are listed in Table I.

It is worthy to note that *cis*-episulfone was produced when phenyldiazomethane was in excess over the quantity of sulfur dioxide, *viz.*, by addition of SO_2 into phenyldiazomethane solution, while no *trans*-episulfone was found in the reaction mixture.

A suggested mechanism for the formation of the *cis*-episulfone is that sulfene II, an intermediate in the initial step of the reaction, first reacts with excess phenyldiazomethanes,[5] to afford a C–S bond. As

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[1] H. Staudinger and F. Pfenninger, *Ber.*, **49**, 1941 (1916).

[2] G. Hesse, E. Reichold, and S. Mayundar, *ibid.*, **90**, 2106 (1957).

[3] The present authors wish to use such an expression preferably than the expression "sulfurous acid solution," since, according to Linchtin,[4] an aqueous solution of sulfur dioxide consists largely, if not entirely, of SO_2 and water.

[4] N. N. Lichtin, *Advan. Phys. Org. Chem.*, **1**, 90 (1963).

[5] Recently, the formation of episulfone was reported, by the reaction of a sulfene derived from the elimination reaction of chlorosulfone with diazo-compounds [G. Opitz and K. Fischer, *Angew. Chem.*, **77**, 41 (1965)].

TABLE I

Expt.	Phenyl-diazomethane solution (A), solvent	Sulfur dioxide or aqueous solution of SO_2 (B)	Vol., of B, ml.	Mixing of A and B	Temp., °C.	Reaction products, %[a]				
						Stilbene		*cis*-1,2-Diphenylethylene episulfone	Benzal-dehyde	Benzyl alcohol
						trans	*cis*			
1	Ether	Liq. SO_2	10	B into A	−20	76.6	Trace	23.4	0	0
2	Benzene	Liq. SO_2	10	B into A	0	59.2	Trace	40.8	0	0
3	*n*-Hexane	Liq. SO_2	10	B into A	−20	39.5	Trace	60.5	0	0
4	Ether	6% aq. SO_2	100	B into A	0	71.5	Trace	28.5	0	Trace
5	Ether	6% aq. SO_2	50	B into A	0	45.1	Trace	54.9	0	Trace
6	Cyclohexane	6% aq. SO_2	60	B into A	0	34.6	0	65.4	0	Trace
7	Ether	Liq. SO_2	50	A into B	−20	73.2	Trace	0	22.0	4.6
8	Ether	Liq. SO_2 saturated with H_2O (1%)	50	A into B	−20	65.7	9.5	0	2.9	22.0
9	Ether	6% aq. SO_2	100	A into B	0	64.8	Trace	10.4	3.0	21.8
10	Ether	Liq. SO_2 H_2O Fuming H_2SO_4	50 1 0.8	A into B	−20	39.3	0.9	0	9.7	49.7
11	Ether	0.8 *N* H_2SO_4	100	B into A	0	15.1	9.4	0	4.5	72.0

[a] Per cents are indicated in molar per cents.

indicated in IIa, the C–C distance thus may be elongated and the London force attraction between the two phenyl rings would be stronger than the repulsive force between them[6]; thus, a *cis*-episulfone might be formed. The similar suggestion has been presented by Neurieter and Bordwell[7] as an intermediate to give *cis*-2-butene when α-chloroethyl ethyl sulfone was treated with alkali.

It is possible that the *trans*-episulfone is also formed and decomposes into *trans*-stilbene owing to the lower stability of the episulfone. Another possible mechanism for the formation of *trans*-stilbene might be the reaction of sulfene II with phenylcarbene (III), arising from decomposition of sulfene, which would lead to formation of a C–C bond (IIb), owing to the electrophilic nature of the carbene,[8] and then result in *trans*-stilbene formation, owing to steric repulsion of the phenyl groups (Scheme I).

Experimental Section

A Typical Reaction.—An ethereal solution of phenyldiazomethane[9,10] (2.26 g. in 100 ml. of ether) was placed in a three-necked flask fitted with a Dry Ice–trichloroethylene reflux condenser (−70°) and stirred, while 10 ml. of liquid sulfur dioxide was added during 15 min. (expt. 1, Table I) The color of the solution changed to yellow on addition of SO_2.

cis-**1,2-Diphenylethylene Episulfone** (V).—The crystalline precipitate was a mixture of V and a small amount of *trans*-stilbene (IV). After washing with ether the sulfone was recrystallized from ether–benzene to give white crystals: 0.547 g.; m.p. 85–86° dec.; $\lambda_{\max}^{\mathrm{EtOH}}$ 268 mμ (log ε 3.65), 274 mμ (log ε 3.61); $\nu_{\max}^{\mathrm{Nujol}}$ 1328, 1143 cm.$^{-1}$ (SO_2 stretching); τ = 2.77 (phenyl), 4.79 p.p.m. (methine).

Anal. Calcd. for $C_{14}H_{12}O_2S$: C, 68.84; H, 4.95. Found: C, 69.01; H, 5.20.

On warming the sulfone at 85–86° without solvent, SO_2 was evolved and *cis*-**stilbene** was formed stereospecifically[11] in 100% yield. The product thus formed has analytical values and weight corresponding to stilbene. A thin layer chromatography (Wako-gel B-5, 0.6 mm., *n*-hexane) showed that the product consisted of a single component, R_f 0.62 (identical with that of *cis*-stilbene synthesized by another method[12]); *trans*-stilbene (R_f 0.55) was not detected. Moreover, the product had $\lambda_{\max}^{\mathrm{EtOH}}$ 223 mμ (log ε 4.28), 276 mμ (log ε 4.05), and $\nu_{\max}^{\mathrm{neat}}$ 1600 cm.$^{-1}$, identical with those of an authentic sample.[12,13] The characteristic absorption at 960 cm.$^{-1}$ due to *trans* olefin was not observed. *trans*-**Stilbene** was isolated from the ether wash and crystallized from methanol: m.p. and m.m.p. 122–123°; $\nu_{\max}^{\mathrm{Nujol}}$ 1620, 960 cm.$^{-1}$; $\lambda_{\max}^{\mathrm{EtOH}}$ 226 mμ (log ε 4.20), 295 mμ (log ε 4.45). The spectra were identical with those of an authentic specimen.[12,13]

Anal. Calcd. for $C_{14}H_{12}$: C, 93.29; H, 6.71. Found: C, 93.19. H, 6.84.

Chromatography of the mother liquor on alumina using petroleum ether (b.p. 40–60°), benzene, and benzene–methanol (9:1) for elution gave successively *cis*-stilbene, *cis*- and *trans*-stilbene mixture (separated by fractional crystallization), and *trans*-stilbene. The total amount of *trans*-stilbene obtained was 1.75 g. Benzalazine,[14] 1.74 g., m.p. and m.m.p. 92°, $\nu_{\max}^{\mathrm{Nujol}}$ 1630 cm.$^{-1}$ (C=N=N=C), was isolated from the final fractions. Benzaldehyde and benzyl alcohol was also obtainable in the case of expt. 7–11. The following is an example in the case of expt. 8, where 4.76 g. of phenyldiazomethane was used.

Benzaldehyde (**IX**), 0.124 g., was obtained, 2,4-dinitrophenylhydrazone m.p. 237°, and the mixture melting point with an authentic sample showed no depression. The elution with benzene–methanol (9:1) gave benzyl alcohol.

Benzyl alcohol (**VIII**), 0.960 g., R_f 0.52 (in benzene) on thin layer chromatography (Wako-gel B-5, 0.63 mm.), was obtained. The infrared spectrum was identical with that of an authentic sample.[15] The phenylurethan had m.p. and m.m.p. 77°.

Since the weights of the products thus obtained involve those of some decomposed products present in the phenyldiazomethane solution in addition to the actual reaction products, blank tests were performed and the yields (Table I) were calculated by subtracting from the weights of the crude products (for example, benzal azine) the amount in the blank runs.

It has been also confirmed by the present authors that an isomerization between *cis*- and *trans*-stilbenes does not occur during the experimental conditions.

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(6) The London force between atoms is believed to fall off with the reciprocal sixth power of the internuclear distance [K. S. Pitzer and E. Catalano, *J. Am. Chem. Soc.*, **78**, 4844 (1956)]. On the other hand, the repulsive force between atoms has been described by a function involving the reciprocal twelfth power of the distance. Accordingly, it seems possible that, at the elongated C–C bond distance (perhaps 2.6 Å. in the transition state IIa but 1.5 Å. in IIb), the attraction force may predominate over the repulsive force.

(7) N. P. Neurieter and F. G. Bordwell, *ibid.*, **85**, 1209 (1963).

(8) P. S. Skell and R. C. Woodworth, *ibid.*, **77**, 4638 (1955).

(9) G. Lock and K. Stack., *Ber.*, **76**, 1252 (1943).

(10) R. J. Mohrbacher and N. H. Cromwell, *J. Am. Chem. Soc.*, **79**, 401 (1957).

(11) The stereospecific thermal decomposition to give the corresponding alkene of a episulfone is known related to diazoethane.[7]

(12) L. F. Fieser, "Experiments in Organic Chemistry," Maruzen, Japan, 1956, pp. 178, 185.

(13) C. C. Price and G. Berti, *J. Am. Chem. Soc.*, **76**, 1219 (1954).

(14) R. G. R. Bacon and W. S. Lindsay, *J. Chem. Soc.*, 1382 (1958); H. H. Hatt, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 395.

(15) S. E. Wiberley, S. C. Bunce, and W. H. Baver, *Anal. Chem.*, **32**, 217 (1960); P. v. R. Schleyer, D. S. Trifan, and R. Bacskai, *J. Am. Chem. Soc.*, **80**, 6691 (1958).