The Friedel–Crafts Reaction in the Carbazole Series. Part IV. Phenylacetyl Compounds.*

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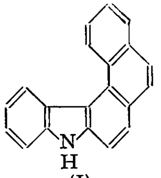
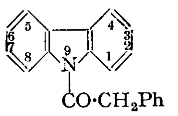
The 1-, 2-, and 3-phenylacetyl derivatives of carbazole, in addition to 3 : 6-bisphenylacetylcarbazole, have been prepared, and their structures established by conversion into known carbazolecarboxylic acids. Several derivatives of these ketones have been obtained, and attempts have been made to convert 3-phenethylcarbazole into naphtho(2′ : 1′-3 : 4)carbazole.

For the preparation of naphtho(2′ : 1′-3 : 4)carbazole (I) it seemed that advantage might be taken of the experience recorded in the previous Parts, in which it was found that 3 : 6-diacylcarbazoles are readily obtained from carbazole and the 2-acyl derivatives from 9-acylcarbazoles, by the Friedel–Crafts reaction, while the 3-acylcarbazoles can be obtained by the action of aluminium chloride on the 9-acyl compounds.

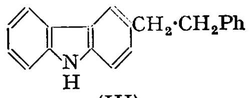
9-Phenylacetylcarbazole (II) was prepared by the action of phenylacetyl chloride on 9-carbazolylmagnesium iodide and was heated with aluminium chloride with the formation of 3-phenylacetylcarbazole, together with a little of the isomeric 1-acyl compound. This conforms with Meitzner's observation (*J. Amer. Chem. Soc.*, 1935, **57**, 2327) that 1-acetylcarbazole accompanies the 3-acetyl compound obtained by a similar process. 3-Phenethylcarbazole (III) was prepared from the corresponding ketone by Huang-Minlon's method (*J. Amer. Chem. Soc.*, 1946, **68**, 2487), but attempts to effect cyclodehydrogenation of this substance under various conditions with the formation of (I) have been unsuccessful. Efforts to obtain 9-*o*-nitrophenylacetylcarbazole, in the hope that the phenanthrene system in (I) might ultimately be formed from a reduction product of its isomer by an application of Pschorr's reaction, also failed.



(I)



(II)



(III)

3 : 6-Bisphenylacetylcarbazole has been obtained by applying the Friedel–Crafts reaction to both carbazole and its 3-phenylacetyl derivative, and has been reduced to 3 : 6-diphenethylcarbazole by the Clemmensen method. The 3 : 6-bisphenylacetyl derivative of 9-methylcarbazole has been obtained by the Friedel–Crafts method as well as by methylation of the above diketone, but attempts to obtain 9-methyl-3-phenylacetylcarbazole by the use of a unimolecular proportion of phenylacetyl chloride gave mixtures. The compound was more conveniently prepared by the methylation of 3-phenylacetylcarbazole. It is of interest in this connexion that Buu-Hoï and Royer (*J. Org. Chem.*, 1951, **16**, 1198) have prepared the 9-*n*-butyl and 9-*iso*amyl derivatives of 3-phenylacetylcarbazole from the appropriate 9-alkylcarbazoles by the Friedel–Crafts method.

2-Phenylacetylcarbazole and its 9-benzoyl derivative have been obtained from the product of a Friedel–Crafts reaction with 9-benzoylcarbazole. The structures of all the above ketones were established by converting the key substances into known carbazolecarboxylic acids by fusion with potassium hydroxide.

Experimental

9-*Phenylacetylcarbazole*.—After magnesium (1·2 g.) had reacted with methyl iodide (7·1 g.) in dry ether (100 c.c.), carbazole (6 g.) was gradually added and the whole refluxed for 10 min.

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* Part III, *J.*, 1947, 937.

Phenylacetyl chloride (7·7 g.) in ether was added in portions with frequent agitation of the syrupy layer, and the whole again refluxed for 10 min. Part of the product was isolated from the ethereal layer after the latter had been washed with dilute hydrochloric acid and dried ($MgSO_4$), and the remainder by treatment of the residual oil with dilute hydrochloric acid. When the whole was crystallised from ethanol, 9-*phenylacetylcarbazole* was obtained in pink plates (5 g.), m. p. 112°. It then separated from acetic acid in colourless plates, m. p. 114° (Found: C, 84·3; H, 5·3. $C_{20}H_{15}ON$ requires C, 84·2; H, 5·3%). It was hydrolysed to carbazole when refluxed with aqueous ethanolic potassium hydroxide for 5 min.

3-*Phenylacetylcarbazole*.—After a mixture of 9-phenylacetylcarbazole (16 g.), aluminium chloride (8·5 g.), and nitrobenzene (160 c.c.) had been gradually brought to 120° and kept at that temperature for 15 min., it was cooled, poured into dilute hydrochloric acid, and the nitrobenzene removed in steam. When the solid residue was dried, distilled under reduced pressure, and crystallised twice from ethanol, 3-*phenylacetylcarbazole* (5 g.) was obtained in plates, m. p. 164° (Found: C, 84·3; H, 5·2%). Its *oxime* crystallised from ethanol in needles, m. p. 214° (Found: C, 80·2; H, 5·3. $C_{20}H_{16}ON_2$ requires C, 80·0; H, 5·3%). Its *phenylhydrazone*, plates, m. p. 239° (from ethanol), was obtained when the ketone (0·5 g.) was heated with phenylhydrazine (1 g.) at 150° for ½ hr. and the mixture treated with carbon tetrachloride (Found: C, 83·5; H, 5·5. $C_{26}H_{21}N_3$ requires C, 83·2; H, 5·6%).

When gradually added to a hot molten mixture of potassium hydroxide (10 g.) and water (1 c.c.), 3-phenylacetylcarbazole (1 g.) dissolved to form a yellow solution. After the aqueous solution of the cold mass had been filtered and acidified with hydrochloric acid, the solid was obtained from acetic acid in plates, m. p. 270°. It was shown to be carbazole-3-carboxylic acid by mixed m. p. and by conversion into its ethyl ester, m. p. 164°, not depressed by admixture with an authentic sample (Plant and Williams, *J.*, 1934, 1142).

After 3-phenylacetylcarbazole (1·9 g.) in acetone (10 c.c.) containing sodium hydroxide (2·3 g.) in water (1·3 g.) had been shaken with methyl sulphate (2 c.c.) for a few minutes, addition of water precipitated an oil which was extracted with carbon tetrachloride. When the extract was dried ($MgSO_4$) and evaporated, the residue, which slowly solidified, gave 9-*methyl*-3-*phenylacetylcarbazole* (0·8 g.) in clusters of pale yellow prisms, m. p. 114°, after being washed with carbon tetrachloride and twice recrystallised from ethanol (Found: C, 84·1; H, 5·8. $C_{21}H_{17}ON$ requires C, 84·3; H, 5·7%). Prepared similarly by using acetyl chloride instead of methyl sulphate, 9-*acetyl*-3-*phenylacetylcarbazole* separated from ethanol in needles, m. p. 113·5° (Found: C, 80·7; H, 5·1. $C_{22}H_{17}O_2N$ requires C, 80·7; H, 5·2%), and gave 3-phenylacetylcarbazole on being refluxed with aqueous ethanolic potassium hydroxide.

1-*Phenylacetylcarbazole*.—When the mother-liquors from the crystallisation of 3-phenylacetylcarbazole referred to above were evaporated and the residue recrystallised from a little ethanol, more 3-phenylacetylcarbazole separated in clusters of plates admixed with yellow needles, m. p. 120—124°, of 1-*phenylacetylcarbazole*, which on occasions could be removed by hand. More conveniently, the residue was ground with carbon tetrachloride (150 c.c.). The insoluble material was reasonably pure 3-phenylacetylcarbazole (about 1·5 g.). When the filtered solution was passed through alumina (4 × 1 cm.) to remove dark coloured material and evaporated, treatment of the residue with ethanol gave 1-phenylacetylcarbazole (1 g.), m. p. 119—122°. Crystallisation from ethanol gave golden needles, m. p. 119·5—123·5°, which, after adsorption on alumina, had m. p. 123—124° (Found: C, 84·1; H, 5·3%). Its *oxime* crystallised from carbon tetrachloride in needles, m. p. 122° (Found: C, 80·2; H, 5·5%). When heated with molten potassium hydroxide as described for the isomeric ketone, carbazole-1-carboxylic acid, m. p. 267° with slight previous softening, identical (mixed m. p.) with an authentic sample (Briscoe and Plant, *J.*, 1928, 1990), was formed.

3-*Phenethylcarbazole*.—A mixture of 3-phenylacetylcarbazole (3 g.), powdered potassium hydroxide (2 g.), hydrazine hydrate (1·2 c.c.; 100%), and diethylene glycol (12·3 c.c.) was heated under reflux at 140—165° for 1½ hr., and then at 185—205° for 4 hr. without the reflux condenser. When the solid obtained by stirring the cold residue with water was crystallised from ethanol, 3-*phenethylcarbazole* was isolated in plates (2 g.), m. p. 213° (Found: C, 88·7; H, 6·3. $C_{20}H_{17}N$ requires C, 88·6; H, 6·3%).

Methyl sulphate (1 c.c.) in acetone (3 c.c.) was gradually added to a boiling mixture of 3-phenethylcarbazole (0·5 g.), sodium hydroxide (1·3 g.), water (0·5 c.c.), and acetone (5 c.c.), and the whole boiled for 5 min. with shaking. Addition of water precipitated 9-*methyl*-3-*phenethylcarbazole*, grey prisms (0·3 g.), m. p. 89° (from ethanol) (Found: C, 88·2; H, 6·9. $C_{21}H_{19}N$ requires C, 88·4; H, 6·7%).

3 : 6-*Bisphenylacetylcarbazole*.—Phenylacetyl chloride (4 g.) was added to a mixture of

carbazole (2 g.), powdered aluminium chloride (3·5 g.), and dry benzene (30 c.c.), with shaking, and the whole left for 12 hr. with exclusion of moisture, and poured into dilute hydrochloric acid. After removal of the benzene in steam, treatment of the solid residue with acetone gave 3 : 6-*bisphenylacetylcarbazole*, which crystallised from nitrobenzene in grey plates (1·5 g.), m. p. 228—236°. Further crystallisation from dioxan and then anisole gave colourless plates, m. p. 242° with slight previous softening (Found : C, 83·5; H, 5·4. $C_{28}H_{21}O_2N$ requires C, 83·4; H, 5·2%). The same compound was prepared by a similar method from 3-phenylacetylcarbazole. After being heated with molten potassium hydroxide as described for 3-phenylacetylcarbazole, this diketone gave an acid which was treated with ethanolic hydrogen chloride with the formation of diethyl carbazole-3 : 6-dicarboxylate, m. p. 202°, identical (mixed m. p.) with an authentic sample (Mitchell and Plant, *J.*, 1936, 1295).

Prepared from the diketone by a method similar to that used for 9-methyl-3-phenylacetylcarbazole, 9-*methyl*-3 : 6-*bisphenylacetylcarbazole* was crystallised from acetic acid and then from ethanol, and obtained in needles, m. p. 145° (Found : C, 83·5; H, 5·8. $C_{29}H_{23}O_2N$ requires C, 83·4; H, 5·5%). This compound (mixed m. p.) was also easily obtained from 9-methylcarbazole by the action of phenylacetyl chloride and aluminium chloride as described above for the unmethylated compound; for purification it was necessary only to crystallise the crude product from ethanol.

After 3 : 6-bisphenylacetylcarbazole (2 g.) in acetone (40 c.c.) containing powdered potassium hydroxide (7 g.) had been shaken for 10 min. with acetyl chloride (10 c.c.), water precipitated 9-*acetyl*-3 : 6-*bisphenylacetylcarbazole*, needles (1 g.), m. p. 157° (from acetic acid and then ethanol) (Found : C, 80·8; H, 5·1. $C_{30}H_{23}O_3N$ requires C, 80·9; H, 5·2%). It gave 3 : 6-bisphenylacetylcarbazole when refluxed for 1 hr. with aqueous ethanolic potassium hydroxide.

3 : 6-*Diphenethylcarbazole*.—A mixture of 3 : 6-bisphenylacetylcarbazole (3 g.), glacial acetic acid (60 c.c.), and amalgamated granulated zinc (90 g.) was refluxed while concentrated hydrochloric acid (60 c.c.) was added in portions during 6 hr. After the liquid had been removed by decantation and the residue extracted with acetic acid, water was added to the combined solution, and the product extracted with carbon tetrachloride. The extract was washed with aqueous sodium carbonate, dried ($MgSO_4$), and evaporated. The residue, which slowly solidified, was ground with a little carbon tetrachloride and crystallised from acetic acid, from which 3 : 6-*diphenethylcarbazole* separated in needles (0·7 g.), m. p. 145° (Found : C, 89·7; H, 6·6. $C_{28}H_{25}N$ requires C, 89·6; H, 6·7%).

2-*Phenylacetylcarbazole*.—After a mixture of 9-benzoylcarbazole (15 g.), aluminium chloride (45 g.), phenylacetyl chloride (26 c.c.), and carbon disulphide (120 c.c.) had been refluxed for 1¼ hr. and the solvent distilled off, the residue was added to dilute hydrochloric acid, and the product extracted with benzene. The benzene solution was washed with dilute hydrochloric acid, then with aqueous sodium carbonate, dried ($MgSO_4$), and evaporated. When the orange coloured gum was dissolved in benzene (250 c.c.) and adsorbed on alumina, elution with benzene gave first 9-*benzoyl*-2-*phenylacetylcarbazole* (about 1·5 g.), colourless rhombs, m. p. 183—185° after slight softening from 179° (from benzene) (Found : C, 83·2; H, 4·9; N, 3·7. $C_{27}H_{19}O_2N$ requires C, 83·3; H, 4·9; N, 3·6%), and then 2-*phenylacetylcarbazole* (about 0·5 g.), colourless plates, m. p. 209—211° (rapid heating) (from ethanol) (Found : C, 83·7; H, 5·5; N, 5·1. $C_{20}H_{15}ON$ requires C, 84·2; H, 5·3; N, 4·9%). The former was converted into the latter either by adsorption on more alumina or by refluxing it with aqueous ethanolic potassium hydroxide.

When 2-phenylacetylcarbazole was heated with molten potassium hydroxide as described for the 3-phenylacetyl compound, carbazole-2-carboxylic acid, m. p. 320° with previous softening, was obtained. It was identified by mixed m. p. and by conversion into its ethyl ester, m. p. 181—183°, not depressed by admixture with an authentic sample (Plant and Williams, *loc. cit.*).

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