360. *The Dicarbazyls. Part V. Synthesis of* 3 : 9′-*Dicarbazyl.*

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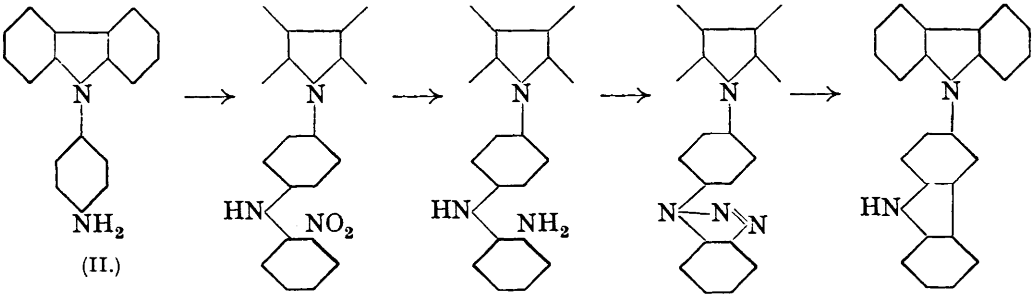
SYNTHESES of 1 : 1′-dicarbazyl (Macrae and Tucker, preceding paper), 3 : 3′-dicarbazyl (Tucker, J., 1926, 3033; Maitland and Tucker, J., 1927, 1388), and 3 : 9′-*dicarbazyl*, herein described, have shown that none of these is identical with the 265°-melting dicarbazyl of Perkin and Tucker (J., 1921, **119**, 216), which also is not 9 : 9′-dicarbazyl (McLintock and Tucker, J., 1927, 1214).

The synthesis of 3 : 9′-dicarbazyl (VI) from 9-*p*-nitrophenylcarbazole (I) has been effected according to the scheme:



(II.) (III.) (IV.) (V.) (VI.)

9-*p*-Nitrophenylcarbazole (I) was prepared by a modification of the method of G. and M. de Montmollin (*Helv. Chim. Acta*, 1923, **6**, 96). Its constitution was established indirectly by them, but we have synthesised it directly by heating together carbazole, *p*-chloronitrobenzene, and potassium carbonate. A synthesis of 9-o-*nitrophenylcarbazole* was effected similarly. In the condensation of nitrobenzene with carbazole no 9-*o*-nitrophenylcarbazole appears to be formed, the sole products being the *p*-analogue and an uncrystallisable liver-coloured solid.

The claim that *p*- is more reactive than *o*-chloronitrobenzene towards amines (7·2 : 1·9) (*Ann. Reports*, 1929, 135) is difficult to test with regard to carbazole; for, although the yield of 9-*p*-nitrophenylcarbazole (58%) is greater than that of the corresponding *o*-compound (10%), the time of heating for the former (10—12 hours) is longer than that which gives the optimum yield for the latter (3 hours).

EXPERIMENTAL.

All m. p.'s are corrected. Micro-analyses were performed by Dr. A. Schoeller, and are marked *. Molecular weights were taken in camphor by Rast's method.

9-p-*Nitrophenylcarbazole* (I).—A mixture of carbazole (100 g.), nitrobenzene (400 c.c.), and potassium hydroxide (75 g. powder) was heated in a water-bath from room temperature to 80° ($\frac{1}{2}$ hour) and kept at this temperature for 1 hour, then in boiling water for $\frac{1}{2}$ hour, with frequent and vigorous shaking. The mixture, poured into a beaker, was left to cool in the water-bath in order to produce large crystals and a product relatively easy to filter. The solid product, washed with ligroin and with warm water and crystallised once from glacial acetic acid, gave practically pure 9-*p*-nitrophenylcarbazole (80 g.), m. p. 209—211° [M. and M., *loc. cit.*, give 212° (uncorr. ?)]. The filtrate, on long standing, gave a second crop (4 g.). The nitrobenzene filtrate, to which the ligroin washings had been added, gave a further small crop and left after steam distillation a liver-coloured residue (160 g.) which contained only a trace of 9-*p*-nitrophenylcarbazole. *p*-Nitrophenol also was present.

The total yield of 9-*p*-nitrophenylcarbazole was thus increased from 33% obtained by the de Montmollins' method (they claim 70%) to 50% : this was never exceeded. Various changes in the temperature and time of heating were possible without lowering the yield by more than 10%. This modified method is being applied to effect reactions excluded by the older method.

9-*p*-Nitrophenylcarbazole is insoluble in ligroin or methyl alcohol and almost insoluble in ethyl alcohol; it is more soluble in benzene or nitrobenzene than in glacial acetic acid or acetone, from all of which it crystallises well.

Synthesis of 9-p-*Nitrophenylcarbazole.*—A mixture of carbazole (5 g.), *p*-chloronitrobenzene (20 g.), and potassium carbonate (20 g. anhydrous) was gently boiled (with frequent shaking) for 10—12 hours. The product was steam-distilled, and the residue dried and extracted with glacial acetic acid. The solid obtained from the acetic acid extract was extracted with alcohol, and the residue extracted with acetic acid. From the alcoholic extract, carbazole (2 g.) was recovered. The acetic acid solution yielded brownish-yellow crystalline 9-*p*-nitrophenylcarbazole (3 g.; yield, calculated on unrecovered carbazole, 58%) melting, alone or mixed with a specimen prepared as above, at 209—211° (Found : *M*, 282, 293. Calc. : *M*, 288).

9-*p*-Aminophenylcarbazole (II) was obtained by reduction of 9-*p*-nitrophenylcarbazole with tin and hydrochloric acid as a golden syrup (uncrystallisable) (yield, 80%). It gave the acetyl derivative, 9-*p*-acetamidophenylcarbazole, m. p. 260°, hydrochloride (Found : HCl, 12·3; Cl, by alcoholic silver nitrate solution, 11·9. Calc. : HCl, 12·4; Cl, 12·1%), and picrate, m. p. 202° (decomp.) (G. and M. de Montmollin, *ibid.*).

9-p-(o-*Nitrophenylamino*)*phenylcarbazole* (III) was prepared by heating a mixture of 9-*p*-aminophenylcarbazole (15 g.), *o*-chloronitrobenzene (150 g.), and sodium carbonate (60 g. anhydrous) at 240° with frequent shaking for 6—8 hours. Unchanged *o*-chloronitrobenzene was removed by steam-distillation, and the remaining brown solid extracted several times with carbon tetrachloride. The solution, on slow evaporation in the air, deposited carmine-red needles, which redissolved with difficulty in solvents and crystallised slowly or only on slow evaporation of the solvent. When nearly pure, however, it crystallised normally from acetone or benzene in ruby-red rods, m. p. 181—185° (6 g.; yield, 40%) (Found : C, 75·9; H, 4·5; N, 11·2; *M*, 365. $C_{24}H_{17}O_2N_3$ requires C, 76·0; H, 4·5; N, 11·1%; *M*, 379). The picrate crystallised from glacial acetic acid in orange needles, m. p. 170°. The *acetyl* derivative, prepared by means of boiling acetic anhydride and a drop of sulphuric acid (15 minutes), crystallised from benzene as orange needles, m. p. 205—207° (Found : N, 10·1; *M*, 416. $C_{26}H_{19}O_3N_3$ requires N, 10·0%; *M*, 421).

9-p-(o-*Aminophenylamino*)*phenylcarbazole* (IV) was obtained by boiling (15 minutes) the nitro-compound with stannous chloride in glacial acetic acid saturated with hydrogen chloride. After most of the mixed acids had been boiled off, the residue was treated with excess of sodium hydroxide solution, and the warm mixture extracted with benzene. The yellow syrup obtained on evaporation was extracted with hot ligroin (b. p. 80—100°); the solution, on cooling, gave clusters of cream-coloured nodules, m. p. 115—116° (yield, about 80%) (Found : C, 82·4; H, 5·4; N, 11·9; *M*, 341. $C_{24}H_{19}N_3$ requires C, 82·5; H, 5·4; N, 12·0%; *M*, 349). It gave a picrate, m. p. 137°, and an acetyl derivative, probably 9-p-(o-*acetamidophenylamino*)*phenylcarbazole*, as white needles, m. p. 180—181° (Found : C, 79·4; H, 5·4; N, 10·6; *M*, 384. $C_{26}H_{21}O_3N_3$ requires C, 79·8; H, 5·4; N, 10·7%; *M*, 391).

9-p-1″ : 2″ : 3″-*Benztriazolylphenylcarbazole* (V).—9-*p*-(*o*-Aminophenylamino)phenylcarbazole (6 g.) was diazotised (in ice) with sodium nitrite and dilute hydrochloric acid solution, and the mixture left (in ice) over-night. The brownish-red solid which separated crystallised from acetic anhydride as salmon-pink cubes (4·8 g.; yield, 80%), m. p. 163° (Found : N, 15·4; *M*, 354. $C_{24}H_{16}N_4$ requires N, 15·6%; *M*, 360).

3 : 9′-*Dicarbazyl* (VI).—The preceding benztriazole (2 g.) was heated gently, in a long Pyrex tube over a small flame, until effervescence ceased. The residue was extracted with toluene (charcoal), and the solution concentrated; white prisms arranged in crosses crystallised (1 g.; yield, 55%), m. p. 212—214° (208—210° uncorr.) (Found * : C, 86·6; H, 4·9; N, 8·3; *M*, 337. $C_{24}H_{16}N_2$ requires C, 86·7; H, 4·8; N, 8·4%; *M*, 332). 3 : 9′-*Dicarbazyl* is fairly readily soluble in benzene, xylene, acetone, ethyl acetate, or chloroform, almost insoluble in methyl, ethyl, or *n*-propyl alcohol, and insoluble in carbon tetrachloride or ligroin. It dissolves in cold concentrated sulphuric acid to give a faintly green solution, which loses its colour on warming, but turns an intense green on addition of a trace of nitric acid; on warming, this colour fades to reddish-yellow. These changes are similar to those exhibited by carbazole and the dicarbazyls.

9-*Acetyl*-3 : 9′-*dicarbazyl*.—A solution of 3 : 9′-dicarbazyl in excess of acetic anhydride containing a drop of concentrated sulphuric acid was boiled for a few minutes and then poured into hot water. The precipitate crystallised from glacial acetic acid in cream-coloured needles, m. p. 197° after softening at 190° (Found * : C, 83·7; H, 4·8; N, 7·4; *M*, 384. $C_{26}H_{18}ON_2$ requires C, 83·4; H, 4·8; N, 7·5%; *M*, 374).

Synthesis of 9-o-*Nitrophenylcarbazole*.—A mixture of carbazole (20 g.), *o*-chloronitrobenzene (40 g.), and potassium carbonate (20 g. anhydrous) was boiled gently, with frequent shaking, for 3 hours, then steam-distilled. The residue was extracted with glacial acetic acid, and the solution evaporated to dryness. The residue was extracted with alcohol. The first two extracts yielded golden-coloured needles of 9-o-*nitrophenylcarbazole*, m. p. 156° (3 g.; yield, 10%) (Found * : C, 74·8; H, 4·4; N, 9·6; *M*, 291. $C_{18}H_{12}O_2N_2$ requires C, 75·0; H, 4·2; N, 9·7%; *M*, 288). Subsequent alcoholic extracts gave carbazole only. 9-*o*-Nitrophenylcarbazole is readily soluble in glacial acetic acid or benzene; it crystallises from aqueous acetic acid or carbon tetrachloride, but best from methyl or ethyl alcohol.

In certain experiments *oo*′-dinitrodiphenyl ether, m. p. 113—114° (uncorr.) (Macrae and Tucker, *loc. cit.*), was also produced : its separation by means of ligroin was difficult (small yield).

An attempt to prepare 9-*o*-nitrophenylcarbazole by heating together carbazole (8 g.), *o*-nitrophenyl *p*-toluenesulphonate (Ullmann and Nádai, *Ber.*, 1908, **41**, 1871) (20 g.), and potassium hydroxide (15 g., dry powder) in acetone (50 c.c.) (Stevens and Tucker, J., 1923, **123**, 2140) gave, instead of the desired compound, a nearly theoretical yield of both 9-*p*-toluenesulphonylcarbazole, m. p. 129—134° (from alcohol) (Cassella, 1909, D.R.-P. 224951; Herz, 1910, A.P. 966092, give m. p. 127—128°), and *o*-nitrophenol.

9-*o*-Aminophenylcarbazole was obtained by reduction (tin and hydrochloric acid solution) of 9-*o*-nitrophenylcarbazole as a golden syrup (uncrystallisable) (yield, 75%). When this syrup was warmed with acetic anhydride, 9-o-*acetamidophenylcarbazole* was obtained, which gave cream-coloured cubes from benzene–ligroin, m. p. 150° (Found : N, 9·2; *M*, 307. $C_{20}H_{16}ON_2$ requires N, 9·3%; *M*, 300).

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