crystalline form by filtering the pasty mass from the solvent at a low temperature and recrystallizing. The product is a mixture of the two isomeric 1,2-*p*-nitrobenzylidene glycerol 1′-methyl ethers. The isomer melting at 47° always tends to crystallize out first in characteristic short, yellowish prisms, while the second isomer (m. p. 42°) separates as white nodules on further cooling.

From the β-methyl ether, on the other hand, the methyl alcohol deposits a mixture of the two markedly crystalline isomeric 1,1′-*p*-nitrobenzylidene glycerol 2-methyl ethers (m. p. 139 and 106°). Recrystallization usually first deposits the higher-melting isomer as gray-white needles but, depending on the amount of solvent used, the lower-melting isomer may simultaneously crystallize as short, white prisms. Although these may be readily separated and identified, the melting point of the mixture (approximately 90°) serves to differentiate the product from that obtained from glycerol α-methyl ether.

Summary

1. The properties of and methods for identifying glycerol β-monomethyl ether are described.
2. The importance of the product as a "type substance" in organic analyses and syntheses is indicated.

MONTREAL, CANADA

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

THE REDUCTION OF PHENYL NAPHTHYL KETONES BY THE BINARY SYSTEM MAGNESIUM + MAGNESIUM IODIDE

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Aromatic ketones[2] are reduced by magnesium + magnesium iodide to free radicals, ketyls, which associate to pinacolates. Addition of water to the pinacolate gives the pinacol. By this method various classes of ketones have been reduced to pinacols. We have now studied the reaction between the binary system and ketones containing a naphthyl group.

We have found that both phenyl α-naphthyl ketone and phenyl β-naphthyl ketone are reduced to the corresponding ketyl $\rightleftharpoons$ pinacolate systems. During the reduction green and brown colors are engendered in the solution. These colors disappear when the solution is exposed to air and reappear when air is prevented from entering. Water likewise removes the color, with concomitant formation of the pinacol.

The pinacol produced from phenyl α-naphthyl ketone by Mg + MgI_2 is different from the pinacol produced from the same ketone by zinc + acetic acid.[3] However, we found that the latter isomer (I) may be trans-

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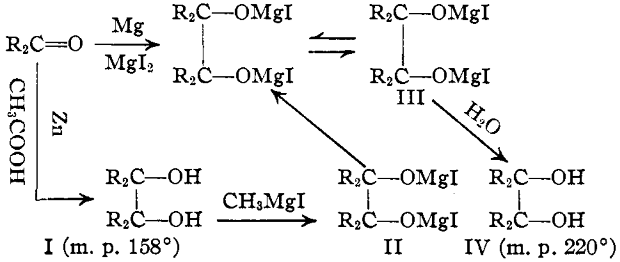
[1] Holder of the Prescott Fellowship in Organic Chemistry.

[2] Gomberg and Bachmann, THIS JOURNAL, **49**, 236 (1927).

[3] Compare the reduction of benzaldehyde which gives rise to mesohydrobenzoin (m. p. 134°) and racemic hydrobenzoin (m. p. 119°).

formed into the former (IV) by converting it to its pinacolate (II) by means of a Grignard reagent. Dissociation into radicals takes place[4] and these radicals become identical with those formed by the addition of MgI to the C=O group of the ketone, and associate to the new pinacolate (III).



Only a single pinacol was produced when phenyl β-naphthyl ketone was reduced by the two different reducing agents.

The pinacols prepared through the agency of the binary system were rearranged to the corresponding pinacolins, and it was found that the naphthyl group wandered in preference to the phenyl group.

Experimental

Reduction of Phenyl α-Naphthyl Ketone

Reduction of the Ketone by Mg + MgI_2.—A colorless mixture of Mg + MgI_2 was prepared from 4.0 g. of magnesium powder and 12 g. of iodine in 75 cc. of anhydrous ether and 75 cc. of dry benzene. To this mixture 10.0 g. of phenyl α-naphthyl ketone was added and the flask was then stoppered and shaken. Almost instantly the solution became olive-green in color and later the color changed to brown. After half an hour the color was a clear green and reduction was considered complete. On exposure to air the green color was quickly destroyed but when the solution was protected from air the green color reappeared. The solution was filtered from the excess of magnesium and was decomposed with ice and ammonium chloride. Experiments in which a rod of magnesium was employed for reduction showed that the magnesium loss was equivalent to 108% of the calculated value, and that the magnesium hydroxide produced on hydrolysis corresponded to 105%. The organic solution was washed with water and dried over sodium sulfate. Evaporation of the solvents at room temperature left an oily residue. The oil was extracted with warm petroleum ether (40–60°) in order to remove unchanged ketone; however, only traces of ketone were found in this extract. During this treatment the oily mass usually solidified. The crude pinacol (9.2 g.) was recrystallized by dissolving it in the minimum amount of hot chloroform, adding twice that volume of hot alcohol and evaporating the solvents until crystallization began. In this way 4.6 g. of pure diphenyl-di-α-naphthyl pinacol was obtained, which represents a yield of 46%. The pinacol crystallizes in glistening prisms, melting at 220° with decomposition.

Anal. Calcd. for $C_{34}H_{26}O_2$: C, 87.52; H, 5.62. Found: C, 87.32; H, 5.60. Mol. wt., calcd.: 466. Found: 469.

Measurement of the gas evolved when the pinacol was treated with methylmagnesium iodide showed the presence of two hydroxyl groups.

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[4] Ref. 2, p. 247.

The low yield of pinacol is attributed to difficulty in crystallization. The crude reduction product was shown to be mostly pinacol by rearranging it to the pinacolin. The crude pinacol from 5.0 g. of ketone gave 4.2 g. (87%) of pure pinacolin.

Rearrangement of the Pinacol to the Pinacolin.—The pinacol readily undergoes dehydration when it is warmed with acetic acid containing a small amount of iodine[5] or when it is treated with acetyl chloride. The pinacolin remaining after the solvent had been evaporated was recrystallized from chloroform–alcohol; yield, practically quantitative; m. p. 216–217°. By its reaction with alcoholic potassium hydroxide the pinacolin was proved to be benzoyl-di-α-naphthylphenylmethane $(C_6H_5)(C_{10}H_7)_2CCO(C_6H_5)$.

Anal. Calcd. for $C_{34}H_{24}O$: C, 91.04; H, 5.40. Found: C, 90.94; H, 5.25. Mol. wt., calcd.: 448. Found: 441.

One gram of the pure pinacolin, heated with alcoholic potassium hydroxide for eight hours, gave 0.260 g. (96%) of benzoic acid.

Reduction of the Ketone by Reagents Other than Mg + MgI$_2$.—The reduction of phenyl α-naphthyl ketone has been studied by a number of investigators.[6] Though many reducing agents were employed, only one method, that of Cohen using zinc and acetic acid, gave a pinacol. No directions, however, were given for carrying out this reduction. We dissolved 10 g. of phenyl α-naphthyl ketone in 175 cc. of cold glacial acetic acid and added 20 g. of zinc dust. After three days the mixture was diluted with water and the insoluble material was filtered off, washed with water and with alcohol. From the insoluble residue the pinacol was extracted by hot benzene. The pinacol obtained after evaporation of the benzene was recrystallized from a mixture of chloroform and alcohol and was obtained in the form of needles of melting point 158°; yield, 4.0 g. Our melting point, analysis and molecular weight were the same as those reported by Cohen for the pinacol. The presence of two hydroxyl groups in the compound was proved by its reaction with methylmagnesium iodide.

We found that the same substance is the product of the action of zinc and ammonium chloride on the ketone.

Rearrangement of the pinacol by warming with acetyl chloride or with acetic acid containing a trace of iodine gave a colorless solid which melted at 232° after it had been recrystallized from chloroform–alcohol. The same compound resulted from the action of zinc and acetyl chloride on phenyl α-naphthyl ketone, a method that usually reduces a ketone to the pinacolin.[7]

Anal. Calcd. for $C_{34}H_{24}O$: C, 91.04; H, 5.40. Found: C, 90.88; H, 5.34. Mol. wt., calcd.: 448. Found: 449.

Unlike a pinacolin, the compound is very resistant to hot alcoholic potassium hydroxide. Even after thirty-six hours of boiling with a saturated solution of potassium hydroxide in alcohol, 70% of the compound was recovered unchanged.

Conversion of the Low-Melting Pinacol into the High-Melting Pinacol.—A benzene solution of 2.0 g. of the low-melting pinacol (158°) was added to a filtered ethereal solution of ethylmagnesium iodide. A vigorous evolution of ethane took place and the solution of the pinacolate became dark green in color. The bottle was stoppered and allowed to stand for twenty-four hours at room temperature. The solution was then

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[5] Ref. 2, p. 246.

[6] Lehne and Caille, *Ber.*, **13**, 359 (1880); Beckmann and Paul, *Ann.*, **266**, 10 (1891); Elbs, *J. prakt. Chem.*, (2) **35**, 504 (1887); Elbs and Brand, *Z. Elektrochem.*, **8**, 785 (1902); Cohen, *Rec. trav. chim.*, **38**, 80, 120 (1919); Montagne, *ibid.*, **27**, 359 (1908).

[7] Zagoumenny, *Bull. soc. chim.*, (2) **34**, 329 (1880); *J. Russ. Phys.-Chem. Soc.*, **12**, 426 (1880).

decomposed with ice and ammonium chloride in the usual manner. The pinacol was recrystallized and was obtained now in the form of prisms having the melting point 215–217°. This new pinacol was found to be identical with the pinacol produced by reduction of the ketone by Mg + MgI_2. For further verification the pinacol was treated with hot acetic acid containing iodine, whereupon the expected pinacolin of melting point 216° resulted.

Reduction of Phenyl β-Naphthyl Ketone

Diphenyl-di-β-naphthyl Pinacol.—2.32 g. of phenyl-β-naphthyl ketone was reduced by 1.0 g. of magnesium and 3.0 g. of magnesium iodide in 30 cc. of ether-benzene (1:1). During the process of reduction the solution became reddish brown in color. This color was instantly destroyed when the solution came in contact with oxygen of the air, but it was restored when the air was prevented from entering. The loss of magnesium corresponded to 105% of the theoretical value and the magnesium hydroxide produced on hydrolysis was equivalent to 102%. The crude pinacol was recrystallized from chloroform–alcohol and was obtained in the form of needles; m. p. 175°; yield of pure pinacol, 91%.

Anal. Calcd. for $C_{34}H_{26}O_2$: C, 87.52; H, 5.62. Found: C, 86.90; H, 5.68. Mol. wt., calcd.: 466. Found: 461.

An identical pinacol resulted from the reduction of the ketone by zinc and acetic acid.

A quantitative yield of the pinacolin $(C_6H_5)(C_{10}H_7)_2CCO(C_6H_5)$, resulted on dehydration of the pinacol. After being recrystallized from a mixture of benzene and acetic acid, the pinacolin melted at 181–182°.

Anal. Calcd. for $C_{34}H_{24}O$: C, 91.04; H, 5.40. Found: C, 90.83; H, 5.24. Mol. wt., calcd.: 448. Found: 450.

One-half gram of this pinacolin heated with alcoholic potassium hydroxide for six hours gave 0.130 g. (96%) of benzoic acid.

Summary

Both phenyl α-naphthyl ketone and phenyl β-naphthyl ketone are reduced by the binary system, Mg + MgI_2 to ketyls, RR'C—OMgI, which associate to pinacolates, RR'C(OMgI)(IMgO)CRR'. Hydrolysis of the pinacolates gives the corresponding pinacols.

On rearrangement of the pinacols to the pinacolins, the naphthyl group wanders in preference to the phenyl group.

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