499. *Syntheses of Heterocyclic Compounds. Part VIII.*[1] *Cyclisation of N-2-Acylaminophenyl Heterocycles with Polyphosphoric Acid.*

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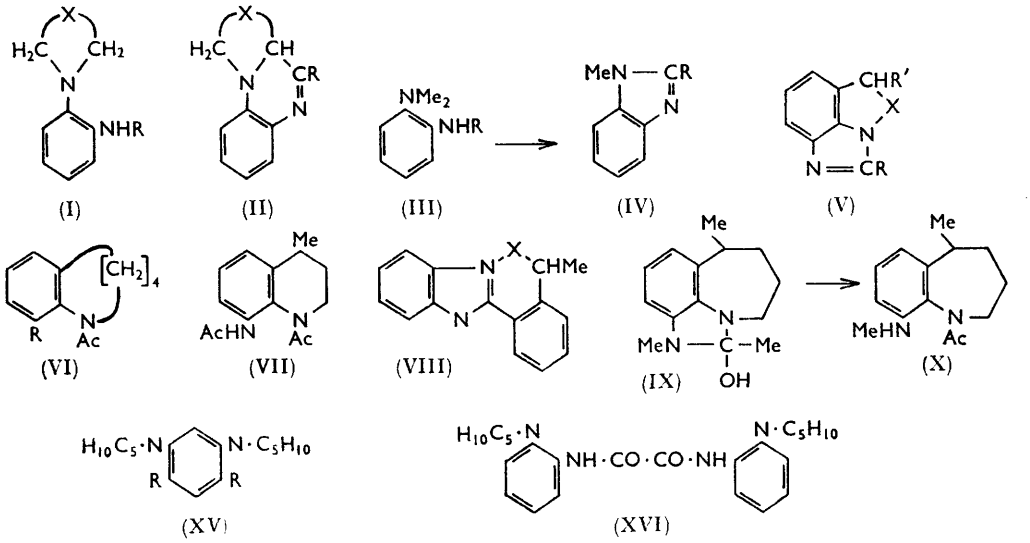
Treatment of *N*-substituted heterocycles of type (I; R = acyl) with hot polyphosphoric acid unexpectedly yields the benzimidazoles (V), with cleavage of the heterocyclic ring. The orientation of the products is discussed and a mechanism for their formation proposed.

We have shown [2] that acylamino-groups can be made to cyclise on to a paraffinic methylene group by using polyphosphoric acid. By analogy, this reaction was expected to give the unknown 1,2-dihydroquinoxalines (II; X = $[CH_2]_3$, $[CH_2]_4$, or $[CH_2]_5$) when applied to the heterocyclic acylated amines (I; R = acyl, X = $[CH_2]_2$, $[CH_2]_3$, or $[CH_2]_4$). The products gave correct analyses for the quinoxalines (II), but their chemical and spectral properties did not support such an assignment. For instance, the product derived from the pyrrolidine (I; R = Ac, X = $[CH_2]_2$) was extremely stable to hydrogenation and dehydrogenation, which is unexpected for a partly hydrogenated quinoxaline.[3] Moreover, its infrared spectrum suggested the presence of a 1,2,3-trisubstituted benzene ring (two strong bands at 754 and 801 cm.$^{-1}$ in Nujol, and characteristic bands at 2000—1700 cm.$^{-1}$ in CCl_4), and its ultraviolet spectrum had two absorption peaks ($\lambda_{max.}$ 275 and 283 mμ) characteristic of 2-alkylbenzimidazoles.[4] The likelihood of benzimidazole rather than quinoxaline formation was enhanced when it was found that the simpler but analogous dimethylaminoanilines (III; R = CHO, Ac, or Bz) cyclised in hot polyphosphoric acid to give the 1-methylbenzimidazoles (IV; R = H, Me, or Ph). This reaction, which entails elimination of a methyl group, is not wholly unexpected since *o*-dimethylaminoaniline (III; R = H) and its acetyl derivative are known to give 1,2-dimethylbenzimidazole (IV; R = Me) when heated in acetic anhydride.[5] Our products (I) were not cyclised by refluxing acetic or propionic anhydride.

It was clearly desirable to synthesise the azepinobenzimidazole (V; R = Me, R′ = H, X = $[CH_2]_3$), since it embodies all the structural features deduced to be present in the product under discussion. The successful route involved nitration of the acetyl compound (VI; R = H) with a mixture of concentrated nitric acid and acetic anhydride, reduction of the resulting nitro-compound (VI; R = NO_2) to the amine (VI; R = NH_2), and cyclisation with hydrochloric acid. The compound was, however, not identical with the substance obtained from the cyclisation of the pyrrolidine (I; R = Ac, X = $[CH_2]_2$), though it had similar spectral features. For this reason the isomeric imidazoquinoline (V; R = R′ = Me, X = $[CH_2]_2$) was considered a likely alternative. It was feasible also on the grounds that the suspected opening of the pyrrolidine ring in (I; X = $[CH_2]_2$), which is the most likely step to account for the trisubstituted benzene in (V), frees an unsaturated side-chain (cf. mechanism below) which could well attach itself to the benzene ring by its penultimate carbon atom under the Friedel–Crafts conditions. The preparation consisted of hydrogenation of 4-methyl-8-nitroquinoline, acetylation to give the tetrahydroquinoline (VII), and cyclisation by acid to the required imidazoquinoline (V; R = R′ = Me, X = $[CH_2]_2$), which was identical with the unknown substance. Structural assignment of all the products made from other acyl derivatives (I; R = H or Bz) and other heterocycles (I; X = $[CH_2]_3$ or $[CH_2]_4$) was based on analogy and corroborated by infrared and nuclear magnetic resonance spectra. Thus, the piperidino-compounds

[1] Part VII, Lathwood and Suschitzky, *J.*, 1964, 2477.
[2] Denton, Smalley, and Suschitzky, *J.*, 1964, 2421.
[3] Rodd, "Chemistry of Carbon Compounds," Elsevier, Amsterdam, 1959, Vol. IV, p. 1368.
[4] Beaven, Holiday, and Johnson, *Spectrochim. Acta*, 1951, **4**, 338; Hunger, Kebrle, Rossi, and Hoffmann, *Helv. Chim. Acta*, 1960, **43**, 800; Smith and Suschitzky, *Tetrahedron*, 1961, **16**, 80.
[5] Pinnow, *Ber.*, 1895, **28**, 3042; 1898, **31**, 2985.

(I; R = CHO, Ac, or Bz; X = $[CH_2]_3$) yielded benzimidazoles (V; R′ = Me, X = $[CH_2]_3$) with a fused methylazepine ring, and the perhydroazepines (I; R as before, X = $[CH_2]_4$) yielded benzimidazoles (V; R′ = Me, X = $[CH_2]_4$) with a fused methylazocine ring. Structural ambiguity could arise in the ring-closure of the benzamido-compounds (I; R = Bz) because two benzene rings are available for alkylation by the aliphatic side-chain (CH_2–X–CH_2·N) to give conceivably a mixture of a three- (V) and a four-ring system (VIII). Only one product was obtained, whose infrared spectrum favoured structure (V) since it was consistent with the presence of a mono- and a tri-substituted benzene ring (bands at **701**, **748**, and **1700—2000** cm.$^{-1}$, in Nujol, characteristic of a phenyl group; also at **720** and **773** cm.$^{-1}$, as expected for a 1,2,3-trisubstituted benzene).



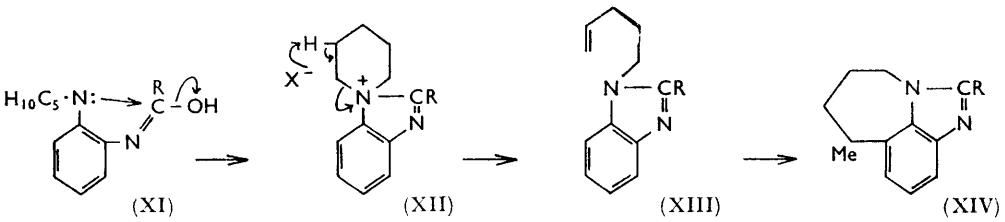
The benzimidazoles (V) were stable to boiling ethanolic sodium hydroxide and aqueous sulphuric acid (30%). Ring fission rapidly occurred, however, when the benzimidazolium methiodide derived from (V; R = R′ = Me, X = $[CH_2]_3$) was heated with aqueous alkali, yielding the diamine (X). Intervention of the appropriate " pseudobase " (IX in this case) s the accepted explanation of benzimidazole cleavage under such mild conditions.[6] It is noteworthy that permanganate treatment of the azepinobenzimidazole (V; R = R′ = Me, X = $[CH_2]_3$) produced an alcohol (V: OH for H; R, R′, and X as before) by oxidation of the only tertiary carbon atom, and did not affect the usually reactive heterocyclic methyl group.

The best yields of benzimidazoles were given by piperidines (I; R = acyl, X = $[CH_2]_3$) on the one hand and acetyl derivatives (I; R = Ac) on the other. Ether-insoluble polymeric material, possibly formed by intermolecular Friedel–Crafts reactions, for which polyphosphoric acid is a good catalyst, and the parent aromatic amines (I; R = H) were among the by-products. No improvement in the yields could be achieved by adding the appropriate anhydride to the reaction mixture, with the object of minimising deacylation.

Our original view on the mechanism of this benzimidazole formation was that first the heterocyclic ring of the starting material (cf. I) is opened by heating in polyphosphoric acid, a reaction which was thought to have some analogy with the behaviour of amine phosphates.[7] This is followed by cyclic dehydration involving the tautomeric form [N:C(OH)R] of the amide, to give an imidazole, and completed by alkylation of the benzene ring to furnish products of type (V). However, the first step of this scheme proved untenable when it

[6] Wright, *Chem. Rev.*, 1951, **48**, 397.
[7] Harries, *Ber.*, 1901, **34**, 300; Harries and Johnson, *ibid.*, 1905, **38**, 1832.

was found that neither piperidino- nor 1-pyrrolidinyl-benzene suffered cleavage of the heterocyclic moiety in hot polyphosphoric acid. The inferred fission of the heterocyclic ring thus seems to be a consequence of imidazole formation and not to precede it. Hence we believe the first step to be cyclisation to a spiro-benzimidazole (*e.g.*, XII). Next, the saturated ring opens with formation of a benzimidazole possessing an unsaturated side-chain (*e.g.*, XIII) which, under the prevailing Friedel–Crafts conditions, attacks the benzene ring. The driving force for the fission is the gain in stability which results from the conversion of a " hetero-olefinic " spiro-compound into a hetero-aromatic benzimidazole. The salient features of this mechanism are shown for the piperidino-compound in the scheme (XI ⟶ XIV; X = anion of polyphosphoric acid).



Other compounds treated with polyphosphoric acid included the dipiperidino-benzene (XV; R = NHAc) which gave tars although its oxidative cyclisation to a di-imidazole has recently been accomplished.[8] Various morpholino-derivatives (I: R = CHO, Ac, or Bz; X = CH_2·O·CH_2) remained unchanged at 150°, and, on prolonged heating with the reagent, gave water-soluble compounds which were not investigated. None of the piperazinyl compounds (I: R = CHO, Ac, or Bz; X = CH_2·NH·CH_2, CH_2·N(CHO)·CH_2, CH_2·NAc·CH_2, or CH_2·NBz·CH_2) could be made to cyclise. They were either hydrolysed to the parent amine or rearranged (cf. Experimental section). Cyclisation also failed with the derivatives (I; R = SO_2·Ph or CO_2Et, X = $[CH_2]_3$), both being deacylated, the latter with evolution of carbon dioxide. The oxamate (I; R = CO·CO_2Na, X = $[CH_2]_3$) liberated carbon dioxide on treatment with polyphosphoric acid, and gave three products on step-wise neutralisation of the mixture with ammonium hydroxide. The first fraction consisted of *NN'-di*-(2-piperidinophenyl)oxamide (XVI), which was readily and unambiguously made from ethyl oxalate and *N*-(2-aminophenyl)piperidine (I; R = H, X = $[CH_2]_3$) in polyphosphoric acid, the second was the ammonium salt (I; R = CO·CO_2NH_4, X = $[CH_2]_3$) of the amide, and the third contained the benzimidazole (V; R = H, R' = Me, X = $[CH_2]_3$).

Experimental

Polyphosphoric acid was commercial tetraphosphoric acid (Albright and Wilson) containing 80—85% of phosphorus pentoxide.

N-2-*Acylaminophenyl Heterocycles*.—These derivatives (I; R = CHO, Ac, or Bz) of pyrrolidine, piperidine, morpholine, and hexahydroazepine were prepared as previously described.[8,9]

The *sulphonamide* (I; R = SO_2·Ph, X = $[CH_2]_3$) had m. p. 130° (Found: C, 65·0; H, 6·6. $C_{17}H_{20}N_2O_2S$ requires C, 64·5; H, 6·4%).

The *sodium oxamate* (I; R = CO·CO_2Na, X = $[CH_2]_3$) was made from a solution of N-2-aminophenylpiperidine (8·8 g.) in benzene (50 ml.) to which ethoxalyl chloride (5·7 ml.) was added dropwise. The mixture was heated on a steam-bath (15 min.), cooled, and acidified (hydrochloric acid). The benzene layer was removed and, on neutralising the aqueous layer, the sodium salt was precipitated as white needles, m. p. 230° (decomp.) (Found: C, 57·2; H, 5·9. $C_{13}H_{15}N_2NaO_3$ requires C, 57·8; H, 5·6%).

N-2-*Dimethylaminophenyl Acylamides*.—*o*-Dimethylaminoaniline was obtained (95%) by heating *o*-chloronitrobenzene and a 26% aqueous solution of dimethylamine in an autoclave for 2 hr. at 150°, and reducing the resulting nitro-compound *in situ* with Raney nickel and hydrogen at 50 atm. The m. p.s. of the acyl acompounds (III; Ac or Bz) made in the usual way

[8] Meth-Cohn and Suschitzky, *J.*, 1963, 4666.
[9] Meth-Cohn, Smalley, and Suschitzky, *J.*, 1963, 1666.

agreed with the literature [10] m. p.s. N-(2-*Dimethylaminophenyl*)*formamide* had m. p. 112° (Found: C, 66·0; H, 7·3. $C_9H_{12}N_2O$ requires C, 65·8; H, 7·4%).

Cyclisation in Polyphosphoric Acid.—(*a*) The acylated dimethylaminoanilines (III; R = CHO, Ac, or Bz) (2 g.) were heated in polyphosphoric acid (20 g.) at 150° for 1 hr. The mixture was poured into water, neutralised with aqueous ammonium hydroxide, and extracted with chloroform. Removal of the solvent gave *N*-methylbenzimidazole (0·8 g.), 2-methyl- (1·6 g.), and 2-phenyl-*N*-methylbenzimidazole (0·92 g.), all of which had the m. p.s quoted.[11]

(*b*) The *N*-2-acylaminophenyl derivatives (I; see Table 1) were heated with a tenfold excess by weight of polyphosphoric acid at 145—150°, and the products, whose details are given in Table 1, were isolated as in (*a*). Some ultraviolet spectra are listed in Table 2 and the nuclear magnetic resonance spectrum of one of the products (in deuterochloroform with tetramethylsilane as internal reference) is given in Table 3. Integrations fitted the suggested structure.

TABLE 1.

Benzimidazoles (V; R′ = Me) derived from *N*-2-acylaminophenyl derivatives (I; R = CHO, Ac, or Bz) of pyrrolidine, piperidine, and hexahydroazepine by heating in polyphosphoric acid for 0·5—1 hr.

					Found (%)			Required (%)	
No.	X	R	M. p. or b. p./mm.	Yield (%)	C	H	Formula	C	H
1	$[CH_2]_2$	H	125°/0·5 [a]	27	—	—	—	—	—
2	$[CH_2]_2$	Me	140	21	77·9	7·6	$C_{12}H_{14}N_2$	77·4	7·6
3	$[CH_2]_2$	Ph	—	10	—	—	—	—	—
4	$[CH_2]_3$	H	157/2 [b]	58	—	—	—	—	—
5	$[CH_2]_3$	Me	117	90	77·5	7·9	$C_{13}H_{16}N_2$	78·0	8·05
6	$[CH_2]_3$	Ph	130	55	82·5	6·8	$C_{18}H_{18}N_2$	82·4	6·9
7	$[CH_2]_4$	H	— [a]	10	—	—	—	—	—
8	$[CH_2]_4$	Me	120	35	78·6	8·2	$C_{14}H_{18}N_2$	78·5	8·5
9	$[CH_2]_4$	Ph	102	14	83·0	7·6	$C_{19}H_{20}N_2$	82·6	7·3

Picrates

	Found (%)			Required (%)		
Compound	C	H	Formula	C	H	M. p.
1	50·4	3·8	$C_{17}H_{15}N_5O_7$	50·9	3·8	175°
2	52·0	4·1	$C_{18}H_{17}N_5O_7$	52·05	4·1	219
3	57·4	4·1	$C_{23}H_{19}N_5O_7$	57·9	4·0	180
4	51·3	4·3	$C_{18}H_{17}N_5O_7$	51·05	4·1	220
5	53·3	4·7	$C_{19}H_{19}N_5O_7$	53·2	4·5	195
6 [c, d]	—	—	—	—	—	—
7	53·1	4·6	$C_{19}H_{19}N_5O_7$	53·2	4·5	214
8	54·1	4·8	$C_{20}H_{21}N_5O_7$	54·2	4·8	165
9 [c]	—	—	—	—	—	—

[a] Unstable and hence unsuitable for analysis. [b] Hygrosopic low-melting solid. Its *methiodide* had m. p. 150° (Found: C, 47·1; H, 5·4. $C_{13}H_{17}IN_2$ requires C, 47·6; H, 5·2%). [c] Did not form a picrate. [d] *Methiodide*, m. p. 224° (Found: C, 56·1; H, 5·5. $C_{19}H_{21}IN_2$ requires C, 56·4; H, 5·2%)

TABLE 2.

Ultraviolet spectra of the benzimidazoles (V; R′ = Me) in methanol.

X	R	$\lambda_{max.}$ (mμ)	log ε	λ_{max} (mμ)	log ε	$\lambda_{max.}$ (mμ)	log ε	$\lambda_{max.}$ (mμ)	log ε
$[CH_2]_2$	H *	212	4·13	254	3·79	275	3·70	282	3·70
$[CH_2]_2$	Me	214	4·77	257	3·80	275	3·70	283	3·69
$[CH_2]_3$	Me	213	4·59	257	3·87	276	3·68	284	3·62
$[CH_2]_3$	Ph	215	4·76	244	4·12	291	4·12		
$[CH_2]_4$	Me	215	4·51	259	3·79	276	3·67	284	3·63

* Measured as picrate against a blank of picric acid of same molar concentration.

TABLE 3.

The chemical shifts (τ-values) of protons of compound (V; R = R′ = Me, X = $[CH_2]_3$).

Group	τ	Bands	Group	τ	Bands
6-Me (aliphatic)	8·74	Doublet	6-H	*ca.* 6·75	Broad, complex
4,5-CH_2·CH_2	8·04	Complex	3-CH_2	*ca.* 6·14	Complex
2-Me	7·74	Singlet	7-H, 8-H, 9-H ...	*ca.* 7·00	Complex

[10] Pinnow, *Ber.*, 1899, **32**, 1688; Bamberger and Tschirner, *ibid.*, 1899, **32**, 1905.
[11] Fischer and Wreszinski, *Ber.*, 1892, **25**, 2711, 2842.

(*c*) The morpholino-compounds (I: R = CHO, Ac, or Bz; X = $CH_2 \cdot O \cdot CH_2$), the sulphonamide (I; R = $SO_2 \cdot Ph$, X = $[CH_2]_3$), and the dipiperidino-compound [8] (XV; R = NHAc), when heated for up to 1 hr. at various temperatures in polyphosphoric acid, gave mixtures of parent amine and starting material. In the last case, tar formation was predominant. The *ester* (I; R = CO_2Et, X = $[CH_2]_3$), m. p. 31° (Found: C, 68·2; H, 8·0. $C_{14}H_{20}N_2O_2$ requires C, 67·7; H, 8·1%), from the parent base and ethyl chloroformate, was decarboxylated under the same conditions to its parent amine.

(*d*) The acylated piperazines listed in Table 4 were heated at 150° for 0·5 hr. in polyphosphoric acid with the following results: the *formyl compounds* (Nos. 1 and 2) were deacylated, the *diacetyl derivative* (No. 4) gave the monoacetyl compound (I; R = H, X = $CH_2 \cdot NAc \cdot CH_2$),[12] m. p. 138°, which on further heating (1 hr.) at 170° rearranged to the 2-*acetamido-compound* (No. 3). The latter was completely deacylated on prolonged heating. The *dibenzoyl derivative* (No. 7) was hydrolysed to the 2-*benzamido-compound* (No. 6), whereas the *benzoyl derivative* (No. 5) gave a mixture of the above dibenzoyl- (27%) and the 2-benzamido-compound (No. 6). The latter compound, when treated alone, was deacylated completely.

TABLE 4.

N-2-Acylaminophenyl derivatives of piperazine.

		Found (%)				Required (%)	
X in (I)	R	M. p.	C	H	Formula	C	H
1. $CH_2 \cdot N(CHO) \cdot CH_2$	H	128°	64·6	7·4	$C_{11}H_{15}N_3O$	64·4	7·4
2. ,,	CHO	197	61·8	6·3	$C_{12}H_{15}N_3O_2$	61·8	6·5
3. $CH_2 \cdot NH \cdot CH_2$	Ac	150	65·6	7·4	$C_{12}H_{17}N_3O$	65·7	7·8
4. $CH_2 \cdot NAc \cdot CH_2$	Ac	174	64·2	7·6	$C_{14}H_{19}N_3O_2$	64·3	7·3
5. $CH_2 \cdot NBz \cdot CH_2$	H	144	72·7	6·7	$C_{17}H_{19}N_3O$	72·6	6·8
6. $CH_2 \cdot NH \cdot CH_2$	Bz	112	72·8	6·8	,,	,,	,,
7. $CH_2 \cdot NBz \cdot CH_2$	Bz	153	75·2	6·0	$C_{24}H_{23}N_3O_2$	74·8	6·0

(*e*) On heating the sodium oxamate (I; R = $CO \cdot CO_2Na$, X = $[CH_2]_3$) (2·5 g.) in polyphosphoric acid (30 g.) at 145° for 0·5 hr., vigorous evolution of carbon dioxide occurred. The mixture was diluted with water (50 ml.) and neutralised with aqueous ammonium hydroxide which first precipitated *NN'-di-(2-piperidinophenyl)oxamide* (XVI) (0·52 g.) m. p. 241° (decomp.) (Found: C, 71·4; H, 7·4. $C_{24}H_{30}N_4O_2$ requires C, 70·9; H, 7·4%) identical with the compound made by heating the parent amine (I; R = H, X = $[CH_2]_3$) (3·6 g.) with ethyl oxalate (1·46 g.) in polyphosphoric acid (40 g.) for 0·5 hr. at 145°. Complete neutralisation gave an oil, from which ether extracted the benzimidazole (V; R = H, R' = Me, X = $[CH_2]_3$) (0·5 g.). The residue was *ammonium* N-*(2-piperidinophenyl)oxamate* (0·5 g.), m. p. 196° (decomp.) (Found: C, 58·1; H, 7·3. $C_{13}H_{19}N_3O_3$ requires C, 58·8; H, 7·2%).

Syntheses of Benzimidazoles.—(*a*) N-*Acetyl-2,3,4,5-tetrahydro*-1H-1-*benzazepine* (VI; R = H) was obtained from its parent amine,[13] using acetic anhydride, as prisms, m. p. 80° (Found: C, 76·5; H, 7·7. $C_{12}H_{15}NO$ requires C, 76·2; H, 8·0%). The compound (6·9 g.) was nitrated in acetic anhydride (15 ml.) and nitric acid (*d* 1·5; 2·6 ml.) at 0° for 0·5 hr. and then at room temperature for 5 hr. On pouring the mixture on to ice and neutralising with ammonium hydroxide, the *nitro-derivative* (6·1 g.) (VI; R = NO_2) was obtained as pale yellow needles, m. p. 131° [from light petroleum (b. p. 100—120°)] (Found: C, 61·9; H, 6·05. $C_{12}H_{14}N_2O_3$ requires C, 61·5; H, 6·0%). The nitro-compound (5 g.) was reduced in benzene (100 ml.) with hydrogen (Raney nickel) at s.t.p., yielding the *amine* (VI; R = NH_2) (4·3 g.), m. p. 100° (Found: C, 79·2; H, 8·0. $C_{12}H_{16}N_2O$ requires C, 70·5; H, 7·9%). The amine (2 g.) was boiled with 4N-hydrochloric acid (20 ml.) for 2 hr., and the mixture neutralised (aqueous sodium hydroxide) and extracted with ether, to give 6,7,8,9-*tetrahydro*-1-*methylazepino*[1,2,3-cd]*benzimidazole* (V; R = Me, R' = H, X = $[CH_2]_3$) (50%), m. p. 134—135° (Found: C, 77·1; H, 7·2. $C_{12}H_{14}N_2$ requires C, 77·4; H, 7·6%). Its *picrate* had m. p. 228° (Found: C, 52·4; H, 4·4. $C_{18}H_{17}N_5O_7$ requires C, 52·05; H, 4·1%).

(*b*) 8-Amino-4-methylquinoline (2·5 g.), prepared by Johnson and Hamilton's method,[14] was refluxed with sodium (6 g.) for 1 hr. in ethanol (75 ml.). Evaporation of the solvent and extraction of the residue with ether gave 8-amino-1,2,3,4-tetrahydro-4-methylquinoline.

[12] Schmutz and Künzle, *Helv. Chim. Acta*, 1956, **39**, 1144.
[13] Baddeley, Chadwick, and Taylor, *J.*, 1956, 448.
[14] Johnson and Hamilton, *J. Amer. Chem. Soc.*, 1941, **63**, 2864.

Its *diacetyl derivative*, m. p. 153° (Found: C, 68·4; H, 7·2. $C_{14}H_{18}N_2O_2$ requires C, 68·2; H, 7·4%) was cyclised as in (*a*), yielding the imidazoquinoline (V; R = R′ = Me, X = $[CH_2]_2$), m. p. and mixed m. p. 140°.

Oxidation of the Azepine (V; R = R′ = Me, X = $[CH_2]_3$).—A boiling solution of the azepine (2 g.) in 30% aqueous pyridine (300 ml.) to which an aqueous solution of potassium permanganate (400 ml.; 3%) had been added during 2 hr., was cooled and filtered, and the filtrate evaporated to dryness, to give the *hydroxy-compound* (V; R = R′ = Me, H = OH, X = $[CH_2]_3$) (0·48 g.) as needles, m. p. 196° (from ethyl acetate) (Found: C, 72·8; H, 7·5; N, 12·7. $C_{13}H_{16}N_2O$ requires C, 72·2; H, 7·5; N, 13·0%), $\nu_{max.}$ (in $CHCl_3$) 3650 (free OH), 1090, and 1050 cm.$^{-1}$ (cyclic tertiary OH with α-unsaturation).[15] The same product was obtained in poor yield by oxidation with a potassium permanganate solution in boiling acetone for 6 hr.

Attempted Ring-fission with Polyphosphoric Acid.—*N*-Phenylpiperidine,[16] b. p. 122°/12 mm., and *N*-phenylpyrrolidine,[17] b. p. 120°/12 mm., were made by diazotising the corresponding *o*-amino-compounds (I; R = H, X = $[CH_2]_3$, or $[CH_2]_2$) (10 g.) and adding an aqueous solution of hypophosphorous acid (30%; 100 ml.) at 0°. The mixture was kept at 0° overnight, basified, and steam-distilled to give the heterocycles in 80 and 75% yield, respectively. Each compound remained unchanged when heated with an excess of polyphosphoric acid at 150 or at 200° for 1 hr.

Ring-fission of the Benzimidazole (V: R = R′ = Me; X = $[CH_2]_3$).—The *methiodide*, m. p. 163° (Found: C, 49·2; H, 5·4. $C_{14}H_{19}IN_2$ requires C, 49·1; H, 5·6%), was boiled for 5 min. with 2N-aqueous sodium hydroxide, and gave a practically 100% yield of *the benzazepine* (X), m. p. 147° (Found: C, 71·9; H, 8·8; N, 12·4. $C_{14}H_{20}N_2O$ requires C, 72·4; H, 8·7; N, 12·1%), $\nu_{max.}$ (in $CHCl_3$) 3330 (>NH), 1640 (tertiary amide carbonyl), 787, and 750 cm.$^{-1}$ (1,2,3-trisubstituted benzene).

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[15] Nakanishi, "Infrared Absorption Spectroscopy," Holden-Day, San Francisco, 1962, p. 31.
[16] Bourns, Embleton, and Hansuld, *Org. Synth.*, 1954, **34**, 79.
[17] von Braun, Blessing, and Zobel, *Ber.*, 1924, **57**, 188.