256. ω-Halogenomethyl-pyridines, -quinolines, and -isoquinolines. Part I. Preparation.

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In order to extend the availability of ω-mono-, -di-, and -tri-halogeno-derivatives of methyl-pyridines, -quinolines, and -*iso*quinolines, ω-chlorination and bromination in acetic acid–sodium acetate mixtures (cf. Koenigs, *Ber.*, 1898, **31**, 2364; Hammick, *J.*, 1923, **123**, 2882; 1926, 1302) has been carried out in a number of new instances (*e.g.*, γ-picoline, 2 : 4-dimethylquinoline, and *N*-methyl-lepidinium iodide). ω-Monohalogeno-derivatives of 3-methylquinoline, lepidine, 1-methyl*iso*quinoline, and 3-methyl*iso*quinoline have been prepared from the corresponding alcohols. Improved methods for the reduction of the ωωω-trihalogeno-compounds to di- and mono-derivatives have been worked out, and the use of the monohalogeno-derivatives illustrated in typical reactions with Grignard reagents, acetoacetic ester, and malonic ester.

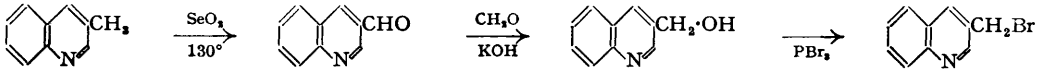
There is apparently no recorded example of chlorination or bromination in the side chain of methyl-pyridines, -quinolines, and -*iso*quinolines by the standard procedures (free halogen in carbon disulphide or acetic acid, etc.). Koenigs (*Ber.*, 1898, **31**, 2364) succeeded, however, in producing ωωω-tribromo-8-nitrolepidine by the action of bromine in acetic acid containing sodium acetate; attempts to obtain ωωω-tribromolepidine by this procedure failed. Subsequently the ω-chlorination and bromination of quinaldine, the ω-chlorination of α-picoline (it has not been found possible to bring about direct ω-bromination of the picolines), the ω-bromination of 5- and 8-nitro-quinaldine and of 2-methylquinoxaline and 9-methylphenanthridine, and the bromination of the 2-methyl group in 2 : 3-dimethyl- and 2 : 6-dimethyl-quinoline were accomplished in acetic acid containing sodium acetate (Hammick, *J.*, 1923, **123**, 2882; 1926, 1302; Dyson and Hammick, *J.*, 1939, 781; Bennett and Willis, *J.*, 1928, 1960; Brown, *J.*, 1949, 2577; Brown and Hammick *J.*, 1950, 628). It was suggested (Dyson and Hammick, *loc. cit.*) that the function of the sodium acetate is to " buffer " the reaction by removing halogen acid as it is formed. We shall, however, produce evidence in a later communication that the process involved is most likely a base-catalysed halogenation, the acetate ion being the base.

The ω-tribromination of quinaldine is readily accomplished in acetic acid–sodium acetate mixture in almost quantitative yield (Hammick, *loc. cit.*, 1923); α-picoline is equally easily trichlorinated, but it is necessary to fractionate the product (Dyson and Hammick, *loc. cit.*). In none of these cases is it possible to control the halogenation and to produce mono- and di-halogenated products directly, the obvious inference being that progressive ω-substitution

increases the rate of substitution. Di- and mono-halogeno-derivatives must therefore be obtained by reduction of the trihalogeno-compounds.

The ready availability of ω-mono-, -di-, and -tri-halogeno-derivatives of methyl-pyridines, -quinolines, and -*iso*quinolines is of some importance in that they provide in many cases convenient alternative routes to carbinols, aldehydes, and carboxylic acids. The ω-trihalogeno-compounds are readily hydrolysed by acids; their ω-di- and -mono-analogues are, surprisingly, extremely resistant to hydrolytic agents, but can nevertheless be readily dehalogenated by treatment with alcoholic-aqueous silver nitrate. We therefore report in this paper (i) improved methods for the reduction of ωωω-tribromoquinaldine to di- and monobromoquinaldines, and (ii) the preparation and characteristation of a number of ω-chloro- and ω-bromo-derivatives of γ-picoline, quinaldine, 3-methylquinoline, lepidine, 1-methyl*iso*quinoline, and 3-methyl*iso*quinoline. In addition, we give examples of the reactivity of ω-monobromoquinaldine with acetoacetic and malonic esters. None of the halogenated substances we have examined appears to form a Grignard reagent.

The success of the direct halogenation of methyl side chains in acetic acid–sodium acetate mixtures is dependent on the position of the side chain, and on the structure of the heterocyclic molecule. The exact relationship will be discussed in a later communication on the mechanism of halogenation, but it is now pointed out that direct halogenation is impossible with β-picoline, 3-methylquinoline, lepidine, and 1-, 3-, and 4-methyl*iso*quinolines. Also, it is sometimes possible to achieve direct chlorination when bromination fails, *e.g.*, with α- and γ-picolines. The ω-monobromo-derivatives of 3-methylquinoline, lepidine, 1-methyl*iso*quinoline, and 3-methyl-*iso*quinoline have therefore been prepared from the corresponding alcohols obtained by formaldehyde reduction of the aldehydes, which were prepared by oxidation of the parent methyl compounds with selenium dioxide, *e.g.*:



All six ω-chloro- and ω-bromo-derivatives of quinaldine have now been prepared. A comparison of their solubilities in acids, and of their facility for forming picrates, indicates an increase of basicity with decrease of halogen substitution. The direct iodination of quinaldine has not been achieved, and no ω-iodo-derivatives are yet known.

Experimental.

M. p.s and b. p.s are uncorrected. Analyses are by Drs. Weiler and Strauss, and by Mr. F. C. Hall.

ωωω-Trichloro-γ-picoline.—A mixture of γ-picoline (21 ml.), acetic anhydride (20 ml.), sodium acetate (60 g.), and acetic acid (250 ml.) was kept at 80°, and dry chlorine passed in until 3 molecules (50 g.) per molecule of picoline had been absorbed. The mixture was poured on ice and made alkaline with ammonia, and an oil isolated by means of ether. Two fractionations under reduced pressure yielded *ωωω-trichloro-γ-picoline* (15·4 g., 37%) as a colourless oil, b. p. 105—107°/18 mm. (Found: Cl, 54·1. $C_6H_4NCl_3$ requires Cl, 54·2%). The product had a smell reminiscent of that of chloroform, and was insoluble in water (dense lower layer); it decomposed on storage, a black deposit forming in a few days. The *picrate* separated from alcohol as small yellow needles, m. p. 154° (Found: Cl, 24·9. $C_{12}H_7O_7N_4Cl_3$ requires Cl, 25·1%). Hydrolysis of ωωω-trichloro-γ-picoline with silver nitrate in aqueous acetic acid yielded *iso*nicotinic acid (32%) (isolated as its copper salt), which separated from alcohol as colourless needles, m. p. 315°. Spath and Spitzer (*Ber.*, 1926, **59**, 1477) record m. p. 315—316°.

ωω-Dichloro-γ-picoline.—A solution of tin (2·5 g.) in hydrochloric acid (*d* 1·16; 10 ml.) was heated with ωωω-trichloro-γ-picoline (4·0 g.) and acetone (30 ml.) on the water-bath for one hour. Removal of the acetone, steam-distillation, and ether-extraction yielded an oil, which on distillation gave *ωω-dichloro-γ-picoline* (1·6 g., 49%) as a colourless oil of penetrating odour, b. p. 78—80°/18 mm. (Found: Cl, 43·6. $C_6H_5NCl_2$ requires Cl, 43·8%). The substance darkened rapidly on storage. Hydrolysis with silver nitrate yielded *iso*nicotinaldehyde (55%) which formed a picrate, m. p. 168—169°, and a phenylhydrazone, m. p. 177—178°. Wibaut, Kroogman, and Boer (*Rec. Trav. chim.*, 1936, **55**, 293) report similar values.

ωω-Dichloroquinaldine.—ωωω-Trichloroquinaldine (5·0 g.) (Hammick, *J.*, 1923, 2882) in acetic acid (50 ml.) was mixed with a solution of tin (2·5 g.) in hydrochloric acid (*d* 1·16; 8·3 ml.) and boiled under reflux for 1 hour. The mixture was poured into water (500 ml.) and neutralised with chalk, and a solid isolated by ether-extraction. Recrystallisation from aqueous methanol yielded *ωω-dichloroquinaldine* (3·1 g., 72%) as small colourless needles, m. p. 82° (Found: Cl, 33·6. $C_{10}H_7NCl_2$ requires Cl, 33·5%).

ω-Monochloroquinaldine.—ωωω-Trichloroquinaldine (5·0 g.) in acetic acid (50 ml.) was reduced as described above with a solution of tin (5·0 g.) in hydrochloric acid (*d* 1·16; 20 ml.). Crystallisation of the isolated oil from light petroleum (b. p. 40—60°) gave *ω-monochloroquinaldine* as colourless needles, m. p. 54° (Found: Cl, 20·2. $C_{10}H_8NCl$ requires Cl, 20·0%). The substance darkened after a time. The *picrate* separated from alcohol as a microcrystalline powder, m. p. 172° (Found: Cl, 8·9. $C_{16}H_{11}O_7N_4Cl$ requires Cl, 8·7%).

The *picrate* of ωω-dibromoquinaldine (Hammick *J.*, 1926, 1302) separated from alcohol as a yellow microcrystalline powder, m. p. 151° (Found : Br, 30·1. $C_{16}H_{10}O_7N_4Br_2$ requires Br, 30·2%).

ω-Monobromoquinaldine.—The following strictly controlled conditions were essential to success. Granulated tin (6·4 g.) was boiled with hydrobromic acid (*d* 1·51; 40 ml.) until dissolution was complete (1—2 hours). ωωω-Tribromoquinaldine (10·0 g.) was dissolved in acetone (50 ml.) in a 500-ml. flask fitted with a condenser, a stirrer, and a delivery funnel with the stem extending below the surface of the liquid, which was boiled on the water-bath and stirred vigorously. The stannous bromide solution was cooled to 50°, swirled round vigorously, and treated with acetone (50 ml.), whereby the temperature rose to 56°; the hot liquid was at once added to the solution of tribromoquinaldine at such a rate as to keep the very vigorous reaction under control. The mixture was refluxed for 1 hour, and the acetone then removed. Treatment of the residue with ice, exact neutralisation with ammonia, and ether-extraction yielded an oil which crystallised overnight. Crystallisation from light petroleum (b. p. 60—80°) gave *ω-monobromoquinaldine* (3·2 g., 54%) as colourless needles, m. p. 57° (Found : Br, 36·2. $C_{10}H_8NBr$ requires Br, 36·0%). The compound decomposes on storage. Hammick (*J.*, 1926, 1302) records m. p. 83° for "ω-monobromoquinaldine." Repetition of the reduction of ωωω-tribromoquinaldine with stannous chloride (Hammick, *loc. cit.*) yielded ω-monochloroquinaldine, m. p. 54°, an exchange of chlorine for bromine occurring on using stannous chloride as reducing agent. The *picrate* of ω-monobromoquinaldine separated from alcohol as a yellow powder, m. p. 178° (Found : Br, 17·8. $C_{16}H_{11}O_7N_4Br$ requires Br, 17·7%).

N-2-*Quinolylmethylpyridinium Bromide.*—ω-Monobromoquinaldine (1·9 g.), pyridine 10 ml.), and benzene (30 ml.) were boiled for 3 hours. The benzene was decanted, and the deposited solid recrystallised from alcohol to yield N-2-*quinolylmethylpyridinium bromide* (2·4 g., 93%) as colourless needles, m. p. 239° (Found : Br, 26·9. $C_{15}H_{13}N_2Br$ requires Br, 26·6%).

2-*Ethylquinoline.*—The Grignard solution from magnesium (0·49 g.), methyl iodide (1·25 ml.), and ether (50 ml.) was boiled for 1 hour with a solution of ω-monobromoquinaldine (4·5 g.) in ether (25 ml.). Decomposition with water and ether-extraction yielded 2-ethylquinoline (2·14 g., 68%) as a colourless oil, b. p. 134—136°/16 mm. (Found : N, 8·7. Calc. for $C_{11}H_{11}N$: N, 8·9%). Delaby and Hiron (*Bull. Soc. chim.*, 1930, **47**, 1395) record b. p. 128—131°/13 mm.

Ethyl α-2-Quinolylmethylacetoacetate.—A solution of sodium (0·25 g.) in alcohol (30 ml.) was cooled to 15°. Ethyl acetoacetate (1·2 ml.) was added, followed by ω-monobromoquinaldine (2·3 g.) in alcohol (5 ml.), and the mixture boiled for 2 hours; it was then neutral to litmus. Removal of alcohol, treatment with water, and ether-extraction gave ethyl α-2-quinolylmethylacetoacetate (2·55 g., 91%) as an oil which was not further purified, since it did not crystallise, and distillation caused decomposition. The 2 : 4-*dinitrophenylhydrazone* separated from alcohol as orange needles, m. p. 140° (Found : C, 58·9; H, 4·5; N, 15·7. $C_{22}H_{21}O_8N_5$ requires C, 58·5; H, 4·6; N, 15·5%).

Acid hydrolysis : β-2-quinolylpropionic acid. Hydrolysis of the foregoing ester with 5% alcoholic potash yielded β-2-quinolylpropionic acid (67%), which separated from benzene as colourless crystals, m. p. 120—121°. Koenigs (*Ber.*, 1900, **33**, 220) records m. p. 122—123°.

Ketonic hydrolysis : methyl β-2-quinolylethyl ketone. Ethyl α-2-quinolylmethylacetoacetate (0·5 g.) and water (10 ml.) were kept at 200° in a sealed tube for 18 hours. The resulting liquid was made acid with hydrochloric acid, boiled with charcoal, and filtered, and the filtrate made slightly alkaline with aqueous ammonia. Ether-extraction gave methyl β-2-quinolylethyl ketone (0·25 g., 70%) as an oil which was not purified further. The 2 : 4-*dinitrophenylhydrazone* separated from alcohol as small orange-coloured needles, m. p. 196° (Found : C, 59·9; H, 4·5; N, 18·1. $C_{19}H_{17}O_4N_5$ requires C, 60·1; H, 4·6; N, 18·5%).

Diamide of 2-Quinolylmethylmalonic Acid.—A solution of sodium (0·25 g.) in alcohol (30 ml.) was treated at 15° with ethyl malonate (1·5 ml.) and ω-monobromoquinaldine (2·3 g.) in alcohol (5 ml.). The mixture was boiled for 2 hours, the alcohol removed, and the residue treated with water and extracted with ether to yield ethyl 2-quinolylmethylmalonate (0·28 g., 90%) as a yellowish oil which was not further purified. After 4 days with excess of aqueous ammonia and sufficient alcohol to produce a homogeneous solution it gave the *diamide*, which separated from aqueous alcohol as colourless plates, m. p. 245° (decomp.) (Found : C, 64·3; H, 5·3; N, 16·6. $C_{13}H_{13}O_2N_3$ requires C, 64·1; H, 5·3; N, 17·2%).

1 : 2-*Di-2'-quinolylethane.*—ω-Monobromoquinaldine (2·2 g.) in xylene (50 ml.) was treated with sodium wire (2·0 g.) and heated under reflux in an oil-bath for 6 hours. The xylene was decanted and evaporated off under reduced pressure. The residue was taken up in light petroleum (b. p. 60—80°) from which 1 : 2-*di-2'-quinolylethane* (0·65 g., 46%) was deposited as light orange needles, m. p. 160° (Found : N, 9·4. $C_{20}H_{16}N_2$ requires N, 9·8%). The *dipicrate* separated from alcohol as fine yellow needles, m. p. 177° (Found : N, 14·9. $C_{32}H_{22}O_{14}N_8$ requires N, 15·1%).

2-*Quinolylmethyl Quinaldinate.*—A mixture of ω-monobromoquinaldine (1·0 g.) in alcohol (15 ml.) with a solution of quinaldinic acid (1·0 g.) in 2N-sodium carbonate (5 ml.) was refluxed for 3 hours. In the cold the *ester* separated as small pale yellow needles (0·8 g., 57%). Two recrystallisations from alcohol yielded slender colourless needles, m. p. 185—186° (Found : C, 76·6; H, 4·6. $C_{20}H_{14}O_2N_2$ requires C, 76·4; H, 4·45%).

Quinoline-3-aldehyde.—3-Methylquinoline (4·0 g.) and freshly prepared and sublimed selenium dioxide (3·4 g.) were heated over a low flame. At about 130° a violent reaction occurred, the temperature rising to 200°. When the reaction had slackened, the mixture was kept at 260—270° for 10 minutes to distil out unchanged 3-methylquinoline. The cold mixture was extracted with ether, the ether removed from the extract, and the residue crystallised from water. Quinoline-3-aldehyde (1·8 g., 41%) formed colourless needles, m. p. 69·5° (Found : N, 8·8. Calc. for $C_{10}H_7ON$: N, 8·9%). Cook, Heilbron, and Steger (*J.*, 1943, 415) record m. p. 70°.

3-*Quinolylmethanol* (3-*Hydroxymethylquinoline*).—A mixture of quinoline-3-aldehyde (1·8 g.), 40% formaldehyde solution (2·9 ml.), potassium hydroxide (2·0 g.), and water (7·5 ml.) was shaken for 3 hours. It was then extracted with chloroform, and the extract washed with sodium hydrogen sulphite solution, sodium carbonate solution, and finally with water. Evaporation yielded a solid residue which crystallised from benzene to yield the *alcohol* (1·5 g., 79%), m. p. 65—67° (Found: C, 75·7; H, 5·5; N, 8·6. $C_{10}H_9ON$ requires C, 75·5; H, 5·7; N, 8·9%).

3-*Bromomethylquinoline*.—3-Quinolylmethanol (2·0 g.) in benzene (20 ml.) was cooled in ice and treated with phosphorus tribromide (1·0 ml.) in benzene (10 ml.). The hydrobromide of the product separated as a yellow solid. The mixture was treated with aqueous ammonia until alkaline, and the precipitate was decomposed, and the product passed into the benzene layer. This was separated, washed, dried, and evaporated. The residue was extracted with light petroleum (b. p. 60—80°) to give 3-*bromomethylquinoline* (2·0 g., 72%) as small needles, m. p. 54·5° (Found: C, 54·2; H, 3·4; Br, 36·7. $C_{10}H_8NBr$ requires C, 54·1; H, 3·6; Br, 36·0%).

2 : 4-*Dinitrophenylhydrazone of Quinoline-4-aldehyde* (Kaplan, *J. Amer. Chem. Soc.*, 1941, **63**, 2654; Kwartler and Lindwall, *ibid.*, 1937, **59**, 524).—The *compound* separated from aqueous pyridine as brick-red crystals, m. p. 258° (Found: C, 57·2; H, 3·9; N, 20·0. $C_{16}H_{11}O_4N_5$ requires C, 57·0; H, 3·3; N, 20·7%).

4-*Quinolylmethanol* (4-*Hydroxymethylquinoline*).—A mixture of quinoline-4-aldehyde (1·8 g.), 40% formaldehyde solution (2·9 ml.), water (7·5 ml.), and potassium hydroxide (2·0 g.) was shaken for 3 hours. The oil which separated crystallised overnight. Recrystallisation from benzene yielded the alcohol (1·6 g., 87%), m. p. 97—98° (Found: N, 8·8. Calc. for $C_{10}H_9ON$: N, 8·9%). Phillips (*J. Amer. Chem. Soc.*, 1946, **68**, 2568) and MacDonald (*ibid.*, 1947, **69**, 1219) record m. p. 99—100° and 96—97°, respectively.

ω-Monobromolepidine.—This was obtained by the method used for 3-bromomethylquinoline. 4-Quinolylmethanol (2·0 g.) yielded *ω-monobromolepidine* (2·1 g., 75%), which separated from light petroleum (b. p. 60—80°) as small plates, m. p. 65° (Found: C, 53·7; H, 4·0; Br, 36·0. $C_{10}H_8NBr$ requires C, 54·1; H, 3·7; Br, 36·0%). The *picrate* separated from alcohol as yellow crystals, m.p. 192° (Found: C, 43·6; H, 2·5; Br, 17·7. $C_{16}H_{11}O_7N_4Br$ requires C, 43·1; H, 2·5; Br, 17·7%).

N-4-*Quinolylmethylpyridinium Bromide*.—ω-Monobromolepidine (1·5 g.), pyridine (10 ml.), and benzene (30 ml.) were refluxed for 3 hours. The solid product which separated crystallised from alcohol to yield N-4-*quinolylmethylpyridinium bromide* (1·9 g., 92%) as colourless needles, m. p. 217° (Found: C, 59·3; H, 4·7; Br, 26·6. $C_{15}H_{13}N_2Br$ requires C, 59·8; H, 4·3; Br, 26·6%).

1 : 2-*Di-4'-quinolylethane*.—This compound was prepared from ω-monobromolepidine (2·0 g.) by the method described above for the preparation of the 2'-isomer. 1 : 2-*Di-4'-quinolylethane* (0·53 g., 42%) separated from light petroleum (b. p. 60—80°) as colourless plates, m. p. 182° (Found: C, 83·9; H, 5·5; N, 9·85. $C_{20}H_{16}N_2$ requires C, 84·5; H, 5·6; N, 9·85%).

ωωω-Tribromo-N-methyl-lepidinium Bromide.—A solution of methyl-lepidinium iodide (5·7 g.) (Hoogewerff and Van Dorp, *Rec. Trav. chim.*, 1883, **2**, 318) and sodium acetate (20 g.) in water (100 ml.) was stirred and kept at 80—90° while bromine (7·0 ml.) was slowly added. The iodine at first precipitated gradually disappeared and a dark oil separated. Eventually the aqueous layer became clear. The mixture was stirred for a further ½ hour and allowed to cool, the aqueous layer decanted, and the semi-solid residue crystallised several times from alcohol. The *bromide* (5·8 g., 61%) separated as dark orange needles, m. p. 159° (Found: Br, 67·1. $C_{11}H_9NBr_4$ requires Br, 67·4%).

Hydrolysis. ωωω-Tribromo-*N*-methyl-lepidinium bromide (5·0 g.) in acetic acid (50 ml.) was treated with a solution of silver nitrate (9·0 g.) in water (20 ml.), and the mixture heated on the water-bath for 2 hours. It was then treated with excess of hydrochloric acid and filtered, and the filtrate diluted and made just alkaline with ammonia. The resulting white precipitate crystallised from alcohol to yield 2-hydroxy-*N*-methylcinchoninic acid (1·3 g., 62%) as colourless needles, m. p. 249°, unchanged on admixture with an authentic specimen.

4-*Methyl-2-tribromomethylquinoline*.—Bromination of 2 : 4-dimethylquinoline (2·5 g.) (Vaughan, *Org. Synth.*, 1948, **28**, 49) by Hammick's method (*J.*, 1923, **123**, 2882) yielded 4-*methyl-2-tribromomethylquinoline* (5·2 g., 78%), which separated from alcohol as colourless needles, m. p. 162° (Found: Br, 60·9. $C_{11}H_8NBr_3$ requires Br, 60·9%). Hydrolysis with aqueous-alcoholic silver nitrate yielded 4-methylquinoline-2-carboxylic acid (62%), which separated from light petroleum (b. p. 80—100°) as small slightly yellow needles, m. p. 153°. Koenigs and Mengel (*Ber.*, 1904, **37**, 1327) record m. p. 153—154°.

1-iso*Quinolylmethanol* (1-*Hydroxymethyl*iso*quinoline*).—*iso*Quinoline-1-aldehyde (1·8 g.) (Barrows and Lindwall, *J. Amer. Chem. Soc.*, 1942, **64**, 2430) was reduced to the carbinol by the method used for 3-quinolylmethanol. 1-iso*Quinolylmethanol* (1·3 g., 69%) formed crystals, m. p. 65°, from benzene (Found: C, 75·5; H, 5·8; N, 8·6. $C_{10}H_9ON$ requires C, 75·5; H, 5·7; N, 8·9%).

1-*Bromomethyl*iso*quinoline*.—The method used for 3-bromomethylquinoline was employed. 1-*iso*-Quinolylmethanol (2·0 g.) yielded 1-*bromomethyl*iso*quinoline* (1·95 g., 70%), which formed small needles, m. p. 56°, from light petroleum (Found: C, 54·4; H, 3·85. $C_{10}H_8NBr$ requires C, 54·1; H, 3·6%).

iso*Quinoline*-3-*aldehyde*.—3-Methyl*iso*quinoline (20 g.) and freshly prepared and sublimed selenium dioxide (17 g.) were heated over a low flame. At 140° a violent reaction occurred, the temperature rising to 230°. When this had slackened, the mixture was kept at 250° for 10 minutes. Distillation yielded a fraction distilling at 140—180°/25 mm.; redistillation gave an oil, b. p. 165—175°/25 mm., which solidified on cooling. Recrystallisation from light petroleum (b. p. 60—80°) yielded iso*quinoline*-3-*aldehyde* (8·1 g., 37%) as small colourless needles, m. p. 39—40° (Found: N, 8·8. $C_{10}H_7ON$ requires

N, 8·9%). The 2 : 4-*dinitrophenylhydrazone* separated from pyridine as small flocculent, orange needles, m. p. 276° (Found : C, 57·2; H, 3·5. $C_{16}H_{11}O_4N_5$ requires C, 57·0; H, 3·3%).

3-iso*Quinolylmethanol* (3-*Hydroxymethyl*iso*quinoline*).—*iso*Quinoline-3-aldehyde (5·0 g.) was reduced to the carbinol by the method used for 3-quinolylmethanol. 3-*iso*Quinolylmethanol (3·9 g., 77%) separated from benzene–light petroleum as crystals, m. p. 81°. Erlenmeyer, Baumann, and Serkin (*Helv. Chim. Acta*, 1948, **31**, 1988) record m. p. 81°.

3-*Bromomethyl*iso*quinoline*.—The method used for 3-bromomethylquinoline was employed. 3-*iso*-Quinolylmethanol (3·0 g.) yielded 3-bromomethyl*iso*quinoline (2·8 g., 67%) as small needles, m. p. 103·5°, from alcohol. Erlenmeyer *et al.* (*loc. cit.*) record m. p. 103·5°.

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