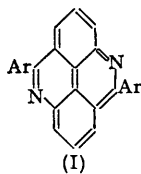


**918. Some Derivatives of 1 : 6-Diazapyrene and 4 : 5-6 : 7-Dibenzo-1 : 3-diazacyclohepta-2 : 4 : 6-triene.**

By A. E. S. FAIRFULL, D. A. PEAK, W. F. SHORT, and T. I. WATKINS.

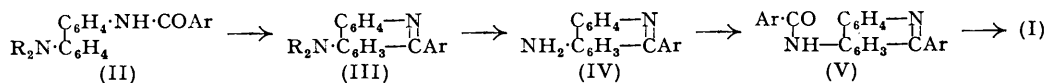
Methods for the synthesis of 2 : 7-diaryl-1 : 6-diazapyrene (I) and certain of its functional derivatives have been developed. A new method for the preparation of 4 : 5-6 : 7-dibenzo-1 : 3-diazacyclohepta-2 : 4 : 6-trienes is described, and the fission of the 7-membered ring by methylating agents is recorded.

THE importance of phenanthridinium compounds in the treatment of trypanosomiasis suggested the desirability of preparing some compounds in which diphenyl is fused with two pyridine nuclei, and we now describe the synthesis of a number of compounds of this type derived from 2 : 7-diaryl-1 : 6-diazapyrene (I).



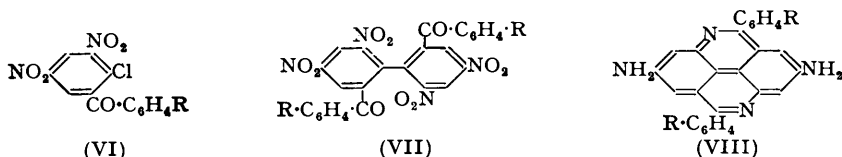
The first synthesis started from 2 : 2'-diaminodiphenyl and involved elaboration of the pyridine nuclei by successive ring closures of the Bischler-Napieralski type, one amino-group being suitably protected during the production of the intermediate phenanthridine (III). A carbethoxy-group was found to be unsuitable for the protection of the amino-group, no phenanthridine being obtained by the action of phosphoryl chloride on 2-benzamido-2'-carbethoxyamino-diphenyl which was prepared from 2-amino-2'-benzamidodiphenyl (Sako, *Mem. Coll. Eng.*

*Kyushu*, 1932, 6, 263), ethyl chloroformate, and diethylaniline in alcohol. Suitable protection was afforded in a number of cases by a phthaloyl group. Thus, 2-amino-2'-phthalimidodiphenyl (Sako, *loc. cit.*) was converted into 2-benzamido-2'-phthalimidodiphenyl [II; Ar = Ph, R<sub>2</sub> = (CO)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>] which afforded 9-phenyl-5-phthalimidophenanthridine [III; Ar = Ph, R<sub>2</sub> = (CO)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>] (62%) when boiled with phosphoryl chloride and nitrobenzene. The phthaloyl group was removed, best by the action of hydrazine, and the resulting 5-amino-9-phenylphenanthridine (IV; Ar = Ph) was successively benzoylated and treated with phosphoryl chloride, giving 2 : 7-diphenyl-1 : 6-diazapyrene (I; Ar = Ph) (76%). A similar series of operations, *p*-nitrobenzoyl chloride being used at the appropriate stages, gave 2 : 7-di-*p*-nitrophenyl-1 : 6-diazapyrene (I; Ar = *p*-NO<sub>2</sub>C<sub>6</sub>H<sub>4</sub>). The two insoluble diazapyrenes were converted successively into the water-soluble bismetho-methylsulphates and dimethobromides. Reduction of 2 : 7-di-*p*-nitrophenyl-1 : 6-diazapyrene dimethobromide with iron powder in faintly acid solution gave 2 : 7-di-*p*-amino-phenyl-1 : 6-diazapyrene dimethobromide, isolated as its hydrobromide dihydrate.



In an attempt to prepare 4 : 9-diamino-2 : 6-diazapyrene, 2 : 2'-dinitrobenzidine (Täuber, *Ber.*, 1890, 23, 795) was converted successively into 4 : 4'-biscarbethoxyamino-2 : 2'-dinitrodiphenyl (Le Fèvre and Turner, *J.*, 1928, 252), 2 : 2'-diamino-4 : 4'-biscarbethoxyaminodiphenyl, 2-amino-4 : 4'-biscarbethoxyamino-2'-phthalimidodiphenyl, and 2-benzamido-4 : 4'-biscarbethoxyamino-2'-phthalimidodiphenyl, but the latter did not yield a phenanthridine. The required compounds were readily obtained by condensing 2-chloro-3 : 5-dinitrobenzoyl chloride with an aromatic compound to give a 2-chloro-3 : 5-dinitrobenzophenone (VI) (cf. Ullmann and Engi, *Annalen*, 1909, 366, 82), and converting this by the action of copper powder into a 2 : 2'-diaryl-4 : 4' : 6 : 6'-tetranitrodiphenyl (VII) which underwent simultaneous reduction and ring closure when treated with stannous chloride. The resulting 4 : 9-diamino-2 : 7-diaryl-1 : 6-diazapyrenes (VIII; R = H, *p*-Me, *p*-Cl, *p*-OMe) were converted into soluble methosalts by successive acetylation, quaternisation, and hydrolysis.

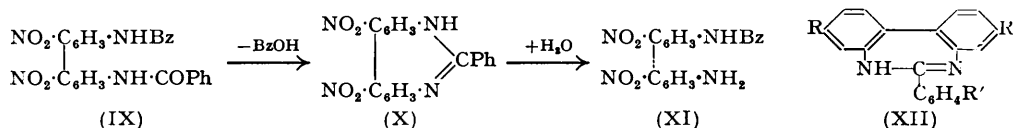
A small amount of 2 : 4-dinitroxanthone was produced during the preparation of 2-chloro-4'-methoxy-3 : 5-dinitrobenzophenone from 2-chloro-3 : 5-dinitrobenzoyl chloride and anisole. This was probably formed by demethylation of anisole, and condensation of phenol with the acid chloride to give 2-chloro-2'-hydroxy-3 : 5-dinitrobenzophenone, which then lost hydrogen chloride to give the xanthone.



2 : 2'-Diamino-4 : 4'-dinitrodiphenyl, prepared by hydrolysing a nitration product of 2 : 2'-succinimidodiphenyl (Sako, *loc. cit.*), was converted into 2 : 2'-dibenzamido-4 : 4'-dinitrodiphenyl (IX), which on treatment with phosphoryl chloride yielded, not a diazapyrene, but 2-amino-2'-benzamido-4 : 4'-dinitrodiphenyl (XI). The monobenzoyl derivative, also prepared directly from 2 : 2'-diamino-4 : 4'-dinitrodiphenyl and by the hydrolysis of 2' : 3'-dinitro-2-phenyl-4 : 5-6 : 7-dibenzo-1 : 3-diazacyclohepta-2 : 4 : 6-triene (see below), probably owes its formation to the production of 2' : 3'-dinitro-2-phenyl-4 : 5-6 : 7-dibenzo-1 : 3-diazacyclohepta-2 : 4 : 6-triene (X) which is hydrolysed when the reaction product is poured into water. Sako (*loc. cit.*) found that 2 : 2'-dibenzamido-6 : 6'-dimethyldiphenyl yields 1'' : 4'-dimethyl-2-phenyl-4 : 5-6 : 7-dibenzo-1 : 3-diazacyclohepta-2 : 4 : 6-triene with phosphorus trichloride at 125°, benzoic acid being eliminated.

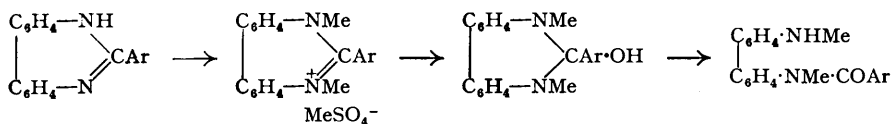
*N*-2-Diphenylamidines are converted into 9-substituted phenanthridines by phosphoryl chloride (Cymerman and Short, *J.*, 1949, 703), but 2 : 2'-diaminodiphenyl, phenyl

cyanide, and benzenesulphonic acid did not yield a diamidine or a diazapyrene but gave 4 : 5-6 : 7-dibenzo-1 : 3-diazacyclohepta-2 : 4 : 6-triene (XII; R = R' = H), a compound previously prepared by Sako (*loc. cit.*) from 2-amino-2'-benzamidodiphenyl and phosphorus trichloride at 130°. 2 : 2'-Diaminodiphenyl, *p*-nitrophenyl cyanide, and benzenesulphonic



acid similarly gave 2-*p*-nitrophenyl-4 : 5-6 : 7-dibenzo-1 : 3-diazacyclohepta-2 : 4 : 6-triene (XII; R = H; R' = *p*-NO<sub>2</sub>), and, in the same way, 2' : 3''-dinitro-2-phenyl-4 : 5-6 : 7-dibenzo-1 : 3-diazacyclohepta-2 : 4 : 6-triene (X) was obtained from 2 : 2'-diamino-4 : 4'-dinitrodiphenyl and phenyl cyanide. The seven-membered rings in these compounds are somewhat unstable. For example, when the dinitro-compound is boiled with ordinary glacial acetic acid it affords 2-amino-2'-benzamido-4 : 4'-dinitrodiphenyl.

The diazacycloheptatriene ring is also ruptured by methylating agents. 2-Phenyl-4 : 5-6 : 7-dibenzo-1 : 3-diazacyclohepta-2 : 4 : 6-triene resisted methylation when heated with methyl sulphate, potassium carbonate, and toluene, being merely converted into its sulphate. Methyl iodide, potassium carbonate, and acetone or formaldehyde and formic acid caused simultaneous methylation and hydrolysis with production of 2-benzomethyl-amido-2'-dimethylaminodiphenyl. 2-*p*-Nitrophenyl-4 : 5-6 : 7-dibenzo-1 : 3-diazacyclohepta-2 : 4 : 6-triene and methyl sulphate in boiling toluene afforded a yellow solid which on being boiled with aqueous ethanol gave the sulphate of the diazacycloheptatriene and orange needles of a base shown to be 2-methylamino-2'-*p*-nitrobenzomethylamidodiphenyl by synthesis of its formyl derivative. The reaction may be formulated as follows (Ar = *p*-NO<sub>2</sub>·C<sub>6</sub>H<sub>4</sub>):



When the diazacycloheptatriene was boiled with methyl sulphate alone and the resulting sticky solid was digested with aqueous methanol, the products were 2-methylamino-2'-*p*-nitrobenzomethylamidodiphenyl and 2-amino-2'-*p*-nitrobenzamidodiphenyl, identical with a specimen prepared from 2 : 2'-diaminodiphenyl and *p*-nitrobenzoic anhydride. 2-Formo-methylamido-2'-*p*-nitrobenzomethylamidodiphenyl was synthesised from 2-amino-2'-nitrodiphenyl by successive formylation, methylation, reduction to 2-amino-2'-formo-methylamidodiphenyl, *p*-nitrobenzoylation, and methylation. 2-Amino-2'-*p*-aminobenzo-methylamidodiphenyl was synthesised from 2-*p*-nitrobenzamido-2'-nitrodiphenyl, since the product obtained by the methylation of the diazacycloheptatriene was first thought to be a monomethyl compound.

The biological activities of the quaternary salts of the 2 : 7-diaryl-1 : 6-diazapyrenes have been examined by Dr. L. Dickinson and her colleagues and detailed results will be published elsewhere. All these compounds possessed antibacterial and antiviral activity and those containing two amino-groups were 1000 times more active against the bacteriophage of *Pseudomonas pyocyanea* than against the host. In an egg test against influenza A virus (PR 8 grade), the amino-compounds were active at one-half to one-quarter of the amount which killed the embryo (1—5 mg.), but the therapeutic index is too small for the compounds to be used therapeutically.

#### EXPERIMENTAL

5-Amino-9-arylphenanthridines and 2 : 7-Diaryl-1 : 6-diazapyrenes.—2 : 2'-Dinitrodiphenyl, m. p. 122—124°, was obtained (average yield of 46% ; with 14% of *o*-chloronitrobenzene) by the action of copper on *o*-nitrobenzenediazonium chloride (Niementowski, *Ber.*, 1901, 34, 3327).

A solution of the dinitro-compound (64 g.) in hot alcohol (500 c.c.) was added in portions with occasional cooling to a warm solution of crystalline stannous chloride (382 g., 6.4 mols.) in 36% hydrochloric acid (440 c.c.), and the mixture was boiled overnight before isolation of 2:2'-diaminodiphenyl, m. p. 77—79° (35.6 g.). The pure compound has m. p. 80—81° (Täuber, *Ber.*, 1891, 24, 198; Niementowski, *loc. cit.*). Ethyl chloroformate (5 c.c., 1.3 mols.) was added dropwise to a boiling solution of 2-amino-2'-benzamidodiphenyl (11.7 g.; Sako, *loc. cit.*) in absolute alcohol (300 c.c.) and diethylaniline (10 c.c., 1.5 mols.), heating was continued for a further hour, and the mixture was then shaken with dilute hydrochloric acid. The resultant oil was collected in ether, and the washed and dried (MgSO<sub>4</sub>) solution was concentrated to 20 c.c., giving 2-benzamido-2'-carbethoxyaminodiphenyl (10.5 g.), which separated from methanol in prisms, m. p. 128—130° (Found: N, 7.7. C<sub>22</sub>H<sub>20</sub>O<sub>3</sub>N<sub>2</sub> requires N, 7.8%). Attempts to cyclise this compound by heating it with phosphoryl chloride, with or without nitrobenzene, were unsuccessful, only unchanged starting material and traces of a solid, m. p. ca. 300°, being obtained. 2-Amino-2'-phthalimidodiphenyl, m. p. 174—176°, was obtained in 71% yield by the method described by Sako (*loc. cit.*), who presented unconvincing evidence for regarding it as *NN'*-2:2'-diphenylene-phthalodiamide. The phthalimido-compound (3.15 g.), benzoyl chloride (1.5 c.c., 1.3 mols.), and chlorobenzene (20 c.c.) were boiled under reflux until evolution of hydrogen chloride ceased (ca. 20 minutes), and addition of light petroleum (80 c.c.) then precipitated 2-benzamido-2'-phthalimidodiphenyl (3.8 g.), m. p. 168—170° (Found: N, 6.9. C<sub>27</sub>H<sub>18</sub>O<sub>3</sub>N<sub>2</sub> requires N, 6.7%). 2-Amino-2'-phthalimidodiphenyl (9.45 g.), *p*-nitrobenzoyl chloride (6.3 g.), and chlorobenzene (30 c.c.) similarly gave 2-*p*-nitrobenzoyl-2'-phthalimidodiphenyl (13.5 g.), needles (from chlorobenzene), m. p. 215—216° (Found: N, 9.4. C<sub>27</sub>H<sub>17</sub>O<sub>5</sub>N<sub>3</sub> requires N, 9.1%).

9-Phenyl-5-phthalimidophenanthridine. 2-Benzamido-2'-phthalimidodiphenyl (20.9 g.), phosphoryl chloride (46 c.c., 0.2 mol.), and nitrobenzene (50 c.c.) were heated under reflux for 16 hours. The mixture was poured on ice, the nitrobenzene was removed in a current of steam, and the phenanthridine (12.4 g.) which separated from the yellow solution was crystallised from alcohol. Recrystallisation from alcohol gave needles of 9-phenyl-5-phthalimidophenanthridine, m. p. 225—226° (Found: C, 81.2; H, 4.25; N, 7.2. C<sub>27</sub>H<sub>16</sub>O<sub>2</sub>N<sub>2</sub> requires C, 81.0; H, 4.0; N, 7.0%). Evaporation of the alcoholic mother-liquors and hydrolysis of the residue with 36% hydrochloric acid gave 5-amino-9-phenylphenanthridine (1.03 g.), and a further quantity (0.41 g.) was obtained by basifying the yellow acid solution remaining after the steam-distillation (above).

5-Amino-9-phenylphenanthridine. The phthaloyl group was removed by boiling 9-phenyl-5-phthalimidophenanthridine (2 g.) for 2½ hours with (a) 36% hydrochloric acid (50 c.c.), (b) 36% hydrochloric acid (20 c.c.) and acetic acid (10 c.c.), or (c) (16 hours) with 20% aqueous potassium hydroxide (50 c.c.). The yields of the amino-compound, 71, 56, and 75.5% respectively, were not always reproducible but hydrolysis by Ing and Manske's method (*J.*, 1926, 2348) in presence of hydrazine was always satisfactory. The phthaloyl compound (6 g.) soon dissolved in a boiling mixture of hydrazine hydrate (3 c.c., 4.2 mols.) and methanol (60 c.c.), and the clear solution soon deposited a mass of white needles. The solid was dissolved in dilute hydrochloric acid and addition of sodium hydroxide to the yellow solution precipitated a solid (96%), which on recrystallisation from alcohol gave pale yellow needles of 5-amino-9-phenylphenanthridine, m. p. 192—193° (Found: C, 84.4; H, 5.3; N, 10.7. C<sub>19</sub>H<sub>14</sub>N<sub>2</sub> requires C, 84.4; H, 5.2; N, 10.4%). The exothermic reaction which occurred on admixture of the amine (5.4 g.) with benzoyl chloride (3 c.c., 1.5 mols.) and nitrobenzene (25 c.c.) was completed by boiling the mixture until the resulting orange solid redissolved. The orange solid precipitated by pouring the solution into light petroleum was dissolved in warm methanol, and the white precipitate, m. p. 210—212° (5.9 g.), obtained on adding ammonia to the solution was recrystallised from ethanol, giving 5-benzamido-9-phenylphenanthridine, plates, m. p. 214° (Found: N, 7.55. C<sub>26</sub>H<sub>18</sub>ON<sub>2</sub> requires N, 7.5%).

9-*p*-Nitrophenyl-5-phthalimidophenanthridine, obtained in 78.5% yield as described for the phenyl analogue, crystallised from chlorobenzene in needles, m. p. 299—300° (Found: C, 72.9; H, 3.5; N, 9.6. C<sub>27</sub>H<sub>15</sub>O<sub>4</sub>N<sub>3</sub> requires C, 72.8; H, 3.4; N, 9.4%).

5-Amino-9-*p*-nitrophenylphenanthridine. The foregoing compound (6 g.), hydrazine hydrate (6 c.c., 9 mols.), and methanol (120 c.c.) were heated under reflux for 3 hours, and the solid (2.1 g.; m. p. 219—220°) was then collected. The solvent was removed from the filtrate and a dilute hydrochloric acid extract of the residue was clarified by filtration, made alkaline with aqueous ammonia, and the precipitate crystallised from chlorobenzene, giving another 1.4 g. of the amine, m. p. 219—220°. 5-Amino-9-*p*-nitrophenylphenanthridine crystallised from chlorobenzene in orange needles, m. p. 221—222° (Found: C, 72.0; H, 4.0; N, 13.5. C<sub>19</sub>H<sub>13</sub>O<sub>2</sub>N<sub>3</sub> requires C, 72.4; H, 4.1; N, 13.3%). This amine (3.15 g.), *p*-nitrobenzoyl chloride

(2.1 g., 1.1 mols.), and nitrobenzene (10 c.c.), brought into reaction in the same way as the corresponding unsubstituted compound, afforded 5-*p*-nitrobenzamido-9-*p*-nitrophenylphenanthridine (81.5%), m. p. 338—341°, raised to 341—342° by recrystallisation from nitrobenzene (Found : N, 12.1.  $C_{28}H_{16}O_5N_4$  requires N, 12.1%).

2 : 7-*Diphenyl*-1 : 6-*diazapyrene*. A mixture of 5-benzamido-9-phenylphenanthridine (2.7 g.), phosphoryl chloride (4.7 c.c.), and nitrobenzene (20 c.c.) was boiled under reflux for 16 hours, the internal temperature being 160°. The excess of chloride was decomposed with ice, nitrobenzene was removed in steam, and the residual solid was washed with hot methanol to remove a coloured impurity. Crystallisation from chlorobenzene gave needles (2.7 g.) of 2 : 7-*diphenyl*-1 : 6-*diazapyrene*, m. p. 320—321° (Found : C, 88.0; H, 4.65; N, 8.0.  $C_{26}H_{16}N_2$  requires C, 87.6; H, 4.5; N, 7.9%). The *dipicrate* (needles from chlorobenzene) had m. p. 205—206° (Found : C, 56.4; H, 2.7; N, 13.9.  $C_{38}H_{12}O_{14}N_8$  requires C, 56.0; H, 2.7; N, 13.8%). White needles separated when methyl sulphate (4 c.c., 2.1 mols.) was added to a solution of the diazapyrene (7.1 g.) in hot nitrobenzene (21 c.c.), and the methomethyl sulphate (6.4 g.) was obtained by boiling the mixture for a few minutes, cooling, and washing the precipitate with benzene and light petroleum. This salt was dissolved in water (20 c.c.) and treated with a hot solution of sodium iodide (10 g.) in water (10 c.c.). The precipitate (4.25 g.) recrystallised from hot water giving red prisms of 2 : 7-*diphenyl*-1 : 6-*diazapyrene dimethiodide dihydrate* (Found : C, 49.45, 50.0; H, 3.8, 3.7; N, 3.9; loss at 100°, 5.1.  $C_{28}H_{22}N_2I_2 \cdot 2H_2O$  requires C, 49.7; H, 3.85; N, 4.15;  $H_2O$ , 5.3%). This salt decomposes at 250—260° with loss of colour and regeneration of 2 : 7-*diphenyl*-1 : 6-*diazapyrene*, m. p. and mixed m. p. 320—321°.

2 : 7-*Di-p-nitrophenyl*-1 : 6-*diazapyrene*. 5-*p*-Nitrobenzamido-9-*p*-nitrophenylphenanthridine (3.5 g.), phosphoryl chloride (7 c.c.) and nitrobenzene (21 c.c.) were heated under reflux for 16 hours and the product was isolated by the procedure described for diphenyldiazapyrene (above). The solid was too insoluble for recrystallisation but successive washing with alcohol, nitrobenzene, and alcohol afforded fine yellow needles of 2 : 7-*di-p-nitrophenyl*-1 : 6-*diazapyrene* (91%) which did not melt below 400° (Found : C, 69.6; H, 3.0; N, 12.3.  $C_{26}H_{14}O_4N_4$  requires C, 69.95; H, 3.2; N, 12.55%). The foregoing compound (13 g.) and methyl sulphate (58.5 c.c.) were boiled under reflux for 15 minutes, and the solid, obtained on cooling the resulting suspension, was washed with benzene and light petroleum and recrystallised from boiling water, giving needles (12.6 g.). Crystallisation from water afforded 2 : 7-*di-p-nitrophenyl*-1 : 6-*diazapyrene bismethomethylsulphate trihydrate* (Found : C, 47.7; H, 4.2; N, 8.0; loss at 100°/vac., 6.3.  $C_{30}H_{26}O_{12}N_4S_2 \cdot 3H_2O$  requires C, 47.9; H, 4.25; N, 7.45;  $H_2O$ , 7.2%), decomp. 312—320°. Addition of ammonium bromide (30 g.) in water (80 c.c.) to the original aqueous mother-liquor afforded a solid (4.6 g.) which on being washed with very dilute hydrobromic acid gave 2 : 7-*di-p-nitrophenyl*-1 : 6-*diazapyrene dimethobromide* (Found : N, 8.9; Br, 23.3.  $C_{28}H_{20}O_4N_4Br_2$  requires N, 8.8; Br, 25.3%). This quaternary salt crystallises in golden-yellow needles which decompose at 200—260° (without melting) to give a white solid, probably the diazapyrene, which does not melt at 360°.

2 : 7-*Di-p-aminophenyl*-1 : 6-*diazapyrene*. The foregoing methobromide (10 g.) was triturated with iron powder (12 g.) and stirred into a mixture of alcohol (300 c.c.), water (300 c.c.), and 0.1*N*-hydrobromic acid (2 c.c.). The mixture was heated on the steam-bath for 4 hours, neutralised with 0.1*N*-sodium hydroxide (2 c.c.), kept overnight, and filtered. The iron residue was washed with alcohol and the united filtrates were evaporated to dryness, the residue being extracted with alcohol (400 c.c.). The filtered alcoholic solution was diluted with water (100 c.c.), brought to pH 4.8 by hydrobromic acid, evaporated to remove the alcohol, cooled, and filtered. The resulting dark red solid (4.2 g.), m. p. 205—206°, was dried at 100°, and then exposed to the atmosphere for several days, giving 2 : 7-*di-p-aminophenyl*-1 : 6-*diazapyrene dimethobromide hydrobromide dihydrate* (Found : N, 8.3; Br, 35.2;  $H_2O$ , 5.6.  $C_{28}H_{24}N_4Br_2 \cdot HBr \cdot 2H_2O$  requires N, 8.1; Br, 34.65;  $H_2O$ , 5.2%). An aqueous solution of this salt (pH 2) was brought to pH 6.6 by sodium hydroxide solution, then concentrated and cooled, giving a red solid, m. p. 212—213°, probably 2 : 7-*di-p-aminophenyl*-1 : 2-*dihydro*-2-*hydroxy*-1-*methyl*-1 : 6-*diazapyrene 6-methobromide* (Found : N, 10.9; Br, 17.2.  $C_{28}H_{25}ON_4Br$  requires N, 10.8; Br, 15.6%).

2-*Benzamido*-4 : 4'-*biscarbethoxyamino*-2'-*phthalimidodiphenyl* and *Phosphoryl Chloride*.—2 : 2'-Dinitrobenzidine was prepared by a modification of Täuber's method (*Ber.*, 1890, **23**, 795). Benzidine (18.4 g.) was dissolved in 10% oleum (282 g.) below 50°, and potassium nitrate (20.2 g.) was added to the stirred solution during an hour, the temperature being kept below 20°. The solution was stirred at room temperature for 3 hours and then poured into ice-water (3 vols.). Most of the 2 : 2'-dinitrobenzidine separated as the sulphate which was collected and decomposed with ammonia. The nitro-amine, purified by reprecipitation from dilute hydrochloric acid and

washed with methanol, had m. p. 209—211° (16.5 g.), and the original acid filtrate afforded a second crop of the same m. p. when it was made alkaline with ammonia (1.8 g.). Ethyl chloroformate (30 c.c., 2.1 mols.) was added dropwise to a boiling solution of the foregoing nitro-compound (45.5 g.) and diethylaniline (60 c.c., 2.3 mols.) in absolute alcohol (1 l.), and the mixture heated for a further hour and poured into water (3 l.) and 5*N*-hydrochloric acid (100 c.c.). The solid (50.4 g.) crystallised from alcohol as orange needles of 4 : 4'-biscarbethoxyamino-2 : 2'-dinitrodiphenyl, m. p. 200—201° as recorded by Le Fèvre and Turner (*J.*, 1928, 252). Reduced iron powder (60 g.) was added to a boiling mixture of the preceding compound (47 g.), alcohol (280 c.c.), water (500 c.c.), and 36% hydrochloric acid (10 c.c.), and heating and stirring were continued for 5 hours before the mixture was poured into ice-water (3 l.). The solid was collected with the aid of kieselgühr and extracted with boiling acetone (2 × 500 c.c.). The acetone extract was washed with methanol, dissolved in dilute hydrochloric acid (charcoal) and reprecipitated with ammonia, giving 2 : 2'-diamino-4 : 4'-biscarbethoxyaminodiphenyl (25 g.), which crystallised from chlorobenzene as colourless needles, m. p. 201—202° (decomp.) (Found : C, 60.1; H, 5.9; N, 15.6.  $C_{18}H_{22}O_4N_4$  requires C, 60.3; H, 6.2; N, 15.6%). A mixture of the diamine (17 g.), phthalic anhydride (8.5 g., 1.2 mols.), and water (170 c.c.) was boiled under reflux for 4 hours; the solid was then collected, powdered, and boiled with the liquid for another 2 hours. The pale yellow solid (18.7 g.) was recrystallised from chlorobenzene, giving yellow needles of 2-amino-4 : 4'-biscarbethoxyamino-2'-phthalimidodiphenyl, m. p. 231—232° (Found : C, 64.3; H, 5.0; N, 11.5.  $C_{26}H_{24}O_6N_4$  requires C, 63.95; H, 4.9; N, 11.5%). The phthaloyl compound (16.3 g.), benzoyl chloride (5 c.c., 1.3 mols.), and nitrobenzene (30 c.c.) were boiled under reflux for 15 minutes and the filtered solution was diluted first with an equal volume of benzene and then with excess of light petroleum. The resulting solid, freed from a brown impurity by boiling it with ethanol (100 c.c.) and washing it with methanol, had m. p. 258—260° (17.6 g.), and a sample recrystallised several times from chlorobenzene afforded prisms of 2-benzamido-4 : 4'-biscarbethoxyamino-2'-phthalimidodiphenyl, m. p. 265—266° (Found : N, 9.3.  $C_{33}H_{28}O_7N_4$  requires N, 9.5%). Attempts to convert this compound into a phenanthridine by the action of phosphoryl chloride were unsuccessful, other substances being produced.

2 : 2'-Diaroyl-4 : 4' : 6 : 6'-tetranitrodiphenyls.—2-Chloro-3 : 5-dinitrobenzophenones. The preparation of these compounds was based on the procedure used by Ullmann and Broido (*Ber.*, 1906, 39, 358) for the preparation of 2-chloro-3 : 5-dinitrobenzophenone. 2-Chloro-3 : 5-dinitrobenzoic acid (Ullmann and Engi, *Annalen*, 1909, 366, 82) was converted into 2-chloro-3 : 5-dinitrobenzoyl chloride, m. p. 62—64°, by means of thionyl chloride as described by Barnett (*Ber.*, 1925, 58, 1610) who does not record the m. p. More usually, the acid and phosphorus pentachloride (1.3 mols.) were brought into reaction in presence of an excess of the appropriate aromatic compound, and the resulting mixture was heated on the steam-bath for  $\frac{1}{2}$  hour, cooled, and treated with aluminium chloride (1.8 mols.), first at room temperature and then at 95—100° for  $\frac{1}{2}$ —3 $\frac{1}{2}$  hours. The mixture was decomposed with ice, and, after being kept for  $\frac{1}{2}$  hour at room temperature, the ketone was collected in benzene and purified by washing it with sodium carbonate solution and recrystallisation, usually from acetic acid (charcoal). The following new compounds were prepared, the yields being shown in parentheses.

2-Chloro-4'-methyl-3 : 5-dinitrobenzophenone (53%), needles (from light petroleum), m. p. 111—112° (Found : N, 9.0.  $C_{14}H_9O_5N_2Cl$  requires N, 8.75%); a lower yield was obtained when carbon disulphide was used as solvent instead of a large excess of toluene. 2 : 4'-Dichloro-3 : 5-dinitrobenzophenone (51.5%), needles (from light petroleum), m. p. 117° (Found : N, 8.5.  $C_{13}H_6O_5N_2Cl_2$  requires N, 8.2%).

2-Chloro-4'-methoxy-3 : 5-dinitrobenzophenone (37%), plates (from alcohol), m. p. 146—147° (Found : N, 8.5.  $C_{14}H_9O_6N_2Cl$  requires N, 8.3%). It was separated from a by-product (8%) which was much more sparingly soluble in benzene and which on crystallisation of this from acetic acid gave long needles, m. p. 206—207° (Found : C, 54.8; H, 2.4; N, 10.0. Calc. for  $C_{13}H_6O_6N_2$  : C, 54.5; N, 2.1; H, 9.8%), undepressed on admixture with a specimen of 2 : 4-dinitroxanthone, prepared in 60% yield as described by Ullmann (*Annalen*, 1909, 366, 87). Reduction with stannous chloride by the method used by Bayer (*Annalen*, 1910, 372, 139) in the case of an isomeric dinitroxanthone, afforded 2 : 4-diaminoxanthone (67%), orange needles (from chlorobenzene), m. p. 230—231° (Found : N, 12.3.  $C_{13}H_{10}O_2N_2$  requires N, 12.4%). 2 : 4-Diacetamidoxanthone had m. p. 315—316° (Found : N, 9.1.  $C_{17}H_{14}O_4N_2$  requires N, 9.0%).

2 : 2'-Diaroyl-4 : 4' : 6 : 6'-tetranitrodiphenyls were prepared from the chlorobenzophenones by the action of copper powder, better yields being obtained by a modification of the method of Ullmann and Broido (*loc. cit.*) in which the nitrobenzene is omitted and a few drops of acetic acid are added to the reaction mixture. The chlorobenzophenone should be pure and the

addition of acetic acid is necessary in order to obtain the yields recorded. 2 : 2'-Dibenzoyl-4 : 4' : 6 : 6'-tetranitrodiphenyl was obtained consistently in 65% yield in place of the 21% yield obtained by Ullmann's procedure. When a drop of acetic acid was added with stirring to a mixture of 2-chloro-3 : 5-dinitrobenzophenone (29 g.) and copper powder (*ca.* 2 g.) heated in an oil-bath at 170°, the internal temperature rose to 175—180°. This temperature was maintained by the addition of copper powder (16 g., 3 atomic proportions in all) during 40 minutes. The bath-temperature was raised to 190° during the next 20 minutes; the internal temperature rose to 195° but fell to 190° during a further 20 minutes' heating. The resulting mixture was extracted with boiling benzene (charcoal), and the filtered solution, after being concentrated to 70 c.c., was precipitated with light petroleum. The final precipitate was sticky but was easily purified by trituration with warm acetic acid and the total yield of the diphenyl, *m. p.* 184—186°, was 16.1 g. Ullmann and Broido (*loc. cit.*) record *m. p.* 186°. The following compounds, crystallised from acetic acid, were prepared by the general method, the bath-temperatures, which are 5—10° lower than the temperatures of the reacting mixtures, being given in parentheses together with yields of crude product.

4 : 4 : 6 : 6'-*Tetranitro-2 : 2'-di-p-toluoxyldiphenyl* (130—150°) (63%), *m. p.* 221—222° (Found : N, 10.0.  $C_{28}H_{18}O_{10}N_4$  requires N, 9.8%).

2 : 2'-*Di-p-nitrobenzoyl-4 : 4' : 6 : 6'-tetranitrodiphenyl* (150—170°) (54%), *m. p.* 232—233° (Found : N, 9.2.  $C_{26}H_{12}O_{10}N_4Cl_2$  requires N, 9.15%).

2 : 2'-*Di-p-methoxybenzoyl-4 : 4' : 6 : 6'-tetranitrodiphenyl* (155—157°) (29%), *m. p.* 227—228° (Found : N, 9.45.  $C_{28}H_{18}O_{12}N_4$  requires N, 9.3%).

4 : 9-*Diamino-2 : 7-diaryl-1 : 6-diazapyrenes*.—Simultaneous reduction and ring closure took place when stirred suspensions of the diaroxytetranitrodiphenyls in alcohol (10 c.c. per g.) were treated with solutions of crystalline stannous chloride (12—13.5 mols.) in 36% hydrochloric acid (1.3 c.c. per g.). The nitro-compounds dissolved in about  $\frac{1}{4}$  hour and reduction was completed by boiling the solutions under reflux for 1—1 $\frac{1}{2}$  hours. The solutions were concentrated under reduced pressure, and the diaminodiazapyrene hydrochlorides were precipitated as red or orange solids by adding 36% hydrochloric acid to the concentrates, and were washed with the concentrated acid. These salts became purple on trituration with water and addition of aqueous sodium hydroxide precipitated the diamines, which were washed with water and alcohol and recrystallised from nitrobenzene or aqueous pyridine. The diamines did not melt below 400° but usually blackened and decomposed at 360—380°. Diacetyl derivatives (80—85%) were obtained by boiling the diamines with acetic anhydride (11—30 c.c. per g.) for 10—15 minutes, the resulting solids being washed with acetic acid and alcohol and recrystallised from nitrobenzene, giving yellow needles which were washed with alcohol and ether. They were recovered unchanged after being boiled with 5% sodium hydroxide solution or with 20% hydrochloric acid but were hydrolysed by dissolving them in concentrated sulphuric acid (5 c.c. per g.), cautiously adding an equal volume of water in small portions, and bringing the resulting solutions to the *b. p.* The amines were obtained by pouring the solutions on ice and sodium hydroxide solution.

4 : 9-*Diamino-2 : 7-diphenyl-1 : 6-diazapyrene* (71%) consisted of orange feathery needles (Found : C, 79.9, 79.6; H, 4.5, 4.8; N, 14.4.  $C_{26}H_{18}N_4$  requires C, 80.8; H, 4.7; N, 14.4%) and the *diacetyl* derivative had *m. p.* 384—385°, with previous sintering (Found : C, 74.1; H, 4.5; N, 12.0.  $C_{30}H_{22}O_2N_4$  requires C, 76.6; H, 4.7; N, 11.9%). The amine and 36% hydrochloric acid afforded the *hydrochloride* which crystallised from methanol containing a little hydrochloric acid in purple needles which did not melt below 400° (Found : N, 12.25; Cl, 14.3.  $C_{26}H_{18}N_4 \cdot 2HCl$  requires N, 12.2; Cl, 15.5%).

4 : 9-*Diamino-2 : 7-di-p-tolyl-1 : 6-diazapyrene* (78%) purified through the *diacetyl* derivative, crystallised from nitrobenzene in orange needles (Found : N, 13.5.  $C_{28}H_{22}N_4$  requires N, 13.5%). The *diacetyl* derivative separated from nitrobenzene in yellow needles, *m. p.* 392—393° (Found : C, 75.8; H, 5.3; N, 11.0.  $C_{32}H_{26}O_2N_4$  requires C, 77.1; H, 5.3; N, 11.25%).

4 : 9-*Diamino-2 : 7-di-p-chlorophenyl-1 : 6-diazapyrene* (92%) crystallised from nitrobenzene in dark red prisms (Found : C, 68.0; H, 3.9; N, 12.2.  $C_{26}H_{16}N_4Cl_2$  requires C, 68.6; H, 3.5; N, 12.3%) and afforded a *diacetyl* derivative, yellow needles (from nitrobenzene) which did not melt below 400° (Found : N, 10.4.  $C_{30}H_{20}O_2N_4Cl_2$  requires N, 10.4%).

4 : 9-*Diamino-2 : 7-di-p-methoxyphenyl-1 : 6-diazapyrene* (70%) crystallised in red needles (Found : N, 12.5.  $C_{28}H_{22}O_2N_4$  requires N, 12.6%) and gave a *diacetyl* derivative, yellow needles (from nitrobenzene), *m. p.* 393—394° (Found : N, 10.45.  $C_{32}H_{26}O_4N_4$  requires N, 10.6%).

*Quaternary Salts of 4 : 9-Diamino-2 : 7-diaryl-1 : 6-diazapyrenes*.—The 4 : 9-diacetamidod-2 : 7-diaryl-1 : 6-diazapyrene was dissolved in boiling nitrobenzene (30—50 c.c. per g.), and

the solution cooled to 180—190°, treated with methyl sulphate (3—3.3 mols.), kept at 180—190° for 20—30 minutes, and cooled in ice-water. The crude methomethylsulphate was collected and extracted with successive quantities of boiling water, and the corresponding methochloride or methobromide was precipitated from the solution by addition of concentrated ammonium chloride or bromide solution. The metho-salts of the diacetamidodiazapyrenes were purified by extracting impurities with boiling *isopropanol* and were hydrolysed by boiling them for 40—75 minutes with 36% hydrochloric or 47% hydrobromic acid (8—10 c.c. per g.). The resulting deacetylated quaternary salts were recrystallised from water.

4 : 9-Diacetamido-2 : 7-diphenyl-1 : 6-diazapyrene dimethobromide (53%) consisted of brown plates, m. p. 310—311° (decomp.) (Found : C, 58.5; H, 4.7; N, 8.5.  $C_{32}H_{28}O_2N_4Br_2$  requires C, 58.2; H, 4.25; N, 8.5%), and was hydrolysed to 4 : 9-diamino-2 : 7-diphenyl-1 : 6-diazapyrene dimethobromide, dark blue plates, m. p. 308—309° (decomp.) (Found : C, 57.8; H, 3.95; N, 10.1.  $C_{28}H_{24}N_4Br_2$  requires C, 58.3; H, 4.2; N, 9.7%). The corresponding dimethochloride consisted of brown plates, m. p. 375—376° (decomp.) (Found : N, 9.55.  $C_{32}H_{28}O_2N_4Cl_2$  requires N, 9.8%), and was hydrolysed to 4 : 9-diamino-2 : 7-diphenyl-1 : 6-diazapyrene dimethochloride monohydrate, m. p. 224° (decomp.) (Found : C, 66.3; H, 5.25; N, 11.3;  $H_2O$ , 2.5.  $C_{28}H_{24}N_4Cl_2 \cdot H_2O$  requires C, 66.5; H, 5.15; N, 11.1;  $H_2O$ , 3.6%).

4 : 9-Diacetamido-2 : 7-di-p-tolyl-1 : 6-diazapyrene dimethochloride (65.5%) crystallised in needles which became discoloured at 320—330° without melting (Found : N, 8.95, 8.85.  $C_{34}H_{32}O_2N_4Cl_2$  requires N, 9.35%). Hydrolysis gave an 84% yield of 4 : 9-diamino-2 : 7-di-p-tolyl-1 : 6-diazapyrene dimethochloride, blue plates, m. p. 341° (Found : C, 70.0; H, 5.5; N, 10.65; Cl, 13.8.  $C_{30}H_{28}N_4Cl_2$  requires C, 69.9; H, 5.4; N, 10.9; Cl, 13.8%).

4 : 9-Diacetamido-2 : 7-di-p-chlorophenyl-1 : 6-diazapyrene dimethochloride (30%) was obtained in brown needles which did not melt below 400° (Found : N, 8.65.  $C_{32}H_{26}O_2N_4Cl_4$  requires N, 8.75%).

4 : 9-Diamino-2 : 7-di-p-chlorophenyl-1 : 6-diazapyrene dimethochloride monohydrate formed turquoise plates, decomp. at 330—340° to a light brown solid [Found : C, 58.4; H, 4.0; N, 10.0, 10.0; Cl, 24.9;  $H_2O$  (Karl Fischer), 2.8.  $C_{28}H_{22}N_4Cl_2 \cdot H_2O$  requires C, 58.5; H, 4.2; N, 9.75; Cl, 24.75;  $H_2O$ , 3.1%].

4 : 9-Diacetamido-2 : 7-di-p-methoxyphenyl-1 : 6-diazapyrene dimethochloride (75%) is a brown solid which decomposes at a high temperature without melting (Found : N, 8.9.  $C_{34}H_{32}O_4N_4Cl_2$  requires N, 8.9%). Hydrolysis gave a 98% yield of 4 : 9-diamino-2 : 7-di-p-methoxyphenyl-1 : 6-diazapyrene dimethochloride, m. p. 321—322° (Found : C, 65.4; H, 5.2; N, 10.1; Cl, 13.1.  $C_{30}H_{28}O_2N_4Cl_2$  requires C, 65.8; H, 5.1; N, 10.2; Cl, 13.0%).

2 : 2'-Dibenzamido-4 : 4'-dinitrodiphenyl and Phosphoryl Chloride.—2 : 2'-Diaminodiphenyl was converted into 2 : 2'-disuccinimidodiphenyl, m. p. 310—312° (60%), and then nitrated as described by Sako (*loc. cit.*). The yield of 4 : 4'-dinitro-2 : 2'-disuccinimidodiphenyl, m. p. 214—316°, was 11% and hydrolysis for 16 hours at 40° with 10% aqueous potassium hydroxide gave 2 : 2'-diamino-4 : 4'-dinitrodiphenyl, m. p. 250—251° (93.5%), for which Sako records m. p. 249—250°. The diamine (2 g.), benzoyl chloride (3 c.c.), and nitrobenzene (10 c.c.) were boiled until the evolution of hydrogen chloride ceased, and the hot solution was poured into benzene (100 c.c.). The solid was collected, mixed with a small second crop obtained by diluting the filtrate with light petroleum, and, after being washed with light petroleum, had m. p. 236—239° (3.25 g.). A sample recrystallised from methanol afforded 2 : 2'-dibenzamido-4 : 4'-dinitrodiphenyl as lemon-yellow plates, m. p. 239—240° (Found : N, 11.9.  $C_{26}H_{18}O_6N_4$  requires N, 11.6%). This compound (2.4 g.), phosphoryl chloride (4.6 c.c., 10 mols.), and nitrobenzene (15 c.c.) were boiled under reflux for 16 hours, cooled, poured on ice, and steam-distilled to remove nitrobenzene. The residual dark brown solid was extracted with methanol, leaving a light brown solid (1.7 g.) which was crystallised from chlorobenzene, giving first a yellow solid, m. p. 238—240° (0.4 g.), and then a more soluble portion (*ca.* 1.05 g.), m. p. 230—234°, shown by a mixed m. p. determination to consist mainly of the unchanged dibenzoyl derivative. A 32% yield of the yellow compound, m. p. 239—240°, was obtained by heating the recovered dibenzoyl derivative with phosphoryl chloride and nitrobenzene for 24 hours. Further crystallisation from chlorobenzene gave yellow needles, m. p. 243—244° (Found : C, 60.7; H, 3.7; N, 14.75.  $C_{19}H_{14}O_5N_4$  requires C, 60.3; H, 3.7; N, 14.8%), and comparison with a specimen prepared by benzylation of 2 : 2'-diamino-4 : 4'-dinitrodiphenyl showed that this compound is 2-amino-2'-benzamido-4 : 4'-dinitrodiphenyl. This compound, which depressed the m. p. of the dibenzoyl derivative, was also obtained (1) by hydrolysis of 2' : 3'-dinitro-2-phenyl-4 : 5 : 6 : 7-dibenzo-1 : 3-diazacyclohepta-2 : 4 : 6-triene (see below), (2) in 35% yield by heating the diamine (0.54 g.) and benzoic anhydride (0.46 g., 1.03 mols.) at 180° for 20 minutes (m. p. 238—240°), and (3)



in 59% yield by keeping the diamine (0.27 g.), benzoyl chloride (0.13 g., 1.04 mols.), and pyridine (6 c.c., 7.5 mols.) at room temperature for 40 hours, pouring the mixture into dilute hydrochloric acid, and crystallising the resulting solid from acetic acid and then from chlorobenzene, the m. p. 243—244°, being undepressed on admixture with samples prepared by the alternative methods.

4 : 5-6 : 7-Dibenzo-1 : 3-diazacyclohepta-2 : 4 : 6-trienes.—2-Phenyl-4 : 5-6 : 7-dibenzo-1 : 3-diazacyclohepta-2 : 4 : 6-triene. 2 : 2'-Diaminodiphenyl (27.6 g.), benzonitrile (15.3 c.c., 1 mol.), and benzenesulphonic acid (23.7 g., 1 mol.) were heated at 180° for an hour, and the resulting solid was washed successively with benzene, light petroleum, and water, leaving a pale yellow salt, m. p. 306—312°. The benzenesulphonate was decomposed by adding sodium hydroxide to an alcoholic suspension, and the precipitate, m. p. 160—164° (18.7 g.), which separated when the alcoholic solution was diluted with water, afforded 2-phenyl-4 : 5-6 : 7-dibenzo-1 : 3-diazacyclohepta-2 : 4 : 6-triene, m. p. 164—165°, on crystallisation from chlorobenzene. Sako (*loc. cit.*) records m. p. 165—166°. An attempt to methylate this base by heating a toluene solution at 100° with methyl sulphate and potassium carbonate, produced greenish-yellow needles of the sulphate, m. p. 262—263° (Found : C, 62.1; H, 4.7; N, 8.1.  $C_{19}H_{16}O_4N_2S$  requires C, 62.0; H, 4.35; N, 7.6%), identical with a specimen prepared by adding dilute sulphuric acid to a toluene solution of the base. Simultaneous methylation and hydrolysis occurred when the base (2 g.), methyl iodide (10 c.c., 22 mols.), potassium carbonate (1 g., 1 mol.), and acetone (100 c.c.) were heated under reflux for 16 hours. The filtered acetone solution was evaporated, and when the residual oil was extracted with acid it afforded a base (1.6 g.; m. p. 110—118°) which crystallised from light petroleum (charcoal) in prisms, m. p. 120—123° (1.05 g.). Further crystallisation gave 2-benzomethylamido-2'-dimethylaminodiphenyl, m. p. 123—124° (Found : C, 79.8; H, 6.7; N, 8.7.  $C_{22}H_{22}ON_2$  requires C, 80.0; H, 6.7; N, 8.5%). A 16% yield of this compound was obtained when the base (2 g.), paraformaldehyde (1 g.), and 100% formic acid (20 c.c.) were boiled under reflux for 16 hours.

2-p-Nitrophenyl-4 : 5-6 : 7-dibenzo-1 : 3-diazacyclohepta-2 : 4 : 6-triene. In the same way, 2 : 2'-diaminodiphenyl (3.68 g.), *p*-nitrobenzonitrile (2.96 g.), and benzenesulphonic acid (3.16 g.) afforded a benzenesulphonate, m. p. 356—358° (3.4 g.), when heated at 180° for 1½ hours. 2-p-Nitrophenyl-4 : 5-6 : 7-dibenzo-1 : 3-diazacyclohepta-2 : 4 : 6-triene, liberated by aqueous ammonia, crystallised from chlorobenzene in yellow-orange needles (1.8 g.), m. p. 186—187° (Found : C, 72.5; H, 3.95; N, 13.6.  $C_{19}H_{13}O_2N_3$  requires C, 72.4; H, 4.1; N, 13.3%). A toluene solution of the base and a little dilute sulphuric acid gave the sulphate, m. p. 307—308° (Found : C, 54.55; H, 4.0; N, 10.4.  $C_{19}H_{15}O_6N_3S$  requires C, 55.2; H, 3.6; N, 10.2%). When the base (9.15 g.), methyl sulphate (9 c.c.), potassium carbonate (2.93 g.), and toluene (500 c.c.) were stirred and heated on the steam-bath for 64 hours a yellow solid was formed. This was washed with benzene and water and heated with methanol (100 c.c.), leaving yellow needles (7.2 g.), m. p. 290—300°, which afforded the above-mentioned sulphate (5.1 g.), m. p. and mixed m. p. 307—308°, when boiled with 95% ethanol (40 c.c.). The united alcoholic solutions on concentration gave a solid (1.8 g.), m. p. 174—180°, which on crystallisation from ethanol afforded orange needles of 2-methylamino-2'-*p*-nitrobenzomethylamidodiphenyl, m. p. 179—180° (Found : C, 69.4; H, 5.3; N, 12.0.  $C_{21}H_{19}O_3N_3$  requires C, 69.8; H, 5.2; N, 11.6%). This compound was recovered unchanged after it had been boiled with formic acid and toluene but acetoformic anhydride (Béhal, *Compt. rend.*, 1899, 128, 1460) at 50° converted it into 2-formomethylamido-2'-*p*-nitrobenzomethylamidodiphenyl, m. p. and mixed m. p. 164—165°. 2-Methylamino-2'-*p*-nitrobenzomethylamidodiphenyl (1 g.), iron powder (10 g.), water (75 c.c.), methanol (75 c.c.), and acetic acid (1 c.c.), when heated and stirred for 4 hours, gave 2-*p*-aminobenzomethylamido-2'-formomethylamidodiphenyl (78.5%), white needles (from chlorobenzene), m. p. 169—170° (Found : C, 76.3; H, 6.3; N, 12.6; NMe, 15.0.  $C_{21}H_{21}ON_3$  requires C, 76.1; H, 6.3; N, 12.7; NMe, 17.5%). A different result was obtained when 2-*p*-nitrophenyl-4 : 5-6 : 7-dibenzo-1 : 3-diazacyclohepta-2 : 4 : 6-triene (7 g.) and methyl sulphate (10 c.c., 7.75 mols.) were boiled together for 4 minutes in absence of potassium carbonate. When the cooled solution was poured into ether (200 c.c.) it afforded a sticky solid, which only became granular after its solution in hot 50% aqueous methanol had been made alkaline with ammonia and heated on the steam-bath for ½ hour. The solid collected from the hot suspension crystallised from chlorobenzene—light petroleum in orange needles (2.45 g.), m. p. 179—180°, undepressed by admixture with 2-methylamino-2'-*p*-nitrobenzomethylamidodiphenyl. The aqueous-methanolic filtrates deposited a solid which was crystallised from chlorobenzene—light petroleum giving an orange solid (1.8 g.), m. p. 128—132°, which dissolved in chlorobenzene to a solution which after several days deposited large prisms (0.2 g.) of 2-amino-2'-*p*-nitrobenzamidodiphenyl, m. p. 143—145°, identical

with a specimen prepared by heating 2 : 2'-diaminodiphenyl, *p*-nitrobenzoic anhydride (1.4 mols.), and benzene for 2 hours (Found : N, 12.9.  $C_{19}H_{15}O_3N_3$  requires N, 12.6%).

2' : 3'-Dinitro-2-phenyl-4 : 5-6 : 7-dibenzo-1 : 3-diazacyclohepta-2 : 4 : 6-triene. A little ammonia was evolved when 2 : 2'-diamino-4 : 4'-dinitrodiphenyl (1.8 g.), benzonitrile (25 c.c.), and benzenesulphonic acid (0.9 g., 0.9 mol.) were boiled under reflux for 7½ hours, and when the product was cooled and washed with benzene and light petroleum, white needles (2.85 g.) of a benzenesulphonate, m. p. 215—220° (decomp.), were obtained. This salt was decomposed by hot water (50 c.c.) and several crystallisations of the resulting solid from nitrobenzene gave 2' : 3'-dinitro-2-phenyl-4 : 5-6 : 7-dibenzo-1 : 3-diazacyclohepta-2 : 4 : 6-triene, red needles, m. p. 348—350° (1.48 g., nearly pure) (Found : C, 63.4; H, 2.9; N, 15.7.  $C_{19}H_{12}O_4N_4$  requires C, 63.3; H, 3.3; N, 15.6%). This (0.2 g.) slowly dissolved in boiling, ordinary, glacial acetic acid (5 c.c.) and the brown solution deposited pale brown needles (0.16 g.) of 2-amino-2'-benzamido-4 : 4'-dinitrodiphenyl, m. p. 243—244° (Found : N, 14.8. Calc. for  $C_{19}H_{14}O_5N_4$  : N, 14.8%), undepressed on admixture with an authentic specimen (see above).

2-Amino-2'-nitrodiphenyl. Reduction of 2 : 2'-dinitrodiphenyl with sodium polysulphide (Purdie, *J. Amer. Chem. Soc.*, 1941, **63**, 2276) gave 2-amino-2'-nitrodiphenyl (53%), m. p. 64—65° (Found : N, 13.3, 13.3. Calc. for  $C_{12}H_{10}O_2N_2$  : N, 13.1%). Hydrolysis of the acetyl derivative, which had m. p. 159—160° as recorded by Purdie, also afforded the nitro-amine, m. p. 64—65°; Purdie states that the nitro-amine has m. p. 94—95°. The hydrochloride crystallised from dilute hydrochloric acid in prisms, m. p. 228—229° (Found : N, 11.3; Cl, 14.6.  $C_{12}H_{11}O_2N_2Cl$  requires N, 11.2; Cl, 14.2%).

2-Formamido-2'-nitrodiphenyl, obtained in 93% yield by slowly distilling a mixture of the nitro-amine (39 g.), 98% formic acid (50 c.c.), and toluene (500 c.c.) through an 18-in. column until the volume was reduced to 50 c.c., crystallised from ethanol in yellow needles, m. p. 130—131° (Found : N, 11.6.  $C_{13}H_{10}O_3N_2$  requires N, 11.6%). 2-Nitro-2'-*p*-nitrobenzamidodiphenyl, obtained by boiling the nitro-amine (4.28 g.), *p*-nitrobenzoyl chloride (3.8 g.), and chlorobenzene (15 c.c.) for 20 minutes, crystallised from ethanol in yellow needles, m. p. 127—128° (Found : N, 11.6.  $C_{19}H_{13}O_5N_3$  requires N, 11.6%).

2-Formomethylamido-2'-nitrodiphenyl. A solution of methyl iodide (9.5 c.c., 1.5 mols.) in acetone (50 c.c.) was added during 15 minutes to a mixture of 2-formamido-2'-nitrodiphenyl (24.2 g.), 85% potassium hydroxide (21 g., 3.2 mols.), and acetone (250 c.c.) heated on the steam-bath. The mixture was heated for a further 25 minutes and the solution was decanted from the solid which was washed with acetone. The united acetone solutions were poured into water (3 l.), and the pale brown solid which separated was recrystallised successively from alcohol (charcoal) and light petroleum (b. p. 80—100°), giving prisms (55.5%) of 2-formomethylamido-2'-nitrodiphenyl, m. p. 97—98° (Found : N, 10.8.  $C_{14}H_{12}O_3N_2$  requires N, 10.9%). 2-Nitro-2'-*p*-nitrobenzomethylamidodiphenyl (88%), similarly prepared from 2-nitro-2'-*p*-nitrobenzamidodiphenyl, crystallised from alcohol in yellow prisms, m. p. 172—174° (Found : N, 11.1.  $C_{20}H_{15}O_5N_3$  requires N, 11.1%). Reduction with iron powder, as described below, gave 2-amino-2'-*p*-aminobenzomethylamidodiphenyl (77%), which crystallised in prisms (from ethanol), m. p. 224—225° (Found : C, 75.1; H, 6.0; N, 13.5.  $C_{20}H_{19}ON_3$  requires C, 75.7; H, 6.0; N, 13.3%).

2-Amino-2'-formomethylamidodiphenyl. 2-Formomethylamido-2'-nitrodiphenyl (10 g.), dissolved in methanol (75 c.c.), was added to a heated mixture of iron powder (10 g.), water (75 c.c.), methanol (75 c.c.), and formic acid (1 g.), and heating and stirring were continued for 4 hours. The acid was neutralised with calcium carbonate, the hot mixture was filtered into water, and the amine was collected in ether and purified through its hydrochloride. 2-Amino-2'-formomethylamidodiphenyl (43%) crystallised from benzene in needles, m. p. 89—90° (Found : N, 12.4.  $C_{14}H_{14}ON_2$  requires N, 12.4%). This compound (4.52 g.), *p*-nitrobenzoyl chloride (3.8 g.), and chlorobenzene (15 c.c.) were boiled for 15 minutes, then poured into light petroleum (150 c.c.) and the solid crystallised from light petroleum, giving prisms (43%) of 2-formomethylamido-2'-*p*-nitrobenzamidodiphenyl, m. p. 170—171° (Found : N, 11.4.  $C_{21}H_{17}O_4N_3$  requires N, 11.2%). Methyl iodide and potassium hydroxide in acetone then gave 2-formomethylamido-2'-*p*-nitrobenzomethylamidodiphenyl (71%), prisms (from ethanol), m. p. 164—165° (Found : C, 67.3; 68.4; H, 5.3, 4.9; N, 11.0.  $C_{22}H_{19}O_4N_3$  requires C, 67.9; H, 4.9; N, 10.8%).