432. *The Friedel–Crafts Reaction in the Carbazole Series. Part V.**

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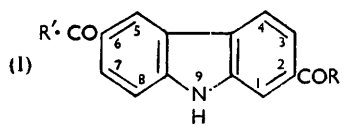
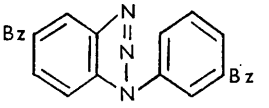
2 : 6-Dibenzoyl-, 2 : 6-diacetyl-, 2-acetyl-6-benzoyl-, and 6-acetyl-2-benzoyl-carbazole and carbazole-2 : 6-dicarboxylic acid have been prepared. Constitutions are assigned to these compounds by analogy.

Under the usual conditions of the Friedel–Crafts reaction two acyl groups are readily introduced into the 3- and the 6-position of carbazole and its 9-alkyl derivatives; with 9-acylcarbazoles substitution of a single acyl group into the 2-position ensues,[1,2] although 3-acylcarbazoles can be obtained by the isomerising action of aluminium chloride on the 9-acyl compounds.[1] Thus, if 2-acylcarbazoles were treated with acid halides in the presence of aluminium chloride, it seemed likely that 2 : 6-diacylcarbazoles (I) would result.



(I)



(II)

Treatment of 2-benzoylcarbazole with one mol. of benzoyl chloride in the presence of aluminium chloride gave 2 : 6-dibenzoylcarbazole. With 2-acetylcarbazole two molecular proportions of benzoyl chloride were required to yield 2-acetyl-6-benzoylcarbazole. Similar treatment with acetyl bromide or chloride gave mixtures containing much starting material, unless a considerable excess of acetyl halide was employed. From these reactions 6-acetyl-2-benzoylcarbazole contaminated with a little 6 : 9-diacetyl-2-benzoylcarbazole, and 2 : 6 : 9-triacetylcarbazole, were obtained. The 9-acetyl groups can be readily removed by hydrolysis, yielding 6-acetyl-2-benzoylcarbazole and 2 : 6-diacetylcarbazole respectively. The Friedel–Crafts reaction with 2-benzoyl-9-methylcarbazole and benzoyl chloride gave 2 : 6-dibenzoyl-9-methylcarbazole identical with the product obtained by methylation of 2 : 6-dibenzoylcarbazole.

2 : 6-Dibenzoylcarbazole and 6-acetyl-2-benzoylcarbazole were also obtained by an isomeric change from 2 : 9-dibenzoylcarbazole and 9-acetyl-2-benzoylcarbazole respectively in the presence of aluminium chloride.

In attempts to apply the Friedel–Crafts reaction to 3 : 9-diacetylcarbazole only unchanged starting material was isolated.

2 : 6-Dibenzoyl- and 2-acetyl-6-benzoyl-carbazole were fused with potassium hydroxide, yielding carbazole-2 : 6-dicarboxylic acid.

There seems little doubt that the structures which have been assigned to these compounds are correct but they have not been rigidly proved. Synthetic experiments were not successful. 4-Bromo-3-nitrobenzophenone was condensed with 3-aminobenzophenone, giving 3′ : 4-dibenzoyl-2-nitrodiphenylamine; this was reduced to the amine and thence

* Part IV, *J.*, 1954, 1341.

[1] Plant, Rogers, and Williams, *J.*, 1935, 741.
[2] Mitchell and Plant, *J.*, 1936, 1295.

converted into 3′ : 5-dibenzoyl-1-phenylbenzotriazole (II) which failed to give 2 : 6-dibenzoylcarbazole on pyrolysis. An attempt to synthesise 2-acetyl-6-benzoylcarbazole was not pursued because 3′-acetyl-4-benzoyl-2-nitrodiphenylamine, prepared from 4-bromo-3-nitrobenzophenone and 3-aminoacetophenone, could not be satisfactorily reduced to the amine.

Experimental

2 : 6-*Dibenzoylcarbazole*.—2-Benzoylcarbazole (3·8 g.), aluminium chloride (2 g.), carbon disulphide (25 c.c.), and benzoyl chloride (1·4 c.c.) were refluxed for 1 hr.; the carbon disulphide was evaporated, and the residue treated with dilute hydrochloric acid. The green solid was washed with hot ethanol and recrystallised from *cyclo*hexanone from which 2 : 6-*dibenzoylcarbazole* (1·2 g.) separated in colourless prisms, m. p. 218° (Found: C, 82·8; H, 4·5. $C_{26}H_{17}O_2N$ requires C, 83·2; H, 4·5%).

A solution of 2 : 9-dibenzoylcarbazole (5 g.) in nitrobenzene (40 c.c.) was treated with aluminium chloride (4 g.) and kept at 120° with occasional shaking for 15 min. The cooled solution was then poured into dilute hydrochloric acid, and the nitrobenzene was removed in steam. The residue was extracted with boiling ethanol (charcoal), and the green solid precipitated by pouring the extracts into dilute hydrochloric acid was then recrystallised from *cyclo*hexanone, from which 2 : 6-dibenzoylcarbazole was obtained in prisms, m. p. and mixed m. p. 218°.

2 : 6-Dibenzoylcarbazole (0·5 g.) was boiled with acetic anhydride (3 c.c.) and one drop of concentrated sulphuric acid for a few minutes. Water precipitated a solid which, recrystallised from acetic acid, gave 9-*acetyl*-2 : 6-*dibenzoylcarbazole* (0·5 g.) as needles, m. p. 184° (Found: C, 80·6; H, 4·7. $C_{28}H_{19}O_3N$ requires C, 80·6; H, 4·6%). This product was converted into 2 : 6-dibenzoylcarbazole by refluxing aqueous-ethanolic potassium hydroxide.

A solution of 2 : 6-dibenzoylcarbazole (0·5 g.) in acetone (15 c.c.) was shaken with potassium hydroxide (0·15 g.) in water (0·1 g.) and benzoyl chloride (0·25 g.). Addition of water precipitated 2 : 6 : 9-*tribenzoylcarbazole*, needles (0·5 g.), m. p. 195° (from ethanol) (Found: C, 82·5; H, 4·5. $C_{33}H_{21}O_3N$ requires C, 82·7; H, 4·4%).

2 : 6-Dibenzoylcarbazole (0·5 g.) in acetone (10 c.c.) was shaken with methyl sulphate (0·5 c.c.) and potassium hydroxide (0·5 g.) in water (0·25 c.c.). Addition of water precipitated 2 : 6-*dibenzoyl*-9-*methylcarbazole*, prisms (0·3 g.), m. p. 140° (from acetic acid) (Found: C, 83·4; H, 5·0. $C_{27}H_{19}O_2N$ requires C, 83·3; H, 4·9%).

2-Benzoylcarbazole (1·65 g.) shaken in acetone solution for 10 min. with methyl sulphate (2 g.) and sodium hydroxide (2 g.) in water gave 2-*benzoyl*-9-*methylcarbazole*, yellow needles (1·35 g.), m. p. 117° (from ethanol) (Found: C, 83·9; H, 5·3. $C_{20}H_{15}ON$ requires C, 84·2; H, 5·3%). This product (1·2 g.), aluminium chloride (0·65 g.), carbon disulphide (10 c.c.), and benzoyl chloride (0·5 c.c.) were refluxed for 1 hr., the carbon disulphide was evaporated, and the residue treated with dilute hydrochloric acid. The green solid was recrystallised from ethanol to give 2 : 6-dibenzoyl-9-methylcarbazole (0·2 g.), m. p. and mixed m. p. 139°.

Diethyl Carbazole-2 : 6-*dicarboxylate*.—2 : 6-Dibenzoylcarbazole (1 g.) was added to potassium hydroxide (10 g.) which had been melted with water (1 c.c.), and the temperature was slowly raised until reaction occurred. When cold, the mixture was dissolved in water; addition of concentrated hydrochloric acid to the filtered solution precipitated carbazole-2 : 6-dicarboxylic acid (0·45 g.), m. p. 384° (decomp.), insoluble in hot *cyclo*hexanone or nitrobenzene. Its suspension in alcoholic hydrogen chloride was refluxed for 6 hr., the solvent distilled off, and the residue ground with dilute aqueous sodium carbonate; crystallisation from methanol gave *diethyl carbazole*-2 : 6-*dicarboxylate* as almost colourless prisms, m. p. 176° (Found: C, 69·1; H, 5·7. $C_{18}H_{17}O_4N$ requires C, 69·4; H, 5·5%).

2-*Acetyl*-6-*benzoylcarbazole*.—2-Acetylcarbazole (2 g.), aluminium chloride (5 g.), carbon disulphide (50 c.c.), and benzoyl chloride (2·4 c.c.) were refluxed for 1½ hr.; the product crystallised from *cyclo*hexanone, to give 2-*acetyl*-6-*benzoylcarbazole* (1·4 g.) as colourless prisms, m. p. 253° (Found: C, 80·5; H, 4·9. $C_{21}H_{15}O_2N$ requires C, 80·5; H, 4·8%). This was converted into diethyl carbazole-2 : 6-dicarboxylate (mixed m. p.) as above.

2-Acetyl-6-benzoylcarbazole (0·2 g.) was boiled with acetic anhydride (3 c.c.) and a few crystals of fused potassium acetate for a few minutes. Water precipitated 2 : 9-*diacetyl*-6-*benzoylcarbazole* which recrystallised from acetic acid as needles (0·1 g.), m. p. 173° (Found: C, 77·0; H, 4·9. $C_{23}H_{17}O_3N$ requires C, 77·8; H, 4·8%).

In the same way as above, 2-acetyl-6-benzoylcarbazole afforded 2-*acetyl*-6 : 9-*dibenzoylcarbazole*, colourless needles, m. p. 198° (from ethanol) (Found : C, 80·4; H, 4·7. $C_{28}H_{19}O_3N$ requires C, 80·6; H, 4·6%), and 2-*acetyl*-6-*benzoyl*-9-*methylcarbazole*, colourless prisms, m. p. 155° (from acetic acid) (Found : C, 80·6; H, 5·2. $C_{22}H_{17}O_2N$ requires C, 80·7; H, 5·2%).

6-*Acetyl*-2-*benzoylcarbazole*.—2-Benzoylcarbazole (4·9 g.) in carbon disulphide (50 c.c.) was refluxed for 1 hr. with aluminium chloride (5 g.) and acetyl bromide (2·8 c.c.). After removal of the carbon disulphide, the product was treated with dilute hydrochloric acid. The resulting green solid was refluxed with ethanol (80 c.c.) and potassium hydroxide (4·8 g.) in water (20 c.c.) for 2 hr. Water was added, and the precipitated 6-*acetyl*-2-*benzoylcarbazole* (1·3 g.) crystallised from acetic acid as almost colourless prisms, m. p. 211° (Found : C, 80·1; H, 4·8. $C_{21}H_{15}O_2N$ requires C, 80·5; H, 4·8%). This was also obtained from 9-acetyl-2-benzoylcarbazole in the same manner as was 2 : 6-dibenzoylcarbazole from 2 : 9-dibenzoylcarbazole.

6-Acetyl-2-benzoylcarbazole was converted in the usual way into 6-*acetyl*-2 : 9-*dibenzoyl*-, prisms, m. p. 160° (from ethanol) (Found : C, 80·7; H, 4·8. $C_{28}H_{19}O_3N$ requires C, 80·6; H, 4·6%), and 6-*acetyl*-2-*benzoyl*-9-*methyl*-*carbazole*, prisms, m. p. 168° (from acetic acid) (Found : C, 80·5; H, 5·4. $C_{22}H_{17}O_2N$ requires C, 80·7; H, 5·2%).

2 : 6-*Diacetylcarbazole*.—A mixture of 2-acetylcarbazole (2·25 g.), carbon disulphide (40 c.c.), and aluminium chloride (8 g.) was treated with acetyl chloride (8 c.c.), the whole refluxed for 1 hr., and the solvent allowed to evaporate. The residue was treated with dilute hydrochloric acid and the brown solid recrystallised twice from *cyclo*hexanone to give 2 : 6 : 9-*triacetylcarbazole* (1·5 g.) in colourless prisms, m. p. 176° (Found : C, 73·5; H, 5·4. $C_{18}H_{15}O_3N$ requires C, 73·7; H, 5·1%). This material (1 g.) in ethanol (40 c.c.) was refluxed with potassium hydroxide (2·4 g.) in water (10 c.c.) for 2 hr. Water precipitated 2 : 6-*diacetylcarbazole* which crystallised from acetic acid as prisms (0·6 g.), m. p. 217° (Found : C, 76·4; H, 5·4. $C_{16}H_{13}O_2N$ requires C, 76·5; H, 5·2%). This gave, in the usual manner, 2 : 6-*diacetyl*-9-*benzoyl*-, prisms, m. p. 180° (from acetic acid) (Found : C, 77·6; H, 4·9. $C_{23}H_{17}O_3N$ requires C, 77·8; H, 4·8%), and 2 : 6-*diacetyl*-9-*methyl*-*carbazole*, prisms, m. p. 180° (from ethanol) (Found : C, 77·2; H, 5·9. $C_{17}H_{15}O_2N$ requires C, 77·0; H, 5·7%).

3′ : 5-*Dibenzoyl*-1-*phenylbenzotriazole*.—4-Bromo-3-nitrobenzophenone (3 g.), 3-aminobenzophenone (2 g.), and potassium carbonate (0·9 g.) were heated at 150° for 4 hr., after which the product was washed with water, dried, and ground with methyl alcohol until all the dark matter had gone into solution. The remaining 3′ : 4-*dibenzoyl*-2-*nitrodiphenylamine* (2 g.) crystallised from acetic acid in yellow plates, m. p. 128° (Found : C, 74·0; H, 4·3. $C_{26}H_{18}O_4N_2$ requires C, 73·9; H, 4·3%). This material (2 g.) in ethanol (90 c.c.) and N-sodium hydroxide (50 c.c.) was treated on the water-bath with a solution of sodium dithionite (12·5 g.) in 0·5N-sodium hydroxide (60 c.c.). The almost colourless solution was filtered hot and the inorganic precipitate washed with ethanol. When the combined filtrates were concentrated under reduced pressure, solid separated as the ethanol was completely removed. Its aqueous suspension was filtered and the base crystallised from ethanol, to give 2-*amino*-3′ : 4-*dibenzoyldiphenylamine* (1·6 g.) as yellow needles, m. p. 150° (Found : C, 79·7; H, 5·3. $C_{26}H_{20}O_2N_2$ requires C, 79·6; H, 5·1%). A solution of this amine (1·4 g.) in glacial acetic acid (20 c.c.) was treated with sodium nitrite (0·5 g.). 3′ : 5-*Dibenzoyl*-1-*phenylbenzotriazole*, which gradually separated, recrystallised from glacial acetic acid as colourless plates (0·9 g.), m. p. 158° (Found : C, 77·2; H, 4·4. $C_{26}H_{17}O_2N_3$ requires C, 77·4; H, 4·2%).

The above triazole (0·5 g.), when heated in liquid paraffin (20 c.c.) for 1½ hr. at 330—335° and then at 360° for ½ hr., gave a mixture from which chromatography afforded an unidentified substance, m. p. 226°, in small amount.

4-Bromo-3-nitrobenzophenone (3 g.), 3-aminoacetophenone (1·4 g.), and potassium carbonate (0·9 g.) were heated at 150° for 2 hr., washed with water, and crystallised from ethanol, to give 3′-*acetyl*-4-*benzoyl*-2-*nitrodiphenylamine* (1·7 g.) in orange prisms, m. p. 140° (Found : C, 70·1; H, 4·6. $C_{21}H_{16}O_4N_2$ requires C, 70·0; H, 4·4%).

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