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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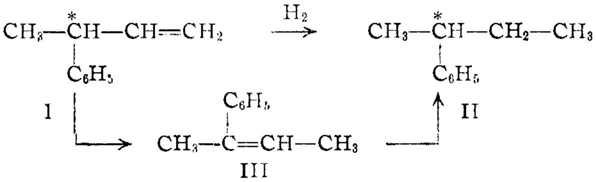
Racemization of an Optically Active Olefin during Catalytic Hydrogenation

BY DONALD J. CRAM

RECEIVED MAY 24, 1952

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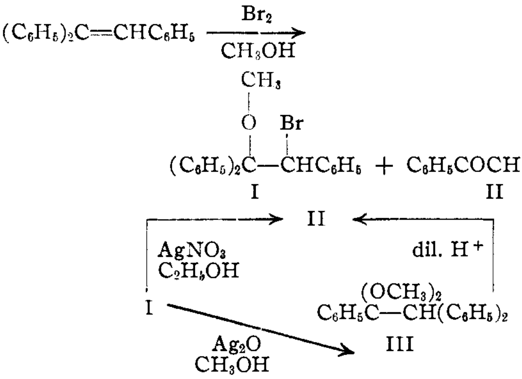
Rearrangement of 2-Bromo-1-methoxy-1,1,2-triphenylethane and 1-*p*-Anisyl-2-bromo-1-methoxy-1,2-diphenylethane[1]

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

RECEIVED JUNE 19, 1952

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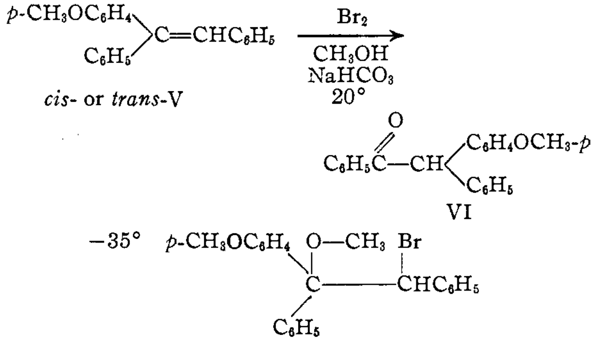
(1) Part of the Ph.D. Thesis submitted by Estelle K. Meislich to Columbia University.

(2) Department of Chemistry, University of Illinois, Urbana, Illinois.

Since *cis*- and *trans*-1-*p*-anisyl-1,2-diphenylethylene (*cis*- and *trans*-V) had been prepared and their configurations established,[3] their reaction with bromine and methanol in the presence of sodium bicarbonate was examined. At room temperature *p*-methoxybenzhydryl phenyl ketone (VI) was obtained (from either *cis*- or *trans*-V) in 97% yield. At −35° both *cis* and *trans*-V gave 70% of what appeared to be a mixture of *erythro*- and *threo*-1-*p*-anisyl-2-bromo-1,2-diphenyl-1-methoxyethane (VII), together with 17% of VI. In a typical experiment the product from *trans*-V melted at 70.5–72.0°, that from *cis*-V melted at 65.5–68° and when mixed they melted at 60.5–64°. When the samples were stored in tightly-stoppered vials in a refrigerator the melting points dropped about 10° during a period of three weeks. Exposure to air caused decomposition to an oil within three hours. A solid appeared after several weeks which was identified as VI. Any sample of VII rearranged to VI on repeated recrystallization from ethanol or methanol or on treatment with silver nitrate in methanol. All attempts to separate pure *erythro*- or *threo*-VII failed.



erythro- and *threo*-VII

Previous work on the rearrangement with nitrous acid of the analogous amino alcohols[4] indicated that *erythro*- and *threo*-VII might under the proper conditions, rearrange stereospecifically to give different ketones. An attempt was therefore made to avoid the isolation of the isomers of VII by carrying out the bromination in methanol containing sodium bicarbonate as above and then proceeding directly with the rearrangement by the addition of silver oxide at −35°. The product from either *cis*- or *trans*-V was the dimethyl ketal (VIII) of VI (formed by migration of *p*-anisyl) in 65–70% yield. VIII was characterized by hydrolysis to VI with dilute hydrochloric acid or even on standing in air for several months. It is not possible on the basis of this work to decide rigorously whether the nonstereospecific reaction is the bromomethoxylation or the rearrangement or both.

Experimental[5]

2-Bromo-1-methoxy-1,2-triphenylethane (I).—Bromine (3.2 g., 0.02 mole) was added to triphenylethylene[6] (5.00 g., 0.0200 mole) in 125 cc. of methanol at 35°. After addition was complete the mixture was stirred for 2 hours. The white solid which had precipitated was filtered, washed with cold methanol and dried to give 1.39 g. of I, m.p. 82–83°. Evaporation of the filtrate to half its volume gave an additional 1.35 g., m.p. 79–81.5°, or a total of 2.74 g. (38% yield). Recrystallization from hexane brought the m.p. to 91–92.5°.

Anal. Calcd. for $C_{21}H_{19}BrO$: C, 68.7; H, 5.2; Br, 21.8. Found: C, 68.7; H, 5.0; Br, 21.8.

Further evaporation of the mother liquor above to dryness gave 2.87 g. of solid. Upon recrystallization from methanol 2.40 g. (45%) of benzhydryl phenyl ketone (II), m.p. 136–137° (mixed m.p. no depression), was obtained.

When the bromination was carried out as above but with the addition of excess sodium bicarbonate the yield of I was 56% and of II, 22%.

Reaction of I with Silver Nitrate.—When I (1.00 g., 0.0027 mole) in 25 cc. of ethanol was treated with a solution of 0.50 g. of silver nitrate in the minimum amount of ethanol an immediate yellow precipitate of silver bromide appeared. The flask was shaken at room temperature for 30 minutes, 25 cc. of ethanol added and the solution filtered while hot. After concentration of the filtrate 0.65 g. (88%) of II, m.p. 136–137° (mixed m.p. showed no depression) was obtained.

Reaction of I with Silver Oxide.—I, prepared by the addition of 1.20 g. (0.0078 mole) of bromine to 2.00 g. (0.0078 mole) of triphenylethylene in the presence of excess sodium bicarbonate was not isolated but allowed to react directly in solution with 5 g. of silver oxide (freshly prepared by the addition of hot 10% sodium hydroxide to 10% aqueous silver nitrate and washed with methanol). The mixture was stirred vigorously for 15 minutes and then allowed to stand overnight. After filtration of the silver salts, concentration of the methanol solution and recrystallization from methanol, 2.0 g. (82%) of the **dimethyl ketal** of II was obtained (m.p. crude 83–86°) which after further crystallization from methane melted at 84.4–85.6°.

Anal. Calcd. for $C_{22}H_{22}O_2$: C, 83.0; H, 7.0. Found: C, 82.7; H, 7.0.

When 0.1 g. of the ketal was dissolved in 5 cc. of 95% ethanol containing four drops of 10% hydrochloric acid, the solution heated to boiling and allowed to cool to room temperature, 0.07 g. (88%) of II, m.p. 137–138°, was obtained. A mixed m.p. with authentic II showed no depression.

Triphenylethylene Glycol Dimethyl Ether.—1,1,2-Triphenyl-2-methoxyethanol[7] (1.00 g., 0.00033 mole) in 50 cc. of benzene was added to a suspension of potassium (0.28 g., 0.0072 mole) in 20 cc. of refluxing benzene. At the end of 1 hour 15.0 g. of methyl iodide was added quickly. The solution was stirred for 1 hour and allowed to stand overnight. The benzene solution was washed with water, dried and evaporated. The oil thus obtained was added to hot petroleum ether from which separated 0.20 g. of starting material. Concentration of the mother liquors gave 0.60 g., m.p. 86–92° which on recrystallization from methanol gave 0.42 g. (51%) of triphenylethylene glycol dimethyl ether, m.p. 90–92°. Further recrystallization brought the melting point to 93.6–95.0°.

Anal. Calcd. for $C_{22}H_{22}O_2$: C, 83.0; H, 7.0. Found: C, 83.0; H, 6.8.

A mixed m.p. with the isomeric ketal obtained above was depressed. This ether was stable to the treatment described above which hydrolyzed the ketal.

Reaction of *cis*- and *trans*-1-*p*-Anisyl-1,2-diphenylethylene (*cis*- and *trans*-V) with Bromine in Methanol.—At room temperature, either *cis*- or *trans*-V (0.50 g., 0.0018 mole) in 20 cc. of methanol containing 0.30 g. of suspended sodium bicarbonate, to which was added 0.30 g. (0.0019 mole) of bromine, gave 0.41 g. (95%) of *p*-methoxybenzhydryl phenyl ketone, m.p. 85–89° (mixed m.p. showed no depression).

At −35°, 1.00 g. of *trans*-V gave 1.14 g. (82%) of a substance, m.p. 70–73°. *cis*-V gave, in a typical run, a product, m.p. 65.5–68°. When the two products were mixed the m.p. was depressed to 60.5–64°. They gave the correct analysis for **1-*p*-anisyl-2-bromo-1,2-diphenyl-1-methoxyethane** (VII).

Anal. Calcd. for $C_{22}H_{21}BrO$: C, 66.5; H, 5.3; Br, 20.1. Found: C, 66.6; H, 5.4; Br, 20.4.

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[3] D. Y. Curtin, Elbert E. Harris and Estelle K. Meislich, THIS JOURNAL, **74**, 2901 (1952).

[4] P. I. Pollak and D. Y. Curtin, *ibid.*, **72**, 961 (1950).

[5] All melting points are corrected. Microanalyses were performed by the Schwarzkopf Microanalytical Laboratory, Middle Village, N. Y.

[6] "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 606.

[7] A. McKenzie and H. Wren, *J. Chem. Soc.*, **97**, 473 (1910).

The m.p. of either product fell about 10° when the sample was allowed to stand in a tightly stoppered vial in the refrigerator. Repeated recrystallization from ethanol or methanol caused rearrangement to the ketone (VI).

Rearrangement of VII.—When 0.500 g. (0.00175 mole) of *trans*-V was brominated in methanol containing 0.30 g. of suspended sodium bicarbonate at −35° and then to the cold solution was added 3.00 g. of freshly prepared silver oxide, an oil was obtained which crystallized from petroleum ether to give 0.42 g. (69%) of *p*-**methoxybenzhydryl** phenyl **ketone dimethyl keta**l (VIII), which on further recrystallization from ethanol melted at 77.4–78°.

Anal. Calcd. for $C_{23}H_{24}O_3$: C, 79.3; H, 6.9. Found: C, 79.5; H, 7.0.

When the same conditions were used for *cis*-V, a 66% yield of VIII was obtained as shown by m.p. and mixed m.p.

The structure of VIII was established by its hydrolysis with 2 drops of 10% hydrochloric acid in 5 cc. of 95% ethanol to VI in 70% yield. It also gave VI after standing at room temperature for one month.

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Some Observations on Phosphinic Anhydrides

BY GENNADY M. KOSOLAPOFF

RECEIVED MAY 28, 1952

Some time ago we reported the synthesis of several dialkylphosphinic anhydrides from alkyl dialkylphosphinates and dialkylphosphinyl chlorides, as[1]

$$R_2P(O)Cl + EtOP(O)R_2 \longrightarrow EtCl + R_2P(O)OP(O)R_2$$

At that time we also reported that the reaction of dimethylphosphinyl chloride with ethyl di-*n*-butylphosphinate gave not the expected mixed anhydride but a mixture of the two symmetric anhydrides.

In order to explore the possibly general nature of this observation we attempted the preparation of several mixed phosphinic anhydrides by this reaction. Equimolar mixtures of chlorides and ethyl esters of dimethyl-, diethyl-, di-*n*-propyl- and di-*n*-butylphosphinic acids were heated as described previously[1]; substantially the theoretical amounts of ethyl chloride were obtained from all possible combinations of the above-mentioned compounds at 140–150°. In all instances, however, the distillation of the reaction mixtures, at 0.05–0.1 mm. pressure, gave only the corresponding pairs of the symmetric phosphinic anhydrides, which were characterized by comparison with the known specimens. The work was done in standard Pyrex apparatus. It is conceivable that the transformation of the expected unsymmetrical substances might have been catalyzed by the glass composition and might have been avoided by the use of fused quartz apparatus. However, it appears that the existence of unsymmetric phosphinic anhydrides at moderately elevated temperatures is purely transient. This points out a similarity of behavior to that of mixed carboxylic anhydrides and acetals, which tend to symmetrize during thermal treatment.

After this work was completed there appeared the paper of Todd and co-workers[2] which reports the preparation of unsymmetrical tetraesters of pyrophosphoric acid. Although the unheated crude reaction mixtures indicate the presence of such unsymmetrical esters, the latter could not be isolated by distillation owing to symmetrization similar to the one reported here.

Phosphinic anhydrides are unique among the known anhydrides of various organic acids of phosphorus, in that they have definite boiling points and, therefore, they can be positively identified and purified by conventional techniques of organic chemistry. Tetraesters of pyrophosphoric acid, probably the most studied anhydrides at this time, on the other hand are prone to decomposition and rearrangement reactions at elevated temperatures which make impossible a true fractional distillation of such compounds. These esters are commonly purified by distillation in molecular stills in which boiling points, in the true sense of the word, have very little significance. Identification of individuals in a mixture of closely related substances under such circumstances becomes dubious.

As a result of our work and that reported by Todd, *et al.*,[2] it appears quite possible that at this time no positively characterized unsymmetrical neutral derivatives of phosphorus acid anhydrides are known. While such compounds have been undoubtedly obtained in low temperature reactions, no methods of isolation at low temperatures have been developed and all distillation techniques, used thus far, require thermal treatment which causes the symmetrization discussed above.[3]

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(1) G. M. Kosolapoff and R. M. Watson, THIS JOURNAL, **73**, 4101 5466 (1951).

(2) N. S. Corby, G. W. Kenner and A. R. Todd, *J. Chem. Soc.*, 1234 (1952).

(3) The material was presented at the 121st National Meeting of the A.C.S., March, 1952.

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Some Salts of Symmetric Phosphinic Acids

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RECEIVED MAY 28, 1952

Many phosphinic acids, *i.e.*, compounds of the general type $R_2P(O)OH$, are known at this time. Qualitative descriptions of a number of metallic salts of a few such acids appear in the literature. However, the only quantitative report dealing with solubility of such salts appears to be that dealing with the copper and lead salts of di-pseudocumylphosphinic acid.[1]

Information about the solubilities of various salts of these acids is of obvious interest for the development of techniques of separation of mixtures of the acids themselves and of mixtures with other substances. We prepared, accordingly, several salts of four phosphinic acids. Two of the latter were aliphatic and two were aromatic, thus encompassing the relatively water-soluble and insoluble acids. Solubilities in water, benzene and 96% ethanol were determined at three temperatures (25, 35 and 45°) by conventional technique.

It is of interest to note the relatively high solu-

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(1) A. Michaelis, *Ann.*, **294**, 1 (1896).