Notes A department for short papers of immediate interest.

Pinacolic Reduction of Aromatic Aliphatic Ketones

Melvin S. Newman

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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.

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[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

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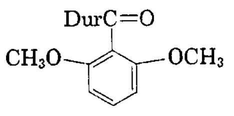
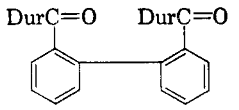
[1] This investigation was supported in part by a grant from the Office of Ordnance Research, U. S. Army (Contract No. DA-11-022-ORD-874).

[2] American Cyanamid Company Fellow, 1958–59.

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



I



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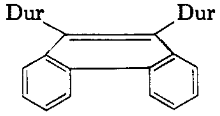

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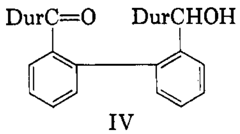
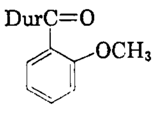


IV

observation is startling because the formation of these products must involve, in addition to reductive coupling, the replacement of two methoxyl groups by hydrogen atoms. It is seen that the demethoxylation has a vinylogous relationship to the reduction of esters to the corresponding aldehydes. Experiments were then undertaken to see whether the demethoxylation could be realized with simpler ketones. Initially it was assumed that the reagent responsible for the demethoxylation was magnesium (I) bromide. Accordingly, duryl *o*-methoxyphenyl ketone (VI) was subjected to the action of the binary mixture, magnesium–magnesium bromide. It had previously been shown that under these conditions the methoxy ketone underwent reductive coupling and cyclization to produce the hydrocarbon III and the diol V.[4]



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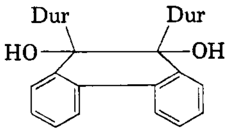
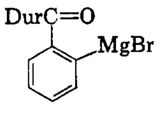


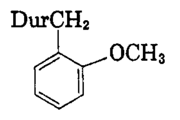
V



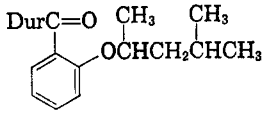
VII

Demethoxylation to give duryl phenyl ketone was indeed observed, although the yield of product was only 4.7%. Similar experiments with 2-methoxy-1-naphthyl mesityl ketone gave mesityl 1-naphthyl ketone in a yield of 11%. Treatment of the reaction mixture with carbon dioxide before work-up failed to produce *o*-duroylbenzoic acid. From this it was concluded that the keto Grignard reagent VII was probably not an intermediate. A similar keto Grignard reagent had been proposed to account for the debromination of *o*-bromophenyl mesityl ketone by the action of the binary mixture, magnesium–magnesium iodide.[5] Attempts to trap this hypothetical intermediate with carbon dioxide, acetic anhydride, and oxygen were not successful, however.

The similarity of this reduction to that of esters suggests that it might occur under conditions used by Hansley.[6] The reaction did not take the expected course, however. When the methoxy ketone VI was treated with sodium and 4-methyl-2-pentanol, the only products isolated were *o*-duroylphenyl 4-methyl-2-pentyl ether (IX) and a compound tentatively assigned the structure of *o*-methoxybenzyldurene (VIII). The keto ether IX presumably was formed by displacement of the methoxyl group by the 4-methyl-2-pentylate anion, a transformation analogous to alcoholysis of esters. The ether IX was synthesized independently from *o*-bromophenyl duryl ketone and sodium 4-methyl-2-pentylate. The formation of the ether VIII is not surprising as similar hindered ketones are reduced by sodium to the corresponding benzyl compounds.[7]



VIII



IX

EXPERIMENTAL[8]

Treatment of duryl 2,6-dimethoxyphenyl ketone with phenyl magnesium bromide in the presence of an excess of magnesium. A solution of 4.00 g. of ketone and 30 ml. of benzene was added over a 5-min. period to the Grignard reagent prepared from 6.30 g. of bromobenzene and 4.00 g. of magnesium in 45 ml. of ether. The mixture was then heated under reflux for 3.5 hr. After dry air had been passed through the mixture, it was poured into 200 ml. of $4N$ sulfuric acid. The organic phase was washed several times with water and dried over sodium sulfate. Removal of solvent left a red oil, which was chromatographed on an alumina column. Elution with 20:1 cyclohexane to ether gave, after combination of fractions and recrystallization, three products, only one of which could be identified with certainty. 9,10-Didurylphenanthrene, m.p. 288–289.5°, yield 0.06 g. (1.0%), was characterized by comparison of its infrared spectrum with that of authentic material. The infrared spectra of the second compound, m.p. 191–193°, yield 0.08 g. (1.1%) and of the the third compound, m.p. 156–160°, yield 0.03 g. (0.4%) did not contain absorption in the 1650 $cm.^{-1}$ region characteristic of hindered aromatic ketones. A band was present, however, at 700 $cm.^{-1}$ assigned to a monosubstituted benzene ring.[9] The spectrum of the third compound had a band at 1265 $cm.^{-1}$ attributed to absorption by an aromatic methoxyl group.[10] Since 9,10-didurylphenanthrene was isolated from the same fractions in the chromatography, it may be that the compounds are phenyl-substituted derivatives of 9,10-didurylphenanthrene. From the later fractions was obtained 0.10 g. (1.6%) of 2,2′-diduroylbiphenyl, m.p. 255.5–257°, identified by comparison of the infrared spectrum with that of authentic material. Removal of the solvent from the combined methanol fractions gave a red oil; it was dissolved in ethanol, and the solution allowed to stand in the cold for many days. Recrystallization of the precipitate from ethanol-chloroform

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[4] R. C. Fuson and R. O. Kerr, *J. Org. Chem.*, **19,** 373 (1954).

[5] R. C. Fuson and M. D. Armstrong, *J. Am. Chem. Soc.*, **63,** 2650 (1941).

[6] V. L. Hansley, *Ind. Eng. Chem.*, **39,** 55 (1947).

[7] R. C. Fuson and B. C. McKusick, *J. Am. Chem. Soc.*, **65,** 60 (1943).

[8] All melting points are corrected. The microanalyses were carried out by Mr. Josef Nemeth, Mr. Rollo Nesset, Mrs. Ruby Ju, Mrs. Alice Terra, Miss Jane Liu, and Miss Claire Higham. The infrared spectra were determined by Mr. James Brader, Mr. Paul McMahon, Mrs. Mary Verkade, Miss Charlene Luebke, Mrs. Louise Griffing, and Mr. Sy Portnow.

[9] M. L. MacMurry and V. Thornton, *Anal. Chem.*, **24,** 319 (1952).

[10] L. J. Bellamy, *The Infrared Spectra of Complex Molecules*, John Wiley and Sons, New York, N. Y., Second Edition, 1958, p. 117.

yielded a small amount of the keto alcohol IV, m.p. 163–166°. A mixture melting point determination with a known sample showed no depression.

Demethoxylation of duryl o-methoxyphenyl ketone. An ether solution of magnesium bromide was prepared according to the procedure of Wotiz, Hollingsworth, and Dessy.[11] A solution of 1.50 g. of ketone in 10 ml. of ether and 10 ml. of toluene was added dropwise to a cooled mixture of 0.50 g. of ground magnesium, 10 ml. of magnesium bromide solution, and 10 ml. of ether. The mixture was then stirred under nitrogen at ice bath temperature for 8 hr. after which time the solution was decanted from the remaining magnesium into 6*N* hydrochloric acid, ether and chloroform being added for solubility. The organic phase was extracted with 5% sodium bicarbonate, washed with water, and dried over sodium sulfate. Evaporation of the solvent left a red solid, which was chromatographed on alumina. From the fractions arising from elution with 15:1 cyclohexane to ether was obtained, after crystallization from chloroform-ethanol, 0.061 g. (4.7%) of duryl phenyl ketone, m.p. 118–121°, identified by a mixture melting point determination and infrared spectral analysis.

Demethoxylation of 2-methoxy-1-naphthyl mesityl ketone. A solution of 2.00 g. of ketone in 15 ml. of toluene and 10 ml. of ether was added over a 10-min. period to a mixture of 0.80 g. of ground magnesium, 10 ml. of magnesium bromide solution, and 10 ml. of ether. The mixture was stirred under nitrogen for 12 hr. at room temperature. Hydrolysis was effected by adding dropwise 25 ml. of 10% hydrochloric acid to the mixture, cooled in an ice bath. After 12 hr. the solution was poured into an additional 25 ml. of acid, to which 25 ml. of toluene and ether had been added. The organic layer was extracted with 5% sodium bicarbonate, washed with water, and dried over sodium sulfate. Evaporation of the solvent left a red solid, which was subjected to chromatography on alumina. Elution with 15:1 cyclohexane to ether gave, after recrystallization from chloroform-ethanol, 0.211 g. (11.7%) of mesityl 1-naphthyl ketone, identified by reference to its infrared spectrum and a mixture melting point determination.

Attempted carbonation of the mixture arising from reaction of duryl o-methoxyphenyl ketone with the binary mixture, magnesium–magnesium bromide. The mixture from the reaction of duryl *o*-methoxyphenyl ketone and the binary mixture was poured into finely divided Dry Ice with vigorous stirring, ether being added to replace that lost by evaporation. The mixture was allowed to warm to room temperature; ice and dilute hydrochloric acid were then cautiously added. When all the magnesium and other solids had dissolved, the organic layer was washed twice with water and extracted with two 50-ml. portions of 10% sodium hydroxide. A gelatinous inorganic precipitate which formed was removed by filtration. Acidification of the basic extract gave a red solid which was taken up in ether. Removal of solvent left a red oil which was reprecipitated by extraction into a 5% sodium bicarbonate solution and acidification of the solution. A tan solid melting over a wide range above 140° was obtained after dissolving the precipitate in ether and removing the solvent. The tan solid, however, could not be recrystallized from ethanol-water. Its infrared spectrum had a single intense band at 1690 cm.$^{-1}$ and a wide band between 3000 and 3500 cm.$^{-1}$. No band was present at 1665 cm.$^{-1}$; the 1665 cm.$^{-1}$ absorption is attributed to the ketone carbonyl group in *o*-duroylbenzoic acid. The organic layer obtained after extraction with sodium hydroxide was worked up in the usual way. Chromatography of the solid obtained after removal of solvent gave 0.028 g. of duryl phenyl ketone.

Treatment of duryl o-methoxyphenyl ketone with sodium and 4-methyl-2-pentanol. A modification of the procedure of Hansley[6] was used. A mixture of 1.00 g. of sodium cut into small pieces and 20 ml. of toluene was heated under nitrogen until the metal had melted. To the mixture was added dropwise, with stirring, 3.00 g. of ketone in 10 ml. of toluene and 20 ml. of 4-methyl-2-pentanol. Heating under reflux was continued until all the sodium had dissolved. An additional 0.30 g. of sodium was then added, and when the metal had dissolved, heating was stopped. The red solution was poured into an acidified ice water mixture, and the organic phase was extracted with 5% sodium bicarbonate, washed with water, and dried over sodium sulfate. Removal of the solvent left a residue which was chromatographed on alumina as before. Elution with 15:1 cyclohexane to ether gave a solid which was recrystallized from chloroform-ethanol to give 0.256 g. (6.8%) of *o*-duroylphenyl 4-methyl-2-pentyl ether, identified by a mixture melting point determination with a sample synthesized independently. The 20:1 cyclohexane to ether fractions gave clear oils, which were crystallized from methylene chloride–methanol to give 0.363 g. (13.1%) of a compound tentatively identified as *o*-methoxybenzyldurene.

Anal. Calcd. for $C_{18}H_{16}O$: C, 84.99; H, 8.72. Found: C, 85.05; H, 8.82.

The infrared spectrum has bands at 1240 and 750 cm.$^{-1}$. The 1240 cm.$^{-9}$ band is assigned to absorption by an aromatic methoxyl group.[10] The 750 cm.$^{-1}$ band is found in a number of *o*-substituted aromatic hindered ketones studied in this laboratory and has been assigned to an *o*-disubstituted benzene ring.[9] No band was present in the 1650 cm.$^{-1}$ region which is characteristic of a hindered aromatic ketone.

Preparation of o-duroylphenyl 4-methyl-2-pentyl ether. A mixture of 1.45 g. of sodium metal cut into small pieces and 25 ml. of 4-methyl-2-pentanol was heated under reflux until all the metal had dissolved. A solution of 10 g. of *o*-bromophenyl duryl ketone in 40 ml. of benzene was then added, and the mixture was heated under reflux for 34 hr., during which time a finely divided colorless precipitate formed. The reaction mixture was poured into 1*N* hydrochloric acid, which dissolved the solid, leaving two clear phases. The organic phase was washed with 5% sodium bicarbonate and with water, dried over sodium sulfate, and heated on a hot plate to remove solvent. When most of the benzene had distilled, *o*-duroylphenyl 4-methyl-2-pentyl ether crystallized from the hot solution; yield 8.10 g. (75.9%), m.p. 117–118°. The analytical sample, crystallized from chloroform-ethanol, melted at 118–119°.

Anal. Calcd. for $C_{23}H_{30}O_2$: C, 81.61; H, 8.93. Found: C, 81.59; H, 8.93.

The infrared spectrum of the material has bands assignable to a hindered conjugated ketone at 1655 cm.$^{-1}$, an aromatic ether at 1245 cm.$^{-1}$, a mesityl group at 865 cm.$^{-1}$, and a 1,2-disubstituted benzene ring at 750 cm.$^{-1}$.

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[11] J. H. Wotiz, C. A. Hollingsworth, and R. E. Dessy, *J. Org. Chem.*, **21**, 1063 (1956).

9,10-*endo*-*o*-Xylylene-9,10-dihydroanthracene

KEIITI SISIDO, YÔKO UDÔ, AND HITOSI NOZAKI

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In view of the remarkable reactivity of anthracene (I) with benzyl radicals as recorded in a previous paper,[1] it appeared of interest to examine

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[1] K. Sisido, Y. Udô, and H. Nozaki, *J. Am. Chem. Soc.*, **82**, 434 (1960). See also R. O. C. Norman and W. A. Waters, *J. Chem. Soc.*, 950 (1957); A. L. J. Beckwith and W. A. Waters, *J. Chem. Soc.*, 1001 (1957).