and 30% *cis*-1,3,5-hexatrnene (5 g.) was added dropwise to the alumina column and the product was collected and isolated as above (*ca.* 80% recovery). G.l.p.c. analysis of the product was conducted at 35 and 50°. No benzene was detected. 1,3-Cyclohexadiene was identified by comparison with an authentic sample. With an alumina column temperature of 300°, only *trans*-1,3,5-hexatriene and 1,3-cyclohexadiene were found. With a column temperature of 200°, *cis*- and *trans*-1,3,5-hexatriene were found in equal amounts, as well as 1,3-cyclohexadiene. In both cases, the amounts of 1,3-cyclohexadiene formed corresponded to the loss of 1,3,5-hexatriene (total area under peaks).

Equilibration of *cis*- and *trans*-1,3,5-Hexatriene.—To samples of freshly distilled 1,3,5-hexatriene (chromatographically pure 70% *trans*, 30% *cis* mixture), a few drops of a saturated iodine-ether solution were added. The resulting samples were equilibrated at 0, 5, 25, 30, and 50° (±0.5°). These were analyzed by g.l.p.c. at various times until the observed *K* values (obtained by measuring the areas under the *cis* and *trans* peaks) were constant. At the higher temperatures, polymer formation was evident before *K* became constant. These runs were discarded for calculation purposes.

Acknowledgment.—The author would like to express his appreciation to the following students for experimental assistance: Mr. Krishnahadi Pribadi, Mr. Curt Harris, and Mr. Tim Bowden.

The Syntheses of (±)-β-Bisabolene and 2-*p*-Tolyl-6-methylhepta-1,5-diene

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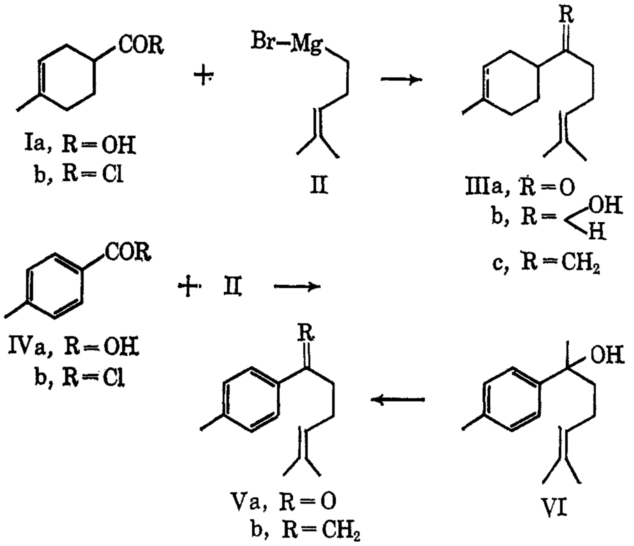
The sesquiterpene hydrocarbon β-bisabolene (IIIc, $C_{15}H_{24}$) has been recently found in nature.[1-4] Navés has prepared it from lanceol,[5] and bisabolene trihydrochloride has been synthesized by Ruzicka and Liguori.[6]

The sesquiterpenoid hydrocarbon 2-*p*-tolyl-6-methylhepta-1,5-diene (Vb, $C_{15}H_{20}$), which has not been found in nature, is the 1-dehydro derivative of the major component in the natural sesquiterpene mixture known as α-curcumene and, so far as we are aware, has not been prepared.

We have obtained both compounds in accordance with Scheme I. The acid chloride of 4-methyl-1-carboxy-Δ^3-cyclohexene (Ib) was coupled with the Grignard reagent from 1-bromo-4-methyl-Δ^3-pentene (II) yielding 2-methyl-6-keto-6-(4′-methyl-$\Delta^{3'}$-cyclohexenyl)-Δ^2-hexene (IIIa). The acid Ia reported by Meldrum and Perkin[7] was prepared by the hydrolysis of the ester obtained by condensation of isoprene and methyl acrylate.[8] The bromo compound II was obtained from α-acetylbutyrolactone according to Julia, *et al.*[9]

SCHEME I



The keto compound IIIa (characterized as its alcohol) was treated with triphenylmethylphosphonium bromide[10] to yield the desired (±)-β-bisabolene (IIIc).

2-*p*-Tolyl-6-methylhepta-1,5-diene (Vb) was prepared in a similar manner by coupling the same Grignard reagent (II) with *p*-toluic acid chloride and treating the 2-methyl-6-keto-6-(*p*-tolyl)-Δ^2-hexene (Va) obtained with triphenylmethylphosphonium bromide, affording an oil that showed infrared and n.m.r. spectra consistent with structure Vb. The same compound (Vb) is obtained when 2-*p*-tolyl-6-methylhept-5-en-2-ol (VI)[11] is dehydrated by means of oxalic acid. It is, therefore, not surprising that the elimination leads predominantly to the 1-olefin, that is, the less-hindered one.[12,13]

Experimental Section[14]

2-Methyl-6-keto-6-(4′-methyl-$\Delta^{3'}$-cyclohexenyl)-Δ^2-hexene (IIIa).—The bromo compound II (45 g.) was slowly added, at room temperature, with stirring to Mg turnings (6.71 g.) in anhydrous ether (200 ml.). When the reaction was completed (45 min.), the organomagnesium compound was slowly added to a mixture of the acid chloride Ib (49 g.), cuprous chloride (200 mg.), and anhydrous ether (60 ml.). Stirring was prolonged overnight and a 5 *N* solution of H_2SO_4 (400 ml.) was then added. After the usual extraction procedure, 73 g. of an oily product was obtained. Fractional distillation afforded a fraction (53 g.): b.p. 123–125° (2 mm.); d^{25}_4 0.920; $n^{25}D$ 1.4869; ν_{max} 2860, 1710, 1375, 910 cm.$^{-1}$; n.m.r. 1.65, 1.8–2.5, 5.0, 5.35.

Reduction of 5 g. of the ketone with 1 g. of $NaBH_4$ in methanol afforded 4 g. of 2-methyl-6-hydroxy-6-(4′-methyl-$\Delta^{3'}$-cyclohexenyl)-Δ^2-hexene (IIIb): b.p. 100–104° (0.25 mm.); d^{25} 0.951; $n^{25}D$ 1.4910; ν_{max} 3040, 2900, 1375 cm.$^{-1}$; n.m.r. 1.6, 3.4, 5.15, 5.35.

Anal. Calcd. for $C_{14}H_{24}O$: C, 80.71; H, 11.61; O, 7.68. Found: C, 80.30; H, 11.48; O, 8.01.

(±)-β-Bisabolene (IIIc).—To a suspension of triphenylmethylphosphonium bromide (7.72 g.) in anhydrous ether (100

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(1) M. Soucek, V. Herout, and F. Sorm, *Collection Czech. Chem. Commun.*, **26**, 2551 (1961).

(2) G. V. Pigulevskii, D. V. Motskus, and L. L. Rodina, *Zh. Prikl. Khim.*, **35**, 1143 (1962); *Chem. Abstr.*, **57**, 7396 (1962).

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(12) H. C. Brown and H. L. Bernies, *J. Am. Chem. Soc.*, **75**, 10 (1953).

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(14) Melting points were determined in a Kofler block. Densities were determined in a Fisher-Davidson gravitometer using ethyl benzene as standard. Refractive indexes were obtained in an Abbé refractometer (Bausch and Lomb). Infrared spectra were run in films on a Perkin-Elmer Model 21 spectrophotometer and the n.m.r. spectra were determined in CCl_4 solutions, containing TMS as internal standard, using a Varian A-60 spectrometer. Chemical shifts are given in parts per million (δ). Distillations were carried out through a 20-cm. Wiedmer column. Microanalyses were performed by Dr. Franz Pascher, Bonn, Germany.

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)-Δ²-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. Navés for a sample of *l*-lanceol.

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

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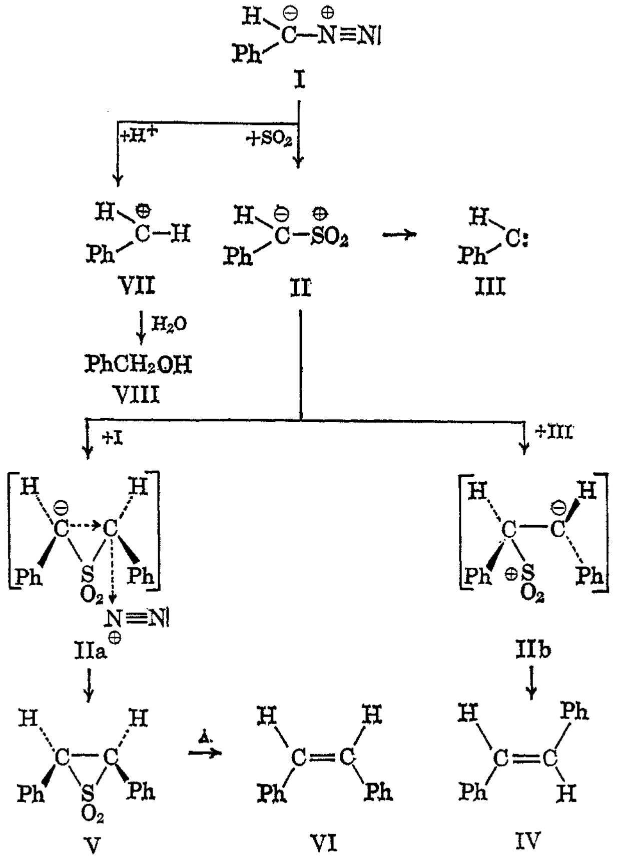
It has long been recognized that by the reaction between a diazomethane derivative and liquid or gaseous sulfur dioxide an alkene is produced, presumably *via* an ethylene sulfone. Tetraphenylethylene sulfone and ethylene sulfone, respectively, have been isolated from diphenyldiazomethane by Staudinger 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)].