150. *Amidines. Part XII. Preparation of 9-Substituted Phenanthridines from N-2-Diphenylylamidines.*

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9-Substituted phenanthridines are produced in good yield by heating *N*-2-diphenylylamidines and phosphoryl chloride in nitrobenzene solution.

THE study of phenanthridine compounds made by Morgan and Walls and their biological investigation by Browning has resulted in the production of a number of compounds having activity against several species of trypanosomes. Moreover, field trials with "Dimidium Bromide" (2 : 7-diamino-9-phenyl-10-methylphenanthridinium bromide) and "Phenidium Chloride" (7-amino-9-*p*-aminophenyl-10-methylphenanthridinium chloride) have given promising results, especially in the treatment of bovine trypanosomiasis (see Walls, *J. Soc. Chem. Ind.*, 1947, **66**, 182). Morgan and Walls (*J.*, 1931, 2447) devised a phenanthridine synthesis of general applicability by extending the Bischler–Napieralski reaction to acyl derivatives of 2-aminodiphenyl:

$$\begin{matrix} C_6H_5 \\ C_6H_4\cdot NH\cdot COR \end{matrix} \xrightarrow{POCl_3} \begin{matrix} C_6H_4\cdot C\cdot R \\ \| \\ C_6H_4\cdot N \end{matrix}$$

The presence of certain substituents, such as a nitro-group in the *m*-position to the hydrogen atom to be eliminated, adversely affected the ring closure, so that the yield of phenanthridines became very small. Walls found that in these cases greatly increased yields can be obtained by using nitrobenzene as solvent (*J.*, 1945, 294; B.P. 511,353), but the yield of 2 : 7-dinitro-9-phenylphenanthridine, the intermediate required for the preparation of "Dimidium Bromide", was still only about 50% after 12 hours' boiling. We now find that good yields of phenanthridines are obtained when the elements of ammonia are eliminated from *N*-2-diphenylylamidines by boiling for 4—5 hours with phosphoryl chloride (10 mols.) in nitrobenzene solution. The yield of 2 : 7-dinitro-9-phenylphenanthridine is 20—30% higher than that obtained by Walls's method, and yields are also 9—20% higher in the case of three other phenanthridines prepared by the two methods. The required amidines are obtained in high yield by the method described in Part I (*J.*, 1946, 147), but the crude amidinium salt resulting from the interaction of a cyanide with a 2-diphenylylammonium arylsulphonate may also be used directly in the phenanthridine synthesis, an arylsulphonyl chloride then being produced as by-product. The method has been used in the preparation of fifteen 9-substituted phenanthridines and the results are collected in Table II. Hydrogen chloride is evolved and intermediates containing phosphorus and chlorine are obtained when the reactants are heated

at the boiling point of phosphoryl chloride; these afford phenanthridines when heated to a higher temperature, but are too unstable for purification. The reaction evidently proceeds in stages, possibly to be represented as follows:

$$\begin{matrix}C_6H_5\\C_6H_4\cdot N{:}CR\cdot NH_2\end{matrix} + POCl_3 \longrightarrow HCl + \begin{matrix}C_6H_5\\C_6H_4\cdot N{:}CR\cdot NH\cdot POCl_2\end{matrix} \longrightarrow \begin{matrix}C_6H_4{-}CR\\C_6H_4{-}N\end{matrix} + NH_2\cdot POCl_2$$

9-p-*Methylsulphonylphenylphenanthridine* is also obtained by boiling N-2-*diphenylyl*-p-*methylsulphonylbenzamidine* with phosphoric oxide in nitrobenzene solution. Phosphorus pentachloride in boiling nitrobenzene converts N-2-(4′-*nitrodiphenylyl*)-p-*chlorobenzamidine* into 3-*chloro*-7-*nitro*-9-p-*chlorophenylphenanthridine*, the position of the additional chlorine atom being established by the preparation of the same phenanthridine from *p*-chlorophenyl cyanide, 5-*chloro*-4′-*nitro*-2-*diphenylylammonium benzenesulphonate*, and phosphoryl chloride.

Experimental.

Preparation of 2-Diphenylylammonium Benzenesulphonates.

2-*Diphenylylammonium Benzenesulphonate*.—This *salt*, prepared from equivalent quantities of its constituents, separated from methanol in white plates, m. p. 282° (Found: N, 4·3. $C_{18}H_{17}O_3NS$ requires N, 4·3%).

4′-*Nitro*-2-*diphenylylammonium Benzenesulphonate*.—2-Aminodiphenyl (4·3 g.) was dissolved in 95% sulphuric acid (60 c.c.; 42 mols.) below 30°. The solution was cooled in ice and stirred during the addition of powdered potassium nitrate (2·6 g.; 1·01 mols.) at such a rate that the temperature remained below 5°. After being stirred at 0—5° for a further 2 hours, the solution was poured into ice-water (500 c.c.); the solid was collected, washed with water, and recrystallised from aqueous alcohol, giving orange-yellow needles of 4′-nitro-2-aminodiphenyl (4·2 g., 77%), m. p. 158°. Scarborough and Waters (*J.*, 1927, 96), who prepared this compound by nitrating 2-acetamidodiphenyl and hydrolysing the resulting nitro-compound, record m. p. 158°. 4′-*Nitro*-2-*diphenylylammonium benzenesulphonate* crystallised from alcohol in pale yellow plates, m. p. 280° (decomp.) (Found: N, 7·65. $C_{18}H_{16}O_5N_2S$ requires N, 7·5%).

4 : 4′-*Dinitro*-2-*diphenylylammonium Benzenesulphonate*.—A solution of 2-aminodiphenyl (43 g.) in 95% sulphuric acid (500 c.c.; 35 mols.) was cooled to 0° and stirred during the slow addition of powdered potassium nitrate (52 g.; 2·02 mols.) so that the internal temperature remained below 5°. After being stirred at 0—5° for a further 4½ hours, the solution was poured into ice-water (500 c.c.) and the yellow solid which separated was triturated with 5N-sodium hydroxide (100 c.c.). After being washed with water and crystallised from 2-ethoxyethanol, 4 : 4′-dinitro-2-aminodiphenyl was obtained in orange needles, m. p. 206° (56 g., 85%). Finzi and Bellavita (*Gazzetta*, 1938, **68**, 77), who prepared this compound from 2-aminodiphenyl and from 4-nitro-2-aminodiphenyl by the action of ethyl nitrate and sulphuric acid, record m. p. 208°. The acetyl derivative, for which Finzi and Bellavita (*loc. cit.*) record m. p. 168—169°, had m. p. 168—169° (decomp.). As stated by Finzi and Bellavita, 4 : 4′-dinitrodiphenyl, m. p. and mixed m. p. 235°, is obtained by deamination of the nitro-amine; the yield was 85% when diazotisation was carried out by Claus's method (*Annalen*, 1891, **266**, 224) and the diazonium salt was reduced with hypophosphorous acid (Kornblum, *J. Amer. Chem. Soc.*, 1941, **63**, 194). 4 : 4′-*Dinitro*-2-*diphenylylammonium benzenesulphonate* separated from absolute alcohol in pale yellow plates, m. p. 249° (decomp.) (Found: N, 10·0. $C_{18}H_{15}O_7N_3S$ requires N, 10·1%).

5-*Chloro*-4′-*nitro*-2-*diphenylylammonium Benzenesulphonate*.—Chlorine was passed into a mixture of 4′-nitro-2-acetamidodiphenyl (7·1 g.), anhydrous sodium acetate (7 g.; 3·1 mols.), and glacial acetic acid (30 c.c.), heated on the steam-bath, until the gain in weight was 2 g. After a further 20 minutes' heating, saturated aqueous sulphur dioxide (10 c.c.) was added, and the solid was collected and crystallised from glacial acetic acid, giving white needles of 5-*chloro*-4′-*nitro*-2-*acetamidodiphenyl*, m. p. 208—209° (Found: N, 9·9. $C_{14}H_{11}O_3N_2Cl$ requires N, 9·65%); yield, 5 g. (62%). Hydrolysis of the acetyl derivative (5·8 g.) by boiling for 4 hours with alcohol (74 c.c.) and concentrated hydrochloric acid (5 c.c.) afforded 5-*chloro*-4′-*nitro*-2-*aminodiphenyl*, m. p. 159·5—160° (Found: N, 11·3. $C_{12}H_9O_2N_2Cl$ requires N, 11·3%). The yield was 4·9 g. (99%) and chlorination is assumed to have taken place at position 5 since 5-bromo-4′-nitro-2-acetamidodiphenyl is obtained by brominating 4′-nitro-2-acetamidodiphenyl (Case, *J. Amer. Chem. Soc.*, 1945, **67**, 118; Walls, *J.*, 1945, 294). 5-*Chloro*-4′-*nitro*-2-*diphenylylammonium benzenesulphonate* crystallised from methanol in pale yellow plates, m. p. 263° (decomp.) (Found: N, 7·2. $C_{18}H_{15}O_5N_2ClS$ requires N, 6·9%).

Preparation of Amidines.

The amidines required for the preparation of phenanthridines were obtained by the method described in Part I (*loc. cit.*). A mixture of the 2-diphenylylammonium benzenesulphonate and the cyanide (1—1·1 mols.) was heated at 200° (bath temp.) for 1½—3½ hours (as indicated in Table I), and the product was repeatedly extracted with boiling water faintly acidified with hydrochloric acid. The filtered extracts were cooled to 0°, and the amidine was liberated with 5N-sodium hydroxide, and collected by filtration, or, if oily, by solution in chloroform. The amidines were purified by crystallisation from chloroform or benzene. The experiments recorded in Table I were conducted with 0·005—0·05 g.-mol. of cyanide, and the yields are expressed in terms of the amine benzenesulphonate used.

N-2(4′-*Nitrodiphenylyl*)-p-*anisamidine*.—A mixture of 4′-nitro-2-diphenylylammonium benzenesulphonate (8·3 g.) and *p*-methoxyphenyl cyanide (3·3 g.) was heated at 200° for 3½ hours and the cold reaction product was extracted with ether to remove unchanged cyanide. The solid was extracted with boiling water (6 l.) just acidified with hydrochloric acid, and the amidine was liberated from the solution at 0° with 5N-sodium hydroxide. The amidine (6·2 g.) crystallised from chloroform in yellow prisms

TABLE I.

No.		Reaction at 200°, hrs.	Amidine. Yield, %	M. p.	Formula.	N, %: Found.	Reqd.	Amidinium picrate. M. p.	Formula.	N, %: Found.	Reqd.
1	N-2-*Diphenylylbenzamidine*	1½	89	144—144·5°	$C_{19}H_{16}N_2$	10·45	10·3	152—153°	$C_{25}H_{19}O_7N_5$	14·05	14·0
2	N-2-*Diphenylyl*-p-*methoxybenzamidine*	2½	81	152·5—153	$C_{20}H_{18}ON_2$	9·25	9·3	181·5—182	$C_{26}H_{21}O_8N_5$	13·25	13·2
3	N-2-*Diphenylyl*-p-*methylsulphonylbenzamidine*	2½	90·5	171·5	$C_{20}H_{18}O_2N_2S$	8·1	8·0	206	$C_{26}H_{21}O_9N_5S$	12·15	12·1
4	N-2-*Diphenylyl*-p-*nitrobenzamidine*	2	87	145·5—146	$C_{19}H_{15}O_2N_3$	13·3	13·25	202 (decomp.)	$C_{25}H_{18}O_9N_6$	15·7	15·4
5	N-2-(4′-*Nitrodiphenylyl*)-p-*chlorobenzamidine*	2¼	82·5	145	$C_{19}H_{14}O_2N_3Cl$	11·95	11·95	262—263 (decomp.)	$C_{25}H_{17}O_9N_6Cl$	14·2	14·4
6	N-2-(4′-*Nitrodiphenylyl*)-p-*methylsulphonylbenzamidine*	2¼	88·5	192—192·5	$C_{20}H_{17}O_4N_3S$	10·45	10·6	235—236	$C_{26}H_{20}O_{11}N_6S$	13·3	13·5
7	N-2-(4′-*Nitrodiphenylyl*)-p-*anisamidine*	3¼	80	119—120	$C_{20}H_{17}O_3N_3$	12·2	12·1	171—172 / 194—195	$C_{26}H_{20}O_{10}N_6$	14·6 / 14·35	14·6
8	N-2-(4′-*Nitrodiphenylyl*)-p-*nitrobenzamidine*	2¼	83	204	$C_{19}H_{14}O_4N_4$	15·4	15·5	166	$C_{25}H_{17}O_{11}N_7$	16·5	16·6
9	N-2-(4 : 4′-*Dinitrodiphenylyl*)*benzamidine*	2	55 / 27·5	171·5—172 / 146—147	$C_{19}H_{14}O_4N_4$	15·35 / 15·5	15·5	195—196	$C_{25}H_{17}O_{11}N_7$	16·3	16·6
10	N-2-*Diphenylyl*-2′-*amidinopyridine*	2¼	68	99·5—100	$C_{18}H_{15}N_3$	15·5	15·4	85·5—86	$C_{24}H_{18}O_7N_6$	16·75	16·7
11	N-2-*Diphenylyl*-3′-*amidinopyridine*	2½	72·5	133·5—134	$C_{18}H_{15}N_3$	15·4	15·4	176—177	$C_{24}H_{18}O_7N_6$	16·45	16·7
12	N-2-*Diphenylylamidinocyclohexene*	2½	87	124·5—125	$C_{19}H_{20}N_2$	10·1	10·1	163—164	$C_{25}H_{23}O_7N_5$	13·8	13·9
13	N-2-*Diphenylyl*-1′-*amidino*-n-*heptane*	2¼	75	96	$C_{20}H_{26}N_2$	9·5	9·5	—	—	—	—
14	N-2-*Diphenylyl*-1′-*amidino*-n-*nonane*	3½	37	97—98	$C_{22}H_{30}N_2$	8·85	8·7	134—135	$C_{28}H_{33}O_7N_5$	12·95	12·7

(1) N-2-*Diphenylylbenzamidinium chloride* separated from N-hydrochloric acid in white plates, m. p. 179—180° (Found : N, 9·1; equiv., by titration, 309. $C_{19}H_{17}N_2Cl$ requires N, 9·1%; equiv., 308·5).

(4) N-2-*Diphenylyl*-p-*nitrobenzamidinium chloride* formed white needles, m. p. 270° (Found : N, 11·95. $C_{19}H_{16}O_2N_3Cl$ requires N, 11·9%).

(7) and (9) These preparations are described below.

(11) This amidine also afforded a *dipicrate* which separated from aqueous alcohol in yellow prisms, m. p. 209—210° (Found : N, 17·15. $C_{30}H_{21}O_{11}N_9$ requires N, 17·2%).

(13) The *toluene*-p-*sulphonate* consisted of rhombic plates, m.p. 105—106° (Found : N, 5·8. $C_{27}H_{34}O_3N_2S$ requires N, 6·0%).

TABLE II.

No.		Method.	Yield, %.	Phenanthridine. M. p.*	Formula.	N, %: Found.	Reqd.	Picrate. M. p.*	Formula.	N, %: Found.	Reqd.
1	9-Phenylphenanthridine	A	84	105—106°	$C_{19}H_{13}N$	5·6	5·5	246—247° *	$C_{25}H_{16}O_7N_4$	11·6	11·6
2	9-p-*Anisylphenanthridine*	A	85	147·5—148	$C_{20}H_{15}ON$	5·05	4·9	214·5—215	$C_{26}H_{18}O_8N_4$	11·0	10·9
3	9-p-*Methylsulphonylphenylphenanthridine*	A	*ca.* 100	238	$C_{20}H_{15}O_2NS$	4·35	4·2	219—220 *	$C_{26}H_{18}O_9N_4S$	9·8	9·95
		B	91	238	—	—	—	—	—	—	—
4	9-*p*-Nitrophenylphenanthridine	A	88	190—191	$C_{19}H_{12}O_2N_2$	9·45	9·35	235	$C_{25}H_{15}O_9N_5$	13·2	13·25
5	7-*Nitro*-9-p-*chlorophenylphenanthridine*	A	80	291	$C_{19}H_{11}O_2N_2Cl$	8·45	8·4	—	—	—	—
		B	81	290—291	—	—	—	—	—	—	—
6	7-*Nitro*-9-p-*methylsulphonylphenylphenanthridine*	B	79	292	$C_{20}H_{14}O_4N_2S$	7·65	7·4	—	—	—	—
7	7-*Nitro*-9-p-*anisylphenanthridine*	A	88	232—233	$C_{20}H_{14}O_3N_2$	8·6	8·5	229—230 *	$C_{26}H_{17}O_{10}N_5$	12·5	12·5
		B	70	232	—	—	—	—	—	—	—
8	7-Nitro-9-*p*-nitrophenylphenanthridine	A	85	327	$C_{19}H_{11}O_4N_3$	12·3	12·2	—	—	—	—
		B	80	327	—	—	—	—	—	—	—
9	2 : 7-Dinitro-9-phenylphenanthridine	A	80	273—274	$C_{19}H_{11}O_4N_3$	12·25	12·2	—	—	—	—
		B	70	270	—	—	—	—	—	—	—
10	9-2′-*Pyridylphenanthridine*	A	85	133	$C_{18}H_{12}N_2$	10·95	10·95	248—249	$C_{24}H_{15}O_7N_5$	14·5	14·45
11	9-3′-Pyridylphenanthridine	A	70	125—126	$C_{18}H_{12}N_2$	10·95	10·95	234	$C_{24}H_{15}O_7N_5$	14·45	14·45
12	9-cyclo*Hexenylphenanthridine*	A	10	205 *	$C_{19}H_{17}N$	5·95	5·4	—	—	—	—
13	9-n-*Heptylphenanthridine*	A	60	50	$C_{20}H_{23}N$	5·1	5·05	179	$C_{26}H_{26}O_7N_4$	11·3	11·1
14	9-n-*Nonylphenanthridine*	A	72	47·5—48	$C_{22}H_{27}N$	4·85	4·6	144—145	$C_{28}H_{30}O_7N_4$	10·85	10·5
15	3-*Chloro*-7-*nitro*-9-p-*chlorophenylphenanthridine*	B	85	318	$C_{19}H_{10}O_2N_2Cl_2$	7·7	7·6	—	—	—	—

* Compounds having m. p.s marked with an asterisk decompose on melting.

(1) Morgan and Walls (*J.*, 1931, 2450) state that the phenanthridine has m.p. 105—106·5°. Pictet and Hubert (*Ber.*, 1896, **29**, 1188) record m. p. 242° (decomp.) for the picrate (not analysed). This phenanthridine was also prepared from *N*-2′-diphenylylbenzamidinium chloride (see below).

(3) 9-*p*-Methylsulphonylphenylphenanthridine was also prepared from the amidine and phosphoric oxide in nitrobenzene (see below).

(4) The yield was 55% after 3 hrs.' boiling. A 42% yield of this phenanthridine, m. p. and mixed m. p. 190—191°, was obtained by boiling a solution of the amidine (1·6 g.) and phosphoryl chloride (4·6 c.c.) in xylene (10 c.c.) for 5 hours. Morgan and Walls (*loc. cit.*) state that the phenanthridine has m. p. 192°.

(6) This phenanthridine did not give a picrate.

(7) The picrate decomposed into its constituents on attempted recrystallisation from 2-ethoxyethanol.

(8) Morgan and Walls (*J.*, 1938, 389) record the same m. p. for this phenanthridine.

(9) This phenanthridine was prepared by Walls (*J.*, 1945, 294) but no m. p. was recorded. It was converted into the methosulphate which with aqueous ammonia afforded 2 : 7-dinitro-10-hydroxy-9-phenyl-10-methyl-9 : 10-dihydrophenanthridine, m. p. 187—188°, previously prepared by Walls (*loc. cit.*) who records m. p. 186—188°.

(11) After the completion of our experiments, Petrow and Wragg (*J.*, 1947, 1413) prepared 9-3′-pyridylphenanthridine, m. p. 125—127°, in 72% yield by boiling 2-nicotinamidodiphenyl and phosphoryl chloride in nitrobenzene solution for 20 hrs.

(15) This phenanthridine was also prepared from *N*-2-(4′-nitrodiphenylyl)-*p*-chlorobenzamidine and phosphorus pentachloride (see later).

having the properties recorded in Table I. The two forms of the *picrate* (yellow needles, m. p. 171—172°, and yellow plates, m. p. 194—195°) were interconvertible by crystallisation from alcohol, a seed of the desired form being used. Another *picrate*, crystallising in needles, m. p. 160—161° (Found: N, 14·55%), was obtained by adding alcoholic picric acid to mother-liquors from the crystallisation of the amidine.

N-2-(4 : 4′-*Dinitrodiphenylyl*)*benzamidine*.—4 : 4′-Dinitro-2-diphenylylammonium benzenesulphonate (2·1 g.) and phenyl cyanide (0·55 g.; 1·06 mols.) were heated at 200° for 2 hours, and the cooled melt was extracted with boiling water (1 l.) acidified with hydrochloric acid. The undissolved solid (0·85 g.) was removed, the filtrate was made alkaline at 0° with 5N-sodium hydroxide, and the precipitate was crystallised from chloroform, giving yellow prismatic needles (1·0 g., 55%) of the amidine, m. p. 171·5—172° (see Table I). The part of the product which was not dissolved in the boiling dilute acid was triturated with 5N-sodium hydroxide and extracted with chloroform, giving yellow needles, m. p. 146—147°, of the second form of the amidine (see Table I). Repeated crystallisation of the amidine of lower m. p. from chloroform or benzene converted it into the form having m. p. 171·5—172°. Both forms afforded the same *picrate*, which formed yellow prismatic plates, m. p. 195—196° (see Table I).

*Preparation of 9-Substituted Phenanthridines.**

Most of the phenanthridines were prepared by heating the amidine (Method A) or the crude amidine benzenesulphonate (Method B) with phosphoryl chloride in nitrobenzene solution and the results are collected in Table II. The preparations of phenanthridines from the amidinium chloride and phosphoryl chloride in nitrobenzene, and from the amidine and phosphoric oxide in nitrobenzene are described subsequently.

Method A.—A solution of the amidine in 6—10 parts of nitrobenzene was mixed with phosphoryl chloride (10 mols.) and boiled under reflux for 4—5 hours, the internal temperature usually rising from 160° to 175° during the first 20 minutes. (In the preparation of Nos. 13 and 14 the mixtures were boiled for only 2½ and 3½ hours, respectively.) Evolution of hydrogen chloride was vigorous at the outset but ceased after about 15 minutes. Nitrobenzene and phosphoryl chloride were completely removed by distillation at 100° under diminished pressure, and the cooled residue was triturated with 5—10 parts of 5N-sodium hydroxide. The liberated phenanthridine was collected by filtration, or when oily, in chloroform, and was purified by crystallisation from 2-ethoxyethanol or from chloroform. The experiments recorded in Table II were carried out with 0·005—0·036 g.-mol. of amidine and the yields are based on the amidine used.

Method B.—An equimolecular mixture of the cyanide and the 2-diphenylylammonium benzenesulphonate was heated at 200° (bath temp.) for 2½—3 hours, and the reaction mixture was then dissolved in nitrobenzene (5 parts). Phosphoryl chloride (7·5—10 mols. per mol. of cyanide) was then added and the mixture was boiled under reflux for 4—5 hours. Nitrobenzene and phosphoryl chloride were removed at 100° under diminished pressure, and the cooled residue was triturated successively with concentrated ammonia (2—3 parts) and 5N-sodium hydroxide (2—3 parts). The phenanthridine was collected and purified as in Method A. The scale of the preparations varied from 0·01 to 0·05 g.-mol. (of cyanide) and the yields are calculated on the cyanide used.

9-*Phenylphenanthridine*.—Phosphoryl chloride (9 c.c.; 10 mols.) was added to a solution of *N*-2-diphenylylbenzamidinium chloride (3·1 g.) in nitrobenzene (27 c.c.), and the mixture was boiled under reflux for 5 hours. The solvent and excess of phosphoryl chloride were removed at 100° under diminished pressure, and the phenanthridine, liberated with 5N-sodium hydroxide (25 c.c.), was collected in chloroform, from which it separated in white needles, m. p. and mixed m. p. 106°; yield, 2·45 g., 95%.

9-p-*Methylsulphonylphenylphenanthridine*.—A solution of *N*-2-diphenylyl-*p*-methylsulphonylbenzamidine (2·8 g.) in nitrobenzene (30 c.c.) was boiled under reflux for 5 hours with phosphoric oxide (11·2 g.; 10 mols.) and the solvent was then removed by distillation at 100° under diminished pressure. The residue was cautiously mixed with 5N-sodium hydroxide (50 c.c.); the solid was collected, washed with water, and dried. Recrystallisation from chloroform afforded 9-*p*-methylsulphonylphenylphenanthridine (1·85 g.; 70%), m. p. and mixed m. p. 238°.

3-*Chloro*-7-*nitro*-9-p-*chlorophenylphenanthridine*.—Phosphorus pentachloride (3 g.; 1·4 mols.) was added to a solution of *N*-2-(4′-nitrodiphenylyl)-*p*-chlorobenzamidine (3·5 g.) in nitrobenzene (30 c.c.) and, after 5 hours' boiling, the crystals which separated on cooling were collected. The filtrate afforded a second crop of crystals on being concentrated to half its volume by distillation under diminished pressure, and recrystallisation of the total solid from 2-ethoxyethanol afforded pale yellow plates (1·2 g., 33%), m. p. 315°, identical with 3-chloro-7-nitro-9-*p*-chlorophenylphenanthridine prepared from *p*-chlorophenyl cyanide and 5-chloro-4′-nitro-2-diphenylylammonium benzenesulphonate (Table II, No. 15).

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* See also B.P. 614,072 (1.7.1946).