476. 2-*Cyano*-4-*nitrophenylhydrazine and* 3-*Amino*-5-*nitroindazole.*

By E. W. Parnell.

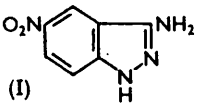
The compound described in the literature as 2-cyano-4-nitrophenylhydrazine (II) is shown to be 3-amino-5-nitroindazole (I). Preparations of the former and of isomeric methyl derivatives of the latter are described.

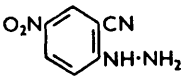
For preparation of 3-amino-5-nitroindazole (I), 2-cyano-4-nitrophenylhydrazine (II) was prepared and its cyclisation examined. Recently the reputed *o*-cyanophenylhydrazine was identified as 3-aminoindazole:[1] we now report that the reputed 2-cyano-4-nitrophenylhydrazine[2,3] (II) is 3-amino-5-nitroindazole, but that the former can be prepared under controlled conditions.

Preparation of the hydrazine (II) from 1-chloro-2-cyano-4-nitrobenzene and hydrazine in boiling ethanol was claimed by Borsche[2] and by Baudet[3] as a red solid, m. p. 250°. From such a reaction at room temperature we obtained a buff-coloured product (A), m. p. 192—194°, which resolidified to a scarlet solid, m. p. 254—258°. From a reaction in boiling ethanol, the product (B), m. p. 259—261°, described by the earlier workers[2,3] was obtained. The product (A) was converted into (B) when heated, or when dissolved in warm dilute hydrochloric acid and re-precipitated by sodium acetate. Product (A) also dissolved in aqueous sodium hydroxide to a deep red solution, and (B) was precipitated on addition of acetic acid. These transformations led to the conclusion that the recorded compound (B) was 3-amino-5-nitroindazole (I) and that (A) was the previously unknown hydrazine (II).

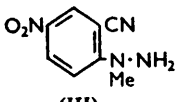
[1] Aron and Elvidge, *Chem. and Ind.*, 1958, **38**, 1234; Cooper, *J.*, 1958, 4212.
[2] Borsche, *Ber.*, 1921, **54**, 665.
[3] Baudet, *Rec. Trav. chim.*, 1924, **43**, 707.

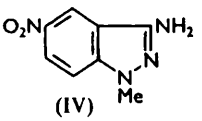
Further evidence that product (B) is the indazole (I) was afforded by methylation. With methyl iodide in alcoholic sodium ethoxide it gave a yellow (C) (m. p. 224—225°) and a less soluble, chocolate-brown monomethyl derivative (D) [m. p. 330—332° (decomp.)].

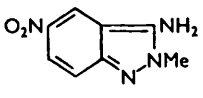

(I)

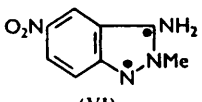

(II)

With one mol. of methyl sulphate in hot nitrobenzene it gave only the monomethyl derivative D. These derivatives gave the same quaternary salt. Now, from 1-chloro-2-cyano-4-nitrobenzene and monomethylhydrazine Hartmanns [4] obtained a product, m. p. 223°, which he formulated as (III). Repetition of this reaction at room temperature gave a mixture which partly melted at 189—195°, then resolidified, and remelted at 210—215°. When this mixture was treated with acid and then reprecipitated, the homogeneous product (C) was obtained. Since 1-chloro-2,4-dinitrobenzene and methylhydrazine give


(III)


(IV)


(V)


(VI)

N-2,4-dinitrophenyl-*N*-methylhydrazine,[5] the initial product from 1-chloro-2-cyano-4-nitrobenzene and methylhydrazine probably has structure (III); it is obtained, mixed with the indazole (IV), when the reaction is carried out at room temperature, but has not been obtained pure. Hartmanns's product is therefore the indazole (IV) and it is identical with compound (C). Since (C) and (D) give the same quaternary salt, it follows that (D) is 3-amino-2-methyl-5-nitroindazole which, according to the work of Barclay *et al.*[6] on the structure of nitroindazoles and their *N*-methyl derivatives, should have the quinonoid structure (V). These structural assignments are supported by the methods of preparation, solubilities, melting points, and colours of the compounds, and by analogy with those of the monomethyl-5-nitroindazoles.[7] The indazole structure (I) for the red product described by Borsche [2] and Baudet,[3] and the structure (IV) for that described by Hartmanns [4] account for the lack of reactivity of these substances towards ketones noted by these authors. The derivatives of aromatic aldehydes described by them are probably 3-benzylideneaminoindazoles.

These conclusions are supported by the spectra. The ultraviolet spectrum of the hydrazine (II) shows a maximum at 358 mμ (log ε 4·14). The infrared spectrum has a band at 2230 cm.$^{-1}$ indicative of a free cyano-group. For the indazole (I) the ultraviolet absorption maximum has shifted to 280 mμ (log ε 4·11), and the infrared band at 2230 cm.$^{-1}$ has disappeared. Similarly in the methyl derivatives (IV) and (V) the maxima are at 285 (log ε 4·05 and 4·15) respectively and in both cases the infrared band at 2230 cm.$^{-1}$ is absent.

It is of interest that the indazoles (I), (IV), and (V) all show a band in the 810 cm.$^{-1}$ region indicative of an intact benzene ring. In the case of the last compound this precludes an *o*-quinonoid structure such as (V), suggested for 2-alkylindazoles by Barclay *et al.*[6] The deep colour of compound (D) suggests that it might exist as a diradical, such as (VI).

Experimental

2-Cyano-4-nitrophenylhydrazine.—60% Hydrazine hydrate (22·8 ml.) was added to 1-chloro-2-cyano-4-nitrobenzene (50 g.) in warm ethanol (750 ml.). After being kept overnight the brown needles which separated were filtered off. The crude product (30 g., 61·5%) could only

[4] Hartmanns, *ibid.*, 1946, **65**, 468.
[5] Blanksma and Wackers, *Rec. Trav. chim.*, 1936, **55**, 655; Vis, *ibid.*, 1939, **58**, 387.
[6] Barclay, Campbell, and Dodds, *J.*, 1941, 113.
[7] Fries, *Annalen*, 1927, **454**, 121.

be crystallised in small amounts from ethanol. Attempts to recrystallise larger quantities resulted in partial transformation into 3-amino-5-nitroindazole. An analytical sample of the *hydrazine* had m. p. 192—194°, resolidifying to a scarlet solid and then remelting at 254—258° (Found: C, 47·1; H, 3·8; N, 31·7. $C_7H_6O_2N_4$ requires C, 47·1; H, 3·4; N, 31·4%). Evaporation of the reaction liquors gave a solid which was dissolved in warm 2N-hydrochloric acid (150 ml.). The solution, after clarification with charcoal, was adjusted to pH 5 with saturated aqueous sodium acetate. A red solid (15 g., 31%), m. p. 254—256°, was precipitated; it was identical with 3-amino-5-nitroindazole (see below).

3-*Amino*-5-*nitroindazole*.—A warm solution of sodium acetate trihydrate (136 g.) in water (300 ml.) was added to a solution of 2-cyano-4-nitrophenylhydrazine (34·5 g.) in 2N-hydrochloric acid (345 ml.) at *ca.* 95°. A deep red solid separated and the mixture (pH *ca.* 5) was cooled and the solid was filtered off. Crystallisation from nitromethane (1·2 l.) gave the product as scarlet needles (26·0 g., 75%), m. p. 259—261° (Found: C, 46·9; H, 3·6; N, 31·95. Calc. for $C_7H_6O_2N_4$: C, 47·1; H, 3·4; N, 31·4%).

Methylation of 3-*Amino*-5-*nitroindazole*.—(1) 3-Amino-5-nitroindazole (1·0 g.) was added to dry ethanol (10 ml.) containing dissolved sodium (0·14 g.). The mixture was refluxed with methyl iodide (0·38 ml.) for 3 hr., then filtered whilst hot to give a deep red solid (D) (0·4 g.), m. p. 280—290° (decomp.); the filtrate deposited a solid (C) (0·4 g.), m. p. 210—220°. Substance (D) crystallised from dimethylformamide in chocolate-brown needles, m. p. 330—332° (decomp.), identical with the product obtained by method (2). Compound (C) recrystallised from ethanol and then from benzene as bright yellow needles, m. p. 218—220°, and was identical with 3-amino-1-methyl-5-nitroindazole prepared from 1-chloro-2-cyano-4-nitrobenzene and monomethylhydrazine (see below).

(2) 3-Amino-5-nitroindazole (11·9 g.) suspended in dry nitrobenzene (119 ml.) was heated and stirred at 150°. Redistilled methyl sulphate (7·7 ml.) was then added; the solid dissolved and a gum separated. After a further hr. the mixture was cooled and mixed with ether (119 ml.), and the gum and ethereal solution were extracted with 2N-hydrochloric acid (*ca.* 300 ml.). After being filtered the aqueous solution was basified with solid sodium hydrogen carbonate, a deep red solid separating. Crystallisation of this from aqueous dimethylformamide gave pure 3-*amino*-2-*methyl*-5-*nitroindazole* (D) (6·0 g., 46·5%), m. p. 330—332° (decomp.) (Found: C, 49·6; H, 4·3; N, 28·9. $C_8H_8O_2N_4$ requires C, 49·9; H, 4·2; N, 29·2%).

3-*Amino*-1-*methyl*-5-*nitroindazole*.—Methylhydrazine (13·2 g.) and 1-chloro-2-cyano-4-nitrobenzene (44 g.) in warm ethanol (440 ml.) reacted exothermally, fine yellow and stouter brownish needles separating. After being kept overnight the solids were filtered off, washed with ethanol, and dried. The product (34 g., 79%) partly melted at 189—195° and melted completely at 210—215°. After being dissolved in warm 2N-hydrochloric acid (340 ml.) and precipitated with sodium acetate (134 g.) in water (300 ml.), the product was homogeneous N-2-*cyano*-4-*nitrophenyl*-N-*methylhydrazine* (C), m. p. 220—224°. Recrystallisation from ethanol then gave yellow needles, m. p. 224—225°, which became red when heated (Found: C, 49·8; H, 4·6; N, 29·1. $C_8H_8O_2N_4$ requires C, 49·9; H, 4·2; N, 29·2%).

3-*Amino*-1,2-*dimethyl*-5-*nitroindazolium Iodide*.—Redistilled methyl sulphate (3·3 ml.) was added to 3-amino-2-methyl-5-nitroindazole (6·15 g.) suspended in dry nitrobenzene (61·5 ml.) stirred and heated at 150°. The product began to separate immediately. After 1 hr. the mixture was cooled and acetone (150 ml.) was added; the methosulphate was filtered off and washed with acetone. It was dissolved in warm water (90 ml.), and the solution neutralised with solid sodium hydrogen carbonate and filtered from a trace of solid. Sodium iodide (30 g.) was added to the filtrate at *ca.* 95°; the *quaternary salt* (9·3 g., 86·5%), m. p. 242—244° (decomp.) crystallised immediately. It recrystallised from water as orange prisms, m. p. 244—245° (decomp.) (Found: N, 15·9; I, 35·7; H_2O, 5·2. $C_9H_{11}O_2N_4I,H_2O$ requires N, 15·9; I, 36·0; H_2O, 5·1%). An identical product was obtained, albeit in lower yield, from 3-amino-1-methyl-5-nitroindazole under the same conditions.

The author thanks Dr. D. F. Muggleton for the spectral determinations, Mr. S. Bance, B.Sc., A.R.I.C., for the semimicro-analyses, and the Directors of May & Baker Ltd. for permission to publish this work.

The Research Laboratories, May & Baker Ltd.,
Dagenham, Essex.

[*Received, February 10th*, 1959.]