389. *The Alleged " Carbazoacridines."*

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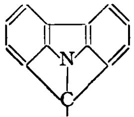
Bizzarri's supposed "carbazoacridines" are shown to be, probably, impure 3-acylcarbazoles.

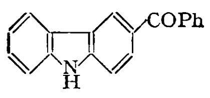
BIZZARRI (*Gazzetta*, 1890, **20**, 407; 1891, **21**, 158, 351; 1892, **23**, 1) claimed to have obtained methyl- and phenyl-" carbazoacridine " (I) by heating *N*-acetyl- and *N*-benzoylcarbazole, or carbazole and the free acids, with zinc chloride, and from the acid amides and carbazole in the presence of phosphoric oxide. The only other reference to " carbazoacridines " in the literature is that of Ilberg and Reichel (*Ber.*, 1943, **76**, 1108) who mention the reaction of the phenyl derivative with tellurium tetrachloride.

The structure (I) suggested is impossible on steric grounds, and as the rearrangement of *N*-acylcarbazoles with aluminium chloride gives 3-acylcarbazoles (Plant and Tomlinson, *J.*, 1932, 2188; Plant, Rogers, and Williams, *J.*, 1935, 741) it was thought that the " carbazoacridines " might be compounds of the latter type. However the melting points of the " carbazoacridines " did not coincide with those of the known acetyl- or benzoylcarbazoles and the analytical data did not agree with such a formulation. Another possibility was that they were acridines formed either by a ring expansion or from diphenylamine present in the carbazole as an impurity. Bizzarri's analytical data and m. p. (186°) for " phenylcarbazoacridine," and the m. p. (172°) and non-basicity of its " dihydro-derivative " corresponded well with the properties of 9-phenylacridine (m. p. 184°) and 9-phenylacridan (m. p. 170°). His claim that " phenylcarbazoacridine methiodide " decomposed, when heated, to methyl iodide and the original " carbazoacridine " supported this view.

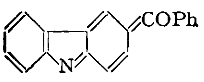
One of Bizzarri's methods was therefore reinvestigated. We should mention that Dr. S. G. P. Plant isolated carbazole and 3-benzoylcarbazole after heating *N*-benzoylcarbazole with zinc chloride for 4 hr. at 130—50° (unpublished work). Benzoic acid, carbazole, and zinc chloride were heated according to Bizzarri's method; the product, after one crystallisation, had the properties ascribed to " phenylcarbazoacridine." Further recrystallisation, however, gave only 3-benzoylcarbazole (II). Chromatography of the crude product or of *N*-benzoylcarbazole gave carbazole and benzoic acid. Diphenylamine, benzoic acid, and zinc chloride gave no 9-phenylacridine under Bizzarri's conditions.



(I)



(II)



(III)

3-Benzoylcarbazole was little affected by zinc and acetic acid, used by Bizzarri for the reduction of " phenylcarbazoacridine " to its " dihydro-derivative," but with hydrogen over Raney nickel gave 3-benzylcarbazole. A mixture of the ketone and 3-benzylcarbazole was obtained if the hydrogenation was stopped before completion. This is a most unusual result as such reductions usually give alcohols; dehydration of the alcohol to (III) followed by further reduction might account for the result, and such a dehydration would be acid-catalysed; addition of alkali to the hydrogenation mixture did not however affect the course of the reaction.

Bizzarri also stated that potassium permanganate oxidised " phenylcarbazoacridine " to " 1 : 8-carbonylcarbazole," m. p. 177—179°, and described nitroso- and acetyl derivatives. The substance may be impure carbazole-3-carboxylic acid; this has m. p. 267—268° (Plant and Williams, *J.*, 1934, 1142).

A repetition of Bizzarri's " methylcarbazoacridine " preparation from acetic acid, etc., gave a product from which nothing crystalline could be isolated. Treatment with 2 : 4-dinitrophenylhydrazine in ethanolic hydrogen chloride gave 3-acetylcarbazole 2 : 4-dinitrophenylhydrazone.

EXPERIMENTAL

3-*Benzoylcarbazole*.—Carbazole (10·0 g.), benzoic acid (7·5 g.), and anhydrous zinc chloride (25 g.) were heated in an oil-bath at 150—170° for 5 hr. No crystalline product could be isolated if the temperature was kept at 205°. The very viscous melt was cooled, dissolved in boiling ethanol, and treated with aqueous ammonia (75 c.c.; *d* 0·880), followed by water until no more dark fawn-coloured precipitate (25 g.) was formed. Nothing could be extracted from this solid by dilute alkali.

A portion, after one recrystallisation from ethanol (charcoal) containing ammonia gave a heterogeneous solid of which the yellow crystalline constituent became green and sintered at 130—150°, had m. p. 180—190°, and corresponded to Bizzarri's " phenylcarbazoacridine " of m. p. 186°. Further recrystallisation of the whole solid from ethanol gave 3-benzoylcarbazole (10—15%) as yellow rhombs, m. p. 206° (Found: C, 83·6; H, 4·9; N, 4·9. Calc. for $C_{19}H_{13}ON$: C, 84·1; H, 4·8; N, 5·2%) alone or mixed with an authentic specimen. The 2 : 4-*dinitrophenylhydrazone* separated from acetic acid as a microcrystalline red powder, m. p. 305° (decomp.) (Found: C, 66·6; H, 3·7. $C_{20}H_{17}O_4N_5$ requires C, 66·6; H, 3·8%). The original condensation gave 63% of 3-benzoylcarbazole, estimated in the crude product by this derivative.

Chromatography of the crude product in benzene on alumina gave carbazole, m. p. 243° alone or mixed with an authentic specimen, and elution with benzene–ether (1 : 1) gave benzoic acid. *N*-Benzoylcarbazole also gave carbazole and benzoic acid on a similar column.

3-*Acetylcarbazole*.—Carbazole (8·0 g.), acetic acid (3·5 g.), and zinc chloride (12 g.) were heated in a sealed tube to 150° for 5 hr. The resulting black tar was dissolved in ethanol and filtered into aqueous ammonia; a fawn-coloured precipitate (2·9 g.) was obtained. Extraction of this precipitate with benzene gave a small quantity of carbazole. The insoluble material gave a red 2 : 4-dinitrophenylhydrazone which after crystallisation from acetic acid and chromatographic purification had m. p. 318—319° (decomp.) (Found: C, 61·7; H, 4·1. $C_{20}H_{15}O_4N_5$ requires C, 61·7; H, 3·9%), unchanged when mixed with authentic 3-*acetylcarbazole* 2 : 4-*dinitrophenylhydrazone* (crystallised from acetic acid), m. p. 320° (decomp.) (Found: C, 61·9; H, 3·8%). The infra-red absorption spectra of the compounds in paraffin paste were identical, and showed the maxima at 10·83, 11·04, 11·24, 11·47, 11·96, 12·48, 13·05, 13·23, 13·52, and 13·76 mμ.

2-*Acetylcarbazole* 2 : 4-*dinitrophenylhydrazone*, also obtained as a microcrystalline red solid from acetic acid, had m. p. 303—305° (decomp.) (Found: C, 61·2; H, 4·0%) and different infra-red absorption maxima, *viz.*, 10·01, 10·82, 10·94, 11·10, 11·33, 11·70, 12·04, 12·20, 12·97, 13·36, 13·58, and 13·73 mμ.

3-*Benzylcarbazole*.—3-Benzoylcarbazole (0·36 g.) in ethanol was hydrogenated over Raney nickel at atmospheric temperature and pressure until absorption (2 mols.) was complete. Evaporation of the filtered solution gave 3-*benzylcarbazole*, colourless plates (from ethanol), m. p. 176° (Found: C, 88·8; H, 5·7; N, 5·3. $C_{19}H_{15}N$ requires C, 88·7; H, 5·8; N, 5·3%).

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