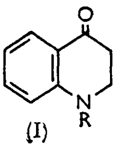
773. *The Structure and Properties of Certain Polycyclic Indolo- and Quinolino-derivatives. Part XIII.* The Cyclisation of Certain 4-Pyridyl- and 4-Quinolyl-hydrazones.*

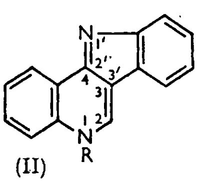
By Frederick G. Mann, A. F. Prior, and Trevor J. Willcox.

The final stage in the preparation of 4-pyridyl- and 4-quinolyl-hydrazine has been considerably improved. In preliminary work, the 4-pyridyl- and the 4-quinolyl-hydrazone of cyclohexanone have been cyclised to 6,7,8,9-tetrahydro-γ-carboline and its 3,4-benzo-derivative respectively. The main object of the investigation was the similar cyclisation of the corresponding hydrazones of 1,2,3,4-tetrahydro-1-methyl(and -1-phenyl)-4-oxoquinoline, which would have given derivatives of great structural interest, but this cyclisation could not be achieved.

The phenylhydrazone of 1,2,3,4-tetrahydro-4-oxo-1-phenylquinoline[1] (I; R = Ph) and of the 1-methyl analogue[2] (I; R = Me) readily undergo indolisation in boiling ethanolic hydrogen chloride to give the bright yellow 1-phenyl- (and 1-methyl)-ψ-indolo(3′,2′:3,4)-quinoline (II; R = Ph or Me). The latter combine vigorously with acids and with cold alkyl iodides to form salts of structure (III), where R′ represents the proton or the alkyl group, the stability of the system being enhanced by the consequent aromatisation of the pyrrole and the pyridine ring. Many compounds analogous to the oxo-quinolines (I) give similar derivatives.[3]



(I)



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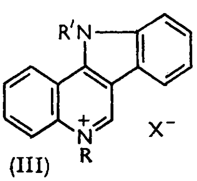

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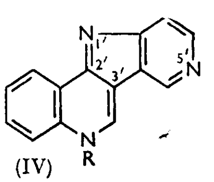

(IV)

We have, therefore, investigated the cyclisation of the 4-pyridylhydrazones of the 4-oxo-quinolines (I; R = Ph and Me), to determine whether this process would give compounds of structure (IV) analogous to the ψ-indoloquinolines (II; R = Ph or Me). Compounds such as (IV) would have great interest, because they could react with, for example, one equivalent of methyl iodide in two different ways, each of which would give considerably enhanced stability. Methyl iodide could react to give a compound analogous in structure to (III): alternatively the pyridine-$N_{(5')}$ of the compound (IV) might undergo quaternisation to give a cyanine iodide, which would be markedly stabilised by the canonical forms in which the positive charge was carried by the pyrrole-$N_{(1')}$ or the pyridine-$N_{(1)}$.

Indolisation of 4-pyridylhydrazones has apparently not been recorded, although the 2-pyridyl-[4] and the 2-methyl-3-pyridyl-hydrazone[5] of cyclohexanone undergo this reaction under more vigorous conditions than the corresponding phenylhydrazones require. A preliminary investigation of the cyclisation of cyclohexanone 4-pyridylhydrazone (V) was therefore undertaken. This hydrazone, when heated with zinc chloride at 240° for 10 min. and then extracted with hydrochloric acid, gave the chlorozincate of 6,7,8,9-tetrahydro-γ-carboline, which with aqueous sodium hydroxide furnished the crystalline base (VI). This compound is isomeric with the 1,2,3,4-tetrahydro-γ-carboline which

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* Part XII, I.G. Hinton and Mann, *J.*, 1959, 2043.

[1] Mann, *J.*, 1949, 2816.

[2] Braunholtz and Mann, *J.*, 1955, 381.

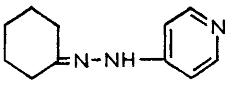
[3] Mann and Smith, *J.*, 1951, 1898; Almond and Mann, *J.*, 1952, 1870.

[4] Okuda and Robison, *J. Amer. Chem. Soc.*, 1959, **81**, 740.

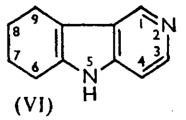
[5] Clemo and Holt, *J.*, 1953, 1313.

Robinson and Thornley[6] obtained by the reduction of γ-carboline with sodium and butan-1-ol.

Attempts similarly to cyclise tetrahydro-1-methyl-4-oxoquinoline 4-pyridylhydrazone (VII; R = Me) failed however. The hydrazone, when heated with ethanolic hydrogen chloride, or anhydrous zinc chloride, or boron trifluoride in acetic acid,[7] gave the hydrochloride, chlorozincate, and boron trifluoride complex of the unchanged hydrazone. Passage of hydrogen chloride over the molten hydrazone,[8] or treatment with hot acetic-sulphuric acid[9] or polyphosphoric acid,[10] left the hydrazone unaffected or considerably decomposed, and sulphuric acid gave the (?6-)sulphonic acid. Cyclisation of the hydrazone (VII; R = Ph) also failed: this hydrazone was much more readily hydrolysed by acids.



(V)



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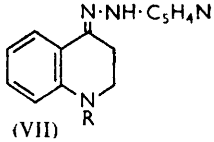
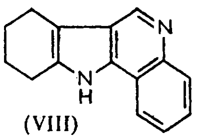


(VII)



(VIII)

It is noteworthy that similar attempts to indolise cyclohexane-1,2-dione bis-4-pyridylhydrazone either left the hydrazone unaffected or caused decomposition: the hydrazone sublimed when heated at low pressures but at atmospheric pressure decomposed with the formation of 4-aminopyridine. These results contrast strongly with the ready indolisation of cyclohexane-1,2-dione bisphenylhydrazone.[11]

The corresponding derivatives of 4-quinolylhydrazine were therefore investigated. Cyclohexanone 4-quinolylhydrazone with zinc chloride at 245° underwent cyclisation, and the product after considerable purification afforded 6,7,8,9-tetrahydro-3,4-benzo-γ-carboline (VIII).

1,2,3,4-Tetrahydro-1-methyl-4-oxoquinoline 4-quinolylhydrazone, m. p. 210°, was unaffected by zinc chloride at 200° and underwent considerable decomposition at higher temperatures: when it was rapidly heated with zinc chloride to 215° and then basified, the product afforded a crude orange-yellow sublimate, m. p. 370—380°, in insignificant yield. The hydrazone was hydrolysed by boiling ethanolic hydrogen chloride to the hydrazine.

Attempts to prepare compounds of type (IV) or their quinolino-analogues were therefore abandoned.

It is noteworthy that 4-pyridylhydrazine hydrochloride has previously been prepared by heating an ethanolic solution of 4-chloropyridine and hydrazine hydrate in a sealed tube,[12] and 4-quinolylhydrazine hydrochloride by boiling under reflux an aqueous-ethanolic solution of 4-chloroquinoline and hydrazine hydrate.[13] The former preparation is laborious and gives an impure product, while the latter gives a low yield. We find that both these hydrazine salts can readily be prepared pure and in high yield by boiling under reflux a propanolic solution of the 4-chloro-base and pure hydrazine hydrate.

The infrared spectrum of 4-quinolylhydrazine hydrochloride shows two bands, at 3170 and 3285 cm.$^{-1}$ respectively, which in relative intensities and spacing almost undoubtedly indicate an $-NH_2$ group: a shoulder at 3120 cm.$^{-1}$ in the former band may be due to the $=NH$ group. A strong rather broad band at 2790 cm.$^{-1}$, with a subsidiary maximum at 2810 cm.$^{-1}$, almost certainly indicates a $\equiv NH^+$ group. Hence salt formation has occurred on the quinolyl nitrogen atom.

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[6] Robinson and Thornley, *J.*, 1924, **125**, 2174.
[7] Snyder and Smith, *J. Amer. Chem. Soc.*, 1943, **65**, 2452.
[8] Robinson and Robinson, *J.*, 1918, **113**, 639.
[9] Clemo and Felton, *J.*, 1951, 677.
[10] Kissman, Farnsworth, and Witkop, *J. Amer. Chem. Soc.*, 1952, **74**, 3948.
[11] Mann and Willcox, *J.*, 1958, 1525.
[12] Koenigs, Weiss, and Zscharn, *Ber.*, 1926, **59**, 317.
[13] Schofield and Swain, *J.*, 1950, 394.

EXPERIMENTAL

M. p.s were determined from room temperature, except those for which the temperature of immersion is noted as (T.I.).

4-*Pyridylhydrazine Hydrochloride.*—A solution of 4-chloropyridine (12·6 g.) and pure hydrazine hydrate (4·9 g., 1·1 mols.) in propan-1-ol (40 c.c.) was boiled under reflux for 2 hr., the hydrochloride crystallising meanwhile. The mixture was cooled to 0°, and the hydrochloride, when collected, washed with propan-1-ol, and recrystallised from methanol, had m. p. 242—243°: a second crop, obtained from the methanolic mother-liquors by precipitation with ether, and then once recrystallised from methanol, had the same m. p. (Found: N, 29·0. Calc. for $C_5H_7N_3,HCl$; N, 28·9%). The total yield was 14·0 g., 85%. The hydrazine gave a benzaldehyde derivative, pale-grey needles, m. p. 200° (lit.,[12] pale yellow prisms, m. p. 195°).

Cyclohexanone 4-*Pyridylhydrazone* (V).—A solution of cyclohexanone (2 g.) in acetic acid (4 c.c.) was added to a solution of the above hydrochloride (3·2 g., 1·1 mols.) and crystalline sodium acetate (5·4 g.) in water (6 c.c.), which was boiled under reflux for 3 hr. and then poured into water (20 c.c.) and aqueous ammonia (*d* 0·880; 6 c.c.). After 1 hr. the colourless precipitated *hydrazone* (V) was collected, washed with water, and recrystallised from aqueous methanol (1 : 1 by vol.); it had m. p. 168—170° (darkening) (2·6 g., 70%) (Found: C, 69·7; H, 7·8. $C_{11}H_{15}N_3$ requires C, 69·9; H, 7·9%).

6,7,8,9-*Tetrahydro-γ-carboline* (VI).—An intimate mixture of the hydrazone (V) (2 g.) and powdered zinc chloride (6 g.) was heated in an oil-bath at 240° for 10 min., and the cold product was extracted with boiling water (40 c.c.) containing dilute hydrochloric acid (5 c.c.). The extract, on cooling, deposited the crystalline *chlorozincate* (2·8 g.), m. p. 275—276° (from very dilute hydrochloric acid), of the carboline (VI) (Found: C, 47·4; H, 4·6; N, 10·5. $2C_{11}H_{12}N_2,H_2ZnCl_4$ requires C, 47·6; H, 4·7; N, 10·2%).

An aqueous solution of this salt, when treated with an excess of aqueous ammonia, deposited a colourless amorphous precipitate. After 4 hr., this was collected, dissolved in aqueous methanol (3 : 1 by vol.), and set aside at 0° overnight. Colourless crystals, m. p. 223—224°, apparently of a *dihydroxydichlorozincate*, were then collected, washed with methanol, and dried at 70°/0·2 mm. [Found: C, 51·4; H, 4·9. $2C_{11}H_{12}N_2,H_2ZnCl_2(OH)_2$ requires C, 51·3; H, 5·1%].

A hot aqueous solution of the chlorozincate, when treated with a large excess of 10% aqueous sodium hydroxide, deposited the *carboline* (VI), which, after being set aside overnight, collected, and recrystallised from aqueous ethanol (1 : 4 by vol.), had m. p. 269—271°, increased to 270—272° after sublimation at 200°/0·1 mm. (Found: C, 77·1; H, 6·6; N, 16·5. $C_{11}H_{12}N_2$ requires C, 76·9; H, 7·0; N, 16·3%).

Dehydrogenation of the carboline with palladium–charcoal was briefly investigated without success.

1,2,3,4-*Tetrahydro*-1-*methyl*-4-*oxoquinoline* 4-*Pyridylhydrazone* (VII; R = Me).—A solution of the oxoquinoline (I; R = Me) (1·3 g.) in ethanol (12 c.c.) was added to a solution of 4-pyridylhydrazine hydrochloride (3·5 g., 3 mols.) and sodium acetate (9·7 g.) in 40% aqueous acetic acid (16 c.c.), which was boiled under reflux for 5 hr. and then poured into an excess of aqueous ammonia. The yellow gum which was deposited slowly solidified when repeatedly kneaded with hot water; recrystallised from aqueous methanol (1 : 4 by vol.) it gave the yellow *hydrazone* (VII; R = Me) (2 g., 95%), m. p. 181—182°, which darkened slowly on exposure to light (Found: C, 70·9; H, 6·6; N, 22·3. $C_{15}H_{16}N_4$ requires C, 71·3; H, 6·5; N, 22·2%).

A solution of the hydrazone in an excess of methyl iodide when set aside for 1 hr., or in methanolic methyl iodide when boiled under reflux for 1 hr. and cooled, deposited pale yellow crystals of the *monomethiodide*, m. p. 228—229° (from methanol) (Found: N, 14·4. $C_{16}H_{19}N_4I$ requires N, 14·25%). A solution of the hydrazone and methyl iodide in nitromethane, when similarly boiled, deposited the colourless *dimethiodide*, m. p. 202—203° (decomp.) (T.I. 190°) after crystallisation from methanol containing *ca.* 3% of water (Found: C, 38·3; H, 4·1; N, 10·5. $C_{17}H_{22}N_4I_2$ requires C, 38·2; H, 4·0; N, 10·45%).

Attempted Cyclisation of the Hydrazone (VII; R = Me).—(i) The yellow solution of the hydrazone (1 g.) in saturated ethanolic hydrogen chloride (10 g.) rapidly deposited the colourless crystalline hydrochloride, a sample of which had m. p. 182—184° (T.I. 170°), but being very deliquescent was not analysed. The mixture, when boiled under reflux for 5 hr., cooled, and basified with aqueous ammonia, deposited the hydrazone. The use of 2N-hydrochloric acid with heating for 1½ hr. gave the same result.

(ii) An intimate mixture of the hydrazone (0·4 g.) and zinc chloride (2 g.), when heated at

200° for 10 min., effervesced and formed a red liquid. The cold melt was extracted with a minimum of hot 10% hydrochloric acid, and the extract, on the addition of concentrated hydrochloric acid, deposited pale red tabular crystals of the *chlorozincate* of the hydrazone; after recrystallisation from dilute hydrochloric acid this had m. p. 320—322° (from room temperature), 327—330° (T.I. 312°) (Found: C, 38·3; H, 3·5; N, 12·3. $C_{15}H_{16}N_4,H_2ZnCl_4$ requires C, 39·3; H, 3·5; N, 12·2%. Low carbon values were obtained). Further similar recrystallisation gave cream-coloured needles, m. p. 314° (decomp.) (from room temperature), 318° (decomp.; T.I. 310°) (Found: C, 39·2; H, 3·8; N, 12·5%). The two crystalline products may be dimorphic forms, or may be structurally different, possibly in the position of the protons in the cation. A solution of the hydrazone in dilute hydrochloric acid, when added to concentrated aqueous zinc chloride, deposited the cream-coloured salt, m. p. and mixed m. p. 318° (decomp., T.I. 310°) after recrystallisation.

Fusion of the hydrazone with zinc chloride at 270° for 1 hr. gave the same result.

(iii) A 40% solution of boron trifluoride in acetic acid (15 c.c.) was added to one of the hydrazone (0·9 g.) in acetic acid (15 c.c.), which was then boiled under reflux for 1 hr., poured into water, and basified with aqueous ammonia. The lemon-yellow precipitate, when collected, washed, and recrystallised from 50% aqueous ethanol, afforded boron-containing needles (1·1 g.), m. p. 208—210°, insoluble in all the usual solvents. It was unaffected by boiling ethanolic ammonia or pyridine, but hot 10% aqueous sodium hydroxide liberated the original hydrazone, m. p. and mixed m. p. 181—182° (Found: C, 71·5; H, 6·4; N, 22·2%).

(iv) A solution of the hydrazone (0·2 g.) in concentrated sulphuric acid (5 c.c.) was heated at 130° for 10 min., cooled, poured on ice, and basified with ammonia. Long yellow needles of the monohydrated (?6-)*sulphonic acid*, m. p. 344—346° (decomp.), separated and were dried at 200°/0·2 mm. for 5 hr. (Found: C, 51·6; H, 5·25; N, 16·5. $C_{15}H_{16}O_3N_4S,H_2O$ requires C, 51·7; H, 5·45; N, 16·0%) The acid is insoluble in organic solvents but freely soluble in mineral acids and in warm 10% aqueous sodium hydroxide, being reprecipitated when such solutions are neutralised. Its infrared spectrum indicates that it is a zwitterion. The solution of the hydrazone in sulphuric acid was unaffected at room temperature, and at 180° underwent hydrolysis to water-soluble constituents.

1,2,3,4-*Tetrahydro*-4-*oxo*-1-*phenylquinoline* 4-*Pyridylhydrazone* (VII; R = Ph).—A solution of the oxoquinoline (1·76 g.) in ethanol (40 c.c.) was added to 4-pyridylhydrazine hydrochloride (4·64 g., 4 mols.) and hydrated sodium acetate (13 g., 12 mols.) in warm 40% aqueous acetic acid (30 c.c.), which was boiled under reflux for 6 hr., poured into an excess of dilute aqueous ammonia, and cooled to 0°. The precipitated *hydrazone*, when recrystallised from methanol, formed pale yellow plates (2·4 g., 95%), m. p. 212° (darkening) (Found: C, 76·9; H, 5·95; N, 17·7. $C_{20}H_{18}N_4$ requires C, 76·4; H, 5·8; N, 17·8%). The hydrazone forms a colourless *acetate*, m. p. 252° (decomp., T.I. 242°) (from methanol) (Found: C, 71·1; H, 6·1. $C_{20}H_{18}N_4,C_2H_4O_2$ requires C, 70·7; H, 5·95%), and a *monomethiodide*, yellow needles, m. p. 289° (decomp.; T.I. 275°) (from aqueous methanol). (Found: C, 55·2; H, 4·5; N, 12·4. $C_{21}H_{21}N_4I$ requires C, 55·4; H, 4·6; N, 12·3%): only this methiodide was formed when the hydrazone and methyl iodide was boiled in methanol or nitromethane for 30 min.

A mixture of the hydrazone and zinc chloride was heated at 200° until effervescence ceased, and on working up afforded the *chlorozincate* of the hydrazone, which on recrystallisation from water formed very pale pink crystals, melting indefinitely at 225—240° (decomp.) (Found: C, 45·9; H, 4·2; N, 10·2. $C_{20}H_{18}N_4,H_2ZnCl_4$ requires C, 45·9; H, 3·9; N, 10·6%).

Cyclohexane-1,2-*dione Bis*-4-*pyridylhydrazone*.—A solution of the dione (1·8 g.), 4-pyridylhydrazine hydrochloride (5·2 g., 2·2 mols.), and hydrated sodium acetate (12·0 g., 4 mols.) in ethanol (20 c.c.) was heated on a steam-bath under nitrogen for 90 min., cooled, and basified with aqueous ammonia. The precipitated *hydrazone*, when recrystallised from ethyl methyl ketone, formed yellow needles (3 g., 63%), m. p. 223—225°, which were dried at 120°/0·2 mm. for 6 hr. (Found: C, 62·0; H, 6·3; N, 26·25. $C_{16}H_{18}N_6,H_2O$ requires C, 61·8; H, 6·4; N, 26·9%). The hydrazone in ethanol readily gave a *dipicrate*, which after recrystallisation from ethanol melted slowly 130—160° (T.I. 80°) and 130—180° (T.I. 120°) (Found: C, 44·9; H, 3·3; N, 22·35. $C_{16}H_{18}N_6,2C_6H_3O_7N_3$ requires C, 44·7; H, 3·2; N, 22·3%). The hydrazone readily gave a colourless *dimethiodide*, m. p. 236—237° (decomp.) (Found: N, 14·5. $C_{18}H_{24}N_6I_2$ requires N, 14·5%).

The hydrazone when heated at atmospheric pressure gave a distillate of 4-aminopyridine, m. p. 158—161° (lit.,[14] 159—160°) (Found: C, 63·8; H, 6·6; N, 29·9. Calc. for $C_5H_6N_2$:

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[14] Leis and Curran, *J. Amer. Chem. Soc.*, 1945, **67**, 79.

C, 63·8; H, 6·4; N, 29·8%), which gave a *picrate*; precipitated from ethanolic solution and recrystallised from water, this had m. p. 216—218° (lit.,[15] 215—216°, without analytical identification) (Found: C, 41·1; H, 2·4. $C_5H_6N_2,C_6H_3O_7N_3$ requires C, 40·9; H, 2·8%).

4-*Quinolylhydrazine Hydrochloride*.—Pure hydrazine hydrate (4·4 g., 1·1 mols.) was added to a solution of 4-chloroquinoline (13 g.) in propan-1-ol (40 c.c.), which was boiled under reflux for 90 min. and cooled. The crystalline hydrochloride was collected, washed with propanol, and dried. Hydrogen chloride was passed through the filtrate to precipitate a second crop of the hydrochloride (total yield, 13·5 g., 87%), m. p. 311° (decomp.) (lit.,[13] 300—301°) (Found: C, 55·5; H, 5·4. Calc. for $C_9H_9N_3$,HCl; C, 55·3; H, 5·1%).

Cyclohexanone 4-*Quinolylhydrazone*.—Cyclohexanone (0·91 g.), 4-quinolylhydrazine hydrochloride (2·0 g., 1·1 mols.), and hydrated sodium acetate (2·52 g., 3 mols.) were added in turn to a mixture of water (6 c.c.) and acetic acid (4 c.c.), which was heated in nitrogen under reflux on a steam-bath for 1 hr., some needles (presumably the hydrazone acetate) being deposited. The cold mixture was basified with dilute ammonia, giving a yellow emulsion which rapidly gave the crystalline *hydrazone* (2·0 g., 90%), m. p. 144—145° after crystallisation from 50% aqueous ethanol (Found: N, 17·5. $C_{15}H_{17}N_3$ requires N, 17·6%).

The addition of hydrogen chloride to the hydrazone, each in ethanolic solution, precipitated the colourless *hydrochloride*, m. p. 329—330° (from ethanol) (Found: N, 15·4. $C_{15}H_{17}N_3$,HCl requires N, 15·2%).

6,7,8,9-*Tetrahydro*-3,4-*benzo*-γ-*carboline* (VIII).—An intimate mixture of this hydrazone (1·5 g.) and zinc chloride (6 g.) was inserted in an oil-bath at 245°, and vigorously stirred until the temperature of the melt attained 235°, and then removed. The yellow glassy product was dissolved in hot dilute hydrochloric acid (30 c.c.) and basified with dilute ammonia. The crude pale yellow carboline was sublimed at 220°/0·2 mm. For further purification, a solution of the carboline in benzene (*ca.* 1 l.) was passed down an alumina column, and afforded an upper brown band and a lower colourless band which was strongly fluorescent in ultraviolet light. The latter band was extracted with methanol and afforded colourless crystals, which were recrystallised from diethyl carbonate and finally sublimed as before to remove tenaciously held solvent. The *carboline* had m. p. 292—293° (Found: C, 80·9; H, 6·6; N, 12·5. $C_{15}H_{14}N_2$ requires C, 81·0; H, 6·35; N, 12·6%): it gave a *picrate*, yellow needles (from ethanol containing 5% of acetone), m. p. 263—266° (T.I. 257°) (Found: C, 55·9; H, 3·7; N, 15·6. $C_{15}H_{14}N_2,C_6H_3O_7N_3$ requires C, 55·9; H, 3·8; N, 15·5%).

A mixture of the carboline and palladium–charcoal, when heated at 250° for 2 hr., gave a very small amount of a colourless sublimate, which was remixed with the charcoal and heated at 250°/0·01 mm., giving a sublimate, m. p. 323—325°, depressed by *ca.* 20° on admixture with the original carboline. This sublimate was insufficient for identification, but it was probably 3,4-benzo-γ-carboline, for which Clemo and Perkin [16] give m. p. " greater than 320°."

1,2,3,4-*Tetrahydro*-1-*methyl*-4-*oxoquinoline* 4-*Quinolylhydrazone*.—The oxoquinoline (I; R = Me) (0·8 g.), 4-quinolylhydrazine hydrochloride (2·0 g., 2 mols.), and hydrated sodium acetate (5 g.) were added to 40% aqueous acetic acid (20 c.c.), which was boiled for 4 hr., cooled, and poured into dilute ammonia. The precipitated solid was collected, washed, and dissolved in acetone, from which, on the careful addition of water, the *hydrazone* separated as yellow needles, m. p. 210° (Found: C, 76·0; H, 6·1; N, 18·9. $C_{19}H_{18}N_4$ requires C, 75·7; H, 6·0; N, 18·6%). The hydrazone in ethanolic solution gave an orange *picrate*, m. p. 232—234°, after collection and washing with hot methanol: it was insoluble in the usual solvents (Found: N, 18·7. $C_{19}H_{18}N_4,C_6H_3O_7N_3$ requires N, 18·5%).

This hydrazone when heated with zinc chloride at 200° was recovered unchanged but at higher temperatures decomposed considerably. A mixture of the hydrazone (0·3 g.) and zinc chloride (1·2 g.) was immersed in a bath at 255° and stirred vigorously until the temperature reached 215°: it was then cooled, digested with dilute hydrochloric acid (10 c.c.), and basified with ammonia. The orange-red deposit when heated at *ca.* 200°/0·01 mm. gave an orange-yellow sublimate, m. p. 370—380°, in too minute yield for identification.

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UNIVERSITY CHEMICAL LABORATORY, CAMBRIDGE. [*Received, June 3rd*, 1959.]

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[15] Koenigs, Kinne, and Weiss, *Ber.*, 1924, **57**, 1175.
[16] Clemo and Perkin, *J.*, 1924, **125**, 1618.