Polycyclic Fused Amidines. Part I. Imidazo- and Pyrimido-[1,2-*f*]-phenanthridines [1]

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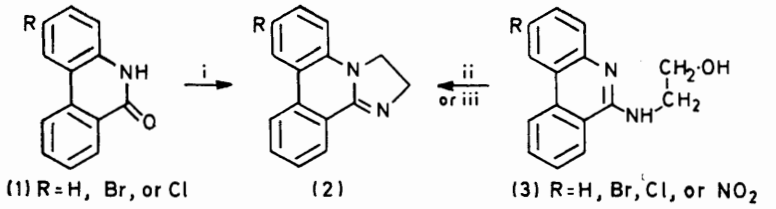
Phenanthridone reacts with 2-aminoethylammonium tosylate at 200—250 °C to give 2,3-dihydroimidazo[1,2-*f*]-phenanthridine (2; R = H) in high yield. This reaction could not be extended to the monotosylate salts of *o*-phenylenediamine, propane-1,3-diamine, and aminoguanidine. Unequivocal syntheses of imidazo[1,2-*f*]-phenanthridine (5) and the 3,4-dihydro-2*H*-pyrimido[1,2-*f*]phenanthridines (14) are reported.

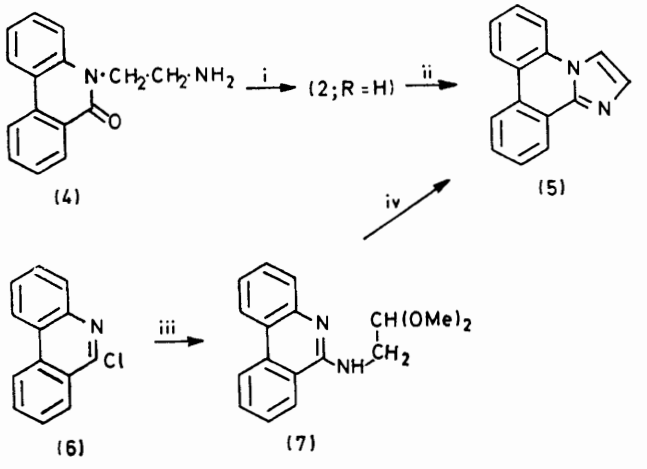
DURING our investigation [1-3] into the preparation of the dihydroimidazophenanthridines (2) by the reaction of phenanthridones (1) with 2-aminoethylammonium tosylate (EDMT), the synthesis of a variety of these dihydro-compounds by nitrosation of the corresponding hydroxyethylaminophenanthridines (3) was reported.[4] As both these reactions result in unexpected cyclisations, giving



Reagents: i, $NH_2{\cdot}CH_2{\cdot}CH_2{\cdot}NH_3^+$ p-$MeC_6H_4{\cdot}SO_3^-$; ii, HNO_2; iii, $POCl_3$ then K_2CO_3

products with marked biological activity,[3,4] we report our studies which establish unequivocally that the reaction products are 2,3-dihydroimidazo[1,2-*f*]phenanthridines.

The dihydroimidazo-compound (2; R = H) was obtained in >90% yield when phenanthridone (1; R = H) was heated with 2—5 mol. equiv. of EDMT at



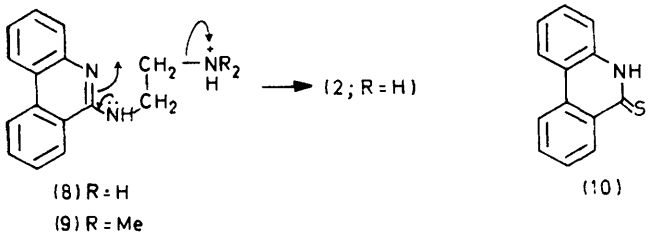
Reagents: i, heat; ii, Pd–C, PhCH:CH·CO_2Me; iii, $NH_2{\cdot}CH_2{\cdot}CH(OMe)_2$; iv, dil. HCl

200—250 °C. The product was identical with that formed by thermal decomposition of the ethylamine (4).[5] Further support for the structure (2; R = H) was obtained by dehydrogenation with palladium–charcoal, in refluxing *p*-cymene in the presence of methyl cinnamate, to give the aromatic system (5). Recently manganese dioxide has been used to dehydrogenate the dihydro-compound to the aromatic heterocycle.[6] Imidazo[1,2-*f*]phenanthridine (5) was also obtained in *ca.* 40% yield by reaction of 6-chlorophenanthridine (6) with aminoacetaldehyde dimethyl acetal, followed by treatment of the crude acetal (7) with acid. This unambiguous synthesis incidentally confirms the structure of the anomalous cycloadduct derived from benzocinnoline *N*-methylimide and dimethyl acetylenedicarboxylate.[6]

As the reaction of cyclic amides with amines in the presence of toluene-*p*-sulphonic acid is known to give amino-heterocycles,[7] the amine (8) is probably an intermediate in the reaction of phenanthridone with EDMT. In support of this hypothesis, heating the monohydrochloride of the amine (8) at 200° gave the dihydroimidazo-compound (2; R = H). Phenanthridone also reacted with the monotosylate salt of *NN*-dimethylethylenediamine at 200 °C to give the same compound, presumably by way of the intermediate (9). As such aminoethylamino-heterocycles were not isolated in any of the reactions of EDMT with phenanthridone or related heterocyclic amides, the formation of intermediates such as the phenanthridine (8) is presumably the rate-determining step in the annulation. This mechanism permits the rationalisation of the present results from attempts to bring about the reactions of phenanthridone with diamines, and the extension of the EDMT condensation to other heterocycles.[8]

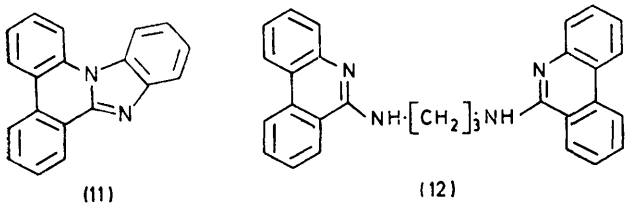
[1] Preliminary communication, R. F. Cookson and R. E. Rodway, *J.C.S. Chem. Comm.*, 1972, 511.
[2] R. F. Cookson, Ph.D. Thesis, University of London, 1971.
[3] R. E. Rodway and R. F. Cookson, B.P. 1,347,493/1974.
[4] H.-L. Pan and T. L. Fletcher, *J. Heterocyclic Chem.*, 1972, **9**, 859.
[5] R. F. Cookson, J. W. James, R. E. Rodway, and R. G. Simmonds, *J. Heterocyclic Chem.*, 1972, **9**, 475.
[6] M. J. Rance, C. W. Rees, P. Spagnolo, and R. C. Storr, *J.C.S. Chem. Comm.*, 1974, 658.
[7] J. V. Earley, R. I. Fryer, and L. H. Sternbach, U.S.P. 3,644,335/1972.
[8] R. F. Cookson and R. E. Rodway, following paper.

In spite of the greater reactivity of thioamides with EDMT,[8] the use of the phenanthridinethione (10) did not



(8) R = H
(9) R = Me

(10)



(11) (12)

allow any moderation of the reaction conditions. Thus the thione (10) did not react with EDMT below 200 °C when heated alone or in refluxing ethylenediamine, or in dimethylformamide at 100 °C.

Treatment of the halogenophenanthridones (1; R = Cl or Br) with EDMT at 200—250 °C gave high yields of the expected dihydroimidazo-compounds (2; R = Cl or Br). However, 2-nitrophenanthridone (1; R = NO_2) underwent extensive decomposition, producing an intractable tar from which no dihydroimidazo-compound could be isolated.

Attempts to prepare the benzimidazophenanthridine (11) by treatment of phenanthridone or phenanthridinethione with the monotosylate salt of *o*-phenylenediamine at 250 °C resulted in no reaction. Presumably the diamine (pK_a 4.57) is insufficiently nucleophilic.

Similarly the extension of the annulation reaction to propane-1,3-diamine did not prove possible. When phenanthridone or phenanthridinethione was heated at 230 °C with a 1 : 1 mixture of propane-1,3-diamine and its ditosylate salt, the only product isolated was a small amount of the diphenanthridinyl compound (12). The differing reactivities of the monotosylate salts of ethylenediamine (pK_a 10.08 and 6.99) and propane-1,3-diamine (pK_a 10.62 and 8.64) may be due to the different stabilities of the two salts. In the equilibrium (i) the large separation of the pK_a's of ethylenediamine (ΔpK_a 3.09) is such as to render the monoprotonated species stable, whereas with propane-1,3-diamine (ΔpK_a 1.98) the monotosylate salt readily dissociates into the free base and the diammonium derivative, neither of which affords the required pyrimido-compound (14; R = H).

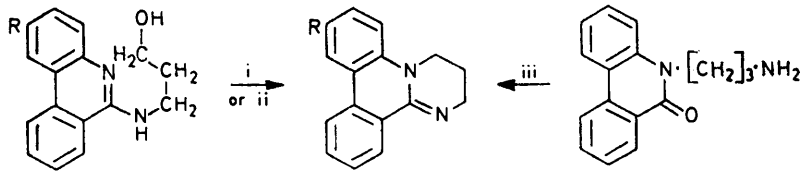
$$2NH_2\cdot[CH_2]_n\cdot NH_3^+ \rightleftharpoons NH_2\cdot[CH_2]_n\cdot NH_2 + NH_3^+\cdot[CH_2]_n\cdot NH_3^+ \quad \text{(i)}$$

The products from the reactions of phenanthridone with ethylene- and propane-1,3-diamine tosylate salts correspond to those obtained from the reaction of 4-chloroquinazoline with the free amines.[9]

Treatment of the hydoxypropyl compounds (13) with phosphoryl chloride, followed by basification of the resultant chloroproply derivatives, gave the 3,4-dihydro-2*H*-pyrimido[1,2-*f*]phenanthridines (14). These were identical (for R = H) with the product from thermal cyclisation of the amine (15), or (for R = Cl) with that obtained [4] from nitrosation of the hydroxypropylamine (13; R = Cl).

An attempt to prepare the triazolo-compound (16) by treatment of phenanthridone with the monotosylate salt of aminoguanidine gave instead a low yield of 6-aminophenanthridine (17).

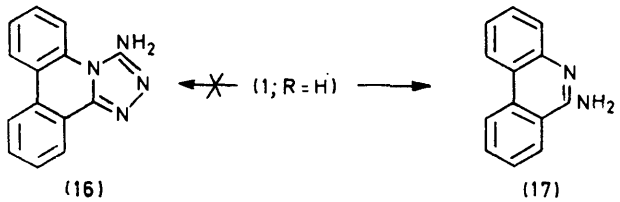
The apparent acidity constants (pK') of 6-aminophenanthridine, imidazo[1,2-*f*]phenanthridine, and the



(13) R = H, Br, Cl, or NO_2 (14) (15)

Reagents: i, $POCl_3$ then heat; ii, HNO_2; iii, heat

related dihydroimidazo- and dihydropyrimido-phenanthridines were determined by titration in 50% aqueous Methylcellosolve.[10] Imidazo[1,2-*f*]phenanthridine (5)



(16) (17)

Reagent: $NH_2\cdot NH\cdot C(NH_2)_2^+$ *p*-$MeC_6H_4\cdot SO_3^-$

(pK' 4.01) is a weaker base than 6-aminophenanthridine (17) (pK' 6.44). This difference is in line with, but more marked than, the differences in the aqueous pK_a values of imidazo[1,2-*a*]pyridine [11] and 2-aminopyridine.[12] Although it is known that 1,2,3,4-tetrahydropyrimidines are stronger bases than 4,5-dihydroimidazoles,[2,13] there

[8] Z. Kolodynska and S. Biniecki, *Acta Polon. Pharm.*, 1964, **21**, 225 (*Chem. Abs.*, 1965, **62**, 13,144g).
[9] R. F. Cookson, *Chem. Rev.*, 1974, **74**, 5.
[10] W. L. F. Armarego, *J. Chem. Soc.*, 1964, 4226.
[11] A. Albert, R. Goldacre, and J. N. Phillips, *J. Chem. Soc.*, 1948, 2240.
[12] D. D. Perrin, 'Dissociation Constants of Organic Bases in Aqueous Solution,' Butterworths, London, 1965, Supplement, 1972.

appear to be no previous reports of the relative pK_a values of dihydroimidazo- and dihydropyrimido-systems. As expected, both the dihydroimidazo-compound (2; R = H) (pK' 8.46) and the pyrimido-analogue (14; R = H) (pK' 9.55) are stronger bases than 6-aminophenanthridine. Moreover the increase in basicity on moving from a five- to a six-membered ring parallels that observed with the monocyclic systems.[13,14]

EXPERIMENTAL

I.r. spectra were recorded with a Perkin-Elmer 157 instrument for Nujol mulls and ^{1}H n.m.r. spectra with a Perkin-Elmer R10 machine operating at 60 MHz. Mass spectra were determined with an A.E.I. MS9 spectrometer at 70 eV. Solutions were dried over magnesium sulphate monohydrate. Identity of samples was established by i.r. spectra and mixed m.p. determinations. Acidity constant determinations were carried out by the method of Albert and Serjeant,[15] except that the titrations were performed in 50% (v/v) water–2-methoxyethanol.

2,3-*Dihydroimidazo*[1,2-f]*phenanthridine*.—(a) *From phenanthridone and 2-aminoethylammonium tosylate* (*EDMT*). An intimate mixture of phenanthridone (8 g, 0.041 mol) and EDMT (20 g, 0.086 mol) was heated in an open flask at 230 °C for 14 h. The cooled mixture was extracted with hot 5N-hydrochloric acid (4 × 100 ml) and unchanged phenanthridone (1.1 g) was filtered off. Basification of the filtrate gave a solid (7.3 g, 94% based on phenanthridone consumed) which was washed, dried, and taken up in chloroform (100 ml). The filtered solution was treated with ethereal hydrogen chloride and an excess of dry ether. The precipitate was collected and crystallised from industrial methylated spirits (charcoal) to yield white crystals of 2,3-dihydroimidazo[1,2-*f*]phenanthridine hydrochloride (5.1 g, 49%), m.p. *ca.* 355° (decomp.) (Found: C, 70.1; H, 5.2; Cl, 13.9; N, 10.9. Calc. for $C_{15}H_{12}N_2$,HCl: C, 70.2; H, 5.1; Cl, 13.8; N, 10.9%). Basification of an aqueous solution of the hydrochloride gave a yellow oil which solidified. The dried solid was crystallised from cyclohexane (45 parts) to give yellow crystals of the free base, m.p. 129—130° (lit.,[4] 127.5—128.5°) (Found: C, 81.8; H, 5.6; N, 12.7. Calc. for $C_{15}H_{12}N_2$: C, 81.8; H, 5.5; N, 12.7%); δ[$(CD_3)_2SO$] 8.25—8.55 (3 H, m, H-8, -9, and -12), 6.90—8.00 (5 H, m, H-5, -6, -7, -10, and -11), and 4.10 (4 H, s, H-2 and -3); *m/e* 221 (36%), 220 (96), 219 (100), 205 (4), 193 (13), 192 (11), 190 (9), 179 (8), 178 (20), 177 (19), 165 (24), 164 (20), 163 (13), 152 (10), and 151 (19), *m** 191 (220 ⟶ 205), 145.3 (220 ⟶ 179), 143 (219 ⟶ 177), 129.3 (179 ⟶ 152), and 124.5 (219 ⟶ 165); pK' 8.46 ± 0.01.

(b) *From compound* (4). 5-(2-Aminoethyl)phenanthridone [5] (0.5 g) was heated above its m.p. until evolution of water ceased. The residue was dissolved in chloroform and treated with ethereal hydrogen chloride. The white precipitate obtained on addition of an excess of ether was recrystallised twice from industrial methylated spirits to give a hydrochloride (0.2 g) identical with that described above.

(c) *From compound* (8). 6-(2-Aminoethylamino)phenanthridine dihydrochloride (1 g) (see below) was dissolved in water (5 ml) and treated with 2N-sodium hydroxide (1.11 ml, 1 equiv.). The solid obtained on evaporation was heated at 160 °C for 4 h. Basification of an aqueous extract of the residue gave an oil which was extracted into methylene chloride. Evaporation of the washed and dried extract gave an oil (0.3 g) which was converted into a hydrochloride identical with that described in (a).

(d) *From phenanthridone and* NN-*dimethyl-*(2-*aminoethyl*)*ammonium tosylate*. Phenanthridone (5 g, 0.0256 mol) and the monotosylate (13 g, 0.05 mol) were mixed and heated at 260 °C for 2 h. Extraction with hot 5N-hydrochloric acid [insoluble phenanthridone (4 g) remained], followed by basification, and extraction of the cooled aqueous extract with chloroform, gave an oil (0.7 g) which was converted into a hydrochloride indistinguishable from those described above.

6-(2-*Aminoethylamino*)*phenanthridine*.—A solution of 6-chlorophenanthridine (11.3 g, 0.053 mol) and ethylenediamine (6.35 g, 0.106 mol) was heated under reflux in dry dioxan (100 ml) for 7 h. The mixture was evaporated to dryness and the residue stirred with a mixture of 5N-hydrochloric acid (500 ml) and chloroform (300 ml). The aqueous layer was separated and basified to give a gummy solid which was taken up in chloroform, dried, and treated with ethereal hydrogen chloride and an excess of dry ether. The precipitate was crystallised from a 2 : 4 mixture of water and industrial methylated spirits to give 6-(2-*aminoethylamino*)*phenanthridine dihydrochloride* (2.0 g, 12%), m.p. 335° (decomp.) (Found: C, 58.1; H, 5.4; N, 13.8. $C_{15}H_{15}N_3$,2HCl requires C, 58.1; H, 5.5; N, 13.6%).

Imidazo[1,2-f]*phenanthridine*.—(a) *From* 2,3-*dihydroimidazo*[1,2-f]*phenanthridine*. 2,3-Dihydroimidazo[1,2-*f*]-phenanthridine (16 g, 0.073 mol), methyl cinnamate (11.5 g, 0.073 mol), and 5% palladium–charcoal (6 g) were stirred and heated under reflux in *p*-cymene (200 ml) for 24 h. The catalyst was filtered off and was washed with chloroform. The combined filtrates were extracted with 5N-hydrochloric acid (3 × 100 ml) and the extracts were washed with chloroform (100 ml). Extraction of the basified solution with chloroform, followed by evaporation of the washed and dried extract, gave a yellow solid (12 g) which was taken up in chloroform and treated with ethereal hydrogen chloride and an excess of dry ether. The white precipitate was crystallised from a 1 : 1 mixture of industrial methylated spirits and light petroleum (b.p. 40—60°) (30 parts) to give white crystals of imidazo[1, 2-*f*]phenanthridine hydrochloride (12.6 g, 68%), m.p. 256—260° (Found: C, 70.7; H, 4.4; Cl, 14.0; N, 11.0. Calc. for $C_{15}H_{10}N_2$,-HCl: C, 70.7; H, 4.4; Cl, 13.9; N, 11.0%). When kept in air, the crystals formed a dihydrate (Found on encapsulation: C, 61.8; H, 5·2; Cl, 12.0; N, 9.6. Calc. for $C_{15}H_{10}N_2$,HCl,$2H_2O$: C, 62.0; H, 5.2; Cl, 12.1; N, 9.6%). Basification of an aqueous solution of the hydrochloride gave an oil which solidified. Crystallisation from acetone (10 parts) gave red crystals of the free base, m.p. 140—141° (lit.,[6] 135—136°) (Found: C, 82.4; H, 4.9; N, 12.9. Calc. for $C_{15}H_{10}N_2$: C, 82.6; 4.6; N, 12.8%); δ ($CDCl_3$) 8.35—8.55 (1 H, m, H-12) and 6.8—8.0 (9 H, other aromatic protons); *m/e* 219 (22%), 218 (100), 191 (3), 178 (7), 164 (32), 163 (15), 151 (8), 109 (8), 63 (12), 51 (8), 50 (8), 43 (13), and 39 (12), *m** 167.5 (218 ⟶ 191), 145.5 (218 ⟶ 178), 128.1 (178 ⟶ 151), and 123.5 (218 ⟶ 164); pK' 4.01 ± 0.06.

(b) *From* 6-*chlorophenanthridine*. A solution of 6-chlorophenanthridine (187.5 g, 0.88 mol) and aminoacetaldehyde

[14] B. Fernandez, I. Perillo, and S. Lamdan, *J.C.S. Perkin II*, 1973, 1371; 1974, 1416.

[15] A. Albert and E. P. Serjeant, ' Determination of Ionization Constants,' 2nd edn., Chapman and Hall, London, 1971.

dimethyl acetal (184.4 g, 1.76 mol) in bis-(2-methoxyethyl) ether (600 ml) was heated under reflux for 18 h. The mixture was evaporated to a thick oil which was dissolved in hot 2N-hydrochloric acid (600 ml). The solution was added to water (2 l) and allowed to cool. Filtration removed traces of phenanthridone formed from the unchanged 6-chlorophenanthridine. The filtrate was basified to pH 7 with concentrated ammonia solution and the crude acetal was separated as a gummy solid (160 g). The crude intermediate was boiled in water (2 l) containing 5N-hydrochloric acid (300 ml) for 5 h. Basification of the cooled and filtered solution gave impure imidazo[1,2-*f*]phenanthridine (122 g, 63%), which was taken up in hot industrial methylated spirits (800 ml; charcoal). The cooled solution was treated with ethereal hydrogen chloride (200 ml). The semi-solid mixture obtained was diluted with a further 200 ml of industrial methylated spirits and the mixture was boiled until the precipitate had dissolved. To the hot stirred solution was added light petroleum (b.p. 40—60°; *ca.* 900 ml) and the crystals that formed on cooling were separated and equilibrated in a humid atmosphere to give the hydrochloride dihydrate (109 g, 42%).

Reaction of 2-Halogenophenanthridones with EDMT.—The substituted phenanthridones were heated with a 4—5 molar excess of EDMT at 260 °C for 7—20 h. The basic products were obtained as described for 2,3-dihydroimidazo[1,2-*f*]-phenanthridine.

(a) 2-*Bromophenanthridone*. Recrystallisation from water gave 7-bromo-2,3-dihydroimidazo[1,2-*f*]phenanthridine hydrochloride (10.1 g, 43%), m.p. 330—333° (Found: C, 53.6; H, 3.6; Cl, 10.7; N, 8.4. Calc. for $C_{15}H_{11}BrN_2$,HCl: C, 53.6; H, 3.6; Cl, 10.6; N. 8.3%). Basification and recrystallisation from benzene–light petroleum (b.p. 40—60°) gave the free base, m.p. 175—176° (lit.,[4] 182—183°), pK' 7.77 ± 0.04.

(b) 2-*Chlorophenanthridone*. Recrystallisation from water (6 parts) gave 7-chloro-2,3-dihydroimidazo[1,2-*f*]phenanthridine hydrochloride (16.1 g, 55%), m.p. 353—360° (Found: C, 61.8; H, 4.0; Cl, 11.9; N, 9.7. Calc. for $C_{15}H_{11}ClN_2$,HCl: C, 61.8; H, 4.1; Cl, 12.2; N, 9.6%).

NN′-*Diphenanthridin-6-ylpropane-1,3-diamine*.—Phenanthridinethione (15·6 g, 0.074 mol) and a mixture of propane-1,3-diamine ditosylate salt (31 g, 0.074 mol) and propane-2,3-diamine (5.5 g, 0.074 mol) were heated in an open flask at 200 °C for 18 h. The mixture was extracted with hot 5N-hydrochloric acid and the cooled, filtered extract was basified. Extraction with chloroform gave an oil which was triturated with ether. The resultant solid (7.6 g) was dissolved in chloroform and treated with ethereal hydrogen chloride to give a crude hydrochloride, which was dissolved in water, basified, and re-extracted. Evaporation of the washed and dried extract gave a gum which was crystallised from benzene (65 parts) to give NN′-*diphenanthridin-6-ylpropane-1,3-diamine* (1.4 g, 4.4%), m.p. 194—196° (Found: C, 81.5; H, 5.7; N, 13.1. $C_{29}H_{24}N_4$ requires C, 81.3; H, 5.6; N, 13.1%). The same product was obtained in 2.4% yield by reaction of phenanthridone with a mixture of propane-1,3-diamine and its ditosylate salt.

3,4-*Dihydro*-2H-*pyrimido*[1,2-f]*phenanthridine*.— 6-(3-Hydroxypropylamino)phenanthridine (21.6 g, 0.084 mol) in phosphoryl chloride (100 ml) was heated under reflux for 6 h. The cooled solution was poured onto ice and ammonia solution, and the mixture was extracted with chloroform. Evaporation of the washed and dried extract gave an oil (19.5 g) which was treated with 1.25N-sodium hydroxide in 50% alcohol (220 ml). The solution was boiled under reflux for 2 h and then cooled, acidified with 5N-hydrochloric acid, and evaporated to dryness. The residue was taken up in water and the solution was basified with saturated potassium carbonate solution and extracted with chloroform. Evaporation of the washed and dried extract gave an oil which was taken up in chloroform and treated with ethereal hydrogen chloride and an excess of dry ether. The crude hydrochloride that precipitated was purified by treatment with water, filtration, basification, extraction with chloroform, and re-formation of the salt with ethereal hydrogen chloride. Crystallisation from a mixture of industrial methylated spirits and ether gave white crystals of the hydrochloride hydrate (5.5 g, 26%), m.p. 285—290° (Found: C, 66.5; H, 5.7; Cl, 12.7; N, 9.9. Calc. for $C_{16}H_{14}N_2$,HCl,H_2O: C, 66.5; H, 5.9; Cl, 12.3; N, 9.7%); δ (D_2O) 6.8—7.6 (8 H, m, aromatic), 2.9—4.0 (4 H, m, H-2 and -4), and 1.7—2.3 (2 H, m, H-3) (all signals unresolved); pK' 9.55 ± 0.07. This hydrochloride was also obtained by heating 5-(3-aminopropyl)phenanthridone [5] above its m. p. until evolution of water had ceased, taking up the residue in chloroform, and treating the solution with ethereal hydrogen chloride. The salt was purified by treatment with water, filtration, basification, re-extraction, and re-formation of the hydrochloride with ethereal hydrogen chloride.

8-*Bromo*-3,4-*dihydro*-2H-*pyrimido*[1,2-f]*phenanthridine*.—This was obtained as the hydrochloride (12 g, 35%) by the method described for the unsubstituted compound; m.p. 341—343° (Found: C, 55.0; H, 3.9; Br, 23.1; Cl, 10.1; N, 8.0. Calc. for $C_{16}H_{13}BrN_2$,HCl: C, 54.9; H, 4.0; Br, 22.9; Cl, 10.2; N, 8.0%); pK' 9.18 ± 0.01.

8-*Chloro*-3,4-*dihydro*-2H-*pyrimido*[1,2-f]*phenanthridine*.—This was prepared as for the unsubstituted compound. The hydrochloride proved hygroscopic but basification of an aqueous solution of the salt gave a solid which crystallised from industrial methylated spirits to give the free base (8.3 g, 35%), m.p. 130—132° (lit.,[4] 125—126°) (Found: C, 71.5; H, 4.8; Cl, 13.5; N, 10.6. Calc. for $C_{16}H_{13}ClN_2$: C, 71.5; H, 4.8; Cl, 13.2; N, 10.4%); δ ($CDCl_3$) 8.2—8.6 (1 H, m, H-13), 6.7—8.0 (6 H, m, remaining aromatic H), 3.5—3.9 (4 H, m, H-2 and -4), and 1.8—2.3 (2 H, m, H-3).

3,4-*Dihydro*-8-*nitro*-2H-*pyrimido*[1,2-f]*phenanthridine*.—This was obtained as the hydrochloride monohydrate (40 g, 72%) by the method described for the unsubstituted compound; m.p. 344—345° (Found: C, 57.6; H, 4.8; Cl, 10.4; N, 12.7. Calc. for $C_{16}H_{13}N_3O_2$,HCl,H_2O: C, 57.6, H, 4.8; Cl, 10.6; N, 12.6%).

Reaction of Phenanthridone with the Monotosylate Salt of Aminoguanidine.—An intimate mixture of phenanthridone (9.75 g, 0.05 mol) and the monotosylate (36.9 g, 0.15 mol) was heated in an open flask at 250—260 °C for 42 h. The mixture was extracted with hot 5N-hydrochloric acid (250 ml) and the unchanged phenanthridone (7.8 g) was filtered off. Basification of the filtrate gave a white solid (1.3 g) which was taken up in chloroform, washed thoroughly with water, dried, and treated with ethereal hydrogen chloride and an excess of dry ether. The solid formed was dissolved in water, and the solution was filtered and basified to give 6-aminophenanthridine. Recrystallisation from acetone gave light brown prisms (0.5 g, 5.2%; 26% based on phenanthridone consumed), m.p. 197—199° (lit.,[16] 195.5°)

[16] G. T. Morgan and L. P. Walls, *J. Chem. Soc.*, 1932, 2225.

(Found: C, 80.4; H, 5.1; N, 14.4. Calc. for $C_{13}H_{10}N_2$: C, 80.4; H, 5.1; N, 14.4%).

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