$C_{32}H_{26}O$: 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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NEWARK, DELAWARE

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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(3) A. Wischnegradsky, *Ann.*, **178**, 103 (1875).

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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.

DEPARTMENT OF CHEMISTRY
UNIVERSITY OF DELAWARE
NEWARK, DELAWARE

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).