# The Cyclisation of Phenolic Nitrochalcones to Compounds containing the [1]Benzopyrano[3,2-*b*]indole Nucleus

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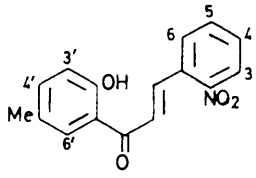
Sodium hydroxide converts 2'-hydroxy-2-nitro-5'-methylchalcone (I) into 10-hydroxy-2-methyl-11*H*-[1]benzopyrano[3,2-*b*]indol-11-one (IIa), a derivative of a new heterocyclic system. Sulphur dioxide in methanol removes the hydroxy-group giving 2-methyl-11*H*-[1]benzopyrano[3,2-*b*]indol-11-one (VIIIa), which is also obtained by the catalytic hydrogenolysis of the methyl ether (IIb). Ethyl phosphite converts 2'-nitro-6-methylflavone into (VIIIa) in a reaction which appears to involve nitrene insertion into a pyrone nucleus and which confirms the constitutions allocated to the new compounds. The 10-hydroxy-1,3-dimethyl (XIV) and the 10-hydroxy-3-methoxy-analogues (XIII), have also been prepared from appropriate chalcones, which are best prepared by the Friedel–Crafts method avoiding basic media. The new heterocyclic nucleus is relatively stable to moderate chemical attack (by acids, bases, oxidising agents, or reducing agents) and to mass spectral fragmentation. These features are attributed to a combination of charge separation phenomena and aromaticity.

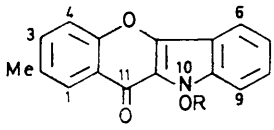
ALKALINE hydrogen peroxide oxidises 2'-hydroxychalcone to 3-hydroxyflavanone in a general reaction now known as the Algar–Flynn–Oyamada reaction. Although we have used the method successfully with chalcones carrying nitro-groups in the 3- or 4-positions,[1] we find that it fails with 2-nitrochalcones because another reaction supervenes. In this, alkali induces a series of reactions terminating in a chromenoindole system and hydrogen peroxide is not involved. For example, alkali

[1] F. M. Dean and V. Podimuang, *J. Chem. Soc.*, 1965, 3978.

converts chalcone (I) into 10-hydroxy-2-methyl-11*H*-[1]benzopyrano[3,2-*b*]indol-11-one (IIa) in yields >60%. Compounds containing this heterocyclic system have not been described previously.



(I)



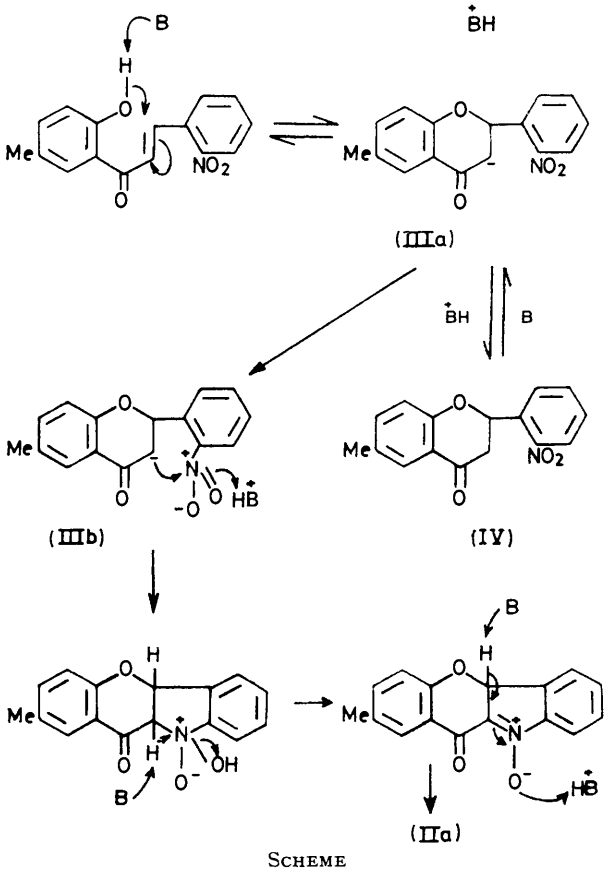
(II)

a; R = H
b; R = Me
c; R = Ac

The presence in the new compound of a slightly acidic hydroxy-group was indicated by the solubility in aqueous sodium hydroxide, and by the formation of a methyl ether (IIb) with methyl sulphate and potassium carbonate. The acetate (IIc) absorbed in the i.r. region at 1800 $cm^{-1}$, an exceptionally high frequency excluding either aryl acetate or acetamide groupings. A broad absorption band at 3110 $cm^{-1}$ together with a strong colour developed by (IIa) with ethanolic iron(III) chloride seemed to point to a chelated system and therefore to the presence of a carbonyl group which might also be responsible for one of the strong bands between 1600 and 1640 $cm^{-1}$. But this region is complex, and the shifts to higher frequency produced by methylation or acetylation (*ca.* 10 $cm^{-1}$) too small for any clear result to emerge. The n.m.r. spectra served to monitor the methyl groups and aromatic protons in these molecules without providing a clue on the skeletal structure. The mass spectrum contained but three major peaks, these corresponding to the parent ion (*m/e* 265) and fragments (*m/e* 249 and 248) resulting from the loss of the hydroxy-group or of water. Losses of 28 or 29 units which might have confirmed the presence of a carbonyl group could be identified but were relatively weak. Degradative studies gave no further information because the compound either resisted acids, bases, oxidising agents, and most reducing agents or, in very vigorous conditions, disintegrated. Structure (IIa) was therefore adduced from the mechanistic considerations summarised in the Scheme.

The sequence in the Scheme begins with cyclisation to the flavanone carbanion (IIIa). The flavanone (IV) can be isolated if treatment with base is mild, and it functions as well as the chalcone in the formation of the chromenoindole derivative (IIa). Following earlier work [1] we had expected the carbanion to effect nucleophilic substitution at peroxide oxygen but clearly the nitro-group at the 2-position is uniquely placed to react by nucleophilic addition as shown in (IIIb). The subsequent steps are all of conventional kinds. A number of reactions between carbanionic centres and nitro-groups are known,[2] though few proceed as smoothly as this one. On the other hand it is possible to attain the same result in terms of oxidation–reduction sequences involving nitroso-intermediates and it may be significant that the reaction mixture acquires a green tint. However, reactions with nitroso-intermediates are commonly radical reactions catalysed by light and we have not found any such catalysis in this case.

Confirmation of structure (IIa) was sought by synthesis. The ester (V) was converted by standard methods into diketone (VI) and so into 2'-nitro-6-methylflavone (VII), which exhibited the appropriate i.r. absorption bands at 1642 (flavone), and 1530 and 1350 $cm^{-1}$ ($NO_2$), and n.m.r. peaks at $\tau$ 7·57 (s, 3H, Ar$CH_3$) and 3·47 (1H, s, pyrone 3-H) besides those due to aromatic protons. On heating with ethyl phosphite this compound was transformed into the indole derivative (VIIIa) presumably through a nitrene (IX) which then effected insertion into the pyrone system. This appears to be the first example of such an insertion reaction.[3]

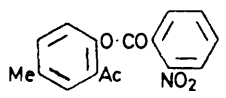


Scheme

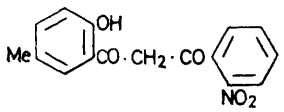
The new chromenoindole (VIIIa) has a mass spectrum very like that of (IIa) but it shows only one strong peak (the molecular ion), ready loss of water or of a hydroxy-group now being impossible, and loss of CO being again unimportant. The i.r. spectra are also very similar. The new compound is also slightly acidic, giving a yellow solution in aqueous, ethanolic alkali and suffering

[2] J. D. Loudon and G. Tennant, *Quart. Rev.*, 1964, **18**, 389.
[3] J. I. G. Cadogan, *Quart. Rev.*, 1968, **22**, 222; *Accounts Chem. Res.*, 1972, **5**, 303.

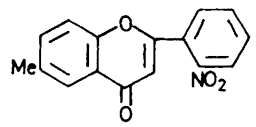
methylation by methyl sulphate and potassium carbonate. Derivative (VIIIb) gives a methyl resonance at $\tau$ 5·67, the low field being typical of *N*-methylindole derivatives.[4]



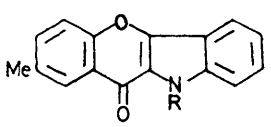
(V)



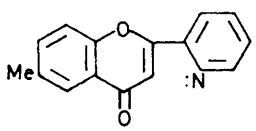
(VI)



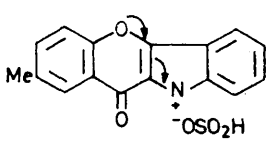
(VII)



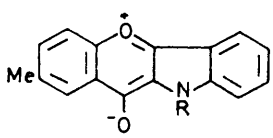
(VIII)
a; R = H
b; R = Me



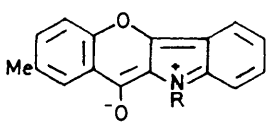
(IX)



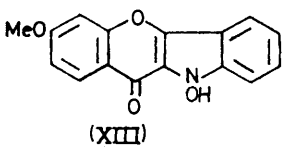
(X)



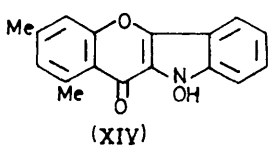
(XI)



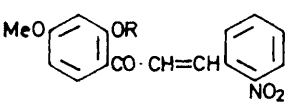
(XII)



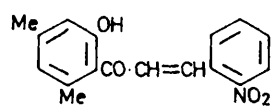
(XIII)



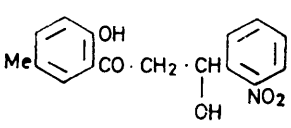
(XIV)



(XV)
a; R = H
b; R = Me



(XVI)



(XVII)

Attempts to oxidise chromenoindole (VIIIa) to chromenoindole (IIa) failed, the compound resisting attack by hydrogen peroxide in acid or in base, or in neutral solutions containing ferrous sulphate. It also resisted benzoyl peroxide, perbenzoic acid, and lead(IV) acetate at 80°. Attempts to reduce the hydroxyindole (IIa) were therefore renewed. Catalytic hydrogenation failed, as did reduction by zinc and acid, lithium aluminium hydride, and diborane. Use of the acetate (IIc) instead led only to hydrolysis of the ester function. Since in all these cases chelation with the reducing agent is possible and might contribute to the stability of the compound, we next used systems avoiding it and found that sulphur dioxide in acidic methanol slowly effects the required reduction of (IIa) to (VIIIa). Diagram (X) suggests a mechanism in which a sulphite (or perhaps sulphate) ester is produced first and then dissociates leaving a nitrenium ion stabilised by the ether oxygen atom as shown but capable of accepting hydride ion from sulphurous acid. However, catalytic hydrogenolysis of the methyl ether (IIb) was a quicker and more convenient method of reduction.

This correlation with (VIIIa) proves that the chromenoindole (IIa) contains a flavone nucleus. The absence of an n.m.r. band near $\tau$ 3·5 shows that the flavone nucleus is substituted at the 3-position, and structure (IIa) follows unambiguously. The resistance of the two chromenoindoles and their derivatives to a wide variety of reagents and conditions can be partly explained in terms of aromaticity and partly in terms of the contributions to the system made by dipolar species such as (XI) and (XII). Indeed, the latter can be regarded as an [18]heteroannulene system devoid of a carbonyl group and possessing an electron-deficient nitrogen atom, and a large contribution by this species would explain both the difficulty of recognising the carbonyl i.r. bands and the acidity of (VIIIa) along with its resistance to oxidation.

Two further chromenoindole derivatives (XIII) and (XIV) were obtained by the action of alkali upon the corresponding chalcones (XVa) and (XVI), respectively, but not studied in detail. The chalcones for this work were not usually made by the standard method in which an acetophenone derivative is condensed with 2-nitrobenzaldehyde in alkaline media because the further reactions leading to chromenoindoles could not easily be prevented. With barium hydroxide as base, 2′-hydroxy-5′-methylacetophenone and 2-nitrobenzaldehyde supplied the aldol (XVII) and dehydration with sulphuric acid furnished the chalcone (I). The same chalcone could be obtained from the acetophenone directly by acid catalysis, but neither method was reliable. In the best general method the methyl ether of the requisite phenol was condensed with 2-nitrocinnamoyl chloride by means of aluminium chloride. For example, 1,3-dimethoxybenzene gave rise to a mixture of chalcones (XVa) and (XVb) in which selective demethylation was completed by boron trichloride.[5]

[4] M. L. Martin, G. J. Martin, and P. Caubere, *Bull. Soc. chim. France*, 1964, 3066.

[5] F. M. Dean, J. Goodchild, L. E. Houghton, J. A. Martin, R. B. Morton, B. Parton, A. W. Price, and N. Somvichien, *Tetrahedron Letters*, 1966, 4153.

EXPERIMENTAL

Molecular weights were determined by mass spectrometry. I.r. spectra were obtained from mulls in paraffin, and n.m.r. spectra from solutions in deuteriochloroform. Light petroleum refers to the fraction with b.p. 60—80°.

*2′-Hydroxy-5′-methyl-2-nitrochalcone* (I).—(i) Powdered aluminium chloride (4·8 g) was stirred into a solution of 2-nitrocinnamoyl chloride (10 g) and 4-methoxytoluene (6 g) in carbon disulphide (50 ml) cooled in ice, and after the vigorous reaction had subsided the mixture was heated under reflux for 1 h. Removal of the solvent left a complex which was decomposed with an excess of dilute hydrochloric acid and the product (a mixture of the required chalcone and its methyl ether) was purified by recrystallisation from methanol. Demethylation was completed by dissolving the crystals in dichloromethane (60 ml) and adding boron trichloride (10 ml) in the same solvent (30 ml) at 0°. Next day dilute hydrochloric acid was stirred in and the organic layer was separated and the solvent allowed to escape. Purified from acetic acid, the product gave the *chalcone* as feathery, yellow needles (5·8 g), m.p. 158°, $\nu_{max.}$ 2900—2700 (hydrogen-bonded OH), 1660 (conj. C:O), and 1550 $cm^{-1}$ ($NO_2$) (Found: C, 67·6; H, 4·45; N, 4·9. $C_{16}H_{13}NO_4$ requires C, 67·8; H, 4·6; N, 4·9%).

(ii) A solution of 2′-hydroxy-5′-methylacetophenone (5 g) and 2-nitrobenzaldehyde (5 g) in methanol (50 ml) was cooled in an ice–salt mixture during the slow addition of sodium hydroxide solution (50%; 20 ml) and for another 1 h. The yellow precipitate was collected and crystallised from acetic acid yielding the chalcone as yellow needles (1 g), m.p. and mixed m.p. 158—159°.

(iii) A solution of 2′-hydroxy-5′-methylacetophenone (2 g) and 2-nitrobenzaldehyde (2 g) in ether (50 ml) was saturated with hydrogen chloride and kept at room temperature for 14 h whereafter volatile materials were allowed to escape. The residue crystallised from acetic acid giving the chalcone as yellow needles (1·4 g), m.p. and mixed m.p. 158—159°.

*3-Hydroxy-1-(2-hydroxy-5-methylphenyl)-3-(2-nitrophenyl)-propan-1-one* (XVII).—2′-Hydroxy-5′-methylacetophenone (2 g) and 2-nitrobenzaldehyde (1·9 g) interacted in ethanol (30 ml) containing barium hydroxide (4·7 g) in water (10 ml) and cooled in ice. After 12 h the base was neutralised with solid carbon dioxide and the mixture filtered. Obtained by concentrating the filtrate to a small bulk and letting it stand, the crystalline product was purified from acetic acid or methanol and formed faintly greenish yellow plates (3·1 g), m.p. 167—168°, identified as the *propanone* (Found: C, 63·8; H, 5·15; N, 4·65. $C_{16}H_{15}NO_5$ requires C, 63·8; H, 5·0; N, 4·65%). The *diacetate* had m.p. 99—100° (Found: C, 61·9; H, 4·9; N, 4·0. $C_{20}H_{19}NO_7$ requires C, 62·3; H, 5·0; N, 3·9%). Dissolved in a little cold sulphuric acid and poured into water, this propanone generated 2′-hydroxy-5′-methyl-2-nitrochalcone, m.p. and mixed m.p. 158°, almost quantitatively.

*2′-Hydroxy-4′,6′-dimethyl-2-nitrochalcone* (XVI).—A solution of 2′-hydroxy-4′,6′-dimethylacetophenone (2·7 g) and 2-nitrobenzaldehyde (2·5 g) in ether (50 ml) was saturated with hydrogen chloride and kept at room temperature for 14 h. Evaporation of volatile materials left a solid which, purified from acetic acid, gave the *chalcone* as yellow plates (2·6 g), m.p. 155°, which imparted a brown colour to iron(III) chloride in ethanol (Found: C, 68·6; H, 5·0; N, 4·7. $C_{17}H_{15}NO_4$ requires C, 68·7; H, 5·1; N, 4·7%).

*2′-Hydroxy-4′-methoxy-2-nitrochalcone* (XVa).—The interaction of 2-nitrocinnamoyl chloride (6 g) and 1,3-dimethoxybenzene (4·25 g) under the influence of aluminium chloride (3·6 g) was conducted as in the example above and the gummy product in methanol was allowed to percolate through a short alumina column to remove resin before being subjected to demethylation by boron trichloride. The *chalcone* crystallised from methanol as yellow needles (2·9 g), m.p. 149—150° (Found: C, 64·4; H, 4·4%; *M*, 299. $C_{16}H_{13}NO_5$ requires C, 64·2; H, 4·35%; *M*, 299).

*2′-Nitro-6-methylflavanone* (IV).—2′-Hydroxy-5′-methyl-2-nitrochalcone (0·46 g) in methanol (60 ml) was mixed with barium hydroxide (0·05 g) in water (5 ml) and heated on the steam-bath for 35 min. The red precipitate was added to acetic acid (50 ml) giving a yellow solution which was diluted next day with water giving a solid that was purified from benzene on a column of silica. The chief fraction crystallised from methanol giving the *flavanone* as faintly yellow leaflets, m.p. 132°, $\nu_{max.}$ 1675 (C:O) and 1515 and 1355 $cm^{-1}$ ($NO_2$), giving no colour with iron(III) chloride (Found: C, 67·7; H, 4·5. $C_{16}H_{13}NO_4$ requires C, 67·8; H, 4·6%).

*2-Acetyl-4-methylphenyl 2-Nitrobenzoate* (V).—2′-Hydroxy-5′-methylacetophenone (13 g) and 2-nitrobenzoyl chloride (32·5 g) were kept together in benzene (150 ml) containing pyridine (20 ml) for 8 h and the mixture was then kept at the b.p. for 4 h and filtered while hot. The filtrate deposited crystals when cooled and further crops were obtained by concentrating it. The combined crops were purified from ethanol giving the *nitrobenzoate* as plates (18 g), m.p. 142—144°, $\nu_{max.}$ 1753 (ester C:O), 1675 (acetyl C:O), 1533 and 1355 ($NO_2$), and 803 $cm^{-1}$, τ 7·6 (3H, s, ArC$H_3$), 7·49 (3H, s, COC$H_3$), and 2·9—1·8 (7H, mm, Ar*H*) (Found: C, 64·5; H, 4·65; N, 4·4%; *M*, 299. $C_{16}H_{13}NO_5$ requires C, 64·2; H, 4·4; N, 4·7%; *M*, 299).

*1-(2-Hydroxy-5-methylphenyl)-3-(2-nitrophenyl)propane-1,3-dione* (VI).—The foregoing ester (1 g) was heated in refluxing pyridine (10 ml) with potassium carbonate (1·2 g) for 35 min. The mixture was cooled and poured into an excess of 10% hydrochloric acid and the precipitate was washed with water and purified from ethanol to give the *propane-1,3-dione* as yellow needles (0·5 g), m.p. 136—137°, $\nu_{max.}$ 1630, 1540, 1365, 840, and 795 $cm^{-1}$, τ 7·72 (3H, s, ArC$H_3$), 5·46 (1H, s, OH), 3·49 (1H, s, COC*H*:COH), and 3·2—2·1 (7H, m, Ar*H*) (Found: C, 64·1; H, 4·3; N, 4·45%; *M*, 299. $C_{16}H_{13}NO_5$ requires C, 64·2; H, 4·4; N, 4·7%; *M*, 299).

*6-Methyl-2′-nitroflavone* (VII).—A solution of the foregoing dione (0·30 g) in acetic acid (15 ml) containing concentrated hydrochloric acid (1 ml) was heated on the steam-bath for 2 h, then cooled and poured into water. The precipitate crystallised from ethanol giving the *nitroflavone* as long needles (0·24 g), m.p. 177—178°, $\nu_{max.}$ 1643, 1618, 1533, 1355, and 807 $cm^{-1}$, τ 7·55 (3H, s, ArC$H_3$), 3·46 (1H, s, pyrone 3-H), and 2·85—1·85 (7H, m, Ar*H*) (Found: C, 68·3; H, 4·1%; *M*, 281. $C_{16}H_{11}NO_4$ requires C, 68·3; H, 3·9%); *M*, 281).

*10-Hydroxy-2-methyl-11H-[1]benzopyrano[3,2-b]indol-11-one* (IIa).—A mixture of 2′-hydroxy-5′-methyl-2-nitrochalcone (1·2 g) or the corresponding flavanone (IV) in ethanol (100 ml) and 5N-sodium hydroxide (60 ml) was kept on the steam-bath for 10 min. and then at room temperature for 4 h. An orange-red crystalline mass of a sodium salt separated and was collected, washed with a little sodium hydroxide solution, and dissolved in hot acetic acid. Gradual addition of water to the yellow solution precipitated a solid which, after three recrystallisations from methanol

supplied the *benzopyranoindolone* as pale yellow needles (0·7 g), m.p. 233—235°, $\nu_{max.}$ 3110, 1635, 1603, 1530, 1283, and 748 $cm^{-1}$, readily soluble to a straw-coloured solution in dilute sodium hydroxide and imparting an intense green colour to ethanol containing iron(III) chloride (Found: C, 72·4; H, 4·25; N, 5·4%; *M*, 265. $C_{16}H_{11}NO_3$ requires C, 72·4; H, 4·2; N, 5·3%; *M*, 265). The *acetate* separated from methanol as plates, m.p. 143°, $\nu_{max.}$ 1800 (NOAc), 1645 (γ-pyrone), and 1615 $cm^{-1}$ (aromatic) (Found: C, 67·2; H, 4·3; N, 4·6. $C_{18}H_{13}NO_4$ requires C, 70·35; H, 4·3; N, 4·6%).

Methylation of the hydroxybenzopyranoindolone (1 g) with methyl sulphate and potassium carbonate in refluxing acetone gave 10-*methoxy*-2-*methyl*-11H-[1]*benzopyrano*[3,2-b]*indol*-11-*one* (IIb) which separated from benzene–light petroleum as needles (0·85 g), m.p. 172°, $\nu_{max.}$ 1655, 1623, 1285, 823, and 750 $cm^{-1}$, τ 7·55 (3H, s, Ar$CH_3$), 5·7 (3H, s, $OCH_3$), 2·94—1·8 (7H, mm, Ar*H*), insoluble in dilute acids or bases and giving no reaction with iron(III) salts (Found: C, 73·2; H, 4·65; N, 3·9%; *M*, 279. $C_{17}H_{13}NO_3$ requires C, 73·1; H, 4·7; N, 4·0%; *M*, 279).

10-*Hydroxy*-1,3-*dimethyl*-11H-[1]*benzopyrano*[3,2-b]*indol*-11-*one* (XIV).—2′-Hydroxy-4′,6′-dimethyl-2-nitrochalcone (0·2 g) in methanol (10 ml) was treated with dilute sodium hydroxide (10%; 1 ml) and warmed on the steam-bath for 5 min, then allowed to stand for 12 h. Acidification gave a solid that crystallised from methanol yielding the *pyranoindolone* as pale greenish yellow needles (0·1 g), m.p. 240—242°, having a bright green ferric reaction in ethanol (Found: C, 73·0; H, 4·7; N, 5·0. $C_{17}H_{13}NO_3$ requires C, 73·1; H, 4·7; N, 5·0%). The *acetate* separated from methanol as needles, m.p. 147—148° (Found: C, 71·1; H, 4·8; N, 4·35. $C_{19}H_{15}NO_4$ requires, C, 71·0; H, 4·7; N, 4·4%).

10-*Hydroxy*-3-*methoxy*-11H-[1]*benzopyrano*[3,2-b]*indol*-11-*one* (XIII).—2′-Hydroxy-4′-methoxy-2-nitrochalcone (0·09 g) in ethanol (75 ml) was mixed with 5N-sodium hydroxide (60 ml) and kept for 9 h while a red precipitate formed. This was dissolved in acetic acid and the yellow product precipitated by water and purified from methanol giving the *methoxybenzopyranoindolone* as pale yellow needles (0·05 g), m.p. (rapid heating) 215—217° but solidifying and remelting at 282—284° (slow heating produces only shrinking over a long range), $\nu_{max.}$ 3250, 1630, 1010, and 842 $cm^{-1}$, τ 6·08 (3H, s, $OCH_3$) and 3·00—1·70 (7H, m, Ar*H*) (Found: C, 68·1; H, 4·1%; *M*, 281. $C_{16}H_{11}NO_4$ requires C, 68·3; H, 3·9%; *M*, 281).

2-*Methyl*-11H-[1]*benzopyrano*[3,2-b]*indol*-11-*one* (VIIIa).—(i) A solution of 10-hydroxy-2-methyl-11*H*-[1]benzopyrano[3,2-*b*]indolone (0·3 g) in methanol (80 ml) containing 2N-hydrochloric acid (8 ml) was heated under reflux for 6 h while a stream of sulphur dioxide was passed in. It was then concentrated under reduced pressure and left. The crystals that separated were recrystallised from methanol giving the *benzopyranoindolone* as fine needles (0·23 g), m.p. 318—319° (shrinks above 300°), $\nu_{max.}$ 3150, 1635, 1615, 840, 325, and 750 $cm^{-1}$, giving a yellow solution in sodium hydroxide solution and an intense green colour with ethanolic iron(III) chloride (Found: C, 77·0; H, 4·6; N, 5·4%; *M*, 249. $C_{16}H_{11}NO_2$ requires C, 77·1; H, 4·45; N, 5·6%; *M*, 249).

Methylation of this compound (0·10 g) in acetone was very slow but treatment in refluxing butan-2-one with methyl sulphate and potassium carbonate for 3 h supplied 2,10-*dimethyl*-11H-[1]*benzopyrano*[3,2-b]*indol*-11-*one* which crystallised from benzene–light petroleum as needles (0·09 g), m.p. 205—207°, $\nu_{max.}$ 1643, 1623, 1510, 1290, 813, and 755 $cm^{-1}$, τ 7·52 (Ar$CH_3$) and 5·67 (3H, s, $NCH_3$) (Found: C, 77·4; H, 4·7; N, 5·1. $C_{17}H_{13}NO_2$ requires C, 77·4; H, 5·0; N, 5·3%).

(ii) 10-Methoxy-2-methyl-11*H*-[1]benzopyrano[3,2-*b*]-indol-11-one (50 mg) in 95% ethanol (30 ml) was shaken with palladium–charcoal (10%; 10 mg) in an atmosphere of hydrogen for 5 h; removal of the catalyst and the solvent left a solid that crystallised from ethanol giving the benzopyranoindole as needles (35 mg), m.p. and mixed m.p. 318—319°, further identified spectroscopically.

(iii) A solution of 6-methyl-2′-nitroflavone (0·5 g) in triethyl phosphite (50 ml) was refluxed under nitrogen for 9 h. Removal of the phosphite under reduced pressure left a solid which crystallised from ethanol giving the benzopyranoindole as needles (0·2 g), m.p. and mixed m.p. 318—319°, further identified spectroscopically.

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