451. *The Reaction of 4-Hydroxycinnoline-3-carboxylic Acid with Pyridine and Acetic Anhydride.*

By J. S. Morley.

The constitution of the product formed by warming together the reactants named in the title has been shown to be (II; R′ = H) and not (IIS) * as reported previously.[1] The degradative work involved in this proof (see the "New Scheme") illustrated the ready nuclear halogenation of 2-arylazopyridines by aqueous halogen acids (VII $\longrightarrow$ VIII and IX). Syntheses of 2-*o*-carboxyphenylazopyridine (VII) (involving condensation of *o*-nitrosobenzoic acid with 2-aminopyridine in 50% aqueous sodium hydroxide), its 4-chloro-derivative (VIII), the indazolone (IX), and a number of intermediate or related products are described.

In 1946, Schofield and Simpson [1] found that treatment of 4-hydroxycinnoline-3-carboxylic acid (I; R′ = H) (1 part) with a mixture of pyridine (4·5 parts) and acetic anhydride (6·5 parts) produced a substance, m. p. 217°, of formula $C_{16}H_{11}O_3N_3$, in good yield, according to the equation $C_9H_6O_3N_2 + C_5H_5N + Ac_2O \longrightarrow C_{16}H_{11}O_3N_3 + AcOH + H_2O$. Using the production of "Reissert" compounds from quinoline, acid chlorides, and potassium cyanide as a model, they formulated the product as a resonance hybrid of three species with the carbonium form (IIS) * making a major contribution. The substance was highly reactive and various reactions were described; when, for example, it was refluxed with the lower alcohols, or with aniline in benzene, it gave a series of amphoteric adducts, which were assigned the structures (IIIS; R = Me, Et, and Pr^i; and also NHPh in place of OR). Schofield and Simpson attempted to verify these structures by degradation, which they considered to follow the scheme given as "Schofield and Simpson's Scheme." The key product, produced from several of the compounds in the series, was a yellow base, $C_{13}H_9N_3,2H_2O$, m. p. 152·5—153·5°, which Schofield and Simpson formulated as 4-2′-pyridylcinnoline (VIS). It was, however, difficult to explain the ease of oxidation of this base to an acid, $C_{12}H_9O_2N_3$, m. p. 146—147° (formulated as VIIS), and the conversion of this by boiling 5N-hydrochloric acid into a mixture of an orange-pink amphoteric compound, m. p. 195°, and a colourless weak ampholyte, m. p. 254° (formulated as VIIIS and IXS respectively). Doubt was later cast on the whole proposed scheme by the synthesis [2] of 4-2′-pyridylcinnoline (VIS), which was not identical with the base, m. p. 152·5—153·5°, as postulated.

An alternative explanation seemed possible. Formation of the initial product, $C_{16}H_{11}O_3N_3$, appeared analogous to the production of "Besthorn's Red" (X) from similar reactants.[3,4] The resulting expression (II; R′ = H) explained the various transformations satisfactorily. Thus the action of alcohols would lead to β-keto-esters (III; R = Me, Et, Pr^i) (these substances were soluble in alkali and gave characteristic red-violet ferric reactions), and other products in the scheme could be formulated as (IV) and (V).

However, it was still difficult to assign a constitution to the yellow base (VIS), m. p. 152·5—153·5°. Its formula, $C_{13}H_9N_3,2H_2O$ was considered by Schofield and Simpson to be "eventually proved by analysis of the picrate, which was solvent-free; the styphnate was monohydrated, and the hydrochloride was a dihydrate." Nevertheless, their analytical figures agreed equally with a formula $C_{13}H_9ON_3,H_2O$ (the hydrochloride as monohydrate, and picrate and styphnate anhydrous) with the possible exception of those for the picrate. Our own figures for the picrate differed somewhat from Schofield and

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* The use, in this paper, of the suffix S against a formula number, *e.g.* (IIS), denotes a structure proposed by Schofield and Simpson [1] for a substance now shown to have the structure carrying the unmodified formula number, *e.g.*, (II).

[1] Schofield and Simpson, *J.*, 1946, 472.

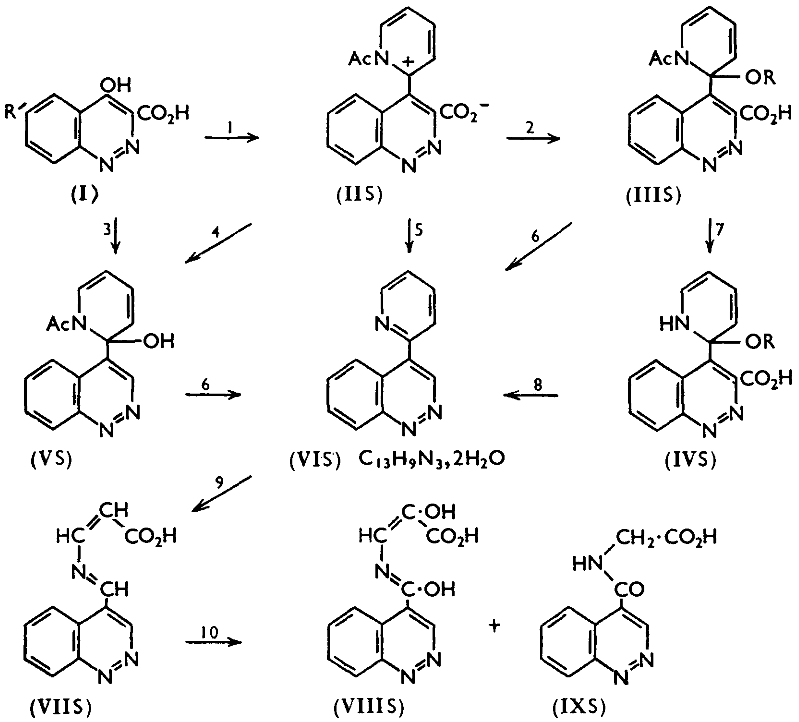
[2] Schofield, *J.*, 1949, 2408.

[3] Besthorn and Ibele, *Ber.*, 1904, **37**, 1236; 1905, **38**, 2127.

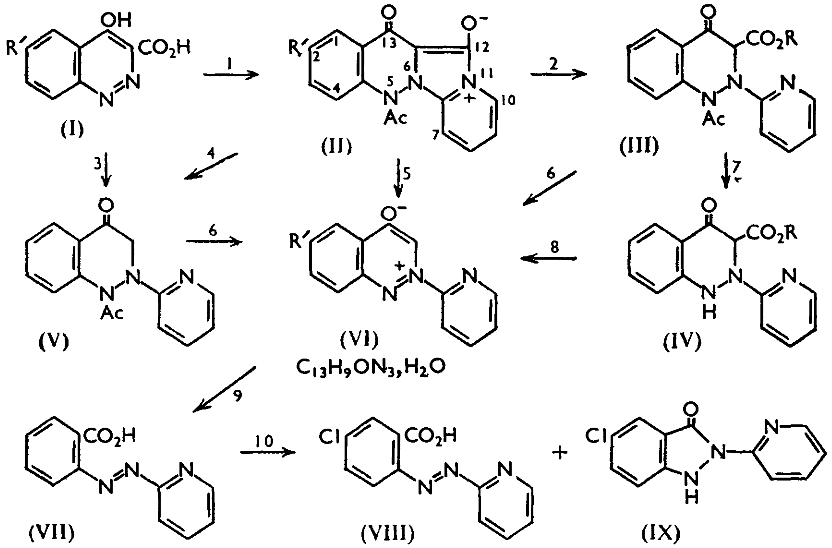
[4] Besthorn, *Ber.*, 1913, **46**, 2762.

Simpson's and agreed closely with a formulation $C_{13}H_9ON_3$ for the base. Moreover, after drying for 16 hours over phosphoric oxide at 60° *in vacuo*, the base gave figures corresponding to the anhydrous formula, $C_{13}H_9ON_3$. The betaine structure (VI; R′ = H) then

Schofield and Simpson's Scheme.



New Scheme.

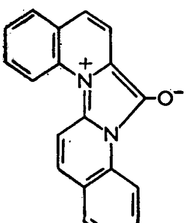


Reagents: 1, C_5H_5N-Ac_2O (4·5 + 6·5 pts.). 2, ROH. 3, C_5H_5N-Ac_2O (3 + 1 pt.). 4, C_5H_5N or H_2O. 5, Hot dil. HCl. 6, Hot dil. HCl or NaOH. 7, ROH-H_2SO_4. 8, Hot NaOH. 9, $KMnO_4$. 10, 5N-HCl.

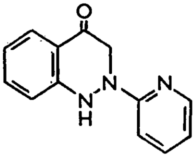
became possible for the base. Its formation, by oxidation of the hypothetical precursor (XI) (which can arise from II, III, IV, or V by normal hydrolytic processes), is not abnormal in view of the ready oxidation of dihydrocinnolines to cinnolines, and a somewhat similar betaine (XII) is readily produced by the dehydrogenation of (XIII) and crystallises as a hydrate.[5]

The oxidation of the base became readily understood on the basis of this proposed structure. The expected oxidation product, 2-*o*-carboxyphenylazopyridine (VII), possessed the empirical formula assigned to the acid (VIIS) and its expected properties agreed well with those described by Schofield and Simpson. Moreover, the constitution of the products (VIIS) and (IXS) of the action of boiling 5N-hydrochloric acid became clear. Under such conditions, 4-phenylazopyridine gives 4-(*p*-chlorophenylhydrazino)pyridine,[6] and similar nuclear halogenations of 2-arylazopyridines have been reported by Colonna *et al.*[7,8] By analogy, (VII) should give 2-(2-carboxy-4-chlorophenylhydrazino)pyridine (XIV; R' = Cl) which by cyclisation could give the indazole (IX), and by oxidation the azo-compound (VIII). The presence of chlorine in the two products was not suspected in the original work, but it is present and the analyses agree with the new structures postulated.

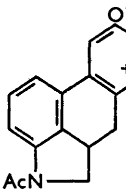
Our interpretations are shown in the " New Scheme." To test its correctness the pyridine–acetic anhydride reaction was applied to 6-chloro-4-hydroxycinnoline-3-carboxylic acid. A chloro-zwitterion (II; R' = Cl) was thereby obtained which, by degradations analogous to (II ⟶ VI, and VI ⟶ VII), gave a chloro-acid corresponding to (VII), which was identical with (VIII).



(X)



(XI)



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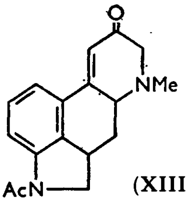

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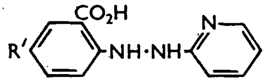
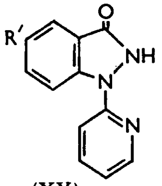
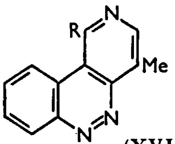


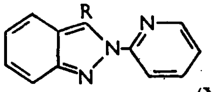
(XIV)



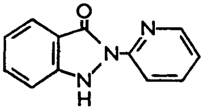
(XV)



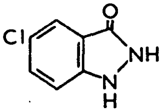
(XVI)



(XVII)



(XVIII)



(XIX)

Final proof was by synthesis. 2-*o*-Carboxyphenylazopyridine (VII) was obtained by condensing *o*-nitrosobenzoic acid with 2-aminopyridine in 50% aqueous sodium hydroxide (after abortive attempts to perform this reaction in acetic acid).[9] 5-Chloro-2-2'-pyridyl-3-indazolone (IX) was obtained as one product on condensation of 5-chloro-2-hydrazinobenzoic acid with 2-chloropyridine and was identical with Schofield and Simpson's colourless ampholyte, m. p. 254° (as were the monomethyl derivatives). The 1-2'-pyridyl isomer (XV; R' = Cl) was a second product from the latter condensation. Reducing the acid

[5] Kornfeld, Fornefeld, Kline, Mann, Morrison, Jones, and Woodward, *J. Amer. Chem. Soc.*, 1956, **78**, 3094, 3111.

[6] Koenigs, Freigang, Lobmayer, and Zscharn, *Ber.*, 1926, **59**, 321.

[7] Colonna and Risaliti, *Gazzetta*, 1955, **85**, 1148; 1956, **86**, 288.

[8] Colonna, Risaliti, and Serra, *ibid.*, 1955, **85**, 1508.

[9] Cf. Campbell, Henderson, and Taylor, *J.*, 1953, 281.

(VIII) catalytically or by stannous chloride or thiol compounds gave 2-(2-carboxy-5-chlorophenylhydrazino)pyridine (XIV; R′ = Cl), the hydrochloride of which, when heated in ethanol at 170—180°, likewise gave the indazole (IX).

A further point deserves mention. Degradation of the ketone (V) to the betaine (VI) by alkaline hydrolysis gave two by-products to which Schofield and Simpson[1] assigned the structures (XVI; R = OH and CO_2H). When the analogy of the hypothetical precursor (XI) [arising from (V) by a normal hydrolysis] to indoxyl is considered, oxidation by air in alkaline media may be considered likely. Ring contraction, by unexceptional processes, of the oxidation products could then lead to indazoles. One of Schofield and Simpson's by-products was an acid, m. p. 169—170° (decomp.). This is probably 2-2′-pyridylindazole-3-carboxylic acid (XVII; R = CO_2H), and the derived base, obtained by decarboxylation, is probably (XVII; R = H). The other by-product, an ampholyte, m. p. 186·5—187·5°, was identified as 2-2′-pyridyl-3-indazolone (XVIII); it was synthesised by heating the hydrochloride of 2-*o*-carboxyphenylhydrazinopyridine (XIV; R = H) [obtained by reduction of (VII)] in ethanol at 170—180°. *o*-Hydrazinobenzoic acid with 2-chloropyridine gave only one pyridylindazolone (the corresponding reaction of 5-chloro-2-hydrazinobenzoic acid led to both isomers), which was not identical with (XVII; R = OH) and must therefore be the 1-isomer (XV; R′ = H); this conclusion was supported by the infrared absorption spectrum.

5-Chloro-2-hydrazinobenzoic acid, used in the synthetical work, was obtained in moderate yield from 5-chloroanthranilic acid by the general procedure of Pfannsteil and Janecke,[10] together with an unidentified nitrogenous product which was converted into *m*-chlorobenzoic acid by aqueous sodium hydroxide. 5-Chloro-2-hydrazinobenzoic acid readily gave 5-chloro-3-indazolone (XIX) when boiled with dilute aqueous hydrochloric acid.

EXPERIMENTAL

Reaction of 6-*Chloro*-4-*hydroxycinnoline*-3-*carboxylic Acid with Pyridine and Acetic Anhydride*.—6-Chloro-4-hydroxycinnoline-3-carboxylic acid (10 g.), pyridine (45 ml.), and acetic anhydride (65 ml.) were heated together on the steam-bath for 1 hr. The olive-green crystals of *anhydro*-(5-*acetyl*-2-*chloro*-5 : 13-*dihydro*-12-*hydroxy*-13-*oxocinnolino*[2,3-c]*pyrido*[1,2-a]*imidazolinium hydroxide*) (II; R′ = Cl) (13·8 g., 94%), decomp. >240°, were collected, washed with dry ether, and dried at 80° *in vacuo* (Found: C, 58·8; H, 3·0; N, 12·8. $C_{16}H_{10}O_3N_3Cl$ requires C, 58·65; H, 3·1; N, 12·8%).

Anhydro-6-*chloro*-4-*hydroxy*-2-*pyridylcinnolinium Hydroxide* (VI; R′ = Cl).—A suspension of the anhydride (II; R = Cl) (13·8 g.) in 2N-hydrochloric acid (800 ml.) was heated under reflux for 5 hr., after which the clear, yellow solution was cooled and neutralised to pH 6—7 with solid sodium carbonate. Yellow crystals separated first during the neutralisation, whilst the mixture was acid to Congo Red; at pH 5—7 this changed to a red gum which was slowly converted into a granular yellow solid. The resulting mixture was stirred for 1 hr. at room temperature, then the solid (9·6 g., 88%), m. p. 158—161°, was collected, washed with water, and recrystallised from ethanol, yielding yellow needles (8·0 g.), m. p. 162—163° (after drying at 80°), of *anhydro*-6-*chloro*-4-*hydroxy*-2-2′-*pyridylcinnolinium hydroxide* (VI; R′ = Cl) (Found: C, 60·4; H, 3·1; N, 16·2. $C_{13}H_8ON_3Cl$ requires C, 60·6; H, 3·1; N, 16·3%). The hydrate, m. p. 132—133°, obtained by air-drying, reverted to the anhydrous material after drying at 80°. The compound was sparingly soluble in boiling water and in ether, and easily soluble in cold, dilute mineral acids.

The annexed Table gives analytical figures for the analogue (VI; R = H).

2-(2-*Carboxy*-4-*chlorophenylazo*)*pyridine* (VIII).—2% Aqueous potassium permanganate (450 ml.) was added during 1 hr. to a vigorously stirred suspension of compound (VI; R′ = Cl) (3 g.) in water (200 ml.) at 40—45°. The mixture was stirred for a further ½ hr. at 40—45°, the excess of permanganate was removed by addition of ethanol, and the mixture was filtered. Acidification of the orange-yellow filtrate to pH 3·8—4·2 with hydrochloric acid gave almost pure 2-(2-carboxy-4-chlorophenylazo)pyridine (VIII) (2·3 g.), m. p. 190—192°, which separated from aqueous ethanol in orange-red needles, m. p. 192—193° (Found: C, 54·9; H, 3·2; N, 16·0.

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[10] Pfannsteil and Janecke, *Ber.*, 1942, **75**, 1104.

Analytical values found (a) by Schofield and Simpson [1] *and (b) in the present work for the base* (VI; R′ = H) *and its salts.*

		Found (%)				Required (%)		
		C	H	N	Formula	C	H	N
Base (VI; R′ = H)	(*a*)	63·75	4·6	17·25	$C_{13}H_9N_3,2H_2O$	64·2	5·35	17·3
					$C_{13}H_9ON_3,H_2O$	64·7	4·6	17·4
	(*b*)	69·7	4·0	18·7	$C_{13}H_9N_3,H_2O$	69·3	4·9	18·6
					$C_{13}H_9ON_3$	69·9	4·05	18·8
Hydrochloride ...	(*a*)	57·3	4·15	15·55	$C_{13}H_9N_3,HCl,2H_2O$	55·8	5·0	15·0
					$C_{13}H_9ON_3,HCl,H_2O$	56·2	4·35	15·1
Picrate	(*a*)	51·75	2·75	18·85	$C_{13}H_9N_3,C_6H_3O_7N_3$	5·23	2·8	19·3
	(*b*)	50·3	2·7	—	$C_{13}H_9ON_3,C_6H_3O_7N_3$	50·45	2·7	18·6
		50·7	2·6	—				
Styphnate	(*a*)	48·3	2·45	18·85	$C_{13}H_9N_3,C_6H_3O_8N_3,H_2O$	48·5	3·0	17·9
					$C_{13}H_9ON_3,C_6H_3O_8N_3$	48·7	2·6	17·95

Calc. for $C_{12}H_8O_2N_3Cl$: C, 55·1; H, 3·1; N, 16·05%). Schofield and Simpson's sample [1] (Found: C, 54·95; H, 3·0; N, 16·05%) prepared by the action of hydrochloric acid on 2-*o*-carboxyphenylazopyridine (described by them as a $C_{12}H_9O_4N_3$ acid, m. p. 194—195°), and a mixture of the two samples also had m. p. 192—193°. The infrared absorption spectra of the two samples were identical.

2-o-*Carboxyphenylazopyridine* (VII).—*o*-Nitrosobenzoic acid [11] (15·9 g., 0·105 mole), 2-aminopyridine (9·4 g., 0·1 mole), and 50% aqueous sodium hydroxide (94 ml.) were vigorously stirred at 85—90° for 5 hr., after which water (125 ml.) was added. The mixture was stirred for a further ½ hr. at 80—85°, then cooled and filtered. The solid residue was dissolved in warm water (250 ml.), and the warm filtered solution was acidified with acetic acid, yielding 2-*o*-carboxyphenylazopyridine (11·45 g., 51%), which separated from ethyl acetate in orange-red prisms, m. p. 144—145° (Found: C, 63·3; H, 4·0; N, 18·1%. Calc. for $C_{12}H_9O_2N_3$: C, 63·45; H, 4·0; N, 18·5%). A sample prepared by the method described by Schofield and Simpson [1] (referred to *in their paper* as substance XIV, m. p. 146—147°), and a mixture of the two samples also had m. p. 144—145°. The infrared absorption spectra of the two samples were identical, and both samples gave the same picrate, m. p. 173—174° (Found: C, 47·3; H, 2·6; N, 18·5. Calc. for $C_{12}H_9O_2N_3,C_6H_3O_7N_3$: C, 47·4; H, 2·65; N, 18·4%).

Acidification of the alkaline mother-liquors gave a red-brown solid (4·9 g.), m. p. 233—235°, which on recrystallisation from ethyl acetate and ethanol gave pale-yellow prisms (0·84 g.), m. p. 253—255° (decomp.), of azoxybenzene-2 : 2′-dicarboxylic acid (Found: C, 59·0; H, 3·6; N, 9·9. Calc. for $C_{14}H_{10}O_5N_2$: C, 58·75; H, 3·5; N, 9·8%).

5-*Chloro-2-hydrazinobenzoic Acid.*—A stirred suspension of 5-chloroanthranilic acid (57 g., 0·31 mole), water (300 ml.), and concentrated hydrochloric acid (340 ml.) was diazotised at 0—3° with sodium nitrite (21·6 g., 0·3 mole) in water (200 ml.), then added in 30 min. to water (2400 ml.) saturated with sulphur dioxide at 0—5°. During the addition sulphur dioxide was bubbled through the mixture, and the temperature was kept at 5—10°. The mixture was left at room temperature overnight, then filtered (residue A). Addition of concentrated hydrochloric acid (3 l.) to the ice-cooled filtrate gave a colourless precipitate of a hydrochloride, m. p. 197° (decomp.), which yielded 5-*chloro-2-hydrazinobenzoic acid* (25 g.) (44%), m. p. 230—235° (decomp.), when stirred with aqueous sodium acetate. Recrystallisation from aqueous 2-ethoxyethanol gave almost colourless needles of the pure product (16·1 g.), m. p. (variable with rate of heating) 265° (decomp.; sintered at 160—180°) (Found: C, 45·2; H, 3·8; N, 14·9. $C_7H_7O_2N_2Cl$ requires C, 45·1; H, 3·8; N, 15·0%) The *benzylidene derivative*, which rapidly separated when benzaldehyde was added to a solution of the crude or recrystallised product in acetic acid, separated from ethanol in yellow prismatic needles, m. p. 249—250° (decomp.) (Found: C, 60·9; H, 3·8; N, 10·4. $C_{14}H_{11}O_2N_2Cl$ requires C, 61·2; H, 4·0; N, 10·2%).

The residue A (33 g.), m. p. 160° (decomp.), reduced warm Fehling's solution and was recovered unchanged after treatment with aqueous sodium acetate. Rapid recrystallisation from aqueous ethanol gave colourless needles of a substance, m. p. 160° (decomp.) (Found: C, 41·7; H, 2·5; N, 7·2; S, 7·0%). A solution of this (1 g.) in 3N-sodium hydroxide (5 ml.) was heated under reflux for 15 min. Acidification then gave *m*-chlorobenzoic acid (0·55 g.), needles (from water), m. p. and mixed m. p. 154—155°.

5-*Chloroindazolone.*—5-Chloro-2-hydrazinobenzoic acid (2 g.) (recrystallised), water (200 ml.),

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[11] Bamberger and Pyman, *Ber.*, 1909, **42**, 2306.

and concentrated hydrochloric acid (5 ml.) were heated under reflux for 1 hr. Pure 5-*chloroindazolone* (1·8 g.), which separated, was collected and recrystallised from acetic acid as colourless needles, m. p. 273—275° (decomp.) (Found: C, 50·3; H, 3·0; N, 16·7. $C_7H_5ON_2Cl$ requires C, 49·9; H, 3·0; N, 16·6%).

5-*Chloro*-1- *and* -2-2′-*pyridyl*-3-*indazolone*.—Crude 5-chloro-2-hydrazinobenzoic acid (9·15 g., 0·048 mole), 2-chloropyridine (5 g., 0·044 mole), and ethanol (40 ml.) were heated at 170—180° for 5 hr. The crystals (0·9 g.) which separated on cooling were collected (mother-liquor A) and dissolved in boiling water (25 ml.) containing sufficient sodium hydroxide to give alkalinity to Clayton Yellow paper. Acidification of the hot solution with acetic acid gave a colourless precipitate of 5-chloro-2-2′-pyridyl-3-indazolone (0·32 g.) (IX), which separated from acetic acid in pale-yellow prisms, m. p. 251—252° (Found: C, 58·7; H, 3·3; N, 17·2. Calc. for $C_{12}H_8ON_3Cl$: C, 58·65; H, 3·3; N, 17·1%). A sample prepared by the method described by Schofield and Simpson,[1] and a mixture of the two samples, also had m. p. 251—252° (Schofield and Simpson [1] give m. p. 253—254° and C, 58·05; H, 3·25; N, 17·6%). Infrared analysis (Nujol mull) showed the absence of a broad band in the 2500—2700 cm.$^{-1}$ region and the presence of strong bands at 3120 and 1660 cm.$^{-1}$. Ultraviolet absorption in methanol (1 mg. per 100 ml.): $\lambda_{max.}$ 254, 292, 298, 340—345 mμ (log ε 4·17, 4·15, 4·14, 3·61). An identical indazolone was produced when an ethanolic solution of 2-(2-carboxy-5-chlorophenylhydrazino)pyridine hydrochloride was heated at 170—180° as described below for preparation of 2-2′-pyridyl-3-indazolone.

The alcoholic mother-liquor A was treated with water (60 ml.), and the solid (3·6 g.), m. p. 209—211°, which separated, was collected. Recrystallisation from acetic acid and then from ethanol afforded pale fawn needles of 5-*chloro*-1-2′-*pyridyl*-3-*indazolone* (1·1 g.), m. p. 251—252° (Found: C, 59·3; H, 3·4; N, 17·2%) (a mixture of this with the 2-isomer had m. p. 218—220°), $\nu_{max.}$ (Nujol mull) 2500—2700, 1600 w cm.$^{-1}$, $\lambda_{max.}$ (in methanol; 1 mg. per 100 ml.) 260, 337 mμ (log ε 4·32, 4·14). The infrared and ultraviolet data indicate that the 1-isomer exists mainly in the enol form, and the 2-isomer in the keto-form.

Methylation of 5-*Chloro*-2-2′-*pyridyl*-3-*indazolone*.—A solution of the indazolone (0·1 g.) in hot 0·5N-potassium hydroxide (5 ml.) was cooled rapidly to 50°, then shaken with dimethyl sulphate (0·06 ml.) for 10 min. at 45—50°. The solid (0·06 g.), m. p. 125—126°, which separated, was isolated by ether-extraction and recrystallised from aqueous methanol, affording colourless prismatic needles of 5-*chloro*-1 : 3-*dihydro*-1-*methyl*-3-*oxo*-2-2′-*pyridylindazole*, m. p. 123—124° (Found: C, 60·2; H, 3·9%; *M*, 249. $C_{13}H_{10}ON_3Cl$ requires C, 60·1; H, 3·9%; *M*, 260).

2-o-*Carboxyphenylhydrazinopyridine*.—(*a*) 2-*o*-Carboxyphenylazopyridine (2·27 g., 0·01 mole) in ethanol (100 ml.) was shaken with hydrogen at room temperature pressure in the presence of palladium oxide. Absorption of hydrogen (1 mol.) ceased after ~1 hr. The solid, which separated, was collected and digested with cold 0·5N-sodium hydroxide (30 ml.). Acidification of the filtered digests with acetic acid gave the crude *hydrazine* (2·05 g.), m. p. 220° (decomp.), which separated from 2-ethoxyethanol in almost colourless needles, m. p. 232° (decomp.) (Found: C, 62·7; H, 4·8; N, 18·2. $C_{12}H_{11}O_2N_3$ requires C, 62·9; H, 4·85; N, 18·3%). The *hydrochloride* separated when a hot solution of the base (1 g.) in water (10 ml.) and concentrated hydrochloric acid (2 ml.) was cooled; recrystallisation from methanol-ether afforded needles, m. p. 243—244° (decomp.) (Found: C, 54·4; H, 4·8; N, 15·5. $C_{12}H_{11}O_2N_3,HCl$ requires C, 54·3; H, 4·6; N, 15·8%).

(*b*) A solution of 2-*o*-carboxyphenylazopyridine (2·27 g., 0·01 mole) in chloroform (25 ml.) was treated dropwise with thiophenol (1·13 ml., 0·011 mole) at 20—22°, then set aside at room temperature for 2 days. The solid (1·84 g.), m. p. 215° (decomp.), was collected and recrystallised from 2-ethoxyethanol, yielding fawn needles of the hydrazine, identical with a sample described in (*a*). Similar results were obtained by using ethanethiol.

2-(2-*Carboxy*-4-*chlorophenylhydrazino*)*pyridine*.—Prepared by methods (*a*) and (*b*), this *compound* separated from 2-ethoxyethanol in almost colourless needles, m. p. 252—253° (decomp.) (Found: C, 54·6; H, 3·7; N, 15·5. $C_{12}H_{10}O_2N_3Cl$ requires C, 54·6; H, 3·8; N, 15·9%).

2-2′-*Pyridyl*-3-*indazolone* (XVIII).—2-*o*-Carboxyphenylhydrazinopyridine hydrochloride (2 g.) and ethanol (20 ml.) were heated at 170—180° for 5 hr. The *indazolone* (0·75 g.), m. p. 185—186°, separated on cooling, and a further crop (0·3 g.), m. p. 176—178°, was obtained by addition of water to the mother-liquors. Recrystallisation from ethanol containing a trace of aqueous sodium hydrogen carbonate gave pale-yellow prismatic needles, m. p. 186—187°. A sample prepared by alkaline degradation of compound (V) by Schofield and Simpson's procedure,[1] and a mixture of the two, had m. p. 186—187° (Found: C, 68·1; H, 4·4; N, 19·8.

Calc. for $C_{12}H_9ON_3$: C, 68·2; H, 4·3; N, 19·9%). Infrared analysis (in Nujol) showed the absence of a broad band at 2500—2700 cm.$^{-1}$ and the presence of strong bands at 3180 and 1655 cm.$^{-1}$, indicating, as with the 5-chloro-derivative, that the compound exists mainly in the enol form.

1-2′-*Pyridyl*-3-*indazolone*.—*o*-Hydrazinobenzoic acid (7·4 g.), 2-chloropyridine (5 g.), and ethanol (40 ml.) were heated together at 170—180° for 5 hr. The cooled product was treated with water (80 ml.), yielding crystals of 1-2′-*pyridyl*-3-*indazolone* (1·21 g.), pale-yellow needles (from methanol), m. p. 204—205° (Found: C, 68·6; H, 4·4; N, 19·9. $C_{12}H_9ON_3$ requires C, 68·2; H, 4·3; N, 19·9%), broad band (Nujol mull) between 2500 and 2700 cm.$^{-1}$, weak band at 1660 cm.$^{-1}$, $\lambda_{max.}$ (in methanol) (1 mg. per 100 ml.) 255 mμ (log ε 4·32, 4·25).

The author thanks Professor R. B. Woodward for helpful discussion, and Dr. J. M. Pryce and Mr. W. K. Thompson for the ultraviolet and infrared spectroscopic examinations.

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[*Received, February 6th*, 1959.]