ing material, only diene dimer as condensation product, b.p. 87.5–88° (15.0 mm.).

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Confirmation of the *ortho* Substitution Rearrangement of the Benzhydryltrimethylammonium Ion by Sodium Amide

BY WALLACE R. BRASEN[1] AND CHARLES R. HAUSER

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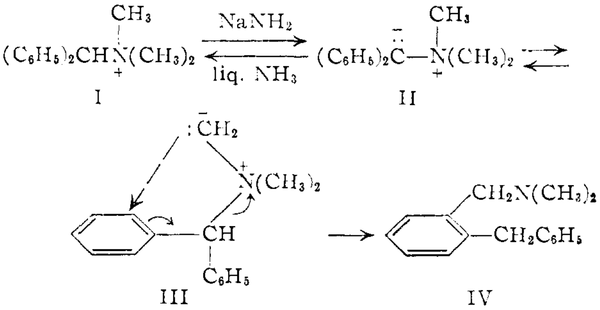
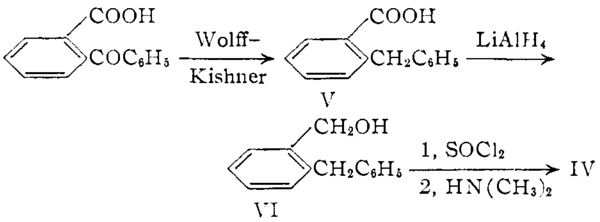
One of the *ortho* substitution rearrangements of benzyl type quaternary ammonium ions by sodium amide in liquid ammonia reported recently,[2] is that of the benzhydryltrimethylammonium ion (I) to form tertiary amine IV (88%). This example is particularly remarkable[3] since the reactive intermediate is carbanion III (an ylide),[4] not carbanion II which is presumably present in much higher concentration.



$$(C_6H_5)_2CH\overset{CH_3}{\underset{+}{N}}(CH_3)_2 \underset{\text{liq. } NH_3}{\overset{NaNH_2}{\rightleftarrows}} (C_6H_5)_2\overset{-}{\ddot{C}}-\overset{CH_3}{\underset{+}{N}}(CH_3)_2 \rightleftarrows$$

The product was assigned structure IV because, on oxidation, it produced *o*-benzyl- and *o*-benzoylbenzoic acids. We have confirmed this assignment of structure by unequivocally synthesizing tertiary amine IV from *o*-benzoylbenzoic acid, passing through intermediates V and VI, and showing that it was identical with the tertiary amine obtained from the rearrangement of I.



Experimental[5]

o-Benzylbenzoic acid (V), m.p. 114–115° (lit. m.p. 111–113°,[6] 117°[7]), was prepared in 50% yield by the reduction of *o*-benzoylbenzoic acid by the Wolff–Kishner method according to the general procedure described in "Organic Reactions."[8]

o-Benzylbenzyl Alcohol (VI).—To a stirred suspension of 2.1 g. (0.058 mole) of lithium aluminum hydride in 100 ml. of anhydrous ether was added a solution of 14 g. (0.066 mole) of *o*-benzylbenzoic acid in 50 ml. of anhydrous ether. The resulting mixture was stirred and refluxed for one hour, and the excess hydride destroyed by addition of 5 ml. of ethyl acetate. The ether solution, after washing with 10% sulfuric acid and 10% sodium bicarbonate, was dried over potassium carbonate and the solvent removed. The oily residue was crystallized from 30–60° petroleum ether to give 10.6 g. (81%) of *o*-benzylbenzyl alcohol (VI), m.p. 40–41°.

Anal. Calcd. for $C_{14}H_{14}O$: C, 84.81; H, 7.12. Found: C, 84.93; H, 7.05.

o-Benzylbenzyl-N,N-dimethylamine (IV).—A solution of 9.6 g. (0.049 mole) of *o*-benzylbenzyl alcohol in 10 ml. of benzene and 12 g. (0.1 mole) of thionyl chloride was boiled (after the first vigorous reaction had subsided) until the volume of the solution was 15 ml. An additional 10 ml. of benzene was added, and the volume of the solution again reduced to 15 ml. To this material was added an ice-cold solution of 14 g. (0.31 mole, 500% excess) of dimethylamine in 100 ml. of methanol, and the resulting solution allowed to stand for 30 hours. Methanol and excess dimethylamine were removed at the water aspirator and the residue taken up in water. After washing with ether, the aqueous solution was made basic with 10% sodium hydroxide and the liberated amine taken up in ether. The ether solution was dried over solid potassium hydroxide and the solvent removed. The residue was distilled under reduced pressure to yield 7.1 g. (70%) of *o*-benzylbenzyl-N,N-dimethylamine (IV), b.p. 129.5–130° at 2.3 mm., $n^{25}\text{D}$ 1.5598.

Anal. Calcd. for $C_{16}H_{19}N$: C, 85.31; H, 8.46; N, 6.22. Found: C, 85.52; H, 8.50; N, 6.33.

The picrate melted at 151–152°; reported m.p. 156–156.6°.[3]

Anal. Calcd. for $C_{22}H_{22}N_4O_7$: N, 12.33. Found: N, 12.03.

Amine IV, obtained from the rearrangement of quaternary ion I as described previously,[2] boiled at 133–135° at 2.5 mm.; $n^{25}\text{D}$ 1.5600. It gave a picrate, m.p. 151–152°, which was not depressed on admixture with the picrate (m.p. 151–152°)[2] of the amine prepared from *o*-benzoylbenzoic acid.

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[1] Carbide and Carbon Chemicals Company Fellow, 1954.

[2] S. W. Kantor and C. R. Hauser, THIS JOURNAL, **73**, 4122 (1951).

[3] The rearrangement of I to IV was first observed by M. Sommelet (*Compt. rend.*, **205**, 56 (1937)) who allowed an aqueous solution of the hydroxide of I to evaporate in sunlight. G. Wittig, R. Mangold, and G. Felletschin (*Ann.*, **560**, 116 (1948)) confirmed this result, and showed that the rearrangement may be effected, along with the Stevens 1,2-shift, by means of lithium phenyl.

[4] See G. Wittig and M. Wetterling, *Ann.*, **557**, 193 (1947).

[5] Melting points and boiling points are uncorrected. Analyses are by Clark Microanalytical Laboratory, Urbana, Ill.

[6] E. C. Horning and D. B. Reisner, THIS JOURNAL, **71**, 1036 (1949).

[7] P. H. Dirstine and F. W. Bergstrom, *J. Org. Chem.*, **11**, 55 (1946).

[8] D. Todd, "Organic Reactions," Vol. IV, John Wiley and Sons, Inc., New York, N. Y., 1948, p. 385.

The Synthesis of N$^{\alpha}$-Acetyl-L-kynurenine[1]

BY R. R. BROWN AND J. M. PRICE[2]

RECEIVED FEBRUARY 12, 1955

This communication presents a convenient method for the synthesis of crystalline N$^{\alpha}$-acetyl-L-, -DL- or -D-kynurenine. Previous methods yielded only racemic non-crystalline material,[3] or depended on isolation from biological material.[4] In this method, ozonolysis of N-acetyltryptophan[5] yielded an intermediate (probably N′-formyl-N$^{\alpha}$-acetylkynurenine)[6] which was converted by mild hydrolysis to N$^{\alpha}$-acetylkynurenine as anticipated

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[2] Scholar in Cancer Research of the American Cancer Society.

[3] C. E. Dalgleish, *J. Chem. Soc.*, 137 (1952).

[4] C. Yanofsky and D. M. Bonner, *Proc. Natl. Acad. Sci. U. S.*, **36**, 167 (1950).

[5] J. L. Warnell and C. P. Berg, THIS JOURNAL, **76**, 1708 (1954).

[6] A. H. Mehler and W. E. Knox, *J. Biol. Chem.*, **187**, 431 (1950).