Notes A department for short papers of immediate interest.

Pinacolic Reduction of Aromatic Aliphatic Ketones

MELVIN S. NEWMAN

Received June 28, 1960

The synthesis of 3,4,3′,4′-tetrahydro-7,7′-dimethyl-1,1′-binaphthyl by pinacolic reduction of 7-methyl-1-tetralone followed by dehydration of the resulting pinacol has been described.[1] In that paper further details concerning a new method of pinacolic reduction involved were promised. In this paper[2] this information is given.

The method involves reduction of a ketone in absolute alcohol-benzene solution by aluminum foil which has been sandpapered and to which a small amount of mercuric chloride has been added for amalgamation. *Successful results were obtained only with aromatic aliphatic ketones,* such as acetophenone, propiophenone, *p*-methoxypropiophenone, methyl 2-naphthyl ketone, α-tetralone, and 7-methyl-1-tetralone.[1] With purely aliphatic ketones, such as acetone, methyl ethyl ketone, methyl *i*-propyl ketone, pinacolone, and cyclohexanone, negligible amounts of bimolecular products were obtained. Benzophenone was reduced to benzopinacol in 60% yield in one experiment but, as a better method[3] is available for pinacolic reduction of aromatic ketones, no further studies in this series were made.

EXPERIMENTAL

In a typical experiment 31.8 g. of acetophenone was dissolved in 130 ml. each of absolute ethanol and dry sulfur-free benzene in a 1-l. one necked flask fitted with a ground-in reflux condenser. To this was added 0.5 g. of mercuric chloride and 8 g. of aluminum foil.[4] On heating the mixture a vigorous reaction started and was allowed to proceed without added heat until it moderated. External heat was then applied to maintain reflux until all of the aluminum had disappeared (2 hr.). In other experiments longer heating was occasionally needed. After cooling the reaction mixture was treated with dilute hydrochloric acid and the product extracted by benzene. The combined benzene extracts were washed with acid, sodium carbonate solution, saturated salt solution, and filtered through a funnel containing anhydrous sodium sulfate. After removal of the benzene, the residue was distilled under reduced pressure. The lower boiling fraction, b.p. 95–97° at 9–10 mm., contained monomeric products (in part, acetophenone). The fraction, b.p. 160–170° at about 0.5 mm. (rapid distillation) was dissolved in petroleum ether (b.p. 65–110°). A total of 18.0 g. (56%) of pinacol, 2,3-diphenyl-2,3-butanediol isomers,[5] m.p. 100–123°, was obtained in two crops. In other similar runs, yields of 54–59% of similar material were obtained.

In a similar way propiophenone yielded 34% of crude[6] 3,4-diphenyl-3,4-hexanediol,[5] m.p. 120–138°; *p*-methoxypropiophenone yielded[6] 31% of crude 3,4-di-*p*-methoxyphenyl-3,4-hexanediol,[7] m.p. 163–188°; methyl 2-naphthyl ketone yielded 18% of crude 2,3-di-2-naphthyl-2,3-butanediol,[8] m.p. 158–171°; and 1-tetralone yielded 53% of 3,4,3′,4′-tetrahydro-1,1′-dinaphthyl,[9] after dehydration of the crude pinacol fraction.

DEPARTMENT OF CHEMISTRY
OHIO STATE UNIVERSITY
COLUMBUS 10, OHIO

---

(1) M. S. Newman, *J. Am. Chem. Soc.*, 62, 1683 (1940).

(2) All of the experiments described herein were done in 1939 and 1940.

(3) M. Gomberg and W. E. Bachmann, *J. Am. Chem. Soc.*, 49, 241 (1927).

(4) About 6 inch squares of $^1/_{64}$ inch thick aluminum foil were sandpapered and then cut into one inch squares rapidly.

(5) G. Ciamician and P. Silber, *Ber.*, 47, 1806 (1914) give m.p. 87° and 122° for the acetophenone pinacols and 113° and 139° for the propiophenone pinacols.

(6) In most of these experiments vacuum distillation of the entire reaction product, or of that remaining in the mother liquors after crystallization of part of the pinacols (usually from benzene–petroleum ether solutions) showed that almost no monomolecular products (starting ketone or the corresponding secondary alcohol) were present.

(7) K. Shishido and H. Nozaki, Japanese Pat. 180,100 (1949). *Chem. Abstr.* 46, 4028h (1952), used a procedure almost identical with that described herein and claimed to get only the high melting isomer, m.p. 194°. See also E. C. Dodds, L. Goldberg, W. Lawson, and R. Robinson, *Proc. Roy. Soc.*, B127, 140 (1939).

(8) M. P. Balfe, J. Kenyon, and C. E. Searle, *J. Chem. Soc.*, 380 (1951).

(9) H. A. Weidlich, *Ber.*, 71, 1203 (1938).

Demethoxylation of Hindered *o*-Methoxy Ketones[1]

REYNOLD C. FUSON, BRUNO VITTIMBERGA, AND DAVID E. FRANKHOUSER[2]

Received April 7, 1960

Phenylmagnesium bromide served to convert 2,6-dimethoxyphenyl duryl ketone (I) to 2,6-diphenylphenyl duryl ketone.[3] This process has now been carried out in the presence of excess magnesium; 2,2′-diduroylbiphenyl (II), the corresponding keto alcohol IV, and 9,10-didurylphenanthrene (III) were among the products isolated. This

---

(1) This investigation was supported in part by a grant from the Office of Ordnance Research, U. S. Army (Contract No. DA-11-022-ORD-874).

(2) American Cyanamid Company Fellow, 1958–59.

(3) R. C. Fuson and B. Vittimberga, *J. Am. Chem. Soc.*, 79, 6030 (1957).