Synthesis of 1,2,5,6-Dibenzfluorene

By Jacob Szmuszkovicz and Ernst D. Bergmann

2-(α-Naphthylmethyl)-1-tetralone (V) is converted into 1,2,5,6-dibenzfluorene (I) upon heating with phosphorus pentoxide. The yield is considerably smaller than in the analogous conversion of 2-(β-naphthylmethyl)-1-tetralone (II), although the latter reaction involves an intramolecular rearrangement.

In a previous communication,[1] 1,2,5,6-dibenzfluorene (I) has been obtained by cyclodehydration of 2-(β-naphthylmethyl)-1-tetralone (II) with polyphosphoric acid[2] to the dihydro compound (III) (?) (yield 43%), and subsequent dehydrogenation of the latter (yield, quantitative). A similar isomerization reaction had been observed for the analogous 2-(β-naphthylmethylene)-1-tetralone (IV).[1,3]

It seemed interesting to investigate whether the cyclization of 2-(α-naphthylmethyl)-1-tetralone (V) gives better yields of (I),[4] in view of the facts that this reaction does not involve isomerization and that the cyclization of 2-(α-naphthylmethylene)-1-tetralone proceeds easily.[5] It was found that (V), prepared from α-tetralone and 1-bromomethylnaphthalene, cyclizes directly—i.e., with simultaneous dehydrogenation—to (I) when heated with phosphorus pentoxide. The yield, however,

I   II

III   IV

V

was only 8.1%. Dehydrogenation of the residual oil with sulfur gave an additional 4.6% of (I); the oil appears to contain some dihydro compound of (I), formed in the cyclization reaction.[6]

Experimental

1-Bromomethylnaphthalene.—α-Naphthoic acid (42 g.) was added in small portion to a solution of 11.5 g. of lithium aluminum hydride in one liter of anhydrous ether. The mixture was stirred at room temperature for one hour, refluxed for one hour and stirred overnight at room temperature. Decomposition was carried out with water and then with 200 ml. of 25% sulfuric acid and the aqueous solution extracted once with ether. The combined ethereal solutions were washed with dilute sulfuric acid, dilute sodium hydroxide and water and dried with sodium sulfate. The crude 1-naphthylcarbinol was dissolved in 350 ml. of absolute benzene and 23.2 ml. of phosphorus tribromide and two drops of pyridine were added. The solution was heated at 55° for two hours, then treated with ice and the organic layer washed with water, sodium bicarbonate solution and saturated salt solution, dried and distilled; b.p. 135–137° (1.5 mm.), m.p. 54–55.5°, yield 50 g. (92.5%).[7]

2-(α-Naphthylmethyl)-1-tetralone (V).—α-Tetralone (24.2 g.) in 30 ml. of toluene was added under nitrogen to a suspension of 6.45 g. of sodamide in 160 ml. of toluene and the mixture was refluxed for six hours. After cooling to room temperature, 33.1 g. of 1-bromomethylnaphthalene in 50 ml. of toluene was added and the mixture heated cautiously. When the vigorous reaction had subsided, the mass was refluxed for six hours and decomposed with water and 25% sulfuric acid. The aqueous layer was extracted twice with ether and the ethereal extracts were washed with water and saturated salt solution and dried with sodium sulfate. Distillation at 0.2 mm. under nitrogen gave 10 g. of unchanged α-tetralone, then a viscous brown oil, b.p. 197–200° (22.5 g., yield 53%, based on 1-bromomethylnaphthalene). The residue distilled with some decomposition at 250–280° (probably bis-alkylated material) and was not investigated any further. The main product crystallized immediately on trituration with methanol. Recrystallization from the same solvent afforded prisms, melting at 92–93° (19.5 g.). Further recrystallization from methanol or chromatography on alumina did not raise the melting point.

Anal. Calcd. for $C_{21}H_{18}O$: C, 88.1; H, 6.3. Found: C, 87.7; H, 6.3.

Cyclization to (I).—The ketone (V) proved resistant to boiling 54% sulfuric acid, and also with polyphosphoric acid a great part of the starting material was recovered under the operating conditions described previously.[1] Only a small quantity of a yellow oxygen-containing compound $C_{21}H_{16}O$, from benzene–petroleum ether, m.p. 107°, could be isolated from the product by chromatography on alumina; the infrared spectrum indicated the presence of a carbonyl group (at 1646 cm.$^{-1}$; 0.026 g. plus 1 cc. of CCl₄; cell thickness, 0.5 mm.); ultraviolet spectrum: λ_{max} 255 mμ (E 4.30); 287.5 mμ (E 4.22). The structure of this compound has not been elucidated.

Anal. Calcd. for $C_{21}H_{16}O$: C, 88.7; H, 5.7. Found: C, 89.0; H, 5.7.
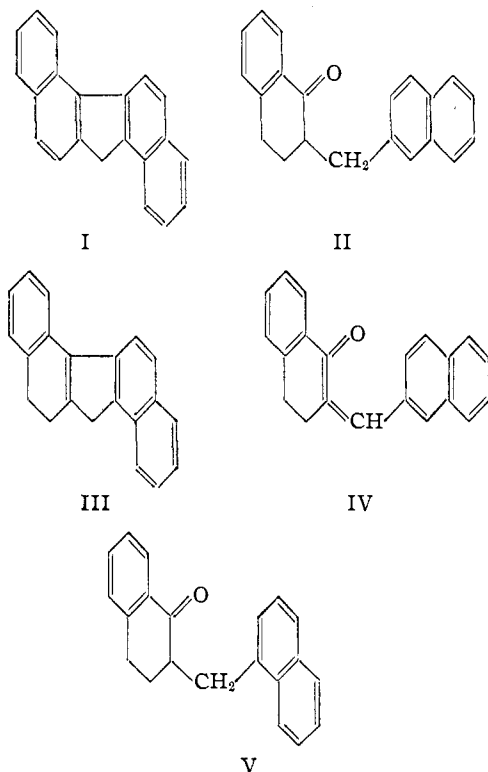
(1) E. D. Bergmann and J. Szmuszkovicz, *Bull. soc. chim. France*, in press.

(2) H. R. Snyder and F. X. Werber, This Journal, **72**, 2962 (1950).

(3) Buu-Hoi and P. Cagniant, *Rev. Sci.*, **81**, 30 (1943) [*C. A.*, **39**, 4861 (1945)].

(4) For the general reaction, see J. Colonge and J. Sibeud, *Compt. rend.*, **232**, 845 (1951).

(5) Buu-Hoi and P. Cagniant, *Rev. Sci.*, **80**, 384 (1942) [*C. A.*, **39**, 3276 (1945)].

(6) For other methods for the preparation of 1,2,5,6-dibenzfluorene, see R. H. Martin, *J. Chem. Soc.*, 679, 683 (1941); *Helv. Chim. Acta*, **30**, 620 (1947); J. W. Cook, *et al.*, *J. Chem. Soc.*, 1319 (1935).

(7) D. T. Keach, This Journal, **55**, 2975 (1933); P. Schorigin, *Ber.*, **59**, 2502 (1926); G. Darzens and A. Lévy. *Compt. rend.*, **202**, 73 (1936).

The following method proved more successful. A mixture of the ketone (V) (4 g.) and *phosphorus pentoxide* (6.3 g.) was heated at 135–140° for one-half hour under nitrogen at 20 mm. and then distilled at 0.5 mm. pressure. The yellow oil (b.p. 195–200°) began to crystallize immediately. The product was recrystallized from benzene–methanol, m.p. 172–174° (0.3 g., 8.1%). Further recrystallization from acetic acid raised the melting point to 174–175°, which was not depressed by admixture of 1,2,5,6-dibenzfluorene. The red residual oil was dissolved in benzene, washed with sodium bicarbonate solution and water and recovered (2 g.) by

evaporation of the solvent. It was dehydrogenated with 0.48 g. of sulfur at 220–260° (20 minutes). After evaporative distillation at 0.1 mm. pressure (170–240°), the dark oil was treated with 3.4 g. of picric acid in glacial acetic acid. The dark-red crystals, after trituration with ethanol containing some picric acid, melted at 184–186° (0.6 g.). The picrate was chromatographed on alumina and eluted with benzene. Recrystallization from glacial acetic acid gave 0.17 g. (4.6%, calcd. on (V)) of slightly pinkish crystals, m.p. and mixed m.p. 174–175°.

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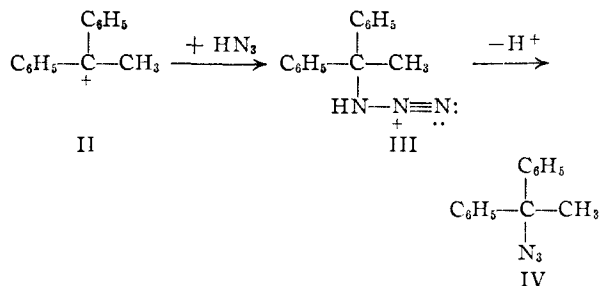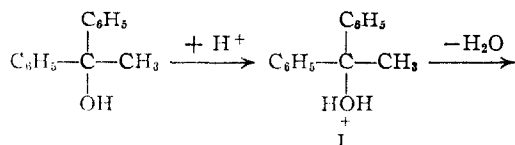# The Formation of Azides in the Reaction of Hydrogen Azide with Diarylethylenes[1]

BY SEYHAN N. EGE AND KENNETH W. SHERK

The Schmidt reaction with 1,1-diarylethylenes in benzene solution using trichloroacetic acid as a catalyst leads to the formation of azides. These azides on treatment with stronger acids, such as sulfuric acid, decompose and undergo the typical Schmidt rearrangement. The migration aptitudes of several para substituted phenyl groups have been measured and correlated with their sigma values.

The investigation of the Schmidt reaction with different classes of compounds[2–6] under varying conditions has led to a better understanding of the factors involved in the rearrangement. Since the Schmidt reaction with olefins carried out by McEwen and co-workers[4] and Kuhn and Di Domenico[7] leads to relatively large amounts of by-product through the polymerization of 1,1-diphenylethylene to 3-methyl-1,1,3-triphenylindane,[4a] it was decided to study the reaction of hydrogen azide with olefins using a milder acid catalyst. The experimental conditions used in the present work involve the passage of dry gaseous hydrogen azide through a benzene solution of the reactant and catalyst. Trichloroacetic acid was chosen as the catalyst because it afforded a homogeneous reaction medium.

From the reaction of hydrogen azide with diphenylmethylcarbinol in the presence of trichloroacetic acid, a neutral product containing nitrogen was obtained instead of the expected aniline and acetophenone. This product, a colorless, high boiling oil, was shown to be 1,1-diphenylethyl azide. The same product was obtained when 1,1-diphenylethylene was allowed to react with hydrogen azide under similar conditions. The steps of the reaction may be outlined as

The azide was found to be very stable, showing no explosive tendencies even when rapidly heated or dropped on a piece of red-hot iron.

One factor that influences the formation of the azide seems to be the acid strength of the reaction medium. It was found experimentally that the concentration and the inherent strength of acids played a large part in effecting the decomposition of 1,1-diphenylethyl azide. While pure trichloroacetic acid caused decomposition only when warmed, slow evolution of nitrogen took place at room temperature with trifluoroacetic acid and with anhydrous stannic chloride. The use of ethanesulfonic acid or sulfuric acid greatly increased the rate of evolution of nitrogen. The role of an acid in the decomposition of azides has been pointed out in earlier publications.[8,9] It is reasonable to assume that the intermediate III and the azide IV are in a state of equilibrium. In this case, the strength of the acid catalyst would influence the degree of ionization of the conjugate acid III of the azide. The stronger acids would depress this ionization and lead to decomposition of the azide, probably through the inhibition of the resonance in the azide group.

This seems to indicate that the decomposition of the azide belongs in the class of specific acid-catalyzed reactions where the rate-determining step is preceded by an equilibrium between the sub-

(1) From the M.A. Thesis of Miss Ege at Smith College, 1952.

(2) P. A. S. Smith, THIS JOURNAL, **70**, 320 (1948).

(3) L. H. Briggs and J. W. Lyttleton, *J. Chem. Soc.*, 421 (1943).

(4) (a) W. E. McEwen, M. Gilliland and B. I. Sparr, THIS JOURNAL, **72**, 3212 (1950); (b) W. E. McEwen and N. B. Mehta, *ibid.*, **74**, 526 (1952).

(5) H. Wolff, The Schmidt Reaction, "Organic Reactions," Vol. 3, John Wiley and Sons, Inc., New York, N. Y., 1946, pp. 307–336.

(6) W. E. McEwen, W. E. Conrad and C. A. VanderWerf, THIS JOURNAL, **74**, 1168 (1952).

(7) L. P. Kuhn and J. Di Domenico, *ibid.*, **72**, 5777 (1950).

(8) K. W. Sherk, A. G. Houpt and A. W. Browne, *ibid.*, **62**, 329 (1940).

(9) P. A. S. Smith and B. B. Brown, *ibid.*, **73**, 2438 (1951).