extraction recrystallized from alcohol in long needles melting undecomposed at 177–178°. A mixed melting point determination of this acid and an authentic sample[6] showed no depression.

Anal. Calcd. for $C_{14}H_{15}O_2N$: C, 73.36; H, 6.55; N, 6.11. Found: C, 73.06; H, 6.50; N, 5.95.

Synthesis of 2,3-Dimethyl-4,8-diethylquinoline.—In accordance with a simplified Beyer procedure for the preparation of 2,4-dimethylquinoline,[5] a mixture of 24.6 cc. of diethyl ketone and 9 cc. of paraldehyde was saturated with dry hydrogen chloride at 0° and, after standing eight hours, was poured into 12.11 g. of *o*-aminoethylbenzene dissolved in 20.4 cc. of concentrated hydrochloric acid and heated on the steam-cone for two hours. The reaction mixture was then diluted with water, non-basic admixtures were extracted with ether and the quinoline base was freed with an over-all yield of 25% from the aqueous layer with caustic. Its picrate, which was prepared in dilute sulfurous acid, on purification showed no depression in a mixed melt with a picrate sample of the petroleum base.

Where the yield of this base is of primary importance, no doubt the lengthy procedure of Beyer may be preferable.

Isolation of 2,3-Dimethyl-4-ethyl-8-*n*-propylquinoline (Base II).—A 130-ml. portion of fraction 2, Table II,[1] was agitated for one hour with an equal volume of saturated sodium nitrate brine in an ice-bath, sulfur dioxide being led in continuously to ensure complete salification of the bases. The acid-sulfite oily layer was separated and dissolved in a liter of acetone. After twelve hours, the precipitated solid base acid-sulfite was removed and dissolved in water. On heating the solution, the salt dissociated with evolution of sulfur dioxide and the water insoluble base. The latter was dissolved in an acetone–ether mixture, and salified with a slight excess of nitric acid (sp. gr. 1.42). The precipitated nitrate crystallized from water in long needles, melting with violent decomposition at 161°. The base was liberated with caustic, ether extracted, and dried over pellets of sodium hydroxide. After evaporation of the solvent, the following constants were determined on the residual odorless base: b. p. 327° (752 mm.), $n^{20}{}_D$ 1.5751, $d^{25}{}_4$ 1.003.

Anal. Calcd. for $C_{16}H_{21}N$: C, 84.72; H, 9.32; N, 6.17. Found: C, 84.84; H, 9.30; N, 6.07.

Acid Sulfate.—Addition of the calculated amount of concentrated sulfuric acid to an acetone–ether solution of the base precipitates this salt as a viscous oil which crystallized from acetone in platelets melting undecomposed at 163–164°.

Anal. Calcd. for $C_{16}H_{21}N \cdot H_2SO_4$: C, 59.02; H, 7.13; N, 4.31. Found: C, 58.78; H, 7.22; N, 4.60.

2,3-Dimethyl-4-ethylquinoline-8-carboxylic Acid.—The base (2 g.) was oxidized in a manner analogous to that employed on 2,3-dimethyl-4,8-diethylquinoline. The acid proved identical with the one from oxidation of base I.

Ozonization of 2,3-Dimethyl-4-ethyl-8-*n*-propylquinoline.—Ozonolysis of the ozonide[4] from 1 g. of base yielded a mixture of aliphatic acids from which *n*-butyric acid was isolated and identified through the anilide, thus establishing the presence of a *n*-propyl substituent in the original compound.

Synthesis of 2,3-Dimethyl-4-ethyl-8-*n*-propylquinoline.—With the exception of a substitution of *o*-amino-*n*-propylbenzene as the primary amine, the procedure was the same as that followed in the synthesis of base I. A mixed melt of picrate samples of the synthetic and petroleum bases showed no depression.

Summary

The isolation of a new quinoline homolog, 2,3-dimethyl-4,8-diethylquinoline, from petroleum is reported. The use of sulfur dioxide in segregation of a second new nitrogen base, 2,3-dimethyl-4-ethyl-8-*n*-propylquinoline, is also described. The structure of these hitherto unknown petroleum bases has been established through degradation and confirmed by synthesis.

AUSTIN, TEXAS RECEIVED JANUARY 20, 1941

[CONTRIBUTION FROM THE HALL LABORATORY OF CHEMISTRY, WESLEYAN UNIVERSITY]

Hexabenzylethane

BY G. ALBERT HILL, W. C. NELSON, R. L. DUNNELL AND L. S. MOODY

In 1909 Schmerda[1] reported the preparation of hexabenzylethane. The same substance was obtained by Trotman,[2] who accepted Schmerda's conclusions regarding its structure. By investigations in this Laboratory[3] the compound was shown to be tribenzylmethane.

The present study was undertaken to prepare the long-sought hydrocarbon, 2,2,3,3-tetrabenzyl-1,6-diphenylbutane, hexabenzylethane. For this purpose tribenzylmethyl bromide[4] was treated in dry ether, and in dry benzene, with sodium, with mercury, and with zinc. The substance most readily obtained, sometimes in yields of 90%, was 2-benzyl-1,3-diphenylpropene, m. p. 33.8°. It was identified by forming the dibromo derivative, 2-benzyl-1,2-dibromo-1,3-diphenylpropane,[5] melting at 127–128°.

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(1) Schmerda, *Monatsh.*, **30**, 387 (1909).

(2) Trotman, *J. Chem. Soc.*, **127**, 88 (1925).

(3) Hill, Little, Wray and Trimbey, THIS JOURNAL, **56**, 911 (1934).

(4) A comprehensive study of the tribenzylmethyl halides is now in progress in this Laboratory.

(5) Orechov and Grinberg, *J. Russ. Phys.-Chem. Soc.*, **48**, 1713 (1916); *J. Chem. Soc.*, **112**, 450 (1917).

The best yield of hexabenzylethane resulted when tribenzylmethyl bromide, in benzene, was acted upon by zinc. Gentle treatment at a relatively low temperature was essential. A hexanitro derivative of the desired hydrocarbon was obtained by direct nitration.

It is a pleasure to acknowledge financial aid from the Atwater Fund, and analytical assistance by Dr. Richard G. Clarke.

Experimental

Tribenzylmethyl Bromide.—Fifty grams of tribenzylcarbinol[6] was dissolved in just sufficient ether and 25 g. of phosphorus tribromide was so added that only very gentle boiling took place. Subsequently, the system was refluxed for six hours. On cooling, crystals appeared and were filtered out. Concentration of the mother liquor yielded another crop and an intractable oil. The solid product, recrystallized from ether and then from acetone, was white, melted at 158°, and weighed 33 g. The yield was 54.6%.

Anal. Calcd. for $C_{22}H_{21}Br$: Br, 21.9. Found (micro catalytic oxidation): Br, 21.79, 21.76, 21.87, 21.94.

Hexabenzylethane.—Thirty-five grams of tribenzylmethyl bromide and 18 g. of zinc dust were heated to 50° for forty-eight hours in dry benzene. The inorganic material was filtered out and the filtrate concentrated in a vacuum. The residue, a pale yellow oil, was dissolved in ether and alcohol was cautiously added until a slight permanent turbidity resulted. By seeding and standing the system yielded some very small white crystals. As concentration of the solution continued an oil, the unsaturated hydrocarbon, 2-benzyl-1,3-diphenylpropene, appeared. The solid product, separated by decantation, was recrystallized from ether and then melted at 195°. It did not contain halogen, nor did it react with a carbon tetrachloride solution of bromine or with an alkaline solution of potassium permanganate. The yield was 3 g., 5.5% of the theoretical value.

Anal. Calcd. for $C_{44}H_{42}$: C, 92.58; H, 7.42; mol. wt., 570. Found: C, 92.85, 92.79; H, 7.86, 7.34; mol. wt. (Rast method), 560, 563.

In some experiments, the unsaturated hydrocarbon was removed from the mixture of products by distillation at 5 mm. (the boiling point was 209°) and the brownish residue, less than 10% of the total product, was recrystallized. The yield of hexabenzylethane was not as large as that obtained by the other method of treatment.

Hexanitrohexabenzylethane.—To 0.8 g. of hexabenzylethane was added 8 ml. of concentrated sulfuric acid. Subsequently, 8 ml. of concentrated nitric acid was introduced carefully and the mixture refluxed for ninety minutes. After cooling, it was poured over 20 g. of cracked ice. The yellow oil, which first appeared, soon solidified. The solid was dissolved in acetone and treated with alcohol, dropwise, until a slight turbidity persisted. A yellow crystalline mass was obtained, m. p. 174–179°. The yield was not recorded.

Anal. Calcd. for $C_{44}H_{36}O_{12}N_6$: N, 10.00. Found (micro modified Kjeldahl): N, 9.94, 9.61, 9.43.

Summary

Tribenzylmethyl bromide has been prepared and converted to hexabenzylethane which in turn was characterized by nitration to a hexanitro derivative.

MIDDLETOWN, CONNECTICUT

RECEIVED FEBRUARY 10, 1941

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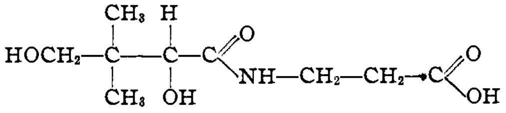
[6] Klages and Heilmann, *Ber.*, **37**, 1456 (1904).

[CONTRIBUTION FROM THE RESEARCH LABORATORY OF MERCK & CO., INC.]

Resolution of *dl*-α-Hydroxy-β,β-dimethyl-γ-butyrolactone

BY RANDOLPH T. MAJOR AND JACOB FINKELSTEIN

In a previous publication[1] from this Laboratory, it was shown that pantothenic acid, I, consists of (+)α,γ-dihydroxy-β,β-dimethylbutyric acid and β-alanine joined through an amide linkage.



$$HOCH_2-\underset{CH_3}{\overset{CH_3}{C}}-\underset{OH}{\overset{H}{C}}-C\begin{smallmatrix}\nearrow O\\ \searrow NH-CH_2-CH_2\rightarrow C\begin{smallmatrix}\nearrow O\\ \searrow OH\end{smallmatrix}\end{smallmatrix}$$

I.

The (+)α,γ-dihydroxy-β,β-dimethylbutyric acid was obtained, as previously described,[2] by resolving the racemic α-hydroxy-β,β-dimethyl-γ-butyrolactone by the application of the method of Pope and Peachey[3] involving the equilibrium of salts. In a more recent publication on this subject, Reichstein and Grüssner[4] resolved the lactone through its quinine salt by refluxing the lactone with quinine in an alcoholic solution for several hours. Although the melting point of their quinine salt is slightly lower than that re-

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[1] Stiller, Keresztesy and Finkelstein, THIS JOURNAL, **62**, 1779 (1940).

[2] Stiller, Harris, Finkelstein, Keresztesy and Folkers, *ibid.*, **62**, 1785 (1940).

[3] Pope and Peachey, *J. Chem. Soc.*, **75**, 1066 (1899).

[4] Reichstein and Grüssner, *Helv. Chim. Acta*, **23**, 650 (1940).