Anal. Calcd. for $C_{18}H_{18}N_4$: C, 74.45; H, 6.25. Found: C, 74.16; H, 6.21.

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Racemization of an Optically Active Olefin during Catalytic Hydrogenation

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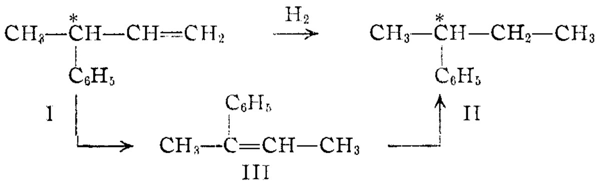
The syntheses and relative configurations of optically pure (−)-3-phenyl-1-butene (I) and (−)-2-phenylbutane (II) have been previously reported.[1] It has now been observed that when I is reduced catalytically to give II, from 1 to 11% loss of optical activity attends the reaction. Since compound II has been demonstrated not to racemize to any detectable extent under the conditions of the experiment, the racemization appears to take place either before or during the reduction. Possibly I isomerizes to III which is subsequently reduced, either with or without leaving the catalyst surface. The results are recorded in Table I.



The palladium-on-calcium carbonate catalyst gives more racemization than the other two catalysts, and the addition of conjugated olefin (2-phenyl-2-butene) to the mixture does not seem to effect the degree of racemization with this catalyst. The results are duplicatable within a few per cent.

TABLE I

DEGREE OF RACEMIZATION OF OPTICALLY ACTIVE 3-PHENYL-1-BUTENE WHEN REDUCED IN THE PRESENCE OF DIFFERENT CATALYSTS[a]

Catalyst	Starting material	Racem. of active material,[b] %
Pd–$CaCO_3$[c]	Opt. pure I	9.1
Pd–$CaCO_3$[c]	86% racemized I[d]	11.1
Pd–$CaCO_3$	15% opt. pure I + 85% III[e]	11.3
Raney Ni	Opt. pure I	2.5
Raney Ni	86% racemized I[d]	1.1
PtO_2[f]	86% racemized I[d]	3.5

[a] The solvent was in each case ethanol, 6 ml. per g. of olefin. The 2-phenylbutane isolated in each case had $n^{25}D$ 1.4878 (see ref. 1b). The hydrogen uptake was the theoretical ±2%. [b] Calculated on the basis that for optically pure 2-phenylbutane, $\alpha^{25}D$ 24.3° (neat, *l* 1 dm.). [c] 0.5% palladium-on-calcium carbonate, 1 g. per g. of olefin [I. M. Heilbron, E. R. H. Jones, J. T. McCombie and B. C. Weedon, *J. Chem. Soc.*, 84 (1945)]. [d] Prepared by diluting optically pure 3-phenyl-1-butene with pure racemic material (see ref. 1a). [e] Equal molar mixture of *cis*- and *trans*-2-phenyl-2-butene. [f] 0.1 g. of PtO_2 per g. of olefin.

Experimental Part

Reduction of Optically Pure 3-Phenyl-1-butene in Presence of Raney Nickel.—The procedure for the experiments reported in Table I is illustrated as follows. A mixture of 1.0 g. of optically pure (−)-3-phenyl-1-butene ($[\alpha]^{22}D$ −6.39°, ref. 1a), 1 ml. (roughly) of freshly prepared Raney nickel catalyst[2] and 6 ml. of absolute ethanol was agitated in an atmosphere of hydrogen with a magnetic stirrer at room temperature until no more hydrogen was absorbed (two hours). A total of 183 ml. (temperature 26°, pressure 752 mm.) was taken up, or 98% of theory. The reduction mixture was filtered, and the catalyst was washed with ethanol (3 ml.). The filtrate was shaken with five volumes of water and two of pure pentane. The pentane layer was washed three times with water, dried, and the solvent was evaporated through a short column. The product was twice flash distilled to give 0.83 g. of pure 2-phenylbutane, $n^{25}D$ 1.4878, $\alpha^{23}D$ −23.7 (neat, *l* 1 dm.), or 2.5% racemized.

When optically active 2-phenylbutane ($n^{25}D$ 1.4878, $\alpha^{23}D$ −22.4°, neat, *l* 1 dm.) was submitted to the above procedure utilizing 0.5% palladium-on-calcium carbonate catalyst, an 84% recovery of the 2-phenylbutane was experienced ($n^{25}D$ 1.4878, $\alpha^{23}D$ −22.4° (neat, *l* 1 dm.)).

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[1] D. J. Cram, (a) THIS JOURNAL, **74**, 2137 (1952); (b) *ibid.*, **74**, 2149 (1952).

[2] R. Mozingo, *Org. Syntheses*, **21**, 15 (1941).

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Rearrangement of 2-Bromo-1-methoxy-1,1,2-triphenylethane and 1-*p*-Anisyl-2-bromo-1-methoxy-1,2-diphenylethane[1]

BY DAVID Y. CURTIN[2] AND ESTELLE K. MEISLICH

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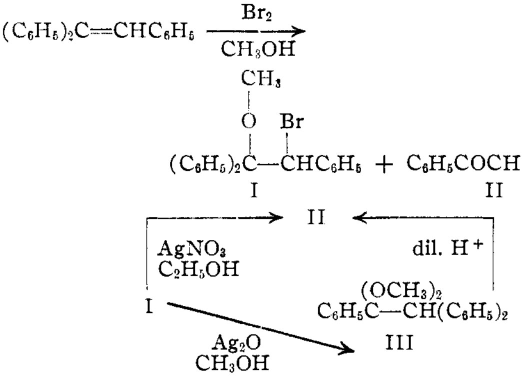
The synthesis of 2-bromo-1-methoxy-1,1,2-triphenylethane (I) was accomplished in 40% yield by the bromination of triphenylethylene in the presence of methanol. Its formation was accompanied by a rearrangement which gave benzhydryl phenyl ketone (II) in 45% yield. It was found that the yield of I was increased to 56% by the addition of sodium bicarbonate.

I reacted with silver nitrate in ethanol to give a 99% yield of II. With silver oxide suspended in ethanol the product was III, the diethyl ketal of II. III was characterized by its ready hydrolysis to II with 0.04% hydrochloric acid. The isomeric ether, triphenylethylene glycol dimethyl ether (IV) was synthesized and found to be stable under the same conditions.



It is possible that benzhydryl phenyl ketone diethyl ketal is an intermediate in the conversion of I to II with aqueous ethanolic silver nitrate but that it is hydrolyzed to II by the nitric acid formed during the reaction.

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[1] Part of the Ph.D. Thesis submitted by Estelle K. Meislich to Columbia University.

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