244. 3-*Acetylcarbazole and Carbazole*-3-*carboxylic Acid.*

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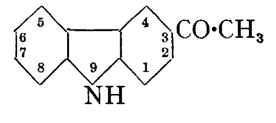
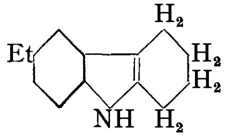
It has recently been stated (I. G. Farbenind. Akt.-Ges., D.R.P. 555,312; *Chem. Zentr.*, 1932, ii, 2532) that the ketone prepared by Borsche and Feise (*Ber.*, 1907, **40**, 378) by the hydrolysis of the product derived from the interaction of 9-acetylcarbazole with acetyl bromide and aluminium chloride is not 3-acetylcarbazole (I), as was originally assumed, but 2-acetylcarbazole. The structure is based upon the fact that the acid obtained from the ketone by oxidation is identical with that obtained from 2-aminocarbazole through the corresponding nitrile. The acid (m. p. 320—322°) prepared by Borsche and Feise by the fusion of their ketone with potassium hydroxide gives an ethyl ester which melts at 184°, while an acid (m. p. 320°) obtained under certain conditions of temperature by the action of alkali and carbon dioxide on carbazole (I. G. Farbenind. Akt.-Ges., D.R.P. 442,609; *Chem. Zentr.*, 1927, ii, 639), and also believed to be carbazole-3-carboxylic acid, gives an ethyl ester, m. p. 184°. The similarity in properties makes it probable that these acids are identical, and the more recent work suggests that they are in reality carbazole-2-carboxylic acid.

(I.)





(II.)

In order to remove any confusion which exists concerning the structures of these simple carbazole derivatives, it seemed desirable to prepare authentic specimens of the apparently hitherto unknown 3-acetylcarbazole and the corresponding carboxylic acid. The former has now been obtained by the action of aluminium chloride on 9-acetylcarbazole, a procedure similar to that used by Plant and Tomlinson (J., 1932, 2188) for the preparation of 3-benzoylcarbazole. The structure assigned to the product was established by reducing it with amalgamated zinc and hydrochloric acid to 3-*ethylcarbazole*, the identity of which was confirmed by synthesis. For this purpose *p*-ethylphenylhydrazine was condensed with *cyclo*hexanone, and the product converted by Fischer's reaction into 6-*ethyl*-1 : 2 : 3 : 4-*tetrahydrocarbazole* (II), which gave 3-ethylcarbazole on oxidation with sulphur in quinoline. A comparison of the properties of 3-*acetylcarbazole* and its 9-*methyl* and 9-*acetyl* derivatives with those of the Borsche and Feise ketone and its corresponding derivatives makes it clear that the products are different, and confirms the more recent views regarding the structure of the latter. *Carbazole*-3-*carboxylic acid* (m. p. 276—278°), obtained from 3-acetylcarbazole by fusion with potassium hydroxide, gave an *ethyl* ester, m. p. 165°, and is obviously different from the acids mentioned above. It therefore follows that the products previously believed to be carbazole-3-carboxylic acid must now be regarded as having the carboxyl group in the 2-position.

2-Acetylcarbazole has been obtained during the present work by the hydrolysis of the 9-*benzoyl*-2-*acetylcarbazole* prepared by the action of acetyl bromide and aluminium chloride on 9-benzoylcarbazole. It has been converted into its 9-*methyl* derivative, from which an *oxime* was readily obtained, and, by reduction with amalgamated zinc and hydrochloric acid, into 2-*ethylcarbazole.*

Experimental.

3-*Acetylcarbazole.*—When a mixture of 9-acetylcarbazole (3·5 g.; Boeseken, *Rec. trav. chim.*, 1912, **31**, 350) and pulverised aluminium chloride (2 g.) had been heated gradually to 110°, frothing ensued. At this stage the whole was vigorously stirred until it became solid, the temperature being slowly raised to 120°. After the product had been boiled in alcohol with charcoal for 10 minutes, 3-*acetylcarbazole*, pale brown prisms, m. p. 167°, from toluene (Found : C, 80·4; H, 5·4. $C_{14}H_{11}ON$ requires C, 80·4; H, 5·3%), was obtained by pouring the filtered solution into dilute hydrochloric acid.

When an acetone solution of this substance (0·8 g.) was shaken for 10 minutes with aqueous potassium hydroxide (2 g. of 50%) and acetyl chloride (2·5 c.c.), and then poured into water, 3 : 9-*diacetylcarbazole*, colourless prisms, m. p. 153°, from alcohol (Found : N, 5·3. $C_{16}H_{13}O_2N$ requires N, 5·6%), was obtained. A similar procedure with methyl sulphate instead of acetyl chloride yielded 3-*acetyl*-9-*methylcarbazole*, practically colourless prisms, m. p. 102°, from alcohol (Found : N, 6·5. $C_{15}H_{13}ON$ requires N, 6·3%).

3-*Ethylcarbazole*.—3-Acetylcarbazole (2 g.) and hydrochloric acid (50 c.c. of 30%) were shaken with granulated zinc (100 g.) which had been amalgamated by standing with aqueous mercuric chloride (200 c.c. of 5%) for an hour, and the mixture was left over-night. Anisole (5 c.c.) was added to dissolve the 3-acetylcarbazole (cf. Ramage and Robinson, J., 1933, 607), and the whole was boiled under reflux for 12 hours. The product was extracted with ether, and, after removal of the solvent, the residue treated with aqueous sodium carbonate and submitted to distillation in steam to remove the anisole. The 3-*ethylcarbazole*, colourless prisms, m. p. 142°, after crystallisation from acetic acid and then from toluene (Found : C, 86·0; H, 6·9. $C_{14}H_{13}N$ requires C, 86·2; H, 6·7%), was again extracted with ether and recovered by evaporation of the solvent.

When *p*-ethylphenylhydrazine, prepared by diazotisation of *p*-aminoethylbenzene (5·8 g., obtained by the method of Day, J., 1930, 252) and subsequent reduction with stannous chloride and hydrochloric acid (cf. Willgerodt and Harter, *J. pr. Chem.*, 1905, **71**, 409), was heated on the steam-bath for a few minutes with *cyclo*hexanone (5 c.c.), and the resulting hydrazone was boiled for 10 minutes with water (90 c.c.) and concentrated sulphuric acid (10 c.c.), 6-*ethyltetrahydrocarbazole*, colourless plates, m. p. 78°, from petroleum (b. p. 40—60°), separated as an oil which solidified on cooling (Found : C, 84·1; H, 8·4. $C_{14}H_{17}N$ requires C, 84·4; H, 8·5%). After this substance (2·6 g.) had been boiled with sulphur (0·85 g.) and pure quinoline (15 c.c.) for ½ hour, the product obtained by pouring the solution into ice–dilute hydrochloric acid was extracted with ether and dried with calcium chloride. When the residue obtained by evaporation of the extract was distilled with iron filings under reduced pressure, 3-ethylcarbazole was collected; it separated from toluene in colourless prisms, m. p. 144°, and was shown to be identical (mixed m. p.) with the compound described above.

Carbazole-3-*carboxylic Acid*.—3-Acetylcarbazole (0·5 g.) was added gradually to potassium hydroxide (5 g.) which had been melted by heating with a little water (about 0·5 c.c.). After the molten mass had been stirred for a short time, it was cooled and dissolved in hot water. The filtered solution was acidified with hydrochloric acid and the precipitate esterified by 6 hours' boiling in alcohol containing a little sulphuric acid; *ethyl carbazole*-3-*carboxylate* separated in colourless prisms, m. p. 165°, after concentration (Found : C, 74·9; H, 5·4. $C_{15}H_{13}O_2N$ requires C, 75·3; H, 5·4%). When the ester was saponified, the *acid*, colourless plates, m. p. 276—278°, from acetic acid, was obtained (Found : C, 74·0; H, 4·5. $C_{13}H_9O_2N$ requires C, 73·9; H, 4·3%).

Derivatives from 2-*Acetylcarbazole*.—2-Acetylcarbazole was prepared not only by the methods already published, but also from 9-benzoylcarbazole. The latter (5 g.; cf. Stevens and Tucker, J., 1923, **123**, 2140) was dissolved in carbon disulphide and treated first with pulverised aluminium chloride (11·5 g.) and then with acetyl bromide (7·5 g.). When the whole had been refluxed for 40 minutes and the solvent distilled off, 9-*benzoyl*-2-*acetylcarbazole*, pale brown plates, m. p. 153°, from alcohol, was obtained by pouring the residue into ice–dilute hydrochloric acid (Found : N, 4·5. $C_{21}H_{15}O_2N$ requires N, 4·5%). 2-Acetylcarbazole, identical (mixed m. p.) with Borsche and Feise's compound, resulted from this substance on hydrolysis with alcoholic alkali.

The oxime of 2-acetylcarbazole crystallised from alcohol in colourless plates, m. p. 278° (Found : N, 12·3. Calc. : N, 12·5%). The m. p. (253°) given by Borsche and Feise (*loc. cit.*) for this oxime appears to be erroneous, since a careful repetition of their experiment gave a product identical with the above.

By a process similar to that used for the isomeric 3-acetyl compound, 2-acetylcarbazole was converted into 2-*acetyl*-9-*methylcarbazole*, pale yellow needles, m. p. 122°, from alcohol (Found : N, 6·5%), which in turn gave an *oxime*, colourless prisms, m. p. 217°, from alcohol (Found : N, 11·9. $C_{15}H_{14}ON_2$ requires N, 11·8%).

When 2-acetylcarbazole was reduced with amalgamated zinc and hydrochloric acid, as described for the corresponding 3-acetyl compound, 2-*ethylcarbazole*, colourless prisms, m. p. 225°, after crystallisation from benzene and then acetic acid, was obtained (Found : C, 86·7; H, 6·7%).

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