CCCCLVI.—*Nitration of Carbazole.*

By GILBERT T. MORGAN and JAMES GIBB MITCHELL.

FROM the mother-liquors obtained in the nitration of carbazole in acetic acid, Ziersch (*Ber.*, 1909, **42**, 3797) isolated a yellow substance melting at 164° which was believed to be 1-nitrocarbazole. Subsequently Lindemann and his colleagues (*Ber.*, 1924, **57**, 555, 1314; 1925, **58**, 1221) isolated another nitrocarbazole (m. p. 187°), probably identical with that reported by Votoček (*Chem. Zeit. Rep.*, 1896, **20**, 190), and showed that the corresponding amino-derivative (m. p. 193°) was identical with 1-aminocarbazole prepared synthetically. Accordingly the yellow substance was assumed to be 2- or 4-nitrocarbazole.

We have, however, failed to obtain this yellow substance in a definite crystalline form with a sharp melting point and when recourse was had to sublimation in a vacuum two fractions in approximately equal amount and in good yield were obtained, the first being 1-nitrocarbazole and the second 3-nitrocarbazole: no trace of any other derivative could be detected. The melting point data offer a complete explanation. The yellow substance is a

Melting Points of Mixtures of 1- *and* 3-*Nitrocarbazoles.*

3-Nitrocarbazole, %	80·0	66·6	64·8	62·0	58·0
M. p.	185—195°	160—164°	157—163°	159—161°	160—163°
3-Nitrocarbazole, %	50·0	43·0	39·0	33·3	20·0
M. p.	162—163°	156—159°	157—162°	161—164°	174—180°

molecular complex (m. p. 162—163°) of the two isomerides, and the isolation of 1-nitrocarbazole in small yields (Votoček, *loc. cit.*; Lindemann, *loc. cit.*; Kehrmann and Zweifel, *Helv. Chim. Acta*, 1928, **11**, 1213) is probably to be attributed to instability of this molecular compound.

In view of the acidity of the carbazole nucleus it was decided to try the effect of basic solvents such as aniline and pyridine in the hope of resolving the molecular compound into its components. The yellow substance dissolved readily in either solvent and addition of alcohol separated 1-nitrocarbazole in almost quantitative yield. This 1-nitrocarbazole was reduced to 1-aminocarbazole, a base from which we did not obtain a 1 : 9-diazoimino-derivative on treatment with nitrous acid or alkyl nitrites, under conditions comparable with those in which *o*-aminodiphenylamine readily yields its diazoimine, $C_6H_5{\cdot}N{\cdot}C_6H_4N_2$.

Nitration Experiments.—(a) A stirred suspension of carbazole (50 g.) in water (100 c.c.) was warmed at 40° for 1 hour while 60% nitric acid (45 c.c.) was added. Thereafter the temperature was raised at the rate of 10° per hour and maintained at 80—90° for 3 hours. The dried product (63 g.) was digested with benzene (400 c.c.) for 2 hours, and the suspension quickly cooled to room temperature. The precipitate (45·3 g.) consisted mainly of 3-nitrocarbazole, and the benzene filtrate contained a yellow product, m. p. about 164°.

(b) The method described by Ziersch * (*loc. cit.*) in glacial acetic acid gave 63·8 g. of mixed nitrocarbazoles, of which 15·6 g. dissolved in benzene. The yellow molecular complex (m. p. 158—162°) contained a small amount of unchanged carbazole.

(c) [With J. R. DOLPHIN.] Benzoyl nitrate, prepared by adding benzoyl chloride (35 g.) and dry petroleum to powdered silver nitrate (50 g.) at − 15°, was after 2 hours filtered into a well-stirred suspension of carbazole (32 g.) in petroleum (200 c.c.) of b. p. 80—100°. The carbazole slowly dissolved and subsequently a dark green solid separated until the mixture became semi-solid. After 1 hour at the ordinary temperature the solid was warmed with aqueous sodium hydroxide to remove benzoic acid, the colour changing from green to dark red. Repeated crystallisations yielded 3-nitrocarbazole (27·4 g.) and the yellow molecular compound (12·5 g.) melting at 164°.

Repeated crystallisations of this molecular compound gave small yields of 1-nitrocarbazole, but the main bulk of the material separated in small crystals with an indefinite melting point round about 164°.

When the yellow molecular compound was heated in a Hedley sublimer in a vacuum at 190—200° a sublimate (1·24 g.) formed which crystallised from glacial acetic acid in long, flat, yellow needles,

* In the original paper the amount of nitric acid given as 15·5 c.c. per 100 g. of carbazole is insufficient and is probably a misprint for 45·5 c.c.

m. p. 186·5—187·5°; further heating at the same temperature gave 0·3 g. (m. p. 164—168°), and at 230—240° a sublimate of 3-nitrocarbazole (1·94 g.) appeared which crystallised from glacial acetic acid in rosettes of needles (m. p. 214°).

A warm solution of the yellow molecular compound (45 g.) in aniline (80 c.c.) was heated with an equal volume of absolute alcohol. 1-Nitrocarbazole (20·8 g.) separated rapidly in characteristic form (m. p. 186—187°). On recrystallisation (18 g.) it melted at 186·5—187·5°, this amount representing a yield of 12 g. of pure material from 100 g. of carbazole.

Warm pyridine (9 c.c.) readily dissolved the molecular compound (8·5 g.) and on addition of three volumes of alcohol 1-nitrocarbazole separated, m. p. 183—184°.

The sintering and liquefying points of weighed mixtures of 1- and 3-nitrocarbazoles were observed (see foregoing table).

CHEMICAL RESEARCH LABORATORY,
TEDDINGTON, MIDDLESEX. [*Received, November 13th,* 1931.]