Cyclic Amidines. Part XXV.[1] Derivatives of 1-Alkyl-2-aminoquinolin-4(1*H*)-ones and 2,3-Dihydroimidazo[1,2-*a*]quinolin-5(1*H*)-one

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Interaction of ethyl cyanoacetate with *N*-alkylarylamine salts, yields 1-alkyl-2-aminoquinolin-4(1*H*)-ones. Alkylation of the aminoquinolinones yields *O*-alkyl derivatives which are strong bases. The same reagents cause alkylation first at O and then on ring N in 2-aminoquinolin-4-ols. 2-Ethoxycarbonylmethylene-1-phenylimidazolidine cyclises to 2,3-dihydroimidazo[1,2-*a*]quinolin-5(1*H*)-one, the 5-chloro-derivative of which reacts readily with alkylamines to yield 5-amino-derivatives; with acyl anhydrides and nitrous acid *N*-substituted derivatives are formed with replacement of Cl by O. The u.v.–visible spectra of the quinolines and imidazoquinolines are discussed.

In previous communications [2a,c] the preparation of 2-aminoquinolin-4-ols was described. This synthesis has now been extended to the preparation of 1-alkyl-2-aminoquinolin-4(1*H*)-ones, and the chemistry of these and the related imidazo[1,2-*a*]quinolin-5(1*H*)-ones is now reported.

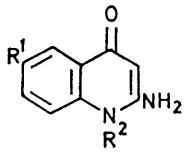
Fusion of an *N*-alkylarylamine salt with ethyl cyanoacetate led directly to 1-alkyl-2-aminoquinolin-4(1*H*)-ones (1) in moderate yields. Six examples are described in the Experimental section; *N*-isopropylaniline did not give the desired compound. The 1-methylquinolinones (1a, d, and e) were also obtained by *O*-demethylation of the appropriate 4-methoxy-1-methylquinolin-2(1*H*)-imine with hydrobromic acid [for (2a and d)] or with hydrochloric acid [for (2f)].

2-Amino-4-methoxyquinolines (3a—c) were prepared by fusion of 2-aminoquinolin-4-ols with methyl toluene-*p*-sulphonate. In one instance (3b) the 1-methyl-substituted ether (2d) was also obtained. Reaction between the methoxyquinolines (3a—c) and alkyl toluene-*p*-sulphonates (R = Me, Et, or $EtO{\cdot}CH_2{\cdot}CH_2$) or between 1-alkyl-2-aminoquinolin-4(1*H*)-ones (1a and f) and methyl toluene-*p*-sulphonate gave 1-alkyl-4-methoxyquinolin-2-imines (2a—g); accompanying the 1-ethyl ether (2g) was the isomeric 2-ethylamino-4,6-dimethoxyquinoline. The 1-alkyl bases had pK_a values in the range 12·44—12·93. The base strengthening which accompanies ring *N*-alkylation in semi-cyclic amidines [3] was used to identify the quinolines where direct comparisons with authentic samples were not possible. Ring alkylation of the amino-ethers contrasts with the

[1] M. W. Partridge and A. Smith, *J.C.S. Perkin I*, 1973, 453.

[2] R. Hardman and M. W. Partridge, *J. Chem. Soc.* (*a*), 1954, 3878; (*b*) 1955, 510; (*c*) 1958, 614.

[3] D. J. Brown and N. W. Jacobsen, *J. Chem. Soc.*, 1960, 1978; 1962, 3172; S. J. Angyal and C. L. Angyal, *ibid.*, 1952, 1461; K. Hoffmann and J. Kebrle, *Helv. Chim. Acta*, 1956, **39**, 116.

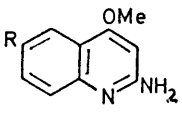


(1)

	R^1	R^2
a;	H	Me
b;	H	Et
c;	H	Bu^n
d;	Me	Me
e;	OMe	Me
f;	OMe	Et

(2)

	R^1	R^2
a;	H	Me
b;	H	Et
c;	H	$CH_2{\cdot}CH_2{\cdot}OEt$
d;	Me	Me
e;	Me	$CH_2{\cdot}CH_2{\cdot}OEt$
f;	OMe	Me
g;	OMe	Et



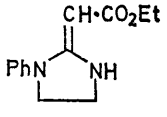
(3)

	R
a;	H
b;	Me
c;	OMe

alkylation of the exocyclic amino-group which occurs [4] with the sodio-derivative of 2-amino-4-butoxyquinoline.

In an attempt to extend further the quinoline synthesis to the preparation of 2,3-dihydroimidazo[1,2-*a*]quinolin-5(1*H*)-ones, *N*-phenylethylenediamine bistoluene-*p*-sulphonate was fused with ethyl cyanoacetate, but no identifiable product was obtained, although in a model experiment benzonitrile and *N*-phenylethylenediamine bistoluene-*p*-sulphonate gave a high yield of 1,2-diphenylimidazoline.

In a stepwise synthesis the intermediate ester (4) was obtained from ethyl β-amino-β-ethoxyacrylate hydrochloride and *N*-phenylethylenediamine. The assigned structure for this and for the methyl ester obtained by



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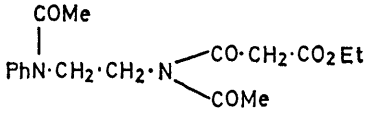

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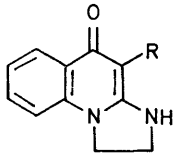
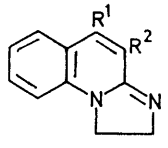


(6)

	R
a;	H
b;	Br
c;	N=O

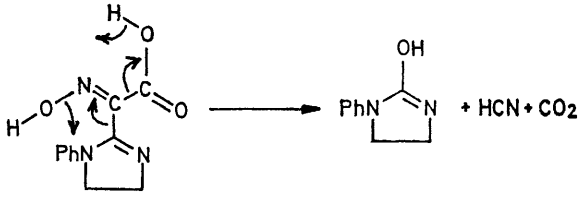


(7)

	R^1	R^2
a;	Cl	H
b;	Cl	Br
c;	NC_5H_{10}	H
d;	NHMe	H
e;	$NH{\cdot}CH_2{\cdot}CH_2{\cdot}OH$	H
f;	H	H
g;	OMe	H
h;	OPr^n	H

alcohol exchange followed from chemical and spectroscopic data. The n.m.r. spectrum of the methyl ester showed signals at τ 6·50—6·03 (m, $CH_2{\cdot}CH_2$ and $CO_2{\cdot}CH_3$), 5·73 (:CH, disappears after addition of D_2O), 2·95—2·45 (m, ArH_5), and 2·15br (NH, disappears on deuteriation); the spectrum of the ethyl ester showed a three-proton absorption at τ 6·06—5·69, which was simplified and integrated for two protons ($CH_2{\cdot}CH_3$) after exchange with D_2O. Their i.r. spectra showed $\nu_{max.}$ at 3380 (NH) and 1644 cm^{-1} (CO_2R, hydrogen-bonded).

With acetic anhydride the imidazolidine (4) underwent ring opening and gave the diacetyl derivative (5) or its isomer, which showed $\nu_{max.}$ 1730 and 1654 (ester and tertiary amide carbonyl stretch) and 1710 and 1695 cm^{-1} {two acyl carbonyls attached to the same nitrogen [*cf.*[5] $(MeCO)_2NMe$, $\nu_{max.}$ 1710 and 1695 cm^{-1}]}. The diacylamino-system lost one acyl group on mild hydrolysis with sodium hydroxide. The ethyl ester (4) readily formed a urea with phenyl isocyanate and with nitrous acid gave a *C*-hydroxyimino-derivative which exhibited very strong hydrogen bonding ($\nu_{max.}$ 2700—2150 and 2040—1800 cm^{-1}). The hydroxyimino-ester was readily hydrolysed to the hydroxyimino-acid (8), which in hot



(8)

dimethylformamide gave 1-phenylimidazolidin-2-one and hydrogen cyanide and not the expected 1-phenyl-2-cyanoimidazoline. The possibility that the nitrile had been formed initially and was hydrolysed by formed water was excluded by the fact that degradation in excess of aniline did not yield 2-anilinoimidazoline; moreover degradation in acetic anhydride gave the acetyl derivative of the imidazolidone. A similar degradation of an α-hydroxyimino-acid does not appear to have been reported.[6] Presumably there is hydrogen bonding between the oxime and the imidazoline and this does not allow the normal degradation of α-hydroxyimino-acids, which involves hydrogen bonding between the HO of the carboxy-group and the oxime. A possible mechanism consistent with the experimental observation is illustrated. A different mechanism may operate for the degradation in acetic anhydride. The n.m.r. spectrum of 1-phenylimidazolidin-2-one showed 40% of lactim and 60% of lactam.

Cyclisation of the ester (4) to the alkali-insoluble imidazoquinolinone (6a) was effected by polyphosphoric acid at 160° but not in boiling diphenyl ether. The imidazoquinoline readily formed *N*-acyl derivatives but with a large excess of benzoyl chloride, in the presence of aqueous alkali, the imidazolidine ring was opened and 1-β-benzamidoethyl-2(or 4)-benzoyloxyquinolin-4(or 2)-one or 1-benzoyl-2-(*N*-2-hydroxyethylbenzamido)quinolin-4(1*H*)-one was formed.

Electrophilic attack at the 3-position of a quinoline having flanking activating groups is well established.[2a,c] The imidazoquinolinone (6a) showed similar reactivity

[4] W. R. Hallows and M. W. Partridge, *J. Chem. Soc.*, 1960, 3675.

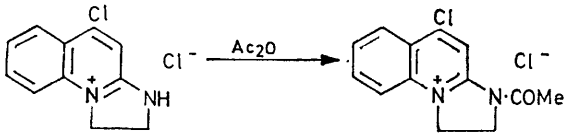
[5] H. K. Hall, jun., and R. Zbinden, *J. Amer. Chem. Soc.*, 1958, **80**, 6428.

[6] A. Ahmad and I. D. Spenser, *Canad. J. Chem.*, 1961, **39**, 1340.

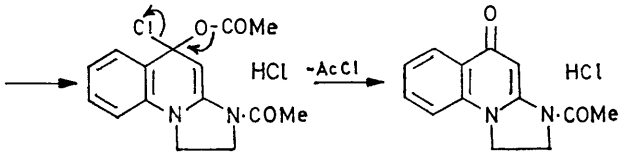
towards nitrous acid and bromine, affording the 4-hydroxyimino- and 4-bromo- (6b) derivatives respectively.

The imidazoquinolinones (6a and b) were readily converted by phosphoryl chloride into their 5-chloro-derivatives, which were resistant to attack by 5N-sodium hydroxide and by sodium butoxide in butanol, but were hydrolysed by boiling potassium hydroxide in ethylene glycol. This low reactivity towards strong nucleophiles recalls similar properties of 2-amino-4-chloroquinoline.[2c] The weaker nucleophilic aliphatic amines (piperidine, $MeNH_2$, $NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}OH$) reacted readily and gave the expected products (7c—e), the last being converted by thionyl chloride into the known β-chloroethylamine.[7]

The chloro-compound (7a) exhibited variable hydration, which was also indicated by integration of its n.m.r. spectrum; the mass spectrum included peaks for an anhydrous parent ion. Attempts to prepare the anhydrous compound were unsuccessful. The chloroimidazoquinoline (7a) and its anhydrous hydrochloride, but not the bromo-chloro-analogue (7b), showed unusual behaviour towards acetic anhydride and nitrous acid. The formation of the 3-acetylimidazoquinoline hydrochloride (9) is interpreted in terms of the illustrated reaction sequence (7a),HCl ⟶ (9). With nitrous acid an *N*-nitroso-5-oxo-derivative was isolated, and this, in



(7a),HCl

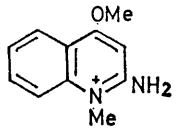


(9)

dilute hydrochloric acid, underwent a Fischer–Hepp rearrangement to the 4-hydroxyimino-compound (6c). Catalytic dehalogenation of the chloro-compounds (7a and b) led to the dihydroimidazo[1,2-*a*]quinoline (7f).

Imidazoquinoline ethers (7g and h) were prepared by alkylation of the imidazoquinolinone (6a) with alkyl toluene-*p*-sulphonates. These ethers were readily dealkylated by hydrobromic acid.

U.v.–Visible Spectra.—The u.v. spectra of the cations of the quinolines (2a) and (1a) were identical, suggesting that the canonical forms (10) and (11) make a major contribution to each. Likewise the spectra of the cations of the corresponding imidazoquinolines (6a) and (7g and h) were identical. The similarity between the spectra of the cations of the alkylamines (7d and e)



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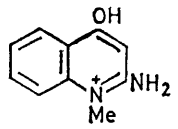
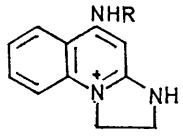


(11)

and the dipolar 5-oxoimidazoquinoline (13) [a canonical form of (6a)] suggests that the former are protonated on a ring nitrogen atom [as in (12)].



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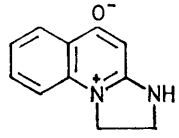

(13)

Dihydroimidazo[1,2-*a*]quinoline (7f) shows a long wavelength n–π^* transition at 392 nm, and introduction of a 5-chloro-substituent (7a) produces the expected bathochromic shift, although the spectrum of the cation does not reveal an auxochromic effect from the chlorine atom. A marked hypsochromic effect on the long wavelength bands is observed with a 5-alkoxy-substituent (7g and h) and this is maintained in the spectra of the cations.

EXPERIMENTAL

M.p.s were determined with a Kofler hot-stage apparatus. I.r. spectra (KBr discs) were measured with a Perkin-Elmer 257 or Unicam SP 200 spectrophotometer. U.v.–visible spectra were recorded for solutions in ethanol unless otherwise indicated, using a Unicam SP 800 spectrophotometer. N.m.r. spectra were obtained with a Perkin-Elmer R10 spectrometer operating at 60 MHz for solutions in deuteriochloroform with tetramethylsilane as internal standard. The u.v.–visible absorption data for compounds (1a), (2a—g), (6a), and (7a—h), and the dissociation constant data for compounds (2a—g), are available in Supplementary Publication No. SUP 20698 (3 pp., 1 microfiche).*

N-Methyl-*p*-anisidine was prepared from *p*-anisidine and trimethyl orthoformate by the method [8] described for *N*-methyl-*p*-chloroaniline. The intermediate formyl derivative, formed in 40% yield, had b.p. 153—154° at 4 mmHg (lit.,[9] b.p. 122—124° at 2 mmHg) (Found: C, 64·9; H, 6·9; N, 8·4. Calc. for $C_9H_{11}NO_2$: C, 65·4; H, 6·7; N, 8·5%) and was hydrolysed (1·5 h) by 10% hydrochloric acid to the amine (92%), b.p. 155—156° at 40 mmHg (lit.,[10] 130° at 15 mmHg). *N*-Ethyl-*p*-anisidine was similarly prepared [92%; b.p. 153—154° at 4 mmHg (lit.,[11] 135—140° at 20 mmHg)]. The intermediate formyl derivative (70%) had b.p. 153—154° at 4 mmHg (lit.,[12] 160—175° at 7 mmHg) (Found: C, 66·8; H, 7·0; N, 7·8. Calc. for $C_{10}H_{13}NO_2$: C, 67·0; H, 7·3; N, 7·8%).

2-Amino-1-methylquinolin-4(1H)-one (1a).—(i) The melt obtained when methylanilinium toluene-*p*-sulphonate (140 g) and ethyl cyanoacetate (57 g) were fused together at 210°

* For details of Supplementary Publications, see *J. Chem. Soc.* (*A*), 1970, Issue No 20 (Notice to Authors No. 7).

[7] J. M. Osbond, *J. Chem. Soc.*, 1950, 1853.

[8] R. M. Roberts and P. J. Vogt, *Org. Synth.*, 1963, Coll. Vol. IV, p. 420.

[9] F. Dallacker and F.-E. Eschelbach, *Annalen*, 1965, **689**, 171.

[10] W. König and G. A. Becker, *J. prakt. Chem.*, 1911, **85**(2), 353.

[11] W. S. Emerson and W. D. Robb, *J. Amer. Chem. Soc.*, 1939, **61**, 3145.

[12] B. I. Ardashev and V. I. Minkin, *Zhur. obschei Khim.*, 1958, **28**, 1578.

for 1 h was digested with chloroform (150 ml) and gave the insoluble *quinoline toluene*-p-*sulphonate* (39·5 g), which separated from methanol–ether as prisms, m.p. 225—234° (decomp.) (Found: C, 58·6; H, 5·3; N, 8·4. $C_{17}H_{18}N_2O_4S$ requires C, 59·0; H, 5·2; N, 8·1%). The *base* (1a) formed needles, m.p. 295—305° (from water) (Found: C, 68·7; H, 5·8; N, 16·4. $C_{10}H_{10}N_2O$ requires C, 69·0; H, 5·8; N, 16·1%). This base was insoluble in aqueous sodium hydroxide. Its *hydrochloride*, prisms from methanol–ether, had m.p. 290—305° (Found: C, 57·0; H, 5·1; N, 13·2. $C_{10}H_{11}ClN_2O$ requires C, 57·0; H, 5·3; N, 13·3%). The alkali-soluble N-*acetyl* derivative (0·4 g) separated when a solution of the base (1 g) and acetic anhydride (5 ml) was kept at room temperature for 1 day. It crystallised from methanol–ether as either prisms or needles, m.p. 246—248° (Found: C, 66·5; H, 5·5; N, 13·1. $C_{12}H_{12}N_2O_2$ requires C, 66·7; H, 5·6; N, 13·0%), $\nu_{max.}$ 2900 (NH) and 1705 cm^{-1} (C:O).

(ii) 4-Methoxy-1-methylquinolin-2(1*H*)-imine (0·2 g) in concentrated hydrobromic acid (3 ml) was refluxed for 1 h. Basification of the solution with ammonia gave the quinolinone (65%), m.p. 290—305°. The i.r. spectra of this base and of a sample prepared by the foregoing method were identical.

Table 1 records 1-alkylquinolin-4(1H)-ones prepared analogously.

2-Amino-4-methoxyquinoline (3a).—2-Aminoquinolin-4-ol (4·0 g) and methyl toluene-*p*-sulphonate (4·75 g) were heated together with stirring in an oil-bath until an exothermic reaction commenced (at 120°; the internal temp. rose to 140°). Heating was continued at 120° for 30 min and the solid obtained by trituration of the cooled mixture with 2N-sodium hydroxide gave the ether (2·9 g), m.p. 193—194° (lit.,[2b] 195—196°). Its *picrate* formed prisms, m.p. 265—267°, from aqueous dimethylformamide (Found: C, 48·1; H, 3·3; N, 17·0. $C_{16}H_{13}N_5O_8$ requires C, 47·7; H, 3·3; N, 17·4%). Larger quantities of the ether were best prepared by replication of the above procedure in a number of boiling tubes; larger scale experiments gave lower yields.

The following methyl ethers were prepared similarly: *2-amino-4,6-dimethoxyquinoline* (55%), prisms, m.p. 186—187° (from aqueous methanol) (Found: C, 65·1; H, 5·8; N, 13·7. $C_{11}H_{12}N_2O_2$ requires C, 64·7; H, 5·9; N, 13·7%); its *picrate*, prisms from aqueous dimethylformamide, had m.p. 264—268° (with resolidification, remelting at 274—275°) (Found: C, 47·3; H, 3·4; N, 15·8. $C_{17}H_{15}N_5O_9$ requires C, 47·1; H, 3·5; N, 16·2%); *2-amino-4-methoxy-6-methylquinoline* (prepared on a 0·02 mol scale in 69% yield) formed prisms, m.p. 204—205° (from aqueous methanol) (Found: C, 69·8; H, 6·3; N, 14·8. $C_{11}H_{12}N_2O$ requires C, 70·2; H, 6·4; N, 14·9%); on a 0·04 mol scale the yield was 58% but 4-methoxy-1,6-dimethylquinoline-2(1*H*)-imine (14%) (Table 2) was also isolated.

1-Alkyl-4-methoxyquinolin-2(1H)-imines.—The appropriate 2-aminoquinolin-4-ol (0·01 mol) and alkyl toluene-*p*-sulphonate (0·01 mol) reacted exothermically when fused together at 100—140°. Heating was continued for 30 min. The mixture was crystallised from the solvent given in Table 2 or digested with a suitable solvent [ethyl acetate for (2c); acetonitrile–ether for (2b)] and the crude salt was isolated prior to crystallisation. The bases were liberated from their salts with 2N-sodium hydroxide and recovered by filtration or extraction into benzene. The bases rapidly absorb carbon dioxide. The 1-alkylquinolines prepared are recorded in Table 2.

TABLE 1

1-Alkyl-2-aminoquinolin-4(1*H*)-ones

	Form	Method	Yield (%)	M.p. (°C)	Solvent for cryst.	Found (%) C	H	N	Formula	Required (%) C	H	N
(1b)	Base			247—249	H_2O	69·9	6·0	14·7	$C_{11}H_{12}N_2O$	70·2	6·4	14·9
	Toluene-*p*-sulphonate	A	9 [b]	236—240	MeOH–Et_2O	59·7	5·5	8·1	$C_{18}H_{20}N_2O_4S$	60·0	5·6	7·8
	Acetyl [c]			174—175	C_6H_6	68·2	5·9	12·1	$C_{13}H_{14}N_2O_2$	67·8	6·1	12·2
(1c)	Base			210—211	MeOH	71·8	7·5	12·8	$C_{13}H_{16}N_2O$	72·2	7·5	13·0
	Toluene-*p*-sulphonate	A	6 [b]	231—232	H_2O	61·7	6·3	6·9	$C_{20}H_{24}N_2O_4S$	61·8	6·2	7·2
(1d)	Base	B	80	316—319 [d]	H_2O	69·7	6·0	14·8	$C_{11}H_{12}N_2O$	70·2	6·4	14·9
	Toluene-*p*-sulphonate			261—265	H_2O	59·6	5·4	7·6	$C_{18}H_{20}N_2O_4S$	60·0	5·6	7·8
(1e)	Base	B [e]	35	298—304	H_2O	64·4	5·7	13·7	$C_{11}H_{12}N_2O_2$	64·7	5·9	13·7
	Toluene-*p*-sulphonate	A	7 [b]	236—238	H_2O	57·2	5·2	7·3	$C_{18}H_{20}N_2O_5S$	57·4	5·4	7·4
(1f)	Base			272—280	H_2O	65·7	6·4	12·9	$C_{12}H_{14}N_2O_2$	66·0	6·5	12·8
	Toluene-*p*-sulphonate	A	5 [b]	252—260	H_2O	58·3	5·6	7·4	$C_{19}H_{22}N_2O_5S$	58·5	5·7	7·2

[a] Yield in method A is of base and in method B of toluene-*p*-sulphonate. [b] Salt continued to separate from the chloroform solution for up to 3 weeks. [c] Formed in cold acetic anhydride (3 days). [d] Decomp. [e] Hydrolysed with 10N-HCl for 6 h; bases from methods A and B had identical i.r. spectra.

Fusion of 2-Amino-4,6-dimethoxyquinoline and Ethyl Toluene-p-*sulphonate*.—The melt obtained by fusing the reactants (0·01 mol of each) at 140° for 30 min was crystallised from acetonitrile and gave *2-ethylamino-4,6-dimethoxyquinoline toluene*-p-*sulphonate* (0·7 g), m.p. 204—212°, raised to 217—220° by recrystallisation (as prisms) from methanol–ether (Found: C, 59·7; H, 6·0; N, 6·8. $C_{20}H_{24}N_2O_5S$ requires C, 59·4; H, 6·0; N, 6·9%). The *base* separated from light petroleum (b.p. 60—80°) as prisms, m.p. 97—99° (Found: C, 67·1; H, 6·8; N, 12·0. $C_{13}H_{16}N_2O_2$ requires C, 67·2; H, 6·9; N, 12·1%). The acetonitrile mother liquor was poured into 2M-sodium picrate (100 ml) and the crude picrate was fractionally crystallised from acetic acid and gave 1-ethyl-4-methoxyquinolin-2(1*H*)-imine picrate (2 g; Table 2).

N-*Phenylethylenediamine toluene*-p-*sulphonate* (needles from butan-1-ol) had m.p. 194—195° (Found: C, 58·8; H, 6·3; N, 9·0. $C_{15}H_{20}N_2O_3S$ requires C, 58·4; H, 6·5; N, 9·1%).

1,2-Diphenylimidazoline toluene-*p*-sulphonate (75%) separated from the hot butanol extract of the melt obtained when *N*-phenylethylenediamine (6·2 g), anhydrous toluene-*p*-sulphonic acid (3·4 g), and benzonitrile (2·1 g) were heated at 210° for 3 h. It formed prisms, m.p. 205—207° (lit.,[13] 205—207°) (from propan-1-ol) (Found: C, 67·1; H, 5·7; N, 7·3. Calc. for $C_{22}H_{22}N_2O_3S$: C, 67·0; H, 5·6; N, 7·1%).

2-Ethoxycarbonylmethylene-1-phenylimidazolidine.—To a suspension of ethyl β-amino-β-ethoxyacrylate hydrochloride [14] (170 g) in ethanol at 0° was added, dropwise, with

[13] M. W. Partridge and H. A. Turner, *J. Chem. Soc.*, 1949, 1308.

[14] A. C. Cope and S. A. Glickman, *J. Amer. Chem. Soc.*, 1945, **67**, 1017.

vigorous stirring during 1 h a solution of *N*-phenylethylenediamine [15] (119 g) in ethanol (300 ml), also at 0°. The suspension was kept at 0—5° for 48 h, then filtered, and the solid (130 g), crystallised from aqueous acetone, gave the *imidazolidine* (110 g) as prisms, m.p. 130—130·5° (Found: C, 67·5; H, 6·7; N, 12·1. $C_{13}H_{16}N_2O_2$ requires C, 67·2; H, 6·9; N, 12·1%), $\nu_{max.}$ 3380 (NH) and 1644 cm^{-1} (CO_2Et, hydrogen-bonded); $\lambda_{max.}$ 248 (log ε 3·94) and 284 nm (4·17). A further 10 g of base (total yield 52%) was isolated from the reaction mixture after refluxing for 2 h, concentrating to 250 ml, and basifying with sodium hydroxide. The petroleum (b.p. 80—100°) as prisms, m.p. 77—78° (Found: C, 61·4; H, 6·5; N, 8·2. $C_{17}H_{22}N_2O_5$ requires C, 61·1; H, 6·6; N, 8·4%), $\nu_{max.}$ 1730, 1710, 1695, and 1654 cm^{-1} (C:O), τ 8·76 (3H, $CH_2{\cdot}CH_3$), 8·16 (3H, $CO{\cdot}CH_3$), 7·55 (3H, $CO{\cdot}CH_3$), 6·24 (2H, $CO{\cdot}CH_2{\cdot}CO$), 6·20—5·96 (4H, $CH_2{\cdot}CH_2$), 5·88 [2H, $CH_2{\cdot}CH_3$ (after D_2O)], and 2·92—2·57 (5H, ArH_5). The same compound was obtained when the reaction mixture was quenched in ethanol, and when sodium benzoate (1·5 mol. equiv.) was dissolved in the acetic anhydride. Acetylation in water gave the triacetyl compound in 76% yield. No recognisable product was obtained when the

TABLE 2

4-Alkoxy-1-alkylquinolin-2(1*H*)-imines

	Form	M.p. (°C)	Reaction temp. (°C)	Yield (%)	Solvent for cryst.	Found (%) C	H	N	Formula	Required (%) C	H	N
(2a)	Base [a]	113—114			LP *	70·0	6·5	14·7	$C_{11}H_{12}N_2O$	70·2	6·4	14·9
	Toluene-*p*-sulphonate	204—205	100	67	MeOH–Et_2O	60·1	5·4	7·9	$C_{18}H_{20}N_2O_4S$	60·0	5·6	7·8
	Hydrochloride	247—249			MeOH–Et_2O	59·0	5·8	12·5	$C_{11}H_{13}ClN_2O$	58·8	5·8	12·5
	Picrate [b]	243—244			HOAc	49·1	3·8	16·6	$C_{17}H_{15}N_5O_8$	48·9	3·6	16·8
	Acetyl	151—152			LP *	68·0	6·1	12·0	$C_{13}H_{14}N_2O_2$	67·8	6·1	12·2
(2b)	Base [a]	89—92			LP *	71·2	7·1		$C_{12}H_{14}N_2O$	71·3	7·0	
	Toluene-*p*-sulphonate	104—109	140	39	Me_2CO	60·7	5·6	7·3	$C_{19}H_{22}N_2O_4S$	61·0	5·9	7·5
	Picrate	226—227			EtOH	50·0	4·0	16·2	$C_{18}H_{17}N_5O_8$	50·1	4·0	16·2
(2c)	Base [c]	Oil										
	Toluene-*p*-sulphonate	170—172	160	39	MeCN	60·1	6·0	6·7	$C_{21}H_{26}N_2O_5S$	60·3	6·3	6·7
	Hydrochloride	179—180			MeOH–Et_2O	59·3	6·5	9·4	$C_{14}H_{19}ClN_2O_2$	59·5	6·8	9·9
(2d)	Base [a]	135—138			LP †	71·3	7·0	13·9	$C_{12}H_{14}N_2O$	71·3	7·0	13·9
	Toluene-*p*-sulphonate	229—230	110	63	MeCN	61·1	5·7	7·4	$C_{19}H_{22}N_2O_4S$	61·0	5·9	7·5
(2e)	Base [a]	69—72			LP †	69·6	7·5	11·1	$C_{15}H_{20}N_2O_2$	69·2	7·7	10·8
	Toluene-*p*-sulphonate	197—199 [d]	140	42	MeCN	61·1	6·6	6·4	$C_{22}H_{28}N_2O_5S$	61·1	6·5	6·5
(2f)	Base [a]	141—144			LP *	65·7	6·5	12·6	$C_{12}H_{14}N_2O_2$	66·0	6·5	12·9
	Toluene-*p*-sulphonate	189—190	120	72	MeCN	58·3	5·7	7·0	$C_{19}H_{22}N_2O_5S$	58·5	5·7	7·2
	Hydrochloride	229—231			MeOH–Et_2O	56·8	6·1	10·6	$C_{12}H_{15}ClN_2O_2$	56·6	6·0	11·0
(2g)	Base [a]	Oil				66·6	6·8	11·9	$C_{13}H_{16}N_2O_2$	67·2	6·9	12·1
	Picrate [e]	222—223	140	24	HOAc	49·6	4·2	14·8	$C_{19}H_{19}N_5O_9$	49·5	4·2	15·2
	Hydrochloride	238—240			MeOH–Et_2O	58·2	6·4	9·8	$C_{13}H_{17}ClN_2O_2$	58·1	6·4	10·4

* Light petroleum (b.p. 100—120°). † Light petroleum (b.p. 60—80°).

[a] Analysis obtained on sublimed material. [b] This picrate (75%), m.p. and mixed m.p. 243—244°, was obtained when 2-amino-1-methylquinolin-4(1*H*)-one (1a) and methyl toluene-*p*-sulphonate were fused at 120° and the melt, in water, was added to sodium picrate solution. [c] Unsatisfactory analytical data were obtained for this compound. On brief storage, the *carbonate*, m.p. 43—44°, was formed (Found: C, 62·8; H, 6·9; N, 10·2. $2C_{14}H_{18}N_2O_2,H_2CO_3$ requires C, 62·8; H, 6·9; N, 10·1%). [d] After melting at 183—186° and resolidifying. [e] This picrate (76%), m.p. and mixed m.p. 223—224°, was obtained from the 6-methoxyquinolinone (1f) as described in footnote (*b*).

picrate separated from aqueous ethanol as needles, m.p. 104—105° (Found: C, 49·4; H, 4·3; N, 15·6. $C_{19}H_{19}N_5O_9$ requires C, 49·5; H, 4·2; N, 15·2%).

No imidazoline was isolated when ethyl cyanoacetate (1 mol), *N*-phenylethylenediamine (1 mol), and anhydrous toluene-*p*-sulphonic acid (2 mol) were fused at 210°.

Only phenylethylenediamine was isolated when the base was hydrolysed with 2N-sodium hydroxide at 50° for 3 h.

2-Methoxycarbonylmethylene-1-phenylimidazolidine.— The ethyl ester (4) (1 g) was boiled in methanol (50 ml) containing conc. hydrochloric acid (3 drops) for 4 h. The solvent (35 ml) was removed and the solution poured into water to give the *methyl ester* (0·8 g) as plates, m.p. 132—133°, unchanged by recrystallisation from aqueous ethanol (Found: C, 66·2; H, 6·4; N, 12·8. $C_{12}H_{14}N_2O_2$ requires C, 66·0; H, 6·5; N, 12·8%).

Similar ester exchange with β-dimethylaminoethanol, with hydrochloric acid or sodium hydroxide as catalyst, could not be effected.

N'N' or NN'-*Diacetyl*-N or N'-*ethoxycarbonylacetyl*-N-*phenylethylenediamine* was formed (90%) when the ester (4) (5 g) was heated in acetic anhydride at 50° for 5 min and poured into water. It crystallised from benzene–light ester was treated with isopropenyl acetate, or acetyl chloride–pyridine.

The triacetyl derivative was completely hydrolysed in 0·5 h by boiling 2N-sodium hydroxide, but with 0·1N-sodium hydroxide *NN'*-diacetyl-*N'*-phenylethylenediamine (40%), m.p. and mixed [16] m.p. 117—120°, was obtained.

2-Ethoxycarbonylmethylene-1-phenyl-3-phenylcarbamoylimidazolidine (1·9 g) separated when a solution of the ester (4) (2·32 g) and phenyl isocyanate (1·19 g) in benzene (15 ml) was refluxed for 2·5 h and diluted with light petroleum (b.p. 60—80°). It formed prisms, m.p. 109—111° (from aqueous ethanol), $\nu_{max.}$ 3380 (NH), 1708, and 1650 cm^{-1} (C:O) (Found: C, 69·2; H, 5·7; N, 12·0. $C_{20}H_{21}N_3O_3$ requires C, 68·4; H, 6·0; N, 12·0%).

2-[Ethoxycarbonyl(hydroxyimino)methyl]-1-phenylimidazoline.—To a solution of compound (4) (9·2 g) in 50% aqueous acetic acid (40 ml) at 0° was added dropwise, with stirring, during 10 min, a solution of sodium nitrite (3·2 g) in water (40 ml). After 5 min the solution was basified with 2N-sodium carbonate and the precipitated gum was crystallised

[15] Farbwerke Hoechst A-G., B.P. 1,050,854/1966.

[16] C. Benko and M. Tĭsler, *Croat. Chem. Acta*, 1958, **30**, 243; *Chem. Abs.*, 1960, **54**, 2221).

from aqueous ethanol to give the *hydroxy-imino-compound* (6·0 g) as needles, m.p. 200—202° [Found: C, 59·7; H, 5·5; N, 15·9; *M* (potentiometric titration), 264. $C_{13}H_{15}N_3O_3$ requires C, 59·8; H, 5·8; N, 16·1%; *M*, 261].

2-[*Ethoxycarbonyl*(*phenylsulphonyloxyimino*)*methyl*]-1-*phenylimidazoline*.—To 2-[ethoxycarbonyl(hydroxyimino)-methyl]-1-phenylimidazoline (1·3 g) dissolved in pyridine (10 ml) and cooled to 0° was added, dropwise, with stirring, benzenesulphonyl chloride (0·8 g) in dry benzene (10 ml). The mixture was kept at 0° overnight, heated on a steam-bath for 30 min, and evaporated. The solid obtained when the residual oil was triturated with light petroleum (b.p. 80—100°) crystallised from benzene–light petroleum (b.p. 80—100°) and gave the O-*benzenesulphonate* as needles, m.p. 110—112° (decomp.) (Found: C, 56·7; H, 4·8; N, 10·3. $C_{19}H_{19}N_3O_5S$ requires C, 56·9; H, 4·8; N, 10·5%), $\nu_{max.}$ 1718 cm^{-1} (CO_2Et). The ester rapidly decomposed to give an uncrystallisable gum.

2-[*Carboxy*(*hydroxyimino*)*methyl*]-1-*phenylimidazoline*.—A solution of the hydroxyimino-ester (5 g) in 2N-sodium hydroxide (25 ml) kept at room temperature for 22 h and adjusted to pH 7 with hydrochloric acid slowly deposited the *acid* (4·0 g) as plates, m.p. 170° (decomp.), unchanged by recrystallisation from water (Found: C, 56·7; H, 4·9; N, 18·5. $C_{11}H_{11}N_3O_3$ requires C, 56·7; H, 4·7; N, 18·0%), $\nu_{max.}$ 3100, 2710 [N·OH, CO·OH (hydrogen bonded)], 1650 (C:O), and 1620 cm^{-1} (C:N).

1-*Phenylimidazolidin*-2-*one*.—When the foregoing acid (1 g) was heated in dimethylformamide (5 ml) there was a strong exothermic reaction (HCN evolved); after refluxing for 5 min the mixture was poured into water (20 ml) to precipitate the imidazolidinone (0·35 g), m.p. and mixed [17] m.p. 161—162°, $\nu_{max.}$ 3250 (NH) and 1678 cm^{-1} (C:O), τ 8·08 (0·4H, s, disappears in D_2O), 6·63—5·92 (4H, m), 4·25br (0·6H, s, disappears with D_2O), and 3·12—2·38 (5H, m).

A similar decomposition in boiling acetic anhydride gave 1-*acetyl*-3-*phenylimidazolidin*-2-*one* (57%), which separated from benzene–light petroleum (b.p. 80—100°) as prisms, m.p. 109—109·5° (Found: C, 64·6; H, 5·9; N, 14·2. $C_{11}H_{12}N_2O_2$ requires C, 64·7; H, 5·9; N, 13·7%). This acetyl derivative was hydrolysed by 2N-sodium hydroxide to the imidazolidinone, m.p. and mixed m.p. 161—163°.

2,3-*Dihydroimidazo*[1,2-a]*quinolin*-5(1H)-*one* (6a).—The imidazolidine (4) (15 g) was heated in polyphosphoric acid (60 g) at 160° for 4 h; the melt was poured into water (200 ml) and the solution was basified with 10N-sodium hydroxide. The mixture was evaporated to dryness at reduced pressure and the residue was extracted with boiling ethanol (3 × 200 ml); the extracts were evaporated to dryness and the solid, crystallised from water, gave the *imidazoquinoline* (7·7 g) as prisms, m.p. 256—257° (Found: C, 70·7; H, 5·3; N, 14·7. $C_{11}H_{10}N_2O$ requires C, 71·0; H, 5·4; N, 15·1%), τ ($CF_3{\cdot}CO_2H$) 6·05—5·08 (m, $CH_2{\cdot}CH_2$), 3·52 (s, 4-H), and 2·62—1·62 (m, ArH_4). Its *acetyl* derivative had m.p. 268—276° (prisms from water) (Found: C, 68·6; H, 5·2; N, 12·1. $C_{13}H_{12}N_2O_2$ requires C, 68·4; H, 5·3; N, 12·3%), $\nu_{max.}$ 1690 and 1622 cm^{-1} (C:O); and the *acetyl derivative hydrochloride* crystallised from water as plates, m.p. 265—266° (Found: C, 59·0; H, 4·8; N, 10·6. $C_{13}H_{13}ClN_2O_2$ requires C, 59·0; H, 4·9; N, 10·6%).

The imidazolidine (4) could not be cyclised in boiling diphenyl ether and no imidazolidine was formed by fusion of equimolecular amounts of *N*-phenylethylenediamine toluene-*p*-sulphonate and ethyl cyanoacetate at 210°.

Benzoylation of 2,3-*dihydroimidazo*[1,2-a]*quinolin*-5(1H)-*one*.—(*a*) When the imidazoquinoline (1·7 g) was shaken vigorously with N-sodium hydroxide (40 ml) and benzoyl chloride (2 ml) the 3-*benzoyl* derivative (2·2 g) separated. It formed plates, m.p. 258—259° (from butanol) (Found: C, 74·9; H, 4·6; N, 9·4. $C_{18}H_{14}N_2O_2$ requires C, 74·5; H, 4·9; N, 9·7%), $\nu_{max.}$ 1690 and 1623 cm^{-1} (C:O).

(*b*) The imidazoquinoline with benzoyl chloride (10 mol. equiv.) and sodium hydroxide gave 1-β-*benzamidoethyl*-2(or 4)-*benzoyloxyquinolin*-4(or 2)-*one* or 1-benzoyl-2-(*N*-2-hydroxyethylbenzamido)quinolin-4(1*H*)-one as needles (from ethanol), m.p. 209—210° (Found: C, 72·5; H, 4·8; N, 6·6. $C_{25}H_{20}N_2O_4$ requires C, 72·8; H, 4·9; N, 6·8%), $\nu_{max.}$ 3450 (NH or OH), 1744, 1656sh, and 1632 cm^{-1} (C:O).

2,4-*Dihydro*-4-*hydroxyiminoimidazo*[1,2-a]*quinolin*-5(1H)-*one*.—(*a*) This *compound* (0·4 g) was precipitated when a solution of the imidazoquinoline (6a) (0·37 g) in 50% aqueous acetic acid (8 ml) at 0° was added to a solution of sodium nitrite (0·14 g) in water (5 ml) and the solution was neutralised with 2N-sodium carbonate. It formed dark green prisms, m.p. 290—293° (decomp.) (from dimethylformamide), $\nu_{max.}$ 3290 (OH), 1642 (C:O), and 1618 cm^{-1} (C:N) (Found: C, 61·1; H, 4·4: N, 19·9. $C_{11}H_9N_3O_2$ requires C, 61·4; H, 4·2; N, 19·5%).

(*b*) The hydroxyimino-compound (0·15 g), m.p. and mixed m.p. 290—293° (decomp.) separated from the cooled reaction mixture obtained by boiling 2,3-dihydro-3-nitroso-imidazo[1,2-*a*]quinolin-5(1*H*)-one (0·2 g) in 2N-hydrochloric acid for 5 min.

4-*Bromo*-2,3-*dihydroimidazo*[1,2-a]*quinolin*-5(1H)-*one* (6b).—The *hydrobromide* of this quinoline (2·8 g) separated when a boiling solution of the imidazoquinoline (1·8 g) in acetic acid (25 ml) was treated during 10 min with bromine (1·6 g) in acetic acid (4 ml) and boiling was continued for a further 30 min; it formed prisms, m.p. 259—260° (decomp.) (from ethanol with 1 drop of water) (Found: C, 38·1; H, 2·9; N, 8·3. $C_{11}H_{10}Br_2N_2O$ requires C, 38·2; H, 2·9; N, 8·1%). The *base* crystallised from aqueous 2-ethoxyethanol as prisms, m.p. 252—253° (decomp.) (Found: C, 49·8; H, 3·4; N, 10·9. $C_{11}H_9BrN_2O$ requires C, 49·8; H, 3·4; N, 10·6%), $\nu_{max.}$ 3140 (NH) and 1625 cm^{-1} (C:O).

5-*Chloro*-1,2-*dihydroimidazo*[1,2-a]*quinoline* (7a).—The imidazo[1,2-a]quinolin-5-one (6a) (10 g) was refluxed with phosphoryl chloride (120 ml) for 2·5 h and the solvent was evaporated off at reduced pressure. Water (500 ml) was added cautiously to the residue and the mixture was boiled for 1 h, and filtered. The solid obtained by basifying the filtrate with 2N-sodium hydroxide crystallised from aqueous acetone to give the chloroimidazoquinoline (7·5 g) as yellow prisms, m.p. 98—99°, $\nu_{max.}$ 3300 (OH) and 1638 cm^{-1} (C:N), $\nu_{max.}$ (CCl_4) 1638 cm^{-1} (C:N), τ 7·30 (0·45H, *H*DO), 6·40—5·85 (4H, $CH_2{\cdot}CH_2$), 3·36 (1H, 4-H), and 3·30—2·40 (4H, ArH_4) [Found, for material dried (P_2O_5) *in vacuo*: C, 62·6; H, 4·1; N, 13·3%; *M* (potentiometric titration), 212; *m/e* 204. $C_{11}H_9ClN_2,0{\cdot}4H_2O$ requires C, 62·3; H, 4·6; N, 13·2; *M*, 211·7. $C_{11}H_9ClN_2$ requires *m/e* 204 for ^{35}Cl]. The base decomposed on drying above 100°.

The *hydrochloride* crystallised from butanol as plates, m.p. 354—355° (decomp.) (Found: C, 54·8; H, 4·1; N, 11·7. $C_{11}H_{10}Cl_2N_2$ requires C, 54·8; H, 4·2; N, 11·6%), and its *picrate*, plates from dimethylformamide, had m.p. 258—259° (decomp.) (Found: C, 47·4; H, 3·0; N, 15·9. $C_{17}H_{12}ClN_5O_7$ requires C, 47·0; H, 3·0; N, 16·1%).

The chloro-group was hydrolysed by boiling 20% potassium hydroxide in ethylene glycol, but (7a) was not attacked by aqueous 40% sodium hydroxide or sodium butoxide in butanol.

[17] H. E. Newman, *Ber.*, 1891, **24**, 2192.

4-*Bromo-5-chloro*-1,2-*dihydroimidazo*[1,2-a]*quinoline* (7c).—This was prepared (61%) as described for the corresponding chloro-compound (7a). It crystallised from aqueous ethanol as *needles*, m.p. 175—176° (Found: C, 47·1; H, 3·0; N, 10·1. $C_{11}H_8BrClN_2$ requires C, 46·6; H, 2·8; N, 9·9%), $\nu_{max.}$ 1615 cm^{-1} (C:N). The *picrate* separated from aqueous dimethylformamide as prisms, m.p. 244—245° (Found: C, 39·9; H, 2·2; N, 13·7. $C_{17}H_{11}BrClN_5O_7$ requires C, 39·8; H, 2·2; N, 13·7%).

This compound was resistant to boiling 2N-sodium hydroxide.

1,2-*Dihydro-5-piperidinoimidazo*[1,2-a]*quinoline* (7c).—This compound, produced (65%) by refluxing the 5-chloro-compound with piperidine (3 ml) for 10 min and adding water (10 ml), crystallised from light petroleum (b.p. 80—100°) as yellow *plates*, m.p. 128—129° (Found: C, 76·4; H, 7·6; N, 16·6. $C_{16}H_{19}N_3$ requires C, 75·9; H, 7·6; N, 16·6%), $\nu_{max.}$ 1640 cm^{-1} (C:N). The *hydrochloride* separated from ethyl acetate–butanol as plates, m.p. 269—270° (Found: C, 62·9; H, 7·0; N, 13·4. $C_{16}H_{20}ClN_3,H_2O$ requires C, 62·4; H, 7·2; N, 13·7%).

1,2-*Dihydro-5-methylaminoimidazo*[1,2-a]*quinoline* (7d).—A solution of the 5-chloro-compound (1·1 g) in ethanol containing methylamine (0·3 g), kept for 14 days at room temperature, slowly deposited the *methylamine hydrochloride* (0·8 g), m.p. 320—340° (decomp.). It crystallised from aqueous ethanol as needles of unchanged m.p. (Found: C, 61·5; H, 5·8; N, 18·2. $C_{12}H_{14}ClN_3$ requires C, 61·1; H, 6·0; N, 17·8%). The *base* crystallised from propan-2-ol as prisms, m.p. 238—240° (decomp.) (Found: C, 66·5; H, 6·9; N, 19·0. $C_{12}H_{13}N_3,H_2O$ requires C, 66·3; H, 7·0; N, 19·3%), $\nu_{max.}$ 3280 (NH) and 1630 cm^{-1} (C:N).

1,2-*Dihydro-5-(2-hydroxyethylamino)imidazo*[1,2-a]*quinoline* (7e).—A solution of the chloro-compound (0·75 g) and ethanolamine (0·75 ml) in ethanol (25 ml) was refluxed for 6 h. The solvent was removed under reduced pressure; basification of the residue dissolved in water gave the *hydroxy-amine* (0·6 g), which crystallised from aqueous ethanol as prisms, m.p. 256—257° (Found: C, 68·1; H, 6·2; N, 18·2. $C_{13}H_{15}N_3O$ requires C, 68·1; H, 6·6; N, 18·3%).

5-(2-*Chloroethylamino*)-1,2-*dihydroimidazo*[1,2-a]*quinoline*.—The foregoing hydroxyethylamine (0·25 g) was boiled in thionyl chloride (3 ml) containing dimethylformamide (3 drops), and the residue obtained by evaporation of the solvent, crystallised from water, gave the chloro-amine hydrochloride (0·2 g), m.p. 218—220° (lit.,[8] 220—221°). The base separated from aqueous ethanol as yellow prisms which decomposed above 320° (lit.,[8] m.p. >320°) (Found: C, 62·6; H, 5·6; N, 16·9. Calc. for $C_{13}H_{14}ClN_3$: C, 63·0; H, 5·7; N, 17·0%).

4-*Bromo*-1,2-*dihydro-5-piperidinoimidazo*[1,2-a]*quinoline*.—The base formed from the bromo-chloro-compound and piperidine in ethanol was recovered as its *hydrochloride* (71%) plates, m.p. 155—155·5° (from ethyl acetate–butan-1-ol) (Found: C, 49·3; H, 5·4; N, 10·9. $C_{16}H_{19}BrClN_3,H_2O$ requires C, 49·7; H, 5·5; N, 10·9%).

Reactions of 5-*Chloro*-1,2-*dihydroimidazo*[1,2-a]*quinoline*.—(a) *With acetic anhydride*. The chloro-compound (0·5 g) treated dropwise, with cooling, with acetic anhydride (3 ml) and then heated on a steam-bath for 0·5 h, gave 3-acetyl-2,3-dihydroimidazo[1,2-*a*]quinolin-5(1*H*)-one hydrochloride (0·4 g). This and the base liberated by sodium hydroxide had m.p.s and i.r. spectra identical with those of authentic specimens.

The same product (57%) was obtained when the chloro-hydrochloride was treated with acetic anhydride. No reaction occurred when the chloro-compound was treated with acetyl chloride or acetyl chloride–sodium acetate.

(b) *With benzoic anhydride*. The chloro-compound treated with benzoic anhydride similarly gave the 3-benzoylimidazo[1,2-*a*]quinoline, m.p. and i.r. spectrum identical with those of an authentic specimen.

(c) *With nitrous acid*. When the chloro-hydrochloride (0·75 g) and saturated sodium nitrite solution (2 ml) were warmed on a steam-bath for 2 min and cooled, 2,3-*dihydro*-3-*nitrosoimidazo*[1,2-a]*quinoline*-5(1H)-*one* (0·5 g), m.p. 210—220° (decomp.), separated. It crystallised as pale green needles of unchanged m.p. from aqueous ethanol (Found: C, 61·0; H, 4·1; N, 19·6. $C_{11}H_9N_3O_2$ requires C, 61·4; H, 4·2; N, 19·5%).

1,2-*Dihydroimidazo*[1,2-a]*quinoline* (7f).—(*a*) 5-Chloro-1,2-dihydroimidazo[1,2-*a*]quinoline (2·7 g) in methanol (68 ml) was hydrogenated at atmospheric pressure over 10% palladium–charcoal (0·5 g) in the presence of potassium hydroxide (2·7 g) (uptake 1·05 mol. equiv.). The catalyst was removed; the filtrate was evaporated to 15 ml, acidified with lactic acid, and added to sodium picrate to give the *imidazoquinoline picrate*, which separated (74%) from aqueous dimethylformamide as needles, m.p. 236—237° (Found: C, 51·3; H, 3·4; N, 17·0. $C_{17}H_{13}N_5O_7$ requires C, 51·1; H, 3·3; N, 17·5%). The *base* was obtained as an amorphous solid, m.p. 45—49°, which could not be crystallised (Found: C, 70·0; H, 6·1; N, 15·1. $C_{11}H_{10}N_2,H_2O$ requires C, 70·2; H, 6·4; N, 14·9%), τ 7·44 (1H, exchanges with D_2O), 5·98 (4H, s, $CH_2{\cdot}CH_2$), and 3·48—2·42 (6H, m, ArH_6); its *hydrochloride* formed prisms, m.p. 272—275° (from methanol–ether) (Found: C, 58·6; H, 5·9; N, 12·4. $C_{11}H_{11}ClN_2,H_2O$ requires C, 58·8; H, 5·8; N, 12·5%).

(*b*) 4-Bromo-5-chloro-1,2-dihydroimidazo[1,2-*a*]quinoline, similarly hydrogenated, took up 2 mol. equiv. of hydrogen and gave the same picrate, m.p. and mixed m.p. 236—237°.

1,2-*Dihydro-5-methoxyimidazo*[1,2-a]*quinoline* (7g), prepared by the method described for 1-alkyl-4-methoxyquinolin-2(1*H*)-imines, sublimed at 120° and 0·03 mmHg as prisms, m.p. 110—111° (Found: C, 71·8; H, 5·9; N, 13·6. $C_{12}H_{12}N_2O$ requires C, 72·0; H, 6·0; N, 14·0%); the *toluene*-p-*sulphonate* formed prisms, m.p. 206—208° (from methanol–ether) (Found: C, 61·1; H, 5·4; N, 7·0. $C_{19}H_{20}N_2O_4S$ requires C, 61·3; H, 5·4; N, 7·5%); the *hydrochloride*, m.p. 194—195° (decomp.), formed needles (from methanol–ether) (Found: C, 52·5; H, 6·1; N, 9·6. $C_{12}H_{13}ClN_2O,2H_2O$ requires C, 52·8; H, 6·3; N, 10·3%), and the *picrate*, prisms from dimethylformamide, had m.p. 273—276° (decomp.) (Found: C, 50·7; H, 3·7; N, 15·9. $C_{18}H_{15}N_5O_8$ requires C, 50·4; H, 3·5; N, 16·3%). Similarly, 1,2-*dihydro-5-propoxyimidazo*[1,2-a]*quinoline* (7h) formed prisms, m.p. 137—138°, after sublimation at 130° and 0·01 mmHg (Found: C, 73·6; H, 6·9; N, 12·4. $C_{14}H_{16}N_2O$ requires C, 73·7; H, 7·1; N, 12·3%); the *toluene*-p-*sulphonate*, prisms from acetonitrile, melted at 154° with resolidification, remelting at 160—162° (Found: C, 62·9; H, 6·0; N, 7·0. $C_{21}H_{24}N_2O_4S$ requires C, 63·0; H, 6·0; N, 7·0%), and the *hydrochloride*, prisms from acetonitrile, had m.p. 193—194° (decomp.) (Found: C, 56·2; H, 7·0; N, 8·9. $C_{14}H_{17}ClN_2O,2H_2O$ requires C, 55·9; H, 7·0; N, 9·3%). This, and the foregoing ether, boiled with 48% hydrobromic acid, gave the parent imidazoquinoline (6a) in good yield.

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