

214. Schmidt's so-called "1 : 4-Dihydrocarbazole."

By (MISS) B. M. BARCLAY, NEIL CAMPBELL, and ROBERT S. GOW.

The substance given in the literature as 1 : 4-dihydrocarbazole is shown to be a mixture containing more than 50% of carbazole.

By the reduction of carbazole with sodium and boiling amyl alcohol Zanetti (*Ber.*, 1893, 26, 2006) obtained mainly tetrahydrocarbazole, but by the same method Schmidt and Schall (*Ber.*, 1907, 40, 3226) isolated besides carbazole and tetrahydrocarbazole a substance, m. p. 228—229°, which they regarded as 1 : 4-dihydrocarbazole. It resembled carbazole in many of its physical properties, but Schmidt and Schall concluded that it was a distinct chemical entity because of the *N*-nitroso-compound, which melted with decomposition at 72—73° (*N*-nitrosocarbazole, m. p. 82° without decomposition), and the picrate, which separated in russet-brown elongated prisms, m. p. 179—180° (carbazole picrate, bright red needles, m. p. 186—187°). It seemed to us that this evidence was inconclusive and that the above results were best explained by the presence of a considerable quantity of carbazole in the so-called dihydrocarbazole, especially since acetylation was stated to give carbazole, and the percentage of hydrogen was found to be 5.96 instead of 6.51 required for dihydrocarbazole. Indeed, Schmidt and Schall admitted that traces of carbazole were present even in the purest samples of "dihydrocarbazole," but they followed this with the puzzling statement that their analyses agree best with a compound of equimolecular quantities of carbazole and dihydrocarbazole in the form of mixed crystals. We have therefore repeated and amplified their work.

The first product obtained by pouring the amyl alcohol solution into water was stated by Schmidt and Schall to consist mainly of carbazole, but we were unable to distinguish its properties and those of its picrate from those given for "dihydrocarbazole" and its picrate respectively. A second product was obtained by distilling off most of the amyl alcohol; by repeated crystallisation of this from toluene, glacial acetic acid, or ethyl alcohol, "dihydrocarbazole," m. p. 229°, was obtained with great loss in yield. Further crystallisation and chromatographic purification did not raise the m. p., and analyses of several samples gave substantially the same results as those of Schmidt and Schall (*loc. cit.*). All samples gave with sulphuric and nitric acids the blue colour characteristic of carbazole, and crystallised from alcohol in rhombic or hexagonal plates with the same profile angles as carbazole. The substance, therefore, seems to contain a considerable proportion of carbazole.

The *N*-nitroso-derivative melted over a much wider range than stated by Schmidt and Schall, and the attendant decomposition may well be due to the presence of a compound such as *N*-nitrosotetrahydrocarbazole [m. p. 33—35° (decomp.)], the main component probably being *N*-nitrosocarbazole. The picrate, although homogeneous in appearance under the microscope, also melted over a wider range than found by Schmidt and Schall and is clearly a mixture, since the picrates of carbazole derivatives melt sharply. An examination of the picrates, styphnates, and *s*-trinitrobenzene derivatives of carbazole, tetrahydrocarbazole, and "dihydrocarbazole" showed that the m. ps. and colours of the "dihydrocarbazole" derivatives were intermediate between those of carbazole and tetrahydrocarbazole. Moreover, mixtures of carbazole (2 parts) and tetrahydrocarbazole (1 part) gave molecular compounds similar in colour and m. p. to those of the corresponding derivatives of "dihydrocarbazole." These facts suggested that "dihydrocarbazole" is a mixture of carbazole and tetrahydrocarbazole, but this was excluded by the low m. p. of such a mixture and by its quick separation into pure components merely by crystallisation from alcohol.

The presence of carbazole in "dihydrocarbazole" was proved by the absorption of approximately 1 mol. of hydrogen on hydrogenation with Adams's catalyst. In all such experiments carbazole was isolated in over 50% yield in addition to an unidentified oily product, and in two a considerable quantity of tetrahydrocarbazole was obtained. It would seem therefore as if reduction gave products which were easily separated from carbazole, but it was possible that carbazole formation was due to disproportionation of dihydrocarbazole, just as the methyl ester of Δ^1 -tetrahydroterephthalic acid with hydrogen in the presence of palladium (but not platinum) yields a mixture of the esters of terephthalic and hexahydroterephthalic acids (Zelinski, *Ber.*, 1911, 44, 2305). We found, however, that with the Adams's catalyst no disproportionation occurred, only a mixture of the esters of the hexahydroterephthalic acids being obtained, and conclude that the carbazole isolated from "dihydrocarbazole" is not due to dehydrogenation.

Acetylation of "dihydrocarbazole" gave conflicting results. In one experiment *N*-acetylcarbazole was isolated in poor yield, in others only unchanged material, while Schmidt and Schall obtained carbazole. It is a little difficult to understand the inability of "dihydrocarbazole" to give *N*-acetylcarbazole under conditions in which carbazole is readily acetylated, but Schmidt and Schall's explanation of their result as due to the ease of oxidation of dihydrocarbazole is improbable.

From the above experiments we feel justified in concluding that the "dihydrocarbazole" of Schmidt and Schall is a mixture containing over 50% of carbazole. We have not been successful in identifying the other component (or components). A mixture or molecular compound of carbazole and a dihydrocarbazole would agree with the analytical and hydrogenation results, but would not contain sufficient hydrogen to account for the observed fact that one molecule of chloranil is completely reduced to the quinol by one molecule of "dihydrocarbazole."

EXPERIMENTAL.

Unless otherwise stated, the preparation, purification, and properties are those given in the literature. The purity of compounds was checked by the sharpness of their m. ps. on a Fuchs micro-m. p. apparatus (*Mikrochim. Acta*, 1937, 2, 317); sublimation was also detected on this apparatus. Analyses were done by Drs. Weiler and Strauss, Oxford.

In all the chromatographic adsorption experiments, aluminium oxide (Brockmann) was used as absorbent, benzene as solvent, and benzene (3 parts)-light petroleum (b. p. 100—120°, 1 part) as developer.

Profile angles of crystals [A. C. Shead, *Ind. Eng. Chem. (Anal.)*, 1937, 9, 496] were measured by means of a microscope provided with an ocular with cross-wires and a graduated rotating stage. A suspension of the crystals to be measured was placed on a microscope slide, the crystals were allowed to settle, and the mother liquor was drained off. Several crystals from each sample were measured. The measurements are correct to one degree.

Preparation of "Dihydrocarbazole."—Carbazole was reduced with sodium and amyl alcohol (b. p. 128—132°) by the method of Schmidt and Schall (*loc. cit.*). The product obtained when the mixture was poured into water was crystallised thrice from alcohol. It formed rhombic plates with profile angles 107° and 73° (see below) and m. p. 226—228°. The picrate formed russet-brown elongated prisms, m. p. 175—180° (softening at 150°). The product therefore has the properties of "dihydrocarbazole" given below.

Crude "dihydrocarbazole" obtained by evaporating the amyl alcohol to 200 c.c. was washed with water until all traces of alkali had been removed, and was then crystallised to constant m. p. One sample crystallised thrice from benzene and then four times from toluene had m. p. 229°, while another after chromatographic purification had the same m. p. which was not raised by crystallisation from glacial acetic acid. A third sample, prepared from the picrate which had been crystallised three times from benzene saturated with picric acid, had m. p. 226—227° after crystallisation from benzene. The three samples gave the following analyses. (1) C, 85.2; H, 5.86. (2) C, 85.1; H, 5.57. (3) C, 85.5; H, 5.89. Other purified specimens gave the following figures: C, 84.9, 85.2; H, 5.78, 5.92. These results show decisively that the substance is not dihydrocarbazole (Calc. for $C_{12}H_{11}N$: C, 85.16; H, 6.56%), and probably not an equimolecular mixture of carbazole and dihydrocarbazole (Calc. for $C_{24}H_{20}N_2$: C, 85.66; H, 6.01%).

"Dihydrocarbazole" crystallised from alcohol in transparent rhombic plates (profile angles, 107° and 73°) and to a smaller extent in hexagonal plates (profile angles, two of 107° and four of 127°). The same results were obtained with pure carbazole except that the crystals were better defined.

The substance gave many of the colour reactions of carbazole: blue with sulphuric and nitric acids or with isatin in sulphuric acid; carmine red with benzoquinone in glacial acetic acid with a little sulphuric acid; but red on fusion with oxalic acid (carbazole, blue).

Derivatives of "Dihydrocarbazole," etc.—The nitroso-derivative of "dihydrocarbazole" melted over a range, 60—73° (decomp.), whereas *N*-nitrosocarbazole melted sharply at 82° (no decomp.). *N*-Nitrosotetrahydrocarbazole was prepared by dissolving tetrahydrocarbazole (1.5 g.) in ether (30 c.c.), glacial acetic acid (10 c.c.), and water (20 c.c.), and adding sodium nitrite (1.5 g.) with shaking. The ether layer was washed with water, sodium carbonate solution, and water, dried ($CaCl_2$), and finally evaporated under reduced pressure. The nitroso-compound separated as yellow crystals which were purified by washing with methyl alcohol; m. p. 33—35° (decomp.) (Found: N, 13.0. $C_{12}H_{12}ON_2$ requires, N, 14.0%).

Picrates. That of "dihydrocarbazole" formed russet-brown elongated prisms, m. p. 165—185° (Schmidt and Schall give 179—180°); of carbazole, bright red needles, m. p. 186°; of tetrahydrocarbazole, chocolate brown elongated prisms, m. p. 144°.

s-Trinitrobenzene derivatives. That of "dihydrocarbazole" formed reddish-brown elongated prisms, m. p. 175—188°; of carbazole, bright orange needles, m. p. 199°. The trinitrobenzene derivative of tetrahydrocarbazole formed red needles, m. p. 159° (Found: N, 14.7. $C_{18}H_{14}O_6N_4$ requires N, 14.6%).

Styphnates. That of "dihydrocarbazole" formed orange elongated prisms which sublimed in yellow needles, m. p. 165—175°; of carbazole, orange-red prisms, subliming in yellow needles, m. p. 179°. The styphnate of tetrahydrocarbazole formed reddish-brown elongated prisms (benzene), m. p. 152—154° (Found: N, 13.4. $C_{18}H_{16}O_8N_4$ requires N, 13.5%). All these substances appeared to be homogeneous under the microscope.

Catalytic Hydrogenation of "Dihydrocarbazole," etc.—The apparatus was calibrated by noting the fall in pressure from 60 lb./sq. in. when 1/100 mol. of benzoin was reduced to hydrobenzoin with 0.1 g. of Adams's platinum catalyst in 100 c.c. of glacial acetic acid. A fall of 8 lb. indicated absorption of 1/100 mol. of hydrogen. All reductions were carried out with the above quantities. "Dihydrocarbazole" (1.7 g.) absorbed 1/100 mol. of hydrogen rapidly. From the solution were isolated 0.6 g. of carbazole, m. p. 232—237°, and 0.9 g. of a brown oil, which gave a bright red colour with concentrated sulphuric acid but no blue colour on the further addition of nitric acid. Efforts to purify the oil by crystallisation and chromatographic adsorption failed. In two other experiments more than 50% of carbazole was obtained, with 0.4 g. of tetrahydrocarbazole, identified by m. p., mixed m. p., and picrate.

Under the same conditions carbazole was not reduced, but tetrahydrocarbazole absorbed 1/100 mol. of hydrogen to give an oily product.

Δ^1 -Tetrahydroterephthalic acid [*p*-nitrobenzyl ester, prisms (glacial acetic acid), m. p. 185—187° (Found: N, 6.33. $C_{22}H_{20}O_8N_4$ requires N, 6.4%)] was converted into the dimethyl ester and hydrogenated as above. The solution was evaporated to small bulk after 1/100 mol. of hydrogen had been absorbed, and water added. An oil separated which was washed several times with water and then hydrolysed with a mixture of methyl alcohol and sodium hydroxide. Acidification, followed by partial evaporation of the solution, gave *trans*-hexahydroterephthalic acid, m. p. ca. 300° (Found: C, 56.1; H, 6.90. Calc. for $C_8H_{12}O_4$: C, 55.8; H, 7.0%). From the solution a small quantity of the *cis*-acid, m. p. 167—169°, was obtained. No terephthalic acid, easily distinguished from the above *trans*-acid by its insolubility in hot water and the appearance of its sublimate, was detected.

Acetylation Experiments.—Acetylation of carbazole with acetic anhydride containing a trace of sulphuric acid gave after 1 hour's heating followed by addition of water an excellent yield of *N*-acetylcarbazole, m. p. 76° (Boeseken, *Rec. Trav. chim.*, 1912, 31, 350). Tetrahydrocarbazole under these conditions gave a poor yield of the acetyl compound, unless very pure tetrahydrocarbazole and redistilled acetic anhydride were used. "Dihydrocarbazole" gave unsatisfactory and conflicting results. In one experiment *N*-acetylcarbazole was isolated in poor yield from the oily product, while in others only unchanged material was found.

Acetic anhydride without sulphuric acid did not attack carbazole even after refluxing for 5 hours, but gave with

tetrahydrocarbazole a 70% yield of *N*-acetyltetrahydrocarbazole, b. p. 210—230°/19 mm., m. p. 73—74° (Perkin and Plant, *J.*, 1921, **119**, 1832). The only product obtained by similar treatment of "dihydrocarbazole" was unchanged material.

Chloranil Dehydrogenation.—"Dihydrocarbazole" (0.505 g.; 0.003 g.-mol.) was refluxed with chloranil (0.733 g.; 0.003 g.-mol.) for 27 hours in 15 c.c. of sulphur-free xylene. At least 24 hours were necessary for complete dehydrogenation. Carbazole, identified by its m. p., mixed m. p., and picrate, was obtained in 83% yield. A second experiment gave a 90% yield of crude and 80% of pure carbazole. In both experiments the chloranil was completely used up.

1:4-Dihydronaphthalene under the same conditions was dehydrogenated to naphthalene (70% yield) in 5 hours.

THE UNIVERSITY, EDINBURGH.

[Received, February 12th, 1946.]