411. *The Structure and Properties of Certain Polycyclic Indolo- and Quinolino-derivatives. Part XII.*[1] *1 : 2-Dihydro-2-methylquinolino(3′ : 2′-3 : 4)*iso*quinoline and its Derivatives.*

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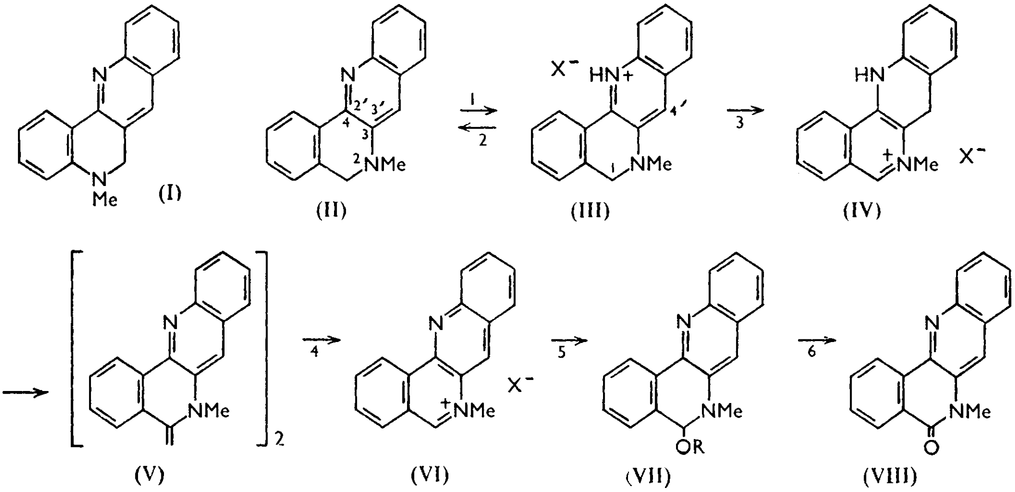
1 : 2-Dihydro-2-methylquinolino(3′ : 2′-3 : 4)*iso*quinoline has been prepared by the condensation of 1 : 2 : 3 : 4-tetrahydro-2-methyl-4-oxo*iso*quinoline and *o*-aminobenzaldehyde. The properties of this base, and particularly the isomerisation of its salts and the products obtained from these salts, have been studied: the base undergoes atmospheric oxidation, both in the solid state and readily in solution, to the corresponding cyclic amide.

The properties of this base, and those of the isomeric 1 : 2-dihydro-1-methylquinolino(3′ : 2′-3 : 4)quinoline studied earlier, show some similarities and also some marked differences.

THE properties of the yellow 1 : 2-dihydro-1-methylquinolino(3′ : 2′-3 : 4)quinoline (I), particularly the formation of its purple monohydrochloride, the conversion of the latter by hot acid into the yellow monohydrochloride of the isomeric 1 : 4′-dihydro-base, the thermal conversion of this isomer into the original base (I), and the ready atmospheric oxidation of both isomers to the cream-coloured 1 : 2-dihydro-1-methyl-2-oxoquinolino-(3′ : 2′-3 : 4)quinoline, have been extensively studied.[2]



Reagents: 1, Cold HCl. 2, Aq. NaOH. 3, Hot HCl. 4, Acids. 5, NaOH–ROH. 6, O_2.

Our recent synthesis of 1 : 2 : 3 : 4-tetrahydro-2-methyl-4-oxo*iso*quinoline[3] has now enabled us to condense this keto-amine with *o*-aminobenzaldehyde to form the yellow 1 : 2-dihydro-2-methylquinolino(3′ : 2′-3 : 4)*iso*quinoline (II), which is isomeric with the base (I), and to study its reactions under comparable conditions.

The structure of the yellow base (II), m. p. 92—93°, is shown by its synthesis, by its analysis and molecular weight, and by its infrared spectrum which shows a sharp moderately strong band at 2780 cm.$^{-1}$ (indicating an =NMe group[4]) but gives no indication of an =NH group. It sublimes without decomposition at 82°/0·002 mm., but undergoes

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[1] Part XI, Braunholtz and Mann, *J.*, 1958, 3377.

[2] *Idem, J.*, 1955, 381; 1958, 3368.

[3] I. G. Hinton and Mann, *J.*, 1959, 599.

[4] Braunholtz, Ebsworth, Mann, and Sheppard, *J.*, 1958, 2780.

atmospheric oxidation readily in cold ethanolic solution and also in the solid state (see p. 2045): consequently its preparation and recrystallisation should be conducted under nitrogen. It acts apparently as a monoacidic base, for the addition of hydrochloric or hydrobromic acid to its cold acetone solution precipitated the red mono-hydrochloride and -hydrobromide, which when treated with aqueous sodium hydroxide regenerated the base (II). These salts have the structure (III), for the infrared spectrum of the hydrochloride has a broad band centred at 2610 cm.$^{-1}$ indicating the $\equiv NH^+$ group, and a band of moderate strength at 2780 cm.$^{-1}$ indicating the $=NMe$ group.

When the hydrochloride (III; $X = Cl$) in concentrated hydrochloric acid was boiled, isomerisation to the golden-yellow quaternary chloride (IV; $X = Cl$) occurred. The infrared spectrum of the corresponding quaternary perchlorate showed a sharp band at 3350 cm.$^{-1}$ indicating an $=NH$ group, but gave no evidence of an $=NMe$ or $\equiv NH^+$ group.

Adding an excess of aqueous sodium hydroxide to an aqueous solution of the chloride (IV; $X = Cl$) gave a purple precipitate which, however, became yellow when the mixture was stirred in contact with air. This precipitate, when isolated and purified, afforded a bright yellow base, m. p. 214°. The structure of this base remains uncertain, but the evidence discussed below indicates that it is probably (V), being thus equivalent to two molecules of the base (II) which by loss of hydrogen at the 1-position have become linked by a double bond.

FIG. 1. *Ultraviolet spectra of the base* (V) (*A*) *in ethanol and* (*B*) *in ethanol containing* 1 *drop of concentrated hydrochloric acid, and* (*C*) *of the perchlorate* (VI; $X = ClO_4$) *in ethanol.*

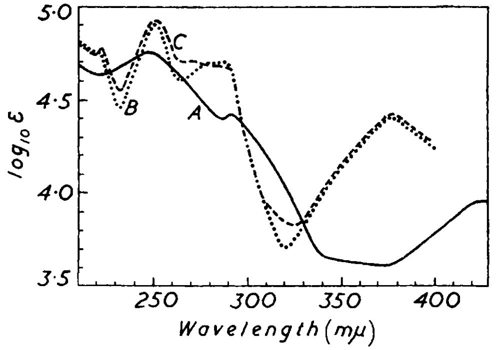
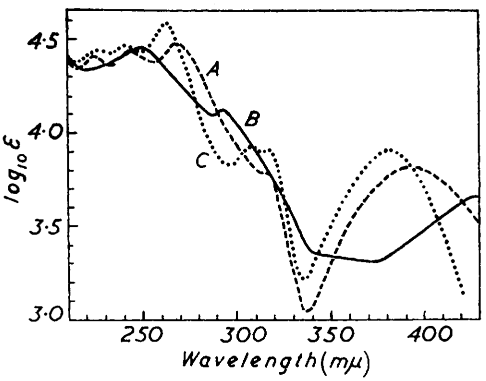


FIG. 2. *Ultraviolet spectra of* (*A*) *the base* (II), (*B*) *the base* (V), *and* (*C*) *the base* (VII; $R = Et$). *For strict comparison with* (*A*) *and* (*C*), *the curve* (*B*) *is plotted for values of* $\log_{10} \varepsilon/2$, *since the intensities are approximately the sum of those of the two halves of the molecule acting independently.*



The base (V) is very sensitive to acids, which convert it into pale yellow quaternary salts of structure (VI). The rapid and fundamental change in structure caused by acidification of the base (V) is shown (Fig. 1) by the marked difference in the ultraviolet absorption spectra of the base (*A*) in ethanol alone and (*B*) in ethanol to which one drop of concentrated hydrochloric acid has been added. The spectrum in the acidified solution is almost identical with that (*C*) of the pure crystalline perchlorate (VI; $X = ClO_4$) obtained similarly by acidification of the base (V). The structure of the perchlorate is confirmed by its infrared spectrum, which shows the absence of $=NH$, $=NMe$, and $\equiv NH^+$ groups, and by its ultraviolet spectrum (Fig. 1), which shows the intense absorption in the 250—260 mμ region which is typical of many extended polycyclic aromatic systems.

A suspension of the perchlorate (VI; $X = ClO_4$) in aqueous sodium hydroxide, when treated with hot ethanol to give complete dissolution, deposited on cooling the yellow 1-ethoxy-base (VII; $R = Et$), m. p. 159—160°, which was stable in boiling ethanolic solution, from which it could be recrystallised: the addition of perchloric acid to this solution, however, rapidly regenerated the perchlorate (VI; $X = ClO_4$). The structure of the base is shown by the infrared spectrum, which gives no evidence for an -OH or =CO group, and the oxygen must therefore be present in a C-O-C unit: the =NMe group appears as a weak band at 2805 cm.$^{-1}$, but as a stronger and sharper band at 2820 cm.$^{-1}$ in the homologue (VII; R = Me). The ultraviolet spectrum of the base (VII; R = Et) is closely similar to that of the base (II) (Fig. 2).

The base (VII; R = Et) is of course the *O*-ethyl derivative of the ψ-base corresponding to the quaternary base (VI; X = OH). This ready reaction of the ψ-base with alcohols to form an ether and with acids to re-form the normal salts represents the usual behaviour of such bases.

A cold ethanolic solution of the initial base (II), when allowed to evaporate spontaneously, underwent oxidation to the colourless 1-oxo-compound (VIII). Fine crystals of the base (II) on exposure to air also underwent this rapid oxidation. The bases (V) and (VII) gave indication of this atmospheric oxidation very much more slowly, but were rapidly oxidised to the compound (VIII) by a warm acetone solution of potassium permanganate. The infrared spectrum of the compound (VIII) shows a band at 1642 cm.$^{-1}$ typical of the amide-carbonyl group; the normal band characteristic of the =NMe group is of course not produced by the CO·NMe unit.[4] The compound (VIII) is weakly basic, and its salts dissociated on attempted recrystallisation. This ready oxidation of the base (II) is thus strictly analogous to that of the base (I), which gives the isomeric 2-oxo-derivative.

The evidence which indicates the structure (V) for the yellow base, m. p. 214°, may now be summarised. (*a*) Analysis and molecular weight determinations: the low solubility in boiling solvents and the small elevation of b. p. precluded accurate determinations but the values for the molecular weight uniformly approached that required for formula (V). (*b*) The ready oxidation of the bases (II), (V), and (VII; R = Me or Et) to the 1-oxo-derivative (VIII) indicate that these bases can differ only at the 1-position, where the atoms or groups attached must, therefore, be reasonably susceptible to replacement by oxygen. (*c*) The infrared spectra of the above bases are very closely similar, except that the spectrum of the base (V) does not show the band characteristic of the =NMe group. This is not surprising, for the band is shown only when the lone pair of electrons on the nitrogen atom is unaffected by neighbouring groups,[4] and the long conjugated chain in the structure (V) might induce some electronic drift from the nitrogen atoms in the =NMe groups. Alternatively, the steric crowding about the central double bond may force the two halves out of coplanarity, which might also affect the nitrogen atom. (*d*) The ultraviolet spectrum of the base (V) has a general similarity to those of the bases (II) and (VII; R = Et), more particularly in the 210—340 mμ region (Fig. 2). (*e*) Each half of the molecule (V) can be regarded systematically as the major portion of an anhydro-base, and the action of acids in splitting this dual system so readily into two molecules of the corresponding salt (VI) would therefore be expected.

The initial purple material produced by the addition of sodium hydroxide to the chloride (IV; X = Cl) was not investigated because of its rapid aerial oxidation. The formation of a base of structure (V) under these circumstances must be a complex process, but quaternary *iso*quinolinium salts are known to give many complex reactions in the presence of alkali and air.[5]

The action of methyl iodide on the above bases may be briefly noted. The base (II) when boiled with an excess of methyl iodide gave pale yellow needles of composition $C_{19}H_{19}ON_2I$ or $C_{19}H_{21}ON_2I$, the structure of which has not been elucidated. The mother-liquor yielded small quantities of the base (VII; R = Me) and also of the 1-oxo-compound (VIII), undoubtedly formed by direct oxidation of the base (II). The base (V) was recovered in high yield after its solution in methyl iodide had been boiled for 6 hours, the

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[5] Cf. Gensler, " Heterocyclic Compounds," ed. by Elderfield, Wiley, New York, 1952, Vol. IV, p. 469.

low reactivity of the =NMe groups being caused probably by steric hindrance. When the base in methyl iodide was heated at 100° for 7 hours, it deposited a crude iodide which furnished a pure yellow perchlorate of composition $C_{19}H_{17-19}O_5N_2Cl$, which has not been identified. The base (VII; R = Me) when boiled in methanolic methyl iodide yielded the iodide (VI; X = I) and the oxo-compound (VIII).

The comparative properties of the isomeric bases (I) and (II) can now be summarised. The conversion of the base (II) by cold hydrochloric acid into the hydrochloride (III; X = Cl) is identical in type with that shown by the base (I). The action of hot hydrochloric acid on the salt (III; X = Cl) is to cause migration of a hydrogen atom to the 4′-position, as in the previous series, but this atom now has to come from the 1-position, with consequent aromatisation of the pyridine ring and the formation of a quaternary chloride, in contrast to the tertiary amine hydrochloride in the earlier series. The base (II), being structurally unable to undergo a strict allylic transformation, cannot exist in an isomeric form, and in this respect differs markedly from the base (I). The stages represented by the compounds (V), (VI), and (VII), being determined specifically by the *iso*quinoline ring, have no parallel in derivatives of the base (I). The close analogy returns, however, at the final oxidation stage (VIII), which is again identical in type with the isomeric oxidation product of the base (I).

One further significant difference arises. The yellow colour of the base (I) and the deep red colour of its salts (corresponding in type to III) can be readily explained by the nature of the canonical contributions of the resonance hybrid of these compounds.[2] A similar explanation of colour cannot be applied to the yellow base (II) and its red salts (III), owing to the " blocking " effect of the methylene group between the =NMe group and the *o*-phenylene ring. Moreover in the case of the salts, it must be borne in mind that the production of marked colour by the addition of one proton to a diamine, owing to the resonance of the cation thus formed, is almost invariably dependent on the nitrogen atoms' being joined by an odd number of carbon (or other) atoms. This requirement is met in the base (I) but is absent in the isomeric base (II). It is clear that the base (II) can be added to the other diamines of comparable structure recently discussed by Murrell,[6] all of which form salts whose marked colour cannot be explained by classical or resonance theories, but for which Murrell has suggested an explanation based on molecular-orbital considerations.

An attempt to prepare the 4′-carboxylic acid of the base (II), by the Pfitzinger reaction (involving isatin in hot alkaline solution) from tetrahydro-2-methyl-4-oxo*iso*quinoline, was unsuccessful. No decisive product was isolated after prolonged heating of the reaction mixture under nitrogen, and the reactants were recovered after milder conditions had been employed.

EXPERIMENTAL

Consistent m. p.s of certain compounds were obtained only by the use of evacuated capillary tubes, noted as (E.T.), the immersion temperature if above room temperature being denoted (I.T.).

o-Aminobenzaldehyde was prepared by Mann and Wilkinson's modification [7] of Smith and Opie's method.[8]

1 : 2-*Dihydro*-2-*methylquinolino*(3′ : 2′-3 : 4)iso*quinoline* (II).—A solution of *o*-aminobenzaldehyde (4·5 g.) in ethanol (40 c.c.) was treated in turn with tetrahydro-2-methyl-4-oxo*iso*quinoline hydrochloride (7 g., 1 mol.) and 10% aqueous sodium hydroxide (32 c.c., 4 mols.), and the solution was set aside under nitrogen overnight. After *ca.* 7 hr. a dark yellow oil separated and later crystallised. The crystals, when both collected and recrystallised from ethanol under nitrogen, gave the iso*quinoline* (II), yellow needles, m. p. 92—93° (E.T.) (Found: C, 83·3; H, 6·0%; *M*, ebullioscopic in 0·702% acetone solution, 220; in 0·656% ethanolic solution, 230. $C_{17}H_{14}N_2$ requires C, 82·9; H, 5·7%; *M*, 246).

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[6] Murrell, *J.*, 1959, 296.
[7] Mann and Wilkinson, *J.*, 1957, 3346.
[8] Smith and Opie, *Org. Synth.*, 1948, **28**, 11.

The addition of dilute hydrochloric acid to an acetone solution of the base deposited the bright red *hydrochloride* (III; X = Cl), m. p. 278° (I.T., 270°) without recrystallisation (Found: C, 71·1; H, 5·4; N, 9·5. $C_{17}H_{14}N_2$,HCl requires C, 72·2; H, 5·3; N, 9·9%). The *hydrobromide* (III; X = Br), prepared by adding 45% hydrobromic acid to the ethanolic base, formed dull red crystals (Found: C, 62·3; H, 4·8; N, 8·6. $C_{17}H_{14}N_2$,HBr requires C, 62·4; H, 4·6; N, 8·6%). The red insoluble *chloroplatinate*, when collected, washed with ethanol, and dried, charred gradually from 120° (Found: C, 45·1; H, 3·4; Pt, 21·3. $2C_{17}H_{14}N_2,H_2PtCl_6$ requires C, 45·2; H, 3·4; Pt, 21·6%).

Picric acid, when added to the base (II), each in ethanolic solution, precipitated a bright red picrate which when recrystallised from ethanol containing a small quantity of picric acid, gave a mixture of yellow and red crystals, m. p. 175—185°, which could not be satisfactorily separated and identified.

A cold aqueous solution of the hydrochloride (III; X = Cl), when treated with aqueous sodium hydroxide, deposited the base (II).

1′ : 4′-*Dihydro*-2-*methylquinolino*(3′ : 2′-3 : 4)iso*quinolinium Chloride* (IV; X = Cl).—A suspension of the base (II) (2·5 g.) in concentrated hydrochloric acid (100 c.c.) was boiled under reflux until the clear red solution, which had become paler, suddenly deposited a thick suspension of orange crystals. The mixture was set aside for 48 hr., and the *chloride* (IV; X = Cl), when collected from the yellow solution and recrystallised from 50% aqueous ethanol, formed golden-yellow crystals, m. p. 288° (Found: C, 72·1; H, 5·3; N, 9·8. $C_{17}H_{15}N_2Cl$ requires C, 72·2; H, 5·3; N, 9·9%). The perchlorate (IV; X = ClO_4), obtained by the addition of 60% perchloric acid to the hot ethanolic solution of the chloride, and recrystallised from aqueous ethanol, had m. p. 270° (I.T. 260°).

Bi-[1 : 2-*dihydro*-2-*methylquinolino*(3′ : 2′-3 : 4)iso*quinol*-1-*ylidene*] (V).—A large excess of 10% aqueous sodium hydroxide was added to a stirred aqueous solution of the chloride (IV; X = Cl). The purple precipitate became yellow when it was near the surface of the solution, and the mixed product was then twice extracted with ether. The deep-maroon ethereal extract was washed with water and diluted with ethanol, charcoal added, and the ether removed. The residual ethanolic solution, when boiled and filtered, was deep yellow and on cooling deposited bright yellow plates of the *base* (V), m. p. 214° (E.T., I.T., 100°) after crystallisation from ethanol (Found: C, 82·4; H, 5·9; N, 11·2%; *M*, in boiling 0·471% acetone solution, 430; in 0·636% solution, 420; in 0·648% ethyl methyl ketone solution, 400. $C_{34}H_{24}N_4$ requires C, 83·5; H, 5·0; N, 11·5%; *M*, 488. Low carbon but satisfactory hydrogen values were obtained by using normal combustion temperatures: higher temperatures gave rather better carbon values but, as usual, increased the hydrogen values).

2-*Methylquinolino*(3′ : 2′-3 : 4)iso*quinolinium Perchlorate* (VI; X = ClO_4).—A warm ethanolic solution of the base (V), when treated dropwise with 60% aqueous perchloric acid and then cooled, deposited the crude red *perchlorate* (VI; X = ClO_4) which after recrystallisation from 50% aqueous ethanol formed pale yellow needles, m. p. 310—312° (E.T.) (Found: C, 58·6; H, 4·0; N, 8·0. $C_{17}H_{13}O_4N_2Cl$ requires C, 59·2; H, 3·8; N, 8·1%). The similar use of dilute sulphuric acid gave the *hydrogen sulphate* (VI; X = HSO_4), pale yellow crystals, m. p. 307—309° (effervescence) (E.T., I.T. 300°) (from aqueous ethanol) (Found: C, 59·3; H, 4·4; N, 8·1. $C_{17}H_{14}O_4N_2S$ requires C, 59·6; H, 4·1; N, 8·2%). The addition of dilute hydrochloric acid to an acetone solution of the base (V) deposited the crude chloride (VI; X = Cl), for which no suitable solvent for crystallisation was found. All these salts had a marked sternutatory action.

1-*Ethoxy*-1 : 2-*dihydro*-2-*methylquinolino*(3′ : 2′-3 : 4)iso*quinoline* (VII; R = Et).—A suspension of the perchlorate (VI; X = ClO_4) in warm 10% aqueous sodium hydroxide was diluted with sufficient hot ethanol to give a clear solution, which was then cooled and extracted with ether. The ethereal extract was diluted with ethanol, charcoal added, and the ether removed. The residual solution, when boiled under nitrogen, filtered and cooled, deposited the 1-*ethoxy-compound* (VII; R = Et), bright yellow crystals, m. p. 159—160° (E.T.) after four recrystallisations from ethanol under nitrogen and drying at 40°/0·1 mm. in nitrogen (Found: C, 78·6; H, 6·3; N, 9·5%; *M*, in boiling 0·732% ethanolic solution, 300. $C_{19}H_{18}ON_2$ requires C, 78·6; H, 6·2; N, 9·6%; *M*, 290). An ethanolic solution of this base, when treated with perchloric acid, deposited the perchlorate (VI; X = ClO_4), m. p. and mixed m. p. 310° (E.T.).

Oxidation to 1 : 2-*Dihydro*-2-*methyl*-1-*oxoquinolino*(3′ : 2′-3 : 4)iso*quinoline* (VIII).—(*A*) An ethanolic solution of the base (II) was allowed to evaporate to dryness on a clock-glass at room temperature during 24 hr. The brownish-yellow residue, when recrystallised from ethanol, sublimed at *ca.* 200°/0·1 mm., and again recrystallised, afforded the 1-*oxo-derivative* (VIII), colourless plates, m. p. 219—220° (Found: C, 78·2; H, 4·5; N, 11·0. $C_{17}H_{12}ON_2$ requires C, 78·4; H, 4·6; N, 10·8%). The pure powdered crystalline base (II) on exposure to air becomes dull yellowish-brown in *ca.* 2 hr. as this oxidation proceeds.

(*B*) Potassium permanganate was added to the base (V), each in warm acetone solution, until decolorisation of the former ceased. The solvent was evaporated and the residue extracted with ether. Removal of the ether left a residue of the compound (VIII), m. p. and mixed m. p. 217—220° after purification as before.

(*C*) A similar result was obtained when the base (VII; R = Et) was thus oxidised.

The onset of atmospheric oxidation of the crystalline bases (V) and (VII; R = Et) at room temperature is revealed only by their colours, which very slowly become duller and darker.

An ethereal solution of the base (VIII) when treated with hydrogen chloride deposited the hydrochloride: an ethanolic solution of the base, with perchloric acid, deposited the perchlorate. Both these yellow salts dissociated on attempted recrystallisation.

Action of Methyl Iodide.—(A) *The base* (II). A solution of this base in an excess of methyl iodide was boiled under reflux in nitrogen for 4 hr., pale yellow crystals separating from the orange solution. The crystals, when collected from the cold mixture and recrystallised from methanol, formed very pale yellow needles, m. p. 140—141° (effervescence) (E.T., I.T. 115°) (Found: C, 54·8; H, 4·8; N, 7·0. $C_{19}H_{19}ON_2I$ requires C, 54·6; H, 4·6; N, 6·7. $C_{19}H_{21}ON_2I$ requires C, 54·3; H, 5·0; N, 6·7%). The infrared spectrum showed a band caused by an $-$OH or =NH group. A methanolic solution of this compound with perchloric acid gave an almost colourless *perchlorate*, m. p. 230—233° (E.T., I.T. 220°) (Found: C, 58·7; H, 5·1; N, 7·3. $C_{19}H_{19}O_5N_2Cl$ requires C, 58·4; H, 4·9; N, 7·2. $C_{19}H_{17}O_5N_2Cl$ requires C, 58·7; H, 4·4; N, 7·2%).

The methyl iodide mother-liquor was treated with much ether to precipitate more crude methiodide, and was then filtered and diluted with a small volume of methanol, and the ether was removed. The methanolic solution, when boiled (charcoal), filtered, and cooled, deposited a yellow oil which solidified. Fractional crystallisation of the solid gave (*a*) the 1-oxo-compound (VIII), colourless plates, m. p. 220° (E.T., I.T. 115°), mixed m. p. 222—223° (E.T., I.T. 205°), and (*b*) the 1-*methoxy-compound* (VII; R = Me), yellow crystals, m. p. 111—112° (E.T., I.T. 90°) (Found: C, 78·2; H, 5·8; N, 10·1. $C_{18}H_{16}ON_2$ requires C, 78·2; H, 5·8; N, 10·1%). A methanolic solution of this compound treated with perchloric acid gave the perchlorate (VI; X = ClO_4). The identity of the 1-methoxy-base (VII; R = Me) was confirmed by its preparation as yellow crystals, m. p. 111—113°, by the addition of 10% aqueous sodium hydroxide to a methanolic solution of the perchlorate (VI; X = ClO_4).

(B) *The base* (V). The base in methyl iodide solution, when boiled under reflux in nitrogen for 6 hr., deposited a trace of a reddish solid, but was otherwise unaffected. When the original solution was heated in a sealed tube under nitrogen at 100° for 7 hr., it deposited blackish-brown crystals, a solution of which in boiling methanol (charcoal) gave a yellow solution. Addition of perchloric acid deposited bright yellow crystals, m. p. 252° (effervescence) (E.T.) after three crystallisations from methanol (Found: C, 58·3; H, 4·5; N, 7·2%). Although the composition of this *perchlorate* is almost identical with that of the above perchlorate, m. p. 230—233°, the non-identity of the two salts is shown by their colour and their m. p.s. The infrared spectrum of the perchlorate, m. p. 252°, did not show a band corresponding to an $-$OH or =NH group.

(C) *The base* (VII; R = Me). A solution of this base in methanolic methyl iodide was boiled under reflux in nitrogen for 3 hr., cooled, and poured into much ether, the golden-yellow powder which separated being then collected. The yellow solution when worked up as above afforded the 1-oxo-compound (VIII), m. p. 221—223° (E.T.). The yellow powder when recrystallised from methanol (charcoal) gave the iodide (VI; X = I), m. p. 265° (E.T., I.T. 120°), which in turn gave the perchlorate (VI; X = ClO_4), m. p. 302—305° (E.T.)

The base (VII; R = Me) when treated in ethanolic solution with hydriodic acid also gave the iodide (VI; X = I), m. p. alone and mixed with the above sample, 268—275° (E.T., I.T. 215°): this iodide in turn gave the perchlorate (VI; X = ClO_4), m. p. and mixed m. p. 303° (E.T., I.T. 280°).

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