The benzene solution was then distilled, first at atmospheric pressure to remove all solvent, followed by vacuum distillation at 0.1–0.05 mm. In the first fraction there was collected 0.1 g. of a low boiling liquid, b.p. 35–55°, which was not identified. A second fraction, 0.50 g., was collected at 65–75° and this solidified in the receiver. Some tribromobenzene was also obtained, but because of its tendency to condense as a solid on the walls of the fraction cutter its partial separation from this product was effected. The third fraction was collected at 185°, and consisted of 2.5 g. of (VI).

The last two fractions were redistilled, and the more volatile fraction was collected at 65° and 0.1 mm. Distillation was not continued beyond this point. The product solidified in the receiver and was found to melt at 44–45°.

Anal. Calcd. for $C_7H_6SiBr_2Cl_2$: C, 24.06; H, 1.73; Si, 8.04. Found: C, 24.27; H, 1.78; Si, 7.80.

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Pentaphenylethanol

BY WILLIAM A. MOSHER AND MELVIN L. HUBER[1]

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In connection with other work it was desirable to prepare substantial quantities of pentaphenylethanol, a compound reported by Schmidlin and Wohl[2] from the reaction of phenylmagnesium iodide and β-benzopinacolone under forcing conditions. This same reaction had been attempted previously but with negative results[3] and other reactions which were expected to yield pentaphenylethanol gave other products.[4] Only two other references to the compound have been found,[5] and in these small amounts of a compound corresponding to the Schmidlin and Wohl substance were reported. No proof of structure has yet been presented.

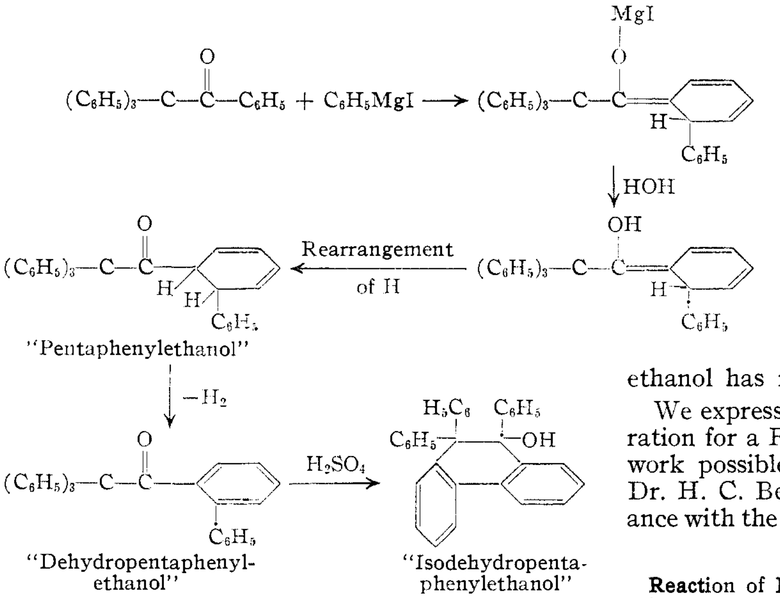

Fig. 1.

Schmidlin and Wohl[2] found that their substance ($C_{32}H_{26}O$) was converted to $C_{32}H_{24}O$ by treatment with hydrochloric acid, acetyl chloride, or phosphorus pentachloride and the new substance was called "dehydropentaphenylethanol." We have recently established the structure of "dehydropentaphenylethanol" as *o*-biphenylyl triphenylmethyl ketone,[6] and this information now permits attack on the structure of the original substance.

When the compound from the reaction of phenylmagnesium iodide and β-benzopinacolone is catalytically dehydrogenated at its melting point with palladium on charcoal, *o*-biphenylyl triphenylmethyl ketone, identical with "dehydropentaphenylethanol," is formed. The original substance shows a strong infrared absorption for carbonyl but hydroxyl absorption is absent. These facts are consistent with a 1,4-addition of the Grignard reagent to the conjugated system of the carbonyl and the aromatic ring, in the matter described by Kohler and Nygaard[7] with diphenylbenzalacetophenone, followed by rearrangement of hydrogen. Figure 1 indicates the complete series of reactions. The only uncertainty is the location of the double bonds in the rather unstable, partially hydrogenated ring. Our formulation is based on the simplest tautomeric shifts.

We have some evidence that the original enol may be present; before recrystallization the infrared absorption is strong at the hydroxyl band and the material decolorizes permanganate. A simple recrystallization removed the hydroxyl absorption completely both from the solid and from the mother liquor.

It seems safe to say that "pentaphenylethanol" as previously reported is actually a dihydroketone, probably 1-triphenylacetyl-2-phenyl-1,2-dihydrobenzene. Pentaphenylethanol has not yet been prepared.

We express our appreciation to Research Corporation for a F. G. Cottrell Grant which made this work possible and to Mrs. Margaret Kraus and Dr. H. C. Beachell of this Department for assistance with the infrared data.

Experimental

Reaction of Phenylmagnesium Iodide and β-Benzopinacolone.—The method was essentially that of Schmidlin and Wohl[2]: 100 g. of benzene, 13 g. (0.54 mole) of magnesium turnings, 102 g. of phenyl iodide (0.5 mole) and 400 ml. of dry ether were used to prepare the Grignard reagent, which was filtered, added to a flask containing 20 g. (0.057 mole) of β-benzopinacolone (m.p. 179–80°) and refluxed for 20 hours. The reaction mixture was cooled in an ice-bath and carefully decomposed with a mixture of ice and water containing 46 ml. of concd. hydrochloric acid. After shaking in a separatory funnel, the solid which separated in the ether layer was filtered off and washed. Recrystallization of this product from acetic acid and then from benzene or a mixture of benzene and petroleum ether (b.p. 65–110°) gave a white solid melting at 175–176°. *Anal.* Calcd. for

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[1] F. G. Cottrell Research Fellow. From the Ph.D. Dissertation of M. L. Huber, Univ. of Delaware School of Graduate Studies, 1950. Presented before Division of Organic Chemistry, American Chemical Society, Chicago, September 7, 1950.

[2] J. Schmidlin and J. Wohl, *Ber.*, **43**, 1145 (1910).

[3] M. Gomberg and L. H. Cone, *ibid.*, **38**, 2454 (1905); **39**, 1461, 1469 (1906).

[4] J. Schmidlin, *ibid.*, **39**, 4200 (1906); **43**, 1137 (1910); W. Schlenk and R. Ochs, *ibid.*, **49**, 608 (1916); W. E. Bachmann, THIS JOURNAL, **53**, 2759 (1931).

[5] W. Schlenk and H. Mark, *Ber.*, **55**, 2298 (1922); H. Gilman and R. E. Fothergill, THIS JOURNAL, **51**, 3149 (1929).

[6] W. A. Mosher and M. L. Huber, *ibid.*, **73**, 795 (1951).

[7] E. P. Kohler and E. M. Nygaard, *ibid.*, **52**, 4128 (1930).

$C_{32}H_{26}O$: C, 90.11; H, 6.14. Found: C, 90.24; H, 5.90.

Infrared absorption spectra in nujol mull were taken using a Baird split beam recording spectrophotometer. The above compound showed very strong absorption at 6 microns, the carbonyl absorption band, and no absorption at 2.9 microns, the hydroxyl band. The compound was unsaturated to bromine and to potassium permanganate.

Dehydrogenation of Pentaphenylethanol.—The above material (0.2 g.) heated at 170–180° with 0.02 g. of palladium on charcoal catalyst[8] yielded *o*-biphenylyl triphenylmethyl ketone, m.p. and mixed m.p. 175–176°,[7] and a small amount of an unidentified product.

Isolation of the Enol Form.—When the crude, ether-insoluble material from the Grignard reaction above, filtered after hydrolysis, was carefully washed with dilute hydrochloric acid (about 2 *M*) and chloroform and then ether, the residue gave an infrared spectrum with absorption at 2.9 μ, indicative of hydroxyl. Tests with bromine in carbon tetrachloride and potassium permanganate in acetone indicated unsaturation. All attempts to recrystallize this material yielded either the unsaturated ketone described above, m.p. 175–176°, or *o*-biphenylyl triphenylmethyl ketone.

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2,2-Dimethyl-3-aminopentane and its Reaction with Nitrosyl Chloride

BY WILLIAM A. MOSHER, JAMES C. COX, JR., AND JAMES KREITZER

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Although rearrangement was expected, we undertook the reaction of 2,2-dimethyl-3-aminopentane with nitrosyl chloride as a possible method of preparing 2,2-dimethyl-3-chloropentane. The amine was prepared by the reduction of the corresponding ketoxime. On treatment of the amine in ether solution with gaseous nitrosyl chloride as employed by Bartlett and Knox[1] the only product isolated was identical with the nitrosochloride from 2,3-dimethyl-2-pentene.

Markownikoff[2] reported the preparation of 2,2-dimethyl-3-aminopentane by reduction of the secondary nitro compound formed by the nitration of 2,2-dimethylpentane. This nitro compound gave on hydrolysis with alkali a ketone erroneously identified as ethyl *t*-butyl ketone on the basis of correspondence with reported physical constants.[3] Markownikoff's ketone must actually have been methyl neopentyl ketone since it gave a semicarbazone of m.p. 175°; the reported values for this derivative from ethyl *t*-butyl ketone[4] and methyl neopentyl ketone[5] are, respectively, 144 and 176°.

Apparently 2,2-dimethyl-3-aminopentane has not been previously reported. The following physical properties were determined in the present study: b.p. 128.0° (760 mm.), n^{25} 0.7615, n^{15}_{D} 1.4306, n^{20}_{D} 1.4287, n^{30}_{D} 1.4249, viscosity at 25°, 24.86 millipoises; surface tension, capillary rise 23.3 dynes/cm. The phenylthiourea melts at 151° and the 3,5-dinitrobenzoate at 149–151°.

Experimental

Preparation of Ethyl-*t*-butylcarbinol.—This compound was prepared from *t*-butylmagnesium chloride and propionaldehyde in the usual manner; yield 45%, b.p. 135° (757 mm.), n^{25}_{D} 1.4180, phenylurethan m.p. 83°.[6] A 45% recovery of propionaldehyde, presumably through enolization, was observed.

Oxidation of Ethyl-*t*-butylcarbinol.—The oxidation was carried out as described by Mosher and Langerak[7] with chromic anhydride in aqueous acetic acid. The ketone was distilled through a column of 15 theoretical plates; yield 88–90%, b.p. 125°,[3] n^{25}_{D} 1.4013, m.p. of semicarbazone 144°,[4,8] of 2,4-dinitrophenylhydrazone 143°,[8] and oxime 84–85°.[8]

Reduction of the Ketoxime.—A total of 190 g. of ketoxime was reduced in the following manner: ethyl *t*-butyl ketoxime, 16.3 g. (0.13 mole), was dissolved in 300 ml. of *n*-amyl alcohol and heated to boiling under reflux; 21 g. of metallic sodium, cut into thin strips, was added slowly. Refluxing was continued for three hours. The reaction mixture was allowed to cool and then poured into 500 ml. of water. The amyl alcohol layer, containing most of the amine, was separated and acidified with concd. hydrochloric acid, the acidified washings were combined, made basic with 10% sodium hydroxide and extracted with several portions of ether. The ether extracts were dried over solid potassium hydroxide, the ether distilled and the amine purified by fractionation. The yields were 75–90% of theory. Chloroplatinate salt: calcd. for $(C_7H_{18}NCl)_2PtCl_4$: Pt, 30.49. Found: Pt, 30.45. Hydrochloride m.p. 221: calcd. for C_7H_8NCl: Cl, 23.38. Found: Cl, 23.35. Phenylthiourea m.p. 151°: calcd. for $C_{14}H_{22}N_2S$: N, 11.19. Found: N, 11.30. 3,5-Dinitrobenzoate m.p. 149–151°: calcd. for $C_{14}H_{19}O_6N_3$: N, 12.87. Found: N, 12.77.

Reaction of 2,2-Dimethyl-3-aminopentane with Nitrosyl Chloride.—This reaction, including the preparation of nitrosyl chloride, was carried out as described by Bartlett and Knox.[1] The reaction temperature was −10° and ether was employed as solvent. Gaseous nitrosyl chloride was added until the persistence of a brown color indicated that an excess had been added. The ether solution was washed with water, dried with sodium sulfate, and evaporated. The solution was blue-green, indicating the presence of a completely substituted double bond,[9] the recrystallized product melted at 124°. For comparison purposes, methylethylisopropylcarbinol was prepared by the reaction of ethylmagnesium bromide on methyl isopropyl ketone and the alcohol formed was dehydrated with potassium acid sulfate. Fractionation gave 2,3-dimethyl-2-pentene, b.p. 97–98°, n^{20}_{D} 1.4212,[10] confirmed by ozonolysis into acetone and methyl ethyl ketone and only a trace of acetaldehyde. The nitrosochloride of 2,3-dimethyl-2-pentene was prepared as above: m.p. and mixed m.p. with the product from 2,2-dimethyl-3-aminopentane, 124°. *Anal.* Calcd. for $C_7H_{14}ONCl$: Cl, 21.67. Found: Cl, 21.80.

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(9) *Cf.* J. L. Simonsen, "The Terpenes," Vol. I, Second Edition, Cambridge Univ. Press, Cambridge, 1947, p. 168.

(10) M. P. Doss, "Physical Constants of the Principal Hydrocarbons," Third Edition, The Texas Co., New York, N. Y., 1942, p. 24.

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A Synthesis of 3,2′-Nornicotyrine[1]

BY HENRY RAPOPORT AND MELVIN LOOK

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Recently[2] it has been shown that the use of N-nitroso-N-(3-pyridyl)-isobutyramide (I) in the Gomberg (or diazo) reaction affords a reasonable method for introducing the 3-pyridyl radical into

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(1) Reported in part in *Abstracts Papers Am. Chem. Soc.*, **122**, 14M (1952).

(2) H. Rapoport, M. Look and G. J. Kelly, THIS JOURNAL, **74**, 6293 (1952).