142. *Some Heterocyclic* N-*Oxides.*

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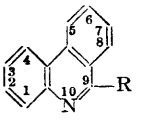
Although the preparation of some *phenanthridine* N-*oxides* has been accomplished, attempts to obtain the "*N*-oxide" analogue of Dimidium bromide (II) have proved unsuccessful.

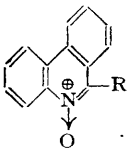
By the action of phosphorus oxychloride on 9-*phenylphenanthridine* N-*oxide*, 3-*chloro*-9-*phenylphenanthridine* has been obtained. 9-*Methylphenanthridine* N-*oxide* similarly gave 9-chloromethylphenanthridine together with what was probably a 3-*chloro*-9-*methylphenanthridine*.

In 1941 McIlwain (*Nature*, **148**, 628) reported that iodinin, the pigment of *Chromobacterium iodinum*, showed marked antibacterial action on a number of organisms. Chemical work on its structure revealed that the compound was a dihydroxyphenazine di-*N*-oxide, a result which led McIlwain (*J.*, 1943, 322) to the synthesis of a number of phenazine and quinoxaline di-*N*-oxides which showed varying degrees of antibacterial action. In 1943 White and Hill (*J. Bact.*, 1943, **45**, 433) reported the isolation of the antibiotic "aspergillic acid" which possessed an antibacterial range greater than that of penicillin (see Glister, *Nature*, 1941, **148**, 470) and

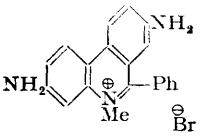
proved to be a hydroxypyrazine *N*-oxide (see Newbold and Spring, *J.*, 1947, 372). The existence of *N*-oxide residues in at least two naturally occuring antibacterial agents appeared significant, particularly as the corresponding "deoxido"-compounds were without biological interest. We therefore undertook the preparation of some phenanthridine *N*-oxides (I*a*) for study as antibacterial agents and, as *N*-oxides bear an electronic resemblance to quaternary salt (*e.g.*, II), for examination as trypanocides. In particular, we wished to prepare the "*N*-oxide" analogue of the effective trypanocide, Dimidium bromide (II) (see Walls, *J.*, 1945, 294). Some new *quinoline* and *quinoxaline* N-*oxides* were also prepared, as we required a range of compounds which could function as mild oxidising agents for chemotherapeutic studies employing the anaerobic organism *Entamoeba histolytica*.



(I.)



(I*a*.)



(II.)

Conversion of phenanthridine itself, and of its 9-methyl and 9-ethyl derivatives, into the corresponding N-*oxides* was smoothly achieved by employing perphthalic acid. Peracetic acid, however, proved to be the reagent of choice for the preparation of the 9-arylphenanthridine *N*-oxides, which generally differed from their 9-alkyl analogues in failing to liberate iodine from potassium iodide under the experimental conditions specified by McIlwain (*J.*, 1943, 342) for this test.

The mononitrophenylphenanthridines were converted into their N-*oxides* with somewhat greater difficulty and required longer reaction periods with peracetic acid. This result is probably due to the electron-attracting effect of the nitro-group on the free electron pair present on the ring nitrogen and available for oxide formation. Similar difficulties were experienced with the dinitrophenylphenanthridines. Although 3-*nitro*-9-p-*nitrophenylphenanthridine* N-*oxide* was obtained from the corresponding dinitro-compound in low yield, all attempts to prepare 2 : 7-dinitro-9-phenylphenanthridine *N*-oxide for conversion into the Dimidium bromide analogue were unsuccessful.

Reduction of the nitro-9-phenylphenanthridine *N*-oxides with stannous chloride in hydrochloric acid solution furnished the corresponding *amino*-9-*phenylphenanthridine* N-*oxides*. Reduction of 3-nitro-9-*p*-nitrophenylphenanthridine *N*-oxide, on the other hand, invariably resulted in loss of the oxido-grouping and formation of 3-amino-9-*p*-aminophenylphenanthridine. Limited success attended efforts at the direct oxidation of 3-*diacetylamino*-9-p-*diacetylamino*-*phenylphenanthridine*, wherein the corresponding N-*oxide* was obtained in very low yield. Attempts to extend this reaction to 7-*diacetylamino*-9-p-*diacetylaminophenyl*-, 2 : 7-*bisdiacetylamino*-9-*phenyl*-, and 2 : 7-dicarbethoxyamino-9-phenyl-phenanthridine proved unsuccessful, however, and further work on the "*N*-oxide" analogue of Dimidium bromide (II) was abandoned.

9-4′-*Pyridylphenanthridine*, prepared by ring closure of 2 : 4′-*picolinamidodiphenyl*, formed a homogeneous *monoxide* on treatment with 1·1 equivalents of perphthalic acid. The constitution of a 9-4′-*pyridylphenanthridine* 1′-*oxide* has been assigned to this compound from analogy with related work on the monoquaternation of 9-3′-pyridylphenanthridine (Petrow and Wragg, *J.*, 1947, 1410) and on general theoretical grounds. Reaction with excess of perphthalic acid led to the formation of the corresponding *dioxide*. Attempts to convert 9-(5-*nitro*-2-*furyl*)*phenanthridine* into its oxide were unsuccessful.

The reaction of phenanthridine *N*-oxide with phosphorus oxychloride followed the pattern established for similar compounds (see, *e.g.*, Baxter, Newbold, and Spring, *J.*, 1948, 1859), 9-chlorophenanthridine being formed. When 9-phenylphenanthridine *N*-oxide was treated in the same way, however, a *chloro*-9-*phenylphenanthridine* was obtained, identical with authentic 3-*chloro*-9-*phenylphenanthridine* prepared by the Sandmeyer reaction from the corresponding amino-compound. When 9-methylphenanthridine *N*-oxide was treated with phosphorus oxychloride, two halogenated products were obtained. One of these was identified with 9-chloromethylphenanthridine previously described by Morgan and Walls (*J.*, 1931, 2447). The other product has, by analogy with its phenyl analogue, been assigned the constitution of a 3-*chloro*-9-*methylphenanthridine*.

Experimental.

(M. p.s are uncorrected. Microanalyses are by the Analytical Department, The British Drug Houses Ltd., and by Drs. Weiler and Strauss, Oxford.)

Substituted 2-Benzamidodiphenyls.—The acid chloride (0·1 mol.) (prepared from the acid and thionyl chloride) was added in portions to a solution of 2-aminodiphenyl (0·1 mol.) in pyridine (15—20 ml.), and the mixture heated on the steam-bath for 2 hours to complete the reaction. Addition of dilute hydrochloric acid usually precipitated the amide as a solid, which was collected, washed, and crystallised from alcohol or alcohol–light petroleum. Occasionally, preliminary vacuum-distillation was required before the amide could be obtained as a solid. The compounds listed in Table I were thus prepared. The yields are based on the acid used.

5-Carbethoxyamino-2-acetamidodiphenyl, prepared by reduction of 5-nitro-2-acetamidodiphenyl followed by carbethoxylation, formed small pale-cream needles, m. p. 127—128° (77%) (Found: C, 68·4; H, 6·0. $C_{17}H_{18}O_3N_2$ requires C, 68·4; H, 6·1%), from benzene–light petroleum.

4′-Carbethoxy-2-acetamidodiphenyl, prepared as for the foregoing compound, formed (91%) silvery leaflets, m. p. 160—161° (cf. Walls, *J.*, 1947, 67).

2-Nitro-4 : 4′-dibenzamidodiphenyl.—2-Nitrobenzidine (23·6 g.) in warm pyridine (30 ml.) was treated with benzoyl chloride (30 g.) in portions. After 30 minutes on the water-bath the *product* was isolated and purified from pyridine–light petroleum, to give pale yellow prisms, m. p. 290—291° (Found: C, 71·7; H, 4·5. $C_{26}H_{19}O_4N_3$ requires C, 71·4; H, 4·4%), in nearly quantitative yield.

2-Amino-4 : 4′-dibenzamidodiphenyl.—Finely powdered 2-nitro-4 : 4′-dibenzamidodiphenyl (16·7 g.) was stirred with concentrated hydrochloric acid (83 ml.) containing a little alcohol to prevent frothing, and a solution of stannous chloride (47 g.) in concentrated hydrochloric acid (50 ml.) added. After 2 hours on the water-bath the mixture was poured, with stirring, into excess of sodium hydroxide solution (30%), and the precipitated solids extracted with boiling pyridine. Evaporation of the extract under reduced pressure, followed by crystallisation of the residue (12·0 g.; m. p. 255—258°) from aqueous pyridine, gave *2-amino-4 : 4′-dibenzamidodiphenyl*, buff-coloured prisms, m. p 270° (Found: C, 76·9; H, 5·2. $C_{26}H_{21}O_2N_3$ requires C, 76·7; H, 5·2%).

4 : 4′-Dicarbethoxyamino-2-dimethylaminodiphenyl.—A well-stirred solution of 2-amino-4 : 4′-dicarbethoxyaminodiphenyl (13 g.) in water (50 ml.) at 80° was treated in portions with aqueous sodium hydroxide (19 g. in 28 ml. of water) and methyl sulphate (35 g.), added alternately so that the mixture remained alkaline. After a further 30 minutes' heating, the product was collected, heated with acetic anhydride (20 ml.) for 10 minutes on the water-bath, and poured into dilute sulphuric acid (20 ml. acid in 300 ml. of water), and the mixture was filtered while hot. The filtrate was made alkaline, giving *4 : 4′-dicarbethoxyamino-2-dimethylaminodiphenyl*, prismatic needles (6·7 g.), m. p. 171—172° (Found: C, 63·7; H, 7·5. $C_{20}H_{25}O_4N_3,C_2H_6O$ requires C, 63·3; H, 7·5%), from ethanol.

2-Benzamido-4′-chlorosulphonyldiphenyl.—2-Benzamidodiphenyl (21·2 g.) was added in portions with stirring to chlorosulphonic acid (42·4 g.) at 10°. The mixture was then heated at 60° for 2 hours and, after cooling, poured on ice. The sticky product was dissolved in chloroform and precipitated with light petroleum, giving *2-benzamido-4′-chlorosulphonyldiphenyl*, needles (12·2 g.), m. p. 162—163° (Found: C, 62·1; H, 3·9; Cl, 9·9. $C_{19}H_{14}O_3ClNS$ requires C, 61·4; H, 3·8; Cl, 9·5%), from benzene (cf. B.PP. 597,809, 597,810 for orientation).

2-Benzamido-4′-2″-pyridylsulphamyldiphenyl, prepared from the above compound, formed prisms m. p. 223°, from ethoxyethyl alcohol (Found: C, 66·5; H, 4·8. $C_{24}H_{19}O_3N_3S$ requires C, 67·1; H, 4·5%). The p-*chlorophenylsulphamyl* derivative separated from ethoxyethyl alcohol in small leaflets, m. p. 239° (Found: C, 64·9; H, 4·5. $C_{25}H_{19}O_3N_2SCl$ requires C, 64·9; H, 4·1%). The *sulphonomorpholide* formed needles, m. p. 161—163° (Found: C, 65·3; H, 5·3. $C_{23}H_{22}O_4N_2S$ requires C, 65·4; H, 5·3%), from aqueous ethoxyethyl alcohol. The *sulphonopiperidide* formed needles, m. p. 102—104° (Found: N, 6·6. $C_{24}H_{24}O_3N_2S$ requires N, 6·7%), from ethanol.

The p-*nitrophenylsulphamyl* derivative formed pale yellow leaflets, m. p. 247° (Found: C, 63·3; H, 3·8. $C_{25}H_{19}O_5N_3S$ requires C, 63·4; H, 4·0%), from ethoxyethyl alcohol.

2-isoNicotinamidodiphenyl.—*iso*Nicotinic acid (30 g.), prepared (56% yield) by the method of Linnell and Vyas (*Quart. J. Pharm.*, 1947, **20**, 120), was heated under reflux with thionyl chloride (85 ml.) for 6 hours. Unchanged thionyl chloride was removed under reduced pressure, and the residue evaporated with benzene. The *iso*nicotinoyl chloride hydrochloride in gently refluxing chlorobenzene (320 ml.) was treated in portions with 2-aminodiphenyl (40 g.) in chlorobenzene (85 ml.). Heating was continued for a further 30 minutes, and the mixture was cooled, the chlorobenzene decanted off, and the semi-solid residue washed by decantation with ether. The product was dissolved in hot methyl alcohol (*ca.* 400 ml.), the base (42·5 g.; m. p. 107—111°) precipitated with aqueous ammonia, and the mixture cooled. 2-iso*Nicotinamidodiphenyl* formed needles, m. p. 113·5° (Found: C, 79·0; H, 5·3. $C_{18}H_{14}ON_2$ requires C, 78·8; H, 5·1%), from aqueous methanol.

The compounds listed in Table II were prepared in a similar way.

4′-Chloro-2-benzamidodiphenyl.—The method of Bradshaw and Wissow (*J. Amer. Chem. Soc.*, 1946, **68**, 405) was modified as follows: 4′-Chloro-2-nitrodiphenyl (11·2 g.), ethanol (45 ml.), water (12 ml.), reduced iron (15 g.), and a few drops of concentrated hydrochloric acid were heated under reflux on the water-bath for 1 hour. The mixture was then made just alkaline with aqueous ammonia and filtered hot. Extraction of the solids with hot ethanol gave an oil from which 4′-chloro-2-benzamidodiphenyl was obtained, on benzoylation, as needles (10·6 g.), m. p. 167—169°, from ethanol.

5-Chloro-2-acetamidodiphenyl.—The following improved method was used: 2-acetamidodiphenyl (10·6 g.) and fused sodium acetate (12·3 g.) in glacial acetic acid (45 ml.) on the water-bath were treated with a stream of chlorine until 3·5 g. had been absorbed. Heating was continued for a further 30 minutes and the mixture was then diluted with water and extracted with chloroform. The product was distilled under reduced pressure, the fraction, b. p. 170—200°/0·05 mm., yielding 5-chloro-2-acetamidodiphenyl, m. p. 120—121° (Found: C, 68·9; H, 5·0. Calc. for $C_{14}H_{12}ONCl$: C, 68·4; H, 4·9%), on crystallisation from alcohol–light petroleum (cf. Scarborough and Waters, *J.*, 1927, 93).

TABLE I.

Substituted diphenyls.

Substituent.	M. p. or b. p.	Yield, %.	Formula.	Found, %. C.	H.	N.	Reqd., %. C.	H.	N.	Description.*
2-o-*Methylbenzamido*-	88—89°	52	$C_{20}H_{17}ON$	83·1	5·6	—	83·4	6·0	—	Needles
2-m-*Methylbenzamido*-	b. p. 185 (0·05 mm.) 89—90 b. p. 180 (0·08 mm.)	63	,,	83·5	6·0	—	83·4	6·0	—	Needles
2-p-*Methylbenzamido*-	107—108	66	,,	83·9	5·8	4·7	83·4	6·0	4·9	Needles
2-o-*Chlorobenzamido*-	103	58	$C_{19}H_{14}ONCl$	73·9	4·5	[c]	74·2	4·3	[c]	Needles [b]
2-m-*Chlorobenzamido*-	107—108	67	,,	74·2	4·6	—	74·2	4·3	—	Wispy needles
2-p-*Chlorobenzamido*-	104	64	,,	73·6	4·5	—	74·2	4·3	—	Wispy needles
5-*Nitro*-2-*benzamido*-	148—149	80	$C_{19}H_{14}O_3N_2$	71·1	4·3	—	71·7	4·4	—	Flat yellow needles [b]
2-o-*Anisamido*-	162	40	$C_{20}H_{17}O_2N$	79·1	5·6	—	79·2	5·7	—	Flat needles [a]
2-m-*Anisamido*-	76—77	58	,,	79·2	5·7	—	79·2	5·7	—	Needles [a]
2-(2 : 5-*Dimethoxybenzamido*)-	134—135	68	$C_{21}H_{19}O_3N$	75·8	5·6	—	75·7	5·8	—	Leaflets
2-(3 : 4-*Dimethoxybenzamido*)-	128—130	73	,,	76·0	5·8	4·1	75·7	5·8	4·2	Small needles [c]
2-p-iso*Propoxybenzamido*-	150 (softens 115)	69	$C_{22}H_{21}O_2N$	79·8	6·4	—	79·7	6·4	—	Wispy needles [c]
2-(p-n-*Propoxybenzamido*)-	116—118	49	,,	79·6	6·5	—	79·7	6·4	—	Long needles
2-(3-*Methoxy*-4-*ethoxybenzamido*)-	111 b. p. 223 (0·07 mm.)	58	$C_{22}H_{21}O_3N$	76·2	6·3	—	76·1	6·1	—	Needles
2-(3-*Methoxy*-4-iso*propoxybenzamido*)-	148·5	73	$C_{23}H_{23}O_3N$	—	—	3·9	—	—	3·9	Needles
2-(3 : 4-*Methylenedioxybenzamido*)-	145—146	66	$C_{20}H_{15}O_3N$	75·6	4·7	—	75·7	4·8	—	Needles
2 : 4 : 4′-*Tribenzamido*-	285	59	$C_{33}H_{25}O_3N_3$	77·2	4·5	—	77·5	4·9	—	Micro-prisms [d]
2-2′-*Furamido*-	76—77·5	71	$C_{17}H_{13}O_2N$	77·0	5·2	—	77·6	5·0	—	Needles
2-(5-*Nitro*-2-*furamido*)-	134—135	55	$C_{17}H_{12}O_4N_2$	65·7	4·1	—	66·2	3·9	—	Yellow leaflets
4′-*Carbethoxyamino*-2-(5-*nitro*-2-*furamido*)-	179—180	50	$C_{20}H_{17}O_6N_3$	60·8	4·4	—	60·8	4·3	—	Flat needles [b]

* Recrystallised from: [a] light petroleum, [b] ethoxyethyl alcohol, [c] benzene, [d] pyridine. [e] Found: Cl, 11·4. Reqd.: Cl, 11·5%.

TABLE II.

Substituted diphenyls.

Substituent.	M. p.	Yield, %.	Formula.	Found, %. C.	H.	N.	Reqd., %. C.	H.	N.	Description.*
2-*Picolinamido*-	100°	82	$C_{18}H_{14}ON_2$	78·3	5·3	—	78·8	5·1	—	Large buff needles [a]
4′-*Nitro*-2-*picolinamido*-	215—217	75	$C_{18}H_{13}O_3N_2$	67·3	4·0	—	67·7	4·1	—	Wispy yellow needles [b]
4′-*Nitro*-2-iso*nicotinamido*-	185—186	85	,,	67·1	4·1	—	67·7	4·1	—	Wispy yellow needles [c]
5-*Nitro*-2-*picolinamido*-	207—208	61	,,	67·8	4·1	—	67·7	4·1	—	Needles [b]
5-*Nitro*-2-iso*nicotinamido*-	138	63	,,	67·8	4·1	—	67·7	4·1	—	Buff prisms [d]
4′-*Carbethoxyamino*-2-*picolinamido*-	181—182 (softens 158)	68	$C_{21}H_{19}O_3N_3,C_6H_6$	73·0	5·6	—	73·8	5·7	—	Needles [e]
2-(2-*Phenyl*-4-*quinolylamido*)-	173	76	$C_{28}H_{20}ON_2$	81·9	4·9	6·8	81·9	5·0	6·9	Prisms [f]
5-*Nitro*-2-(2-*phenyl*-4-*quinolylamido*)-	228	72	$C_{28}H_{19}O_3N_3$	75·1	4·5	—	75·5	4·3	—	Prisms [g]
4′-*Nitro*-2-(2-*phenyl*-4-*quinolylamido*)-	223	83	,,	75·5	4·5	—	75·4	4·3	—	Small needles [h]
4′-*Carbethoxyamino*-2-(2-*phenyl*-4-*quinolylamido*)-	195	81	$C_{31}H_{25}O_3N_3$	76·2	4·9	—	76·4	5·2	—	Flat buff needles [c]
2-(2-o-*Chlorophenyl*-5 : 6-*benz*-4-*quinolylamido*)-	234—236	70	$C_{32}H_{21}ONCl$	79·0	4·7	—	79·3	4·4	—	Cream needles [b]

* Recrystallised from: [a] light petroleum, [b] ethoxyethyl alcohol, [c] methanol, [d] benzene–light petroleum, [e] benzene, [f] acetone, [g] nitrobenzene–ether, [h] nitrobenzene.

2-(p-*Aminobenzamido*)*diphenyl*, prepared by reduction of the corresponding nitro-compound with reduced iron, separated (87%) from ethanol in cubes, m. p. 144—145° (Found: C, 79·3; H, 5·7; N, 9·5. $C_{19}H_{16}ON_2$ requires C, 79·1; H, 5·6; N, 9·7%). It was converted into 2-(p-*carbethoxyaminobenzamido*)-*diphenyl*, needles, m. p. 166—167° (Found: C, 73·7; H, 6·0. $C_{22}H_{20}O_3N_2$ requires C, 73·3; H, 5·6%), from ethanol, by the method of Lesslie and Turner (*J.*, 1943, 1588).

9-*Subsituted Phenanthridines*.—The amidodiphenyl (1 part), phosphorus oxychloride (2 parts), and nitrobenzene (3 parts) were heated under reflux in an oil-bath for 1½—2½ hours. The reaction mixture was poured on excess of ice–sodium hydroxide solution, and the nitrobenzene removed in steam. After cooling, the separated solids were collected, washed, and purified by crystallisation. The compounds listed in Table III were thus prepared.

9-4′-*Pyridylphenanthridine dihydrochloride* formed yellow prisms, m. p. 235° (decomp.) (Found: C, 65·3; H, 4·4. $C_{18}H_{12}N_2$,2HCl requires C, 65·7; H, 4·3%), from ethanol.

3-*Chloro*-9-*phenylphenanthridine*.—3-Amino-9-phenylphenanthridine (5·0 g.), dissolved in concentrated hydrochloric acid (7 ml.) and water (3 ml.), was diazotised at 0° with sodium nitrite (1·4 g.) dissolved in a little water. The diazonium solution was then rapidly added to cuprous chloride solution [prepared from cupric sulphate (6·2 g.), sodium chloride (1·75 g.), and water (20 ml.; saturated with SO_2), the resulting cuprous chloride being dissolved in hydrochloric acid (12 ml.)]. After being kept overnight, the precipitated solids were collected and extracted with sodium hydroxide solution, and the insoluble residue was crystallised from ethanol. 3-*Chloro*-9-*phenylphenanthridine* formed yellow leaflets (1·3 g.), m. p. 141—142° (Found: C, 79·0; H, 4·4. $C_{19}H_{12}NCl$ requires C, 78·7; H, 4·3%).

7-*Amino*-9-*phenylphenanthridine*.—Finely powdered 7-nitro-9-phenylphenanthridine (14·5 g.) was stirred with concentrated hydrochloric acid (60 ml.) while a solution of stannous chloride (40 g.) in hydrochloric acid (43 ml.) was added. After 3 hours on the water-bath the cooled mixture was filtered, the yellow stannichloride dissolved in water, and the solution basified. Hot ethoxyethyl alcohol extracted 7-*amino*-9-*phenylphenanthridine*, yellow needles (10·8 g.), m. p. 168° (Found: C, 83·8; H, 5·3. $C_{19}H_{14}N_2$ requires C, 84·4; H, 5·2%), from ethanol.

3-*Amino*-9-m-*aminophenylphenanthridine*, prepared similarly to the foregoing compound, formed yellow prisms (63%), m. p. 201° (Found: C, 79·5; H, 5·1. $C_{19}H_{15}N_3$ requires C, 80·0; H, 5·3%), from ethanol.

7-*Amino*-9-m-*aminophenylphenanthridine*, prepared similarly to the above compound, formed yellow prismatic needles (64%), m. p. 210° (Found: C, 79·4; H, 5·2. $C_{19}H_{15}N_3$ requires C, 80·0; H, 5·3%), from ethoxyethyl alcohol. The NN′-*diacetyl* derivative formed needles, m. p. >290° (Found: C, 74·5; H, 5·0; N, 11·1. $C_{23}H_{17}O_2N_3$ requires C, 75·2; H, 4·7; N, 11·4%), from alcohol.

5-*Amino*-9-*phenylphenanthridine*, prepared by ring closure of 2 : 2′-dibenzamidodiphenyl (3 g.) with phosphorus oxychloride (6 g.) and nitrobenzene (9 ml.) at 160° for 2 hours, formed yellow prisms, m. p. 164° (Found: C, 84·1; H, 5·3; N, 10·4. $C_{19}H_{14}N_2$ requires C, 84·4; H, 5·2; N, 10·4%), from aqueous ethanol. The *monohydrochloride* formed yellow needles, m. p. 335—338° (decomp.) (Found: C, 74·3; H, 4·9; N, 8·6. $C_{19}H_{14}N_2$,HCl requires C, 74·4; H, 4·9; N, 9·1%), from aqueous alcohol.

9-p-*Diacetylaminophenylphenanthridine*.—9-*p*-Aminophenylphenanthridine (5 g.), acetic anhydride (50 ml.), and one drop of concentrated sulphuric acid were heated under reflux for 4 hours. Excess of acetic anhydride was removed under reduced pressure leaving 9-p-*diacetylaminophenylphenanthridine*, m. p. 207° (Found: C, 78·4; H, 5·3. $C_{23}H_{18}O_2N_2$ requires C, 77·9; H, 5·1%) after crystallisation.

3-*Diacetylamino*-9-p-*diacetylaminophenylphenanthridine* crystallised from ethoxyethyl alcohol–ethanol (1 : 2) in needles, m. p. 221—222° (softening at 217°) (Found: C, 71·0; H, 5·3. $C_{27}H_{23}O_4N_3$ requires C, 71·5; H, 5·1%).

7-*Diacetylamino*-9-p-*diacetylaminophenylphenanthridine* formed small prisms, m. p. 227—229° (Found: C, 71·0; H, 5·1. $C_{27}H_{23}O_4N_3$ requires C, 71·5; H, 5·1%), from aqueous ethanol.

3-*Carbethoxyamino*-9-*methylphenanthridine*, pale yellow prisms (3 g.) from benzene, m. p. 177—179° (Found: C, 72·7; H, 5·8. $C_{17}H_{16}O_2N_2$ requires C, 72·8; H, 5·8%), was obtained by ring closure of 5-carbethoxy-2-acetamidodiphenyl (5·0 g.) with phosphorus oxychloride (10 ml.) under reflux for 45 minutes.

9-p-*Hydroxyphenylphenanthridine*.—9-*p*-Aminophenylphenanthridine (2·0 g.) in 2N-sulphuric acid (20 ml.) was heated on the water-bath and then cooled to 0°. Sodium nitrite (0·8 g.), dissolved in a little water, was then added, and the diazotised solution poured into water (50 ml.) at 70°. After being kept overnight, the solids were collected, purified by solution in alkali, and crystallised from ethanol. 9-p-*Hydroxyphenylphenanthridine* formed prismatic needles (1·4 g.), m. p. 237° (Found: C, 83·7; H, 4·8. $C_{19}H_{13}ON$ requires C, 84·1; H, 4·8%).

9-m-*Hydroxyphenylphenanthridine*, prepared similarly, formed buff-coloured microneedles, m. p. 225—226° (Found: C, 83·7; H, 4·8. $C_{19}H_{13}ON$ requires C, 84·1; H, 4·8%), from aqueous ethanol.

9-*Morpholinomethylphenanthridine*.—9-Chloromethylphenanthridine (6·3 g.), morpholine (8·5 g.), alcohol (25 ml.), and chloroform (5 ml.) were heated under reflux for 2 hours. Water was added, the mixture extracted with chloroform and concentrated to small bulk, and light petroleum added. 9-*Morpholinomethylphenanthridine* separated and was obtained as yellow prisms, m. p. 95° (Found: C, 77·6; H, 6·7. $C_{18}H_{18}ON_2$ requires C, 77·7; H, 6·5%), from light petroleum.

9-(5-*Nitro*-2-*furyl*)*phenanthridine*, yellow needles, m. p. 187° (Found: C, 69·6; H, 3·5. $C_{17}H_{10}O_3N_2$ requires C, 70·3; H, 3·5%), from acetone, was obtained (36%) by heating 2-(5-nitro-2-furamido)-diphenyl (5·0 g.) with phosphorus oxychloride (10 ml.) and nitrobenzene (15 ml.) for 30 minutes at 180°.

9-p-*Diguanidophenylphenanthridine*.—9-*p*-Aminophenylphenanthridine (2·65 g.), dicyandiamide (2·7 g.), water (15 c.c.), and hydrochloric acid (1 c.c.) were heated under reflux for 3 hours. The mixture was basified with ammonia, and the solid collected and crystallised from ethanol, from which it separated as needles (1·0 g.) (Found, in a sample dried at 100°/30 mm.: C, 69·2; H, 5·2; N, 23·0. $C_{21}H_{18}N_6,\frac{1}{2}H_2O$ requires C, 69·4; H, 5·3; N, 23·1%).

7-*Diguanido*-9-*phenylphenanthridine monohydrate*, similarly prepared, formed prismatic needles, m. p. 153° (decomp.) (Found: C, 68·0; H, 5·7; N, 22·4. $C_{21}H_{18}N_6,H_2O$ requires C, 67·7; H, 5·4; N, 22·5%), from alcohol. The *picrate* formed small yellow prisms, m. p. 235° (decomp.) (Found: N, 20·6. $C_{21}H_{18}N_6,C_6H_3O_7N_3$ requires N, 21·6%), from ethoxyethyl alcohol.

TABLE III.

9-Substituted phenanthridines.

Substituent.	M. p.	Yield, %.	Formula.	Found, %. C.	H.	N.	Reqd., %. C.	H.	N.	Description.*
m-*Tolyl-*	98—99°	78	$C_{20}H_{15}N$	89·6	5·9	—	89·2	5·6	—	Prismatic needles [a]
p-*Tolyl-*	108	73	,,	88·8	5·6	—	89·2	5·6	—	Needles [a, (1)]
7-*Chloro*-9-*phenyl-*	120	57	$C_{19}H_{12}NCl$	78·6	4·3	—	78·7	4·3	—	Cream needles [b]
o-*Chlorophenyl-*	125	94	,,	78·5	4·0	—	78·7	4·3	—	Prisms [b]
m-*Chlorophenyl-*	137—138	87	,,	78·5	4·1	—	78·7	4·3	—	Silver needles [c]
p-*Chlorophenyl-*	157·5	84	,,	79·2	4·2	—	78·7	4·3	—	Silver needles [b]
3-*Nitro*-9-*phenyl-*	228—229	96	$C_{19}H_{12}O_2N_2$	75·5	4·0	—	76·0	4·0	—	Pale yellow wispy needles [d, (2)]
2 : 7-*Dibenzamido*-9-*phenyl-*	321—322	89	$C_{33}H_{23}O_2N_3$	79·6	4·8	8·1	80·3	4·7	8·5	Pale cream micro-needles [e, (3)]
o-*Methoxyphenyl-*	127	75	$C_{20}H_{15}ON$	84·2	5·3	5·0	84·2	5·3	4·9	Needles [f]
m-*Methoxyphenyl-*	128—129	89	,,	84·2	5·3	—	84·2	5·3	—	Prisms [f]
p-*Methoxyphenyl-*	146	80	,,	83·7	4·8	—	84·2	5·3	—	Needles [f]
2′-*Methoxy*-5′-*bromophenyl-*	148	77	$C_{20}H_{14}ONBr$	65·8	3·9	—	66·0	3·9	—	Cubes [f]
p-*Ethoxyphenyl-*	149—150	64	$C_{21}H_{17}ON$	84·0	5·9	4·8	84·2	5·7	4·7	Flat needles [f]
2′ : 5′-*Dimethoxyphenyl-*	163	95	$C_{21}H_{17}O_2N$	80·0	5·4	—	80·0	5·4	—	Prisms [f]
3′ : 4′-*Dimethoxyphenyl-*	169	88	,,	79·6	5·3	—	80·0	5·4	—	Prismatic needles [f]
3′ : 4′-*Methylenedioxyphenyl-*	113	70	$C_{20}H_{13}O_2N$	79·8	4·4	4·3	80·4	4·4	4·7	Needles [f]
p-n-*Propoxyphenyl-*	116—117	96	$C_{21}H_{17}O_2N$	—	—	4·1	—	—	4·5	Cream needles [f]
p-iso*Propoxyphenyl-*	118—119	62	,,	91·0	5·8	—	90·3	6·1	—	Needles [f]
3′-*Methoxy*-4′-*ethoxyphenyl-*	118—120	53	$C_{22}H_{19}O_2N$	—	—	4·7	—	—	4·3	Needles [f]
3′-*Methoxy*-4′-iso*propoxyphenyl-*	137—139	86	$C_{22}H_{21}O_2N$	80·4	5·8	—	80·4	6·2	—	Needles [f]
3′-*Methoxy*-4′-n-*propoxyphenyl-*	128—129	77	,,	79·8	6·2	—	80·4	6·2	—	Needles [f]
4′-*Pyridyl-*	160	74	$C_{18}H_{12}N_2$	84·2	4·8	—	84·4	4·7	—	Prismatic needles [g, (4)]
4′-*Pyridyl- dihydrochloride*	235 (decomp.)	—	$C_{18}H_{12}N_2,2HCl$	65·3	4·4	—	65·7	4·3	—	Yellow prisms [f]
2′-*Phenyl*-4′-*quinolyl-*	183—184	63	$C_{28}H_{18}N_2$	87·5	4·8	—	87·9	4·7	—	Pale cream prisms [f, (5)]
3-*Nitro*-9-(2-*phenyl*-4-*quinolyl*)-	>295	70	$C_{28}H_{17}O_2N_3$	79·0	4·1	—	78·7	4·0	—	Small needles [d, (5)]
7-*Nitro*-9-(2-*phenyl*-4-*quinolyl*)-	282	58	$C_{28}H_{17}O_2N_3$	78·2	3·8	—	78·7	4·0	—	Pale yellow needles [d, (5)]
9-(2-o-*Chlorophenyl*-5 : 6-*benz*-4-*quinolyl*-)	260	65	$C_{32}H_{19}NCl$	82·3	4·1	6·0	81·6	3·9	5·3	Leaflets [h]

(1) Since completion of this preparation Gilman and Nelson (*J. Amer. Chem. Soc.*, 1948, **70**, 3316) have described an alternative preparation from phenanthridine and tolyl-lithium.

Periods of refluxing: (2) 16 hours, (3) 3½ hours, (4) 16 hours, (5) 18 hours.

* Recrystallised from: [a] light petroleum, [b] methanol, [c] acetone, [d] nitrobenzene, [e] aq. pyridine, [f] ethanol, [g] acetone–ethanol, [h] ethoxyethyl alcohol.

Phenanthridine 10-*Oxide*.—Phenanthridine (18·1 g.), dissolved in a little chloroform, was added to ethereal perphthalic acid solution (≡ 2·1 g. of active oxygen). After five days at 5° the solids were collected, ground with aqueous 5% ammonium hydroxide, and crystallised from ethanol (87%). *Phenanthridine* 10-*oxide* formed (after drying at 100°/20 mm.) leaflets, m. p. 220° (softening at 215°) (Found: C, 79·5; H, 4·6. $C_{13}H_9ON$ requires C, 80·0; H, 4·7%).

9-*Methylphenanthridine* 10-*oxide hydrochloride* was obtained (89%) in small buff prisms, m. p. 190—192° (decomp.; after drying) (Found: C, 68·1; H, 4·8. $C_{14}H_{12}ONCl$ requires C, 68·4; H, 4·9%).

9-*Ethylphenanthridine* 10-*oxide monohydrate* separated from aqueous acetic acid in pale pink needles, m. p. 252—253° (decomp.) (Found: C, 73·9; H, 6·3. $C_{15}H_{13}ON,H_2O$ requires C, 74·6; H, 6·3%).

9-*Phenylphenanthridine* 10-*Oxide*.—To a peracetic acid solution, prepared by heating 30% hydrogen peroxide (30 g.) and glacial acetic acid (50 g.) at 85° for one hour, was added 9-phenylphenanthridine (5·0 g.), and heating at 85° continued for a further 4—5 hours. The mixture was then poured into water, and the precipitated solids were collected and crystallised from chloroform. 9-*Phenylphenanthridine* 10-*oxide* was obtained (91%) in glistening buff leaflets, m. p. 212—215° (Found: C, 84·4; H, 5·0. $C_{19}H_{13}ON$ requires C, 84·1; H, 4·8%).

The compounds listed in Table IV were thus prepared.

9-p-*Aminophenylphenanthridine* 10-*Oxide*.—Finely powdered 9-*p*-nitrophenylphenanthridine 10-oxide (4·9 g.) was stirred with hydrochloric acid (25 ml.) on a steam-bath, a few drops of ethanol being added to prevent frothing. Stannous chloride (14 g.) in hydrochloric acid (15 ml.) was then added; the suspended solids dissolved and were replaced, after 30 minutes' heating, by yellow crystals. After cooling to 5° the separated stannichloride was collected and decomposed with 10% aqueous sodium hydroxide, and the liberated base crystallised from ethanol. 9-p-*Aminophenylphenanthridine* 10-*oxide monohydrate* separated (40%) in yellow needles, m. p. 264—265° (decomp.) (Found: C, 75·2; H, 5·3. $C_{19}H_{14}ON_2,H_2O$ requires C, 75·0; H, 5·3%). The product is readily soluble in dilute acid and gives a positive primary amine test on diazotisation and coupling with alkaline 2-naphthol. For analysis the compound was dried at room temperature, as appreciable decomposition occurs at 100°.

9-m-*Aminophenylphenanthridine* 10-*oxide hemihydrate* formed yellow needles, m. p. 124—125° (decomp.) (Found: C, 77·8; H, 5·1; N, 9·0. $C_{19}H_{14}ON_2,\frac{1}{2}H_2O$ requires C, 77·3; H, 5·1; N, 9·5%), from ethanol.

3-*Amino*-9-*methylphenanthridine* 10-*oxide hemihydrate* was obtained (42%) in wispy yellow needles, m. p. 214° (Found: C, 72·3; H, 5·6. $C_{14}H_{12}ON_2,H_2O$ requires C, 72·1; H, 5·6%), from aqueous alcohol.

3-*Amino*-9-*phenylphenanthridine* 10-*oxide monohydrate* formed yellow needles (54%), m. p. 248° (decomp.) (Found: C, 75·5; H, 5·4. $C_{19}H_{14}ON_2,H_2O$ requires C, 75·0; H, 5·3%), from ethanol.

7-*Amino*-9-*phenylphenanthridine* 10-*oxide* separated (46%) in yellow needles, m. p. 278° (decomp.) (Found: C, 78·8; H, 5·3. $C_{19}H_{14}ON_2,\frac{1}{4}H_2O$ requires C, 78·6; H, 5·0%), from ethanol.

3-*Diacetylamino*-9-p-*diacetylaminophenylphenanthridine* 10-*oxide hemihydrate*, obtained in very low yield, separated from alcohol as an amorphous yellow powder, m. p. 268° (decomp., preheated bath) (Found: C, 67·7; H, 4·8. $C_{27}H_{23}O_4N_3,\frac{1}{2}H_2O$ requires C, 67·8; H, 5·1%).

9-4′-*Pyridylphenanthridine* 1′-*Oxide*.—The corresponding base was treated with 1·1 equivs. of perphthalic acid solution. After fractional crystallisation to remove unchanged material, the 1′-*oxide* was obtained in prismatic needles, m. p. 266° (Found: C, 79·4; H, 4·6; N, 10·0. $C_{18}H_{12}ON_2$ requires C, 79·4; H, 4·4; N, 10·3%), from aqueous ethanol.

9-4′-*Pyridylphenanthridine* 10 : 1′-*dioxide*, colourless prisms (71%), m. p. 303° (decomp.) (Found: C, 75·3; H, 4·2. $C_{18}H_{12}O_2N_2$ requires C, 75·0; H, 4·2%), from ethoxyethyl alcohol, was similarly obtained by using 3·3 equivs. of perphthalic acid.

Quaternary Salts.—The base was heated with methyl sulphate for 10 minutes in nitrobenzene at 160°. The methosulphate was isolated either by direct filtration or by removal of the nitrobenzene by steam-distillation followed by concentration under reduced pressure. The compounds listed in Table V were thus prepared.

3-*Amino*-9-(2-*phenyl*-4-*quinolyl*)*phenanthridine Dimethiodide*.—3-Nitro-9-(2-phenyl-4-quinolyl)phenanthridine dimethosulphate (1·0 g.), dissolved in concentrated hydrochloric acid (5 ml.), was treated with stannous chloride (3 g.) in hydrochloric acid (4 ml.) for 2 hours on the water-bath. After cooling, the orange-red stannichloride was collected and decomposed with hydrogen sulphide in dilute hydrochloric acid solution. The resulting dimethochloride proved very hygroscopic. The *dimethiodide* was therefore prepared, and formed orange-red needles (0·9 g.), m. p. 228° (decomp.) (Found: C, 51·5; H, 4·2. $C_{30}H_{25}N_3I_2,H_2O$ requires C, 51·5; H, 3·9%), from aqueous ethanol.

2 : 3-*Di*-2′-*furylquinoxaline*.—Furil (9·5 g.), in hot ethanol (100 ml.) and chloroform (70 ml.), was heated with *o*-phenylenediamine (5·4 g.) in ethanol (10 ml.) under reflux for 30 minutes. Concentration gave 2 : 3-*di*-2′-*furylquinoxaline*, yellow needles (12·6 g.), m. p. 130—131° (Found: C, 73·0; H, 3·4. $C_{16}H_{10}O_2N_2$ requires C, 73·3; H, 3·8%). Attempts to convert this compound into the *N*-oxide gave only 2 : 3-dihydroxyquinoxaline, white needles, m. p. >300° (Found: C, 59·0; H, 3·7. Calc. for $C_8H_6O_2N_2$: C, 59·3; H, 3·7%), from water. Attempts to prepare quaternary salt were likewise unsuccessful.

2 : 3-*Dimethylquinoline*-4-*carboxylic acid* 1-*oxide*, prepared by using peracetic acid, formed glistening leaflets (25%), m. p. 229° (decomp.) (Found: C, 66·2; H, 5·1. $C_{12}H_{11}O_3N$ requires C, 66·3; H, 5·1%), from ethanol.

2-*Phenylquinoline*-4-*carboxylic acid* 1-*oxide*, prepared similarly, formed pale yellow prisms (75%), m. p. 260° (decomp.) (Found: C, 71·7; H, 4·3. $C_{16}H_{11}O_3N$ requires C, 72·4; H, 4·2%).

2-*Methyl*-5 : 6-*benzquinoline* 1-*oxide*, prepared by treating 2-methyl-5 : 6-benzquinoline (10 g.) in glacial acetic acid (200 ml.) with hydrogen peroxide (50 ml. of 30%) at 50° for 24 hours, was obtained as the monohydrate, m. p. 87—89°, from which the oxide was obtained after drying, m. p. 128—129° (Found: C, 80·0; H, 5·8; N, 6·7. $C_{14}H_{11}ON$ requires C, 80·4; H, 5·3; N, 6·7%).

The Action of Phosphorus Oxychloride on Some Phenanthridine N-*Oxides*.—*Phenanthridine* 10-*oxide*. The oxide (1·0 g.), in a flask cooled in ice–water was treated with phosphorus oxychloride (4·0 ml.) added dropwise with shaking. The mixture was then heated on the water-bath for 15 minutes, poured on

TABLE IV.

Phenanthridine 10-oxides.

Substituent.	M. p.	Yield, %.	Formula.	Found, %. C.	Found, %. H.	Reqd., %. C.	Reqd., %. H.	Description.*
9-p-*Tolyl-*	196—197°	50	$C_{20}H_{15}ON$	83·3	5·4	84·2	5·3	Buff needles [a]
9-o-*Chlorophenyl-*	200	91	$C_{19}H_{12}ONCl$	74·2	4·0	74·6	4·0	Buff leaflets [b]
9-p-*Chlorophenyl-*	252 (decomp.)	68	,,	74·1	4·0	74·6	4·0	Cream leaflets [c]
3-*Chloro*-9-*phenyl-*	174—175	74	,,	73·8	4·0	74·6	4·0	Pale yellow needles [d]
7-*Chloro*-9-*phenyl-*	218	66	,,	74·5	4·2	74·6	4·0	Pale yellow prisms [d]
9-m-*Nitrophenyl-*	181	63	$C_{19}H_{12}O_3N_2$	71·5	3·8	72·1	3·8	Small buff needles [d]
9-p-*Nitrophenyl-*	242—245 (decomp.)	87	,, ,H_2O	68·5	4·1	68·3	4·2	Golden needles [e]
3-*Nitro*-9-*phenyl-*	231	47	,, ,H_2O	69·0	4·2	68·3	4·2	Yellow needles [c]
7-*Nitro*-9-*phenyl-*	269—271 (decomp.)	68	,,	72·1	4·0	72·1	3·8	Yellow needles [c]
3-*Nitro*-9-m-*nitrophenyl-*	286	26	$C_{19}H_{11}O_5N_3$	63·4	3·3	63·2	3·1	Yellow needles [e] * †
3-*Nitro*-9-*methyl-*	>265	96	(Could not be purified owing to insolubility. Used direct.)					
9-p-*Methoxyphenyl-*	232—234 (decomp.)	50	$C_{20}H_{15}O_2N$	78·9	4·7	79·7	5·0	Cream needles [d]

* Recrystallised from: [a] ethyl acetate, [b] aq. ethanol, [c] aq. acetic acid [d] ethanol, [e] acetic acid. † Period of heating, 16 hours.

TABLE V.

Phenanthridine quaternary salts.

Substituent.*	M. p.	Yield, %.	Formula.	Found, %. C.	Found, %. H.	Reqd., %. C.	Reqd., %. H.	Description.†
9-p-*Tolyl- M.S.*	191—192°	76	$C_{22}H_{21}O_4NS$	67·3	5·6	66·8	5·4	Needles [a]
9-p-*Tolyl- M.I.*	219—221 (decomp.)	76	$C_{21}H_{18}NI$	61·5	4·4	61·3	4·4	Yellow prisms [a]
9-o-*Chlorophenyl- M.I.*	207—208	60	$C_{20}H_{15}NClI$	55·9	3·7	55·7	3·5	Yellow prisms or red needles [b]
9-p-*Chlorophenyl- M.S.*	191—192	47	$C_{21}H_{18}O_4NSCl$	60·4	4·4	60·6	4·4	Needles [b]
9-(5-*Nitro*-2-*furyl*)- *M.S.*	210 (decomp.)	65	$C_{19}H_{16}O_7N_2S$	54·5	3·5	54·8	3·9	Yellow needles [b]
9-*Morpholinomethyl- M.S.*	206—207 (decomp.)	69	$C_{20}H_{24}O_5N_2S$	59·5	5·8	59·4	6·0	Needles [a]
9-*Morpholinomethyl- M.I.*	195 (decomp.)	69	$C_{19}H_{21}ON_2I$	54·8	5·5	54·3	5·0	Needles [c]
9-4′-*Pyridyl- M.S.*	171—174 (decomp.)	80	$C_{20}H_{18}O_4N_2S$	63·1	5·1	62·8	4·7	Cream leaflets [a]
9-4′-*Pyridyl- M.I.*	>290	57	$C_{19}H_{15}N_2I$	57·2	4·0	57·3	3·8	Yellow needles [c]
9-(2-*Phenyl*-4-*quinolyl*)- *di-M.S.*	230 (decomp.)	60	$C_{32}H_{30}O_8N_2S_2,2H_2O$	57·6	5·4	57·3	5·1	Yellow needles [a]
3-*Nitro*-9-(2-*phenyl*-4-*quinolyl*)- *di-M.S.*	260 (decomp.)	77	$C_{32}H_{29}O_{10}N_3S_2,2H_2O$	53·7	4·7	54·2	4·9	Yellow prisms [b]
7-*Nitro*-9-(2-*phenyl*-4-*quinolyl*)- *di-M.S.*	254—255 (decomp.)	70	$C_{32}H_{29}O_{10}N_3S_2$	56·3	4·4	56·5	4·3	Small yellow needles [b]

* M.I. = methiodide; M.S. = methosulphate.

† Recrystallised from: [a] ethanol–ether, [b] ethanol, [c] aqueous ethanol.

ice, and neutralised with sodium hydroxide. The product in light petroleum (50 ml. of b. p. 80—100°; charcoal) deposited a little phenanthridone on storage overnight; this was removed, and the filtrate chilled to −30°. 9-Chlorophenanthridine separated, needles (0·95 g.), m. p. 116·5° (Found: C, 73·1; H, 3·8. Calc. for $C_{13}H_8NCl$: C, 73·1; H, 3·8%), from light petroleum, not depressed in admixture with an authentic specimen.

9-Chlorophenanthridine (10 g.) in alcohol (50 ml.) was added to a solution of sodium (1·2 g.) in alcohol (50 ml.), and the mixture heated under reflux for 3 hours. The product, in light petroleum, was purified by passage through a column of alumina, giving 9-*ethoxyphenanthridine*, needles (2·5 g.), m. p. 60° (Found: C, 80·5; H, 6·4. $C_{15}H_{13}ON$ requires C, 80·7; H, 5·9), from methanol. On reaction with peracetic acid it was converted into phenanthridone.

9-*Phenylphenanthridine* 10-*oxide*. The oxide (2·0 g.) in a flask cooled in ice-water, was treated dropwise with phosphorus oxychloride (8 ml.). When the vigorous reaction had subsided the mixture was heated on the water-bath for 1½ hours, and the product isolated as before. Repeated crystallisation from methanol gave 3-chloro-9-phenylphenanthridine, m. p. 141° (Found: C, 79·0; H, 4·2. Calc. for $C_{19}H_{12}NCl$: C, 78·7; H, 4·3%), not depressed in admixture with an authentic specimen.

9-*Methylphenanthridine* 10-*oxide*. The oxide hydrochloride (2·0 g.) was treated with phosphorus oxychloride (8 ml.) as before, and the mixture heated on the water-bath for 45 minutes. After decomposition with ice and basification with ammonia, the product was fractionated from ethanol, giving 9-chloromethylphenanthridine, m. p. 132° (Found: C, 74·2; H, 4·6. Calc. for $C_{14}H_{10}NCl$: C, 73·8; H, 4·4%), not depressed in admixture with an authentic specimen. The mother-liquors yielded (? 3-)*chloro*-9-*methylphenanthridine*, small needles, m. p. 91·5—92·5° (Found: C, 73·3; H, 4·6%), from light petroleum.

The authors thank the Directors of The British Drug Houses Ltd. for permission to publish these results.

CHEMICAL RESEARCH LABORATORIES,
THE BRITISH DRUG HOUSES LTD., LONDON, N.1. [*Received, December 5th*, 1949.]