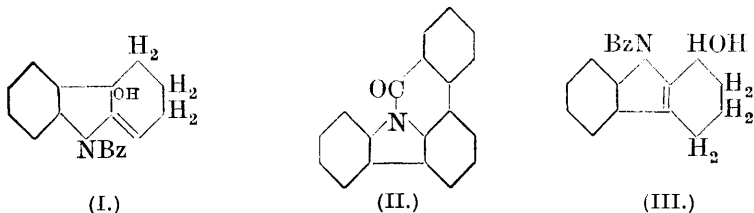


303. Syntheses of 19-Ketophenanthridindocoline, 3-Benzoylcarbazole, and 3:6-Dibenzoylcarbazole.

By S. G. P. PLANT and (MISS) M. L. TOMLINSON.

THE authors have already described (J., 1931, 3324) the preparation of 11-hydroxy-9-benzoyl-2:3:4:11-tetrahydrocarbazole (I) and the formation from it of a compound, $C_{19}H_{11}ON$, which was thought to be 19-ketophenanthridindocoline (II). The validity of this view

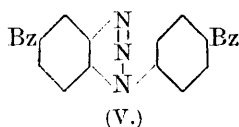
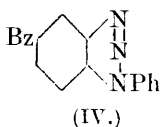


has now been definitely established by the synthesis of the latter product: carbazole was converted through its 9-*o*-nitrobenzoyl derivative into the corresponding *amine*, which was diazotised in methyl-alcoholic sulphuric acid; the product obtained after boiling was identical with the 19-ketophenanthridindocoline previously described. In the formation of (II) from (I) it appears probable that the latter first changes to 1-hydroxy-9-benzoyl-1:2:3:4-tetrahydrocarbazole (III) and then (II) results from ring closure and loss of hydrogen.

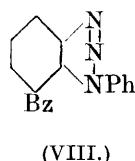
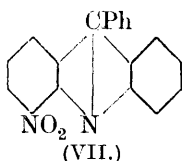
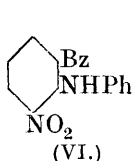
In an attempt to prepare 19-ketophenanthridindocoline directly by the dehydrogenation of 9-benzoylcarbazole by aluminium chloride at 120° (compare the formation of benzanthrone from α -benzoylnaphthalene; Scholl and Seer, *Annalen*, 1912, **394**, 111), isomeric change occurred and 3-benzoylcarbazole was obtained. The synthesis of 3-benzoylcarbazole was achieved by condensing *p*-hydrazinobenzophenone with *cyclohexanone*, heating the product with dilute sulphuric acid, and oxidising the 6-benzoyl-1:2:3:4-tetrahydrocarbazole so formed with sulphur in boiling quinoline.

After the completion of the above experiments, a synthesis of 3-benzoylcarbazole by the elimination of nitrogen from 5-benzoyl-1-phenylbenzotriazole (IV) was described by Hunter and Darling (*J. Amer. Chem. Soc.*, 1931, **53**, 4183). They were unsuccessful, however, in attempts to obtain 3-benzoylcarbazole from 9-benzoylcarbazole.

The action of benzoyl chloride on carbazole in carbon disulphide solution in the presence of aluminium chloride produced 3:6-dibenzoylcarbazole, which was also obtained by the action of benzoyl chloride under similar conditions on 9- and on 3-benzoylcarbazole. Its constitution was established by its formation from 5:4'-dibenzoyl-1-phenylbenzotriazole (V), prepared by condensing 4-bromo-3-nitrobenzophenone and *p*-aminobenzophenone, followed by reduction and treatment with nitrous acid.



In an attempt to synthesise 1-benzoylcarbazole, 2-bromo-3-nitrobenzophenone was condensed with aniline to give 2-nitro-6-benzoyldiphenylamine (VI) (compare Schöpf, *Ber.*, 1891, **24**, 3771).



The condensation proceeded smoothly on the steam-bath, but at 130° the diphenylamine derivative was contaminated with a substance which is apparently Jensen and Rethwisch's 1-nitro-5-phenylacridine (VII) (*J. Amer. Chem. Soc.*, 1928, **50**, 1144). The amine obtained by the reduction of (VI) was converted into 7-benzoyl-1-phenylbenzotriazole (VIII), but all efforts to transform this product into 1-benzoylcarbazole were unsuccessful.

EXPERIMENTAL.

Synthesis of 19-Ketophenanthridindocoline.—A mixture of carbazole (3.3 g.), Me₂CO (50 c.c.), and 66% KOH aq. (6 g.) was shaken and treated gradually with *o*-nitrobenzoyl chloride (6 g.). The product obtained by dilution with H₂O was crystallised from EtOH and from AcOH and 9-*o*-nitrobenzoylcarbazole isolated in yellow prisms, m. p. 148—150° (Found: N, 8.8. C₁₉H₁₂O₃N₂ requires N, 8.8%). This compound was kept at 50° with an excess of Zn dust in AcOH for 4 hrs., the filtered liquid diluted with much H₂O, and the ppt. crystallised from EtOH, 9-*o*-aminobenzoylcarbazole being obtained in pale yellow

needles, m. p. 160—162° (Found: N, 9.7. $C_{19}H_{14}ON_2$ requires N, 9.8%). A solution of the amine (1 g.) in MeOH (120 c.c.) and conc. H_2SO_4 (2 c.c.) was diazotised at 0° ($NaNO_2$, 0.24 g., in H_2O , 5 c.c.) and after $\frac{1}{2}$ hr. the mixture was refluxed for $\frac{1}{2}$ hr. The product, which separated on cooling, was crystallised from EtOH (charcoal), and 19-ketophenanthridindocoline isolated in colourless needles, m. p. 227°, mixed m. p. with Plant and Tomlinson's compound (II) (m. p. 225°) (*loc. cit.*), 226°.

3-Benzoylcarbazole.—9-Benzoylcarbazole (10 g.) (Stevens and Tucker, J., 1923, 123, 2140) and $AlCl_3$ (4 g.) were gradually heated to 120°, the molten mass poured into dil. HCl aq., and the green solid recrystallised twice from EtOH (charcoal), 3-benzoylcarbazole being isolated in pale yellow plates, m. p. 206° (Found: C, 84.0; H, 5.0. Calc.: C, 84.1; H, 4.8%).

A solution of 3-benzoylcarbazole in Ac_2O was refluxed for 6 hrs., cooled, and shaken with H_2O . The ppt., crystallised from EtOH, gave pale yellow needles, m. p. 154° (Found: C, 80.4; H, 5.0. $C_{21}H_{15}O_2N$ requires C, 80.5; H, 4.8%), of 3-benzoyl-9-acetylcarbazole, which was also prepared from 3-benzoylcarbazole and $AcCl$ in Me_2CO containing conc. KOH aq. A similar procedure with $BzCl$ led to 3:9-dibenzoylcarbazole, which separated from EtOH in colourless needles, m. p. 170° (Found: C, 83.1; H, 4.7. $C_{26}H_{17}O_2N$ requires C, 83.2; H, 4.5%).

3-Benzoylcarbazole (1 g.) and phenylhydrazine (1 g.), heated at 150° for $\frac{3}{4}$ hr., gave the phenylhydrazone, colourless plates, m. p. 219°, from AcOH (Found: N, 11.8. $C_{25}H_{19}N_3$ requires N, 11.6%).

Synthesis of 3-Benzoylcarbazole.—Equiv. quantities of cyclohexanone and *p*-hydrazinobenzophenone (Ruhemann and Blackman, J., 1889, 55, 612) were heated, the hydrazone was boiled for 20 mins. with 18% H_2SO_4 aq., and the solid product crystallised from AcOH and from EtOH, from which 6-benzoyltetrahydrocarbazole separated in yellow prisms, m. p. 167—168° (Found: N, 5.2. $C_{19}H_{17}ON$ requires N, 5.1%). This derivative (1 g.) in C_6H_7N was boiled for $\frac{1}{2}$ hr. with S (0.23 g.) and then poured into ice-dil. HCl aq., the solid obtained was mixed with Fe filings and distilled under reduced pressure, and the product crystallised twice from EtOH, 3-benzoylcarbazole being obtained in pale yellow plates, m. p. and mixed m. p. 206°.

3:6-Dibenzoylcarbazole.—Carbazole (12 g.), $AlCl_3$ (10 g.), CS_2 (30 c.c.), and $BzCl$ (10 g.) were refluxed for 1 hr., the CS_2 was evaporated, the residue treated with H_2O , and the product ground with conc. HCl aq. The green solid was then crystallised from AcOH and from EtOH, and 3:6-dibenzoylcarbazole obtained in pale yellow plates, m. p. 258° after sintering at 243° (Found: C, 83.0; H, 4.7. $C_{28}H_{17}O_2N$ requires C, 83.2; H, 4.5%).

When a solution of this compound in Me_2CO was shaken with conc. KOH aq. and $BzCl$ and then diluted with H_2O , 3:6:9-tribenzoylcarbazole was obtained, colourless needles, m. p. 224°, from much EtOH or Me_2CO (Found: N, 2.8. $C_{33}H_{21}O_3N$ requires N, 2.9%). Similar treatment with $AcCl$ gave 3:6-dibenzoyl-9-acetylcarbazole, colourless needles, m. p. 270°, from AcOH (Found: N, 3.3. $C_{28}H_{19}O_3N$ requires N, 3.4%).

A solution of 3:6-dibenzoylcarbazole in xylene containing an excess of phenylacetyl chloride was refluxed for 24 hrs., HCl being evolved. The product was pptd. by petroleum (b. p. 60—80°), washed with EtOH, and crystallised from Me_2CO , from which 3:6-dibenzoyl-9-phenylacetylcarbazole was obtained in colourless needles, m. p. (after drying at 100°) 190—191° (Found: C, 82.8; H, 4.6. $C_{34}H_{23}O_3N$ requires C, 82.8; H, 4.7%). These

three *N*-acyl derivatives were readily hydrolysed to 3 : 6-dibenzoylcarbazole in boiling aq.-alc. KOH.

Synthesis of 3 : 6-Dibenzoylcarbazole.—A mixture of 4-bromo-3-nitrobenzoyl chloride (5 g.), AlCl_3 (6 g.), CS_2 (20 c.c.), and C_6H_6 (7.5 c.c.) was refluxed for $\frac{1}{2}$ hr., the solvent evaporated, and the 4-bromo-3-nitrobenzophenone washed with dil. HCl aq. and with NaOH aq.; it was then isolated from EtOH in almost colourless needles, m. p. 112° (Schöpf, *loc. cit.*, gives m. p. 112 — 113° ; the above method is more satisfactory than his). When this compound (1 g.), *p*-aminobenzophenone (0.66 g.) (Doebner, *Ber.*, 1880, **13**, 1011), and K_2CO_3 (0.3 g.) were heated at 150° for 4 hrs., and the product was washed with H_2O , 2-nitro-4 : 4'-dibenzoyldiphenylamine remained. It separated from EtOH or AcOH in small orange prisms, m. p. 150° (re-solidifying and finally melting at 193°) (Found : C, 74.1; H, 4.3. $\text{C}_{26}\text{H}_{18}\text{O}_4\text{N}_2$ requires C, 73.9; H, 4.3%).

The above nitro-compound (2 g.) in hot AcOH (30 c.c.) was boiled with SnCl_2 in 28% HCl aq. (30 c.c.) for a few mins., the cooled solution made alkaline with NaOH aq., and the ppt. crystallised from aq. EtOH and from MeOH, from which 2-amino-4 : 4'-dibenzoyldiphenylamine was obtained in yellow prisms, m. p. 153° (Found : C, 79.3; H, 5.0. $\text{C}_{26}\text{H}_{20}\text{O}_2\text{N}_2$ requires C, 79.6; H, 5.1%). A suspension of this amine in AcOH was treated gradually with NaNO_2 (rather more than 1 mol.); the 5 : 4'-dibenzoyl-1-phenylbenzotriazole obtained by dilution with H_2O separated from AcOH or EtOH in colourless plates, m. p. 195° (Found : N, 10.4. $\text{C}_{26}\text{H}_{17}\text{O}_2\text{N}_3$ requires N, 10.4%). When this compound was decomposed at 380° in a stream of CO_2 , 3 : 6-dibenzoylcarbazole was produced, m. p. (after crystn. from AcOH and from EtOH) and mixed m. p. 258° after sintering at 243° .

7-Benzoyl-1-phenylbenzotriazole.—2-Bromo-3-nitrobenzoyl chloride was converted by a process similar to that described above for the 4-bromo-3-nitro-analogue, into 2-bromo-3-nitrobenzophenone, which separated from EtOH in colourless needles, m. p. 76° (Found : C, 51.4; H, 2.8. Calc. : C, 51.0; H, 2.6%) (Schöpf, *loc. cit.*, gives m. p. 115°). Equal quantities of this substance and aniline were heated on the steam-bath for several hrs. and the resultant solid was crystallised from EtOH, 2-nitro-6-benzoyldiphenylamine being obtained in scarlet needles, m. p. 137° (Found : C, 72.0; H, 4.7. Calc. : C, 71.7; H, 4.4%) (Schöpf, *loc. cit.*, obtained this product in yellow needles, m. p. 135°). When the latter reaction was carried out at 130° for $\frac{1}{2}$ hr., and the product was fractionally crystallised from EtOH, 1-nitro-5-phenylacridine separated first in yellow needles, m. p. 188° (Found : C, 75.7; H, 4.1. Calc. : C, 76.0; H, 4.0%), and 2-nitro-6-benzoyldiphenylamine was obtained from the mother-liquor. The former of these two compounds was also obtained when the latter was boiled with alc. HCl for 5 mins.; the red colour of the diphenylamine derivative disappeared and the substituted acridine separated on cooling.

NH_3 aq. (11 c.c., *d* 0.880) was added gradually to a boiling mixture of an alc. solution of 2-nitro-6-benzoyldiphenylamine (3 g.) and conc. FeSO_4 aq. (28 g.). The residue after filtration was washed with hot EtOH, the united filtrates were diluted with H_2O , and the ppt. was shaken with dil. HCl aq. The acid solution was made alkaline with NH_3 aq., and the solid obtained was crystallised from petroleum (b. p. 60 — 80°), from which 2-amino-6-benzoyldiphenylamine separated in yellow needles, m. p. 118 — 119° (Found : C, 79.3; H, 5.6. $\text{C}_{19}\text{H}_{16}\text{ON}_2$ requires C, 79.2; H, 5.5%). A solution of this amine (0.8 g.) in AcOH was treated with NaNO_2 (0.3 g.). The solid obtained by

pptn. with H_2O was crystallised from EtOH, and 7-benzoyl-1-phenylbenzotriazole isolated in elongated plates, m. p. 154° (Found: N, 14.1. $C_{19}H_{13}ON_3$ requires N, 14.0%).

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