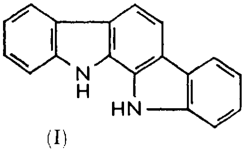
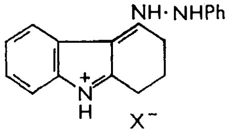
568. *The Fischer Indolisation of Cyclohexane-*1,4*-dione Bisphenylhydrazone.*

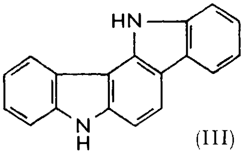
By B. Robinson.

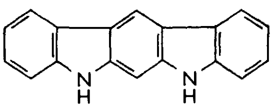
Cyclohexane-1,4-dione bisphenylhydrazone has been converted by treatment with a mixture of glacial acetic acid and concentrated sulphuric acid into indolo(3′,2′-2,3)carbazole and 3-phenylhydrazinocarbazole.

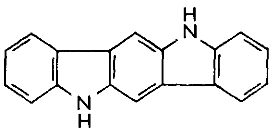
Fischer indolisation of cyclohexane-1,2-dione bisphenylhydrazone or 1,2,3,4-tetrahydro-1-oxocarbazole phenylhydrazone has been found to give indolo(2′,3′-1,2)carbazole (I), dehydrogenation of the proximate 3,4-dihydro-derivative having occurred.[1,2] Although the Fischer indolisation of cyclohexane-1,3-dione bisphenylhydrazone (which could lead to two isomeric products) has not been directly investigated, it has been found that 1,2,3,4-tetrahydro-4-oxocarbazole (which results from indolisation of cyclohexane-1,3-dione monophenylhydrazone [3]) reacts with phenylhydrazine in acid solution, to give compound (II); on pyrolysis under reduced pressure or treatment with refluxing acetic acid this is indolised and dehydrogenated to indolo(3′,2′-3,4)carbazole [2] (III), which had previously been prepared by other routes.[4,5] Besides compounds (I) and (III), compounds (IV) and (V), a further two of the five possible indolocarbazoles, have been prepared by the vapour-phase cyclodehydrogenation of *NN*′-diphenyl-*m*- and -*p*-phenylenediamine, respectively.[6]


(I)


(II)


(III)


(IV)


(V)

The present work was undertaken, not only to investigate the direction of indolisation of cyclohexane-1,4-dione bisphenylhydrazone (VI), but also as a possible route to the remaining, unknown indolocarbazole (VII; $R = H$). Synthesis of the 6-cyano-derivative, (VII; $R = CN$) has been claimed, but proof that it had the angular structure was lacking.[7]

Of several indolisation catalysts used in the present work, including glacial acetic acid which gave a deep-blue solid, and dry ethanolic hydrogen chloride which gave a tan-coloured solid containing an NH^+ group (infrared spectrum), the most satisfactory was a mixture of glacial acetic acid and concentrated sulphuric acid. After treatment of the bisphenylhydrazone (VI) with this catalyst the non-basic product was found to be compound (V) (by comparison with an authentic specimen [6]), dehydrogenation having occurred as in the previous syntheses of indolocarbazoles (I) [1,2] and (III); [2] none of the possible

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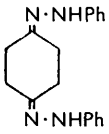
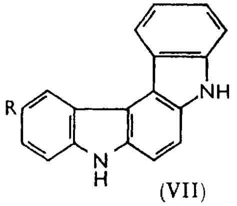
[1] Bhide, Tikotkar, and Tilak, *Chem. and Ind.*, 1957, 363.
[2] Mann and Willcox, *J.*, 1958, 1525.
[3] Clemo and Felton, *J.*, 1951, 700.
[4] Tomlinson, *J.*, 1951, 809.
[5] Hall and Plant, *J.*, 1953, 116.
[6] Grotta, Riggle, and Bearse, *J. Org. Chem.*, 1961, **26**, 1509.
[7] Clifton and Plant, *J.*, 1951, 461.

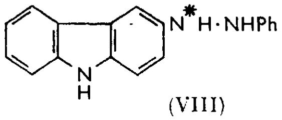
angular isomer, (VII; R = H), or its 12,-dihydro-derivative was detected. A basic product, $C_{18}H_{15}N_3$, was also formed, which was shown to have structure (VIII) on the following evidence: it contained no aliphatic protons (nuclear magnetic resonance spectrum in trifluoroacetic acid with tetramethylsilane as internal reference); its infrared spectrum showed multiple absorption in the NH stretching region and five strong bands in the 700—900 cm.$^{-1}$ region [corresponding to the substitution patterns of the benzenoid nuclei in (VIII)]; and its ultraviolet spectrum (neutral solution) underwent a hypsochromic shift on acidification to a curve almost identical with that of an equimolar mixture of carbazole and phenylhydrazine in ethanol–hydrochloric acid [as would be expected of (VIII) after protonation of N*] (see Figure).



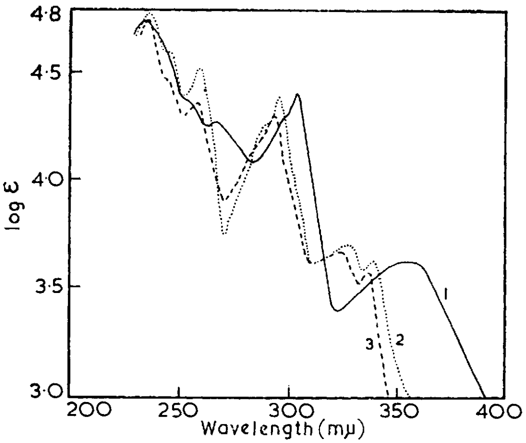
(VI)



(VII)

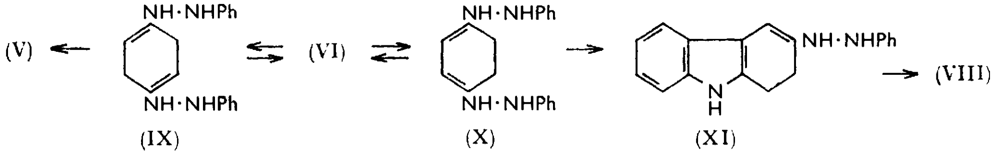


(VIII)



Ultraviolet absorption spectra of 3-phenylhydrazinocarbazole (VIII) (1) in ethanol, and (2) ethanol–hydrochloric acid, and (3) of an equimolar mixture of carbazole and phenylhydrazine in ethanol–hydrochloric acid.

The formation of compound (VIII) probably accounts for the non-formation of the indolocarbazole (VII; R = H) in the indolisation. The first stage in the mechanism of the indolisation [8] is tautomerism of the bishydrazone (VI) to one or both of the hydrazines (IX) and (X). By double intramolecular rearrangement, etc., the former would give 1,4-dihydroindolo(3′,2′-2,3)carbazole and thence the indolocarbazole (V). However,



partial indolisation of the tautomer (X) would give the intermediate (XI) and it appears that this is dehydrogenated to 3-phenylhydrazinocarbazole (VIII) [a similar reaction

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[8] See *e.g.*, Allen and Wilson, *J. Amer. Chem. Soc.*, 1943, **65**, 611; Carlin and Fischer, *ibid.*, 1948, **70**, 3421; Julian, Meyer, and Printy, "Heterocyclic Compounds," ed. Elderfield, Wiley, New York, 1952, p. 8; Sumpter and Miller, "Heterocyclic Compounds with Indole and Carbazole Systems," ed. Weissberger, Interscience, London and New York, 1954, p. 3.

sequence is possible from tautomer (IX) but unlikely (see below)]; a second indolisation, leading to compound (VII; R = H) is thus prevented. Dreiding models of (I), (III), (V), and (VII; R = H) and their corresponding dihydro-precursors, show that in compound (VII; R = H) and its dihydro-precursor the terminal benzenoid nuclei are much closer together than in the other six cases; it is probably this factor which renders the formation of the indolo(2′,3′-3,4)carbazole skeleton relatively more difficult, so that preferential dehydrogenation of intermediate (XI) to 3-phenylhydrazinocarbazole (VIII) occurs. Further attempts to prepare the indolocarbazole (VII R = H) are in progress.

EXPERIMENTAL

Fischer Indolisation of Cyclohexane-1,4-*dione Bisphenylhydrazone* (VI).—The powdered bisphenylhydrazone[9] (VI) (4·4 g.) was added with stirring to a mixture of glacial acetic acid (20 c.c.) and concentrated sulphuric acid (4 c.c.) at 10°. The mixture immediately became red and on being warmed to 30° and stirred for a further 5—10 min. gave a red-purple solution. This was further warmed at 60—70°, changing in 2—3 min. to light-brown; an exothermic reaction ensued (cooling) and crystals separated. After 3 days at room temperature the product was removed, washed with acetic acid and water and obtained as pale yellow crystals (1·35 g., 35%), which did not melt at <350°. They sublimed at 320—330°(bath)/0·1 mm. but considerable decomposition occurred. Recrystallisation from quinoline[6] gave indolo(3′,2′-2,3)-carbazole (V) 0·91 + 0·13 g.; further concentration of the mother-liquors led to decomposition) as pale yellow plates which did not melt or decompose at <350° and were identical [infrared spectrum (in Nujol); qualitative ultraviolet spectrum (in ethanol)] with an authentic specimen (kindly supplied by Dr. H. M. Grotta, Battelle Memorial Institute, Ohio) (Found: C, 83·8; H, 5·25. Calc. for $C_{18}H_{12}N_2$: C, 84·35; H, 4·7%). The crystals were insoluble or only slightly soluble in the common organic solvents, a qualitative ultraviolet spectrum in ethanol (in which the crystals were slightly soluble giving a pale violet fluorescent solution) having $\lambda_{\text{max.}}$ 274, 321—322, 330, and 337 mμ. The NN′-*diacetyl derivative* prepared by refluxing (V) (125·6 mg.) in acetic anhydride (7 c.c.) for 15 min., crystallised (146·9 mg., 88%) from acetic acid (charcoal) as needles, m. p. 289—291° (Found: C, 77·4; H, 4·5; N, 8·0. $C_{22}H_{16}N_2O_2$ requires C, 77·65; H, 4·75; N, 8·25%), $\lambda_{\text{max.}}$ 237, 278—280, 294, 317, 347, $\lambda_{\text{infl.}}$ 249, 270, 305, 325, 332, $\lambda_{\text{min.}}$ 261, 288—289, 296—297, 344 mμ (log ε 4·67, 4·32, 4·29, 4·61, 3·96; 4·49, 4·25, 4·36, 4·50, 4·47, 4·18, 4·28, 4·28, 3·95, respectively, in ethanol).

The acidic filtrate from the main reaction was basified with 6N-sodium hydroxide; the liberated base (1·1 g., 27%) recrystallised from ethanol (charcoal), to give 3-*phenylhydrazinocarbazole* (VIII) as plates, m. p. 262—264° (Found: C, 78·9; H, 5·15; N, 15·0. $C_{18}H_{15}N_3$ requires C, 79·1; H, 5·55; N, 15·4%), $\lambda_{\text{max.}}$ 232, 267, 303, 352—358, $\lambda_{\text{infl.}}$ 253, 297, $\lambda_{\text{min.}}$ 260, 283, 320—323 mμ (log ε 4·74, 4·27, 4·40, 3·62, 4·38, 4·29, 4·25, 4·08, 3·39, respectively, in ethanol), changed to $\lambda_{\text{max.}}$ 234, 258, 295, 328, 339, $\lambda_{\text{infl.}}$ 244, 283, 289, $\lambda_{\text{min.}}$ 250, 268, 309—310, 333 mμ (log ε 4·77, 4·52, 4·38, 3·70, 3·62, 4·59, 4·08, 4·25, 4·38, 3·74, 3·62, 3·58, respectively, in ethanol–hydrochloric acid), $\nu_{\text{max.}}$ (in Nujol) 3480msh, 3442s, 3406s, 3240w (NH stretchings), 861s, 806s, 771s, 756s, 727s cm.$^{-1}$ (aromatic CH out-of-plane deformations).[10]

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[9] Gardner, Haynes, and Brandon, *J. Org. Chem.*, 1957, **22**, 1206; Baeyer and Noyes, *Ber.*, 1889, **22**, 2168.

[10] Bellamy, " The Infrared Spectra of Complex Molecules," Methuen and Co. Ltd., London, 1958, p. 65.