

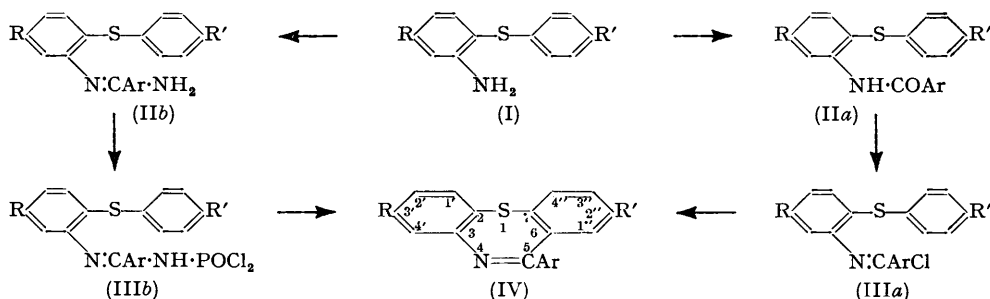
Heterocyclic Derivatives of 1 : 2-5 : 6-Dibenzocyclohepta-1 : 3 : 5-triene.
 Part II.* 5-Aryl-2 : 3-6 : 7-dibenzo-1-thia-4-azacyclohepta-2 : 4 : 6-
 trienes and their 1 : 1-Dioxides.*

By C. I. BRODRICK, J. S. NICHOLSON, and W. F. SHORT.

[Reprint Order No. 5492.]

The thia-aza-compounds (IV) mentioned in the title are obtained from 2-benzamidodiphenyl sulphides (IIa) or from the corresponding amidines (IIb) and phosphoryl chloride. The seven-membered ring in these compounds is readily opened by methylating agents, giving a substituted benzophenone (VI). The 2'' : 3'-dibromo- and -dicyano-thia-aza-compounds are partly desulphurised when they are heated with cuprous bromide, being converted into 2 : 7-disubstituted phenanthridines. Oxidation of the thia-aza-compounds affords the corresponding 1 : 1-dioxides, which cannot be obtained from a 2-benzamidodiphenyl sulphone (VIII) or the related amidine (X), both of which yield an *NN'*-disubstituted amidine (XI) with phosphoryl chloride.

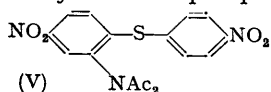
IN Part I of this series * the preparation and properties of a number of 2 : 3-6 : 7-dibenzo-1-oxa-4-azacyclohepta-2 : 4 : 6-trienes were described, and the present paper is concerned with compounds containing $\cdot S\cdot$ or $\cdot SO_2\cdot$ in place of the oxygen atom of the oxa-compounds. The thia-compounds (IV; R, R', Ar = H, H, Ph; H, NO₂, *p*-NO₂·C₆H₄; NO₂, NO₂, Ph; NO₂, NO₂, *p*-NO₂·C₆H₄; Br, Br, Ph, respectively) were prepared by dehydrating the corresponding 2-benzamidodiphenyl sulphides (IIa) with phosphoryl chloride. The action of phosphoryl chloride on two of the amides under milder conditions afforded imidoyl chlorides (IIIa; R = R' = NO₂; Ar = Ph or *p*-NO₂·C₆H₄) and these chlorides, which were also obtained from the amides and phosphorus pentachloride, gave the thia-compounds (IV) on further treatment with phosphoryl chloride. Both imidoyl chlorides afforded 2-diacetyl-amino-4 : 4'-dinitrodiphenyl sulphide (V) on being boiled with acetic anhydride, whereas boiling formic acid reconverted them into the parent benzamido-compound (IIa). *p*-Nitro-*N*-(5-nitro-2-*p*-nitrophenylthiophenyl)benzimidoyl chloride was hydrolysed by aqueous-alcoholic hydrochloric acid to 2-amino-4 : 4'-dinitrodiphenyl sulphide. 2-Amino-4-nitrodiphenyl sulphide, the intermediate required for the synthesis of 3'-nitro-5-phenyl-2 : 3-6 : 7-dibenzo-1-thia-4-azacyclohepta-2 : 4 : 6-triene, could not be obtained from 2 : 4-



dinitrodiphenyl sulphide: reduction of the dinitro-compound with sodium sulphide-sodium hydrogen carbonate gave diphenyl disulphide, also obtained from 2 : 4 : 4'-trinitrodiphenyl sulphide and sodium disulphide. Hodgson and Ward (*J.*, 1949, 136) and Ward and Day (*J.*, 1952, 398) have shown that *o*- and *p*-dinitrobenzenes are converted by sodium hydrogen sulphide into dinitrodiphenyl disulphide, but the total elimination of nitro-groups

* For nomenclature see Part I, Brodrick, Donaldson, Nicholson, Short, and Wibberley, *J.*, 1953, 1079.

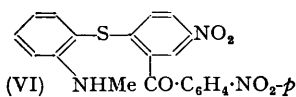
by alkaline sulphides, so far as we are aware, has not been recorded hitherto. The action of phosphoryl chloride on 2:4-dibenzamidodiphenyl sulphide and on 2:4-di-*p*-nitrobenzamidodiphenyl sulphide produced amorphous products, and 3'-benzamido-5-phenyl-2:3:6:7-dibenzo-1-thia-4-azacyclohepta-2:4:6-triene (IV; R = NHBz, R' = H, Ar = Ph) and its dinitro-derivative could not be detected. Application of the synthesis to 2-benzamido-5'-chloro-2'-methyl-diphenyl sulphide gave 1''-chloro-4''-methyl-5-phenyl-2:3:6:7-dibenzo-1-thia-4-azacyclohepta-2:4:6-triene (89%). It was noticed that if freshly distilled phosphoryl chloride was used in this cyclodehydration much starting



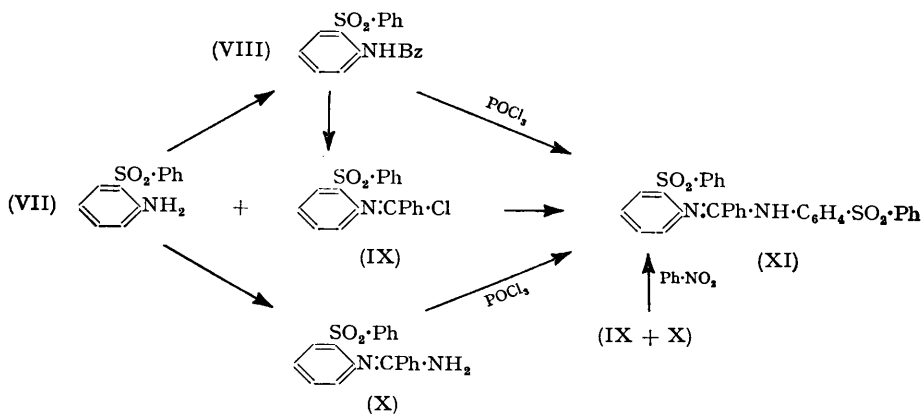
material was recovered, a good yield being obtained only with the aged reagent, and this may also be applicable to the other examples. Snyder and Werber (*J. Amer. Chem. Soc.*, 1950, **72**, 2962) found that the yield of norharman from *N*-formyl-DL-tryptophan depended on the quality of the phosphoryl chloride used and showed that the presence of polyphosphoric acid leads to increased yields.

An alternative method for the preparation of the cyclic compounds is exemplified by the preparation of 5-phenyl-, 5-*p*-nitrophenyl-, and 5-*p*-methylsulphonylphenyl-2:3:6:7-dibenzo-1-thia-4-azacyclohepta-2:4:6-triene (IV; R = R' = H; Ar = Ph, *p*-NO₂·C₆H₄, *p*-Me·SO₂·C₆H₄) and of 2''-nitro-5-*p*-nitrophenyl-2:3:6:7-dibenzo-1-thia-4-azacyclohepta-2:4:6-triene (IV; R = H, R' = NO₂, Ar = *p*-NO₂·C₆H₄) from phosphoryl chloride and the corresponding *N*-(2-arylthioaryl)benzamidines (II*b*; R = H, H, H, H; R' = H, H, H, NO₂; Ar = Ph, *p*-NO₂·C₆H₄, *p*-Me·SO₂·C₆H₄, *p*-NO₂·C₆H₄). In a subsequent communication it will be shown that certain amidines react with phosphoryl chloride to give amino-phosphonyl dichlorides and it is probable that a compound of type (III*b*) is an intermediate in this synthesis.

The thia-aza-compounds, like the oxa-aza-analogues (Part I, *loc. cit.*), undergo fission of the heterocyclic nucleus when they are treated with methylating agents. Dr. A. E. S.



Fairfull finds that 2''-nitro-5-*p*-nitrophenyl-2:3:6:7-dibenzo-1-thia-4-azacyclohepta-2:4:6-triene and methyl sulphate react at 200° to give a grey solid, probably the metho(methyl sulphate), converted into orange needles, m. p. 154—155°, by several crystallisations from methanol, the change being accelerated by the addition of a little water. This transformation product, which behaves as an amino-ketone, gives readily hydrolysed salts with mineral acids, is converted by methyl iodide and potassium carbonate

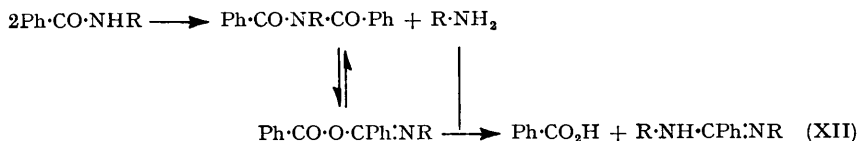


into a dimethyl compound, and is formulated as 2-*o*-methylaminophenylthio-4':5-dinitrobenzophenone (VI).

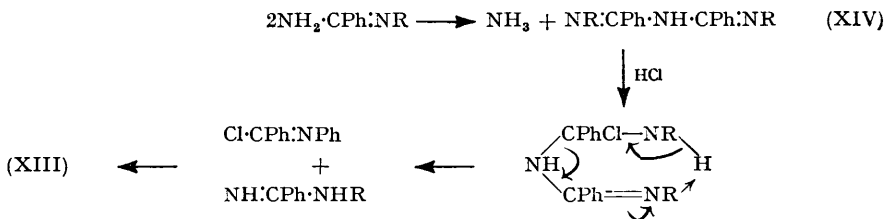
Another example of the fission of the heterocyclic nucleus was encountered during the conversion of 2'':3'-dibromo-5-phenyl-2:3:6:7-dibenzo-1-thia-4-azacyclohepta-2:4:6-triene into the corresponding dicyanide by the action of cuprous cyanide in boiling quinoline. In addition to 2'':3'-dicyano-5-phenyl-2:3:6:7-dibenzo-1-thia-4-azacyclohepta-2:4:6-

triene (47%), the product contained 2 : 7-dicyano-9-phenylphenanthridine (10%), identified by comparison with a specimen prepared from 2 : 7-diamino-9-phenylphenanthridine. The dicyano-thia-compound was not converted into the phenanthridine by cuprous cyanide in boiling quinoline, but cuprous bromide gave a very small yield of the dicyanophenanthridine. The dibromo-thia-compound was converted into 2 : 7-dibromo-9-phenylphenanthridine (20%) on being boiled with cuprous bromide-quinoline, and these reactions recall the production of carbazole by the heating of phenothiazine with copper powder (Goske, *Ber.*, 1887, 20, 232). 9-Phenylphenanthridine could not be detected in the products of the action of cuprous bromide on 5-phenyl-2 : 3-6 : 7-dibenzo-1-thia-4-azacyclohepta-2 : 4 : 6-triene, and the *p*-substituents therefore seem to be necessary for the production of a diradical which is assumed to be an intermediate in the production of the phenanthridine.

Attempts to adapt the two methods for the synthesis of the thia-compounds to the production of the corresponding thia-dioxides were unsuccessful. Both 2-benzamidodiphenyl sulphone (VIII) and *N*-(2-phenylsulphonylphenyl)benzamidine (X) were converted by phosphoryl chloride into an *NN'*-disubstituted amidine which must be *NN'*-di-(2-phenylsulphonylphenyl)benzamidine (XI), since it is also obtained from 2-aminodiphenylsulphone (VII) and *N*-(2-phenylsulphonylphenyl)benzimidoyl chloride (IX). The production of the amidine (XI) from the benzamido-compound (VIII) and phosphoryl chloride probably takes place as follows (cf. Oxley and Short, *J.*, 1946, 765) (R = *o*-Ph·SO₂·C₆H₄) :

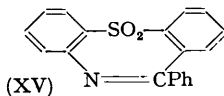


Conversion of the amidine (X) into the substituted amidine (XI) probably involves the formation of the diamide NR·CPh·NR·CPh·NH (XIII) which would be expected to decompose into the amidine (XII) and benzonitrile (Cooper, Partridge, and Short, *J.*, 1951, 396), and this amidine, and not the diamide (XIII), was in fact obtained from the imidoyl chloride (IX) and the amidine (X). It has been shown (unpublished experiments with Mr. D. A. Firth) that certain amidines lose the elements of ammonia when they are treated with phosphoryl chloride and yield diamidides, but the results suggest that the amidine (X) would yield the diamide (XIV). However, the diamide (XIV) might be converted into its isomer (XIII) by addition of the elements of hydrogen chloride, followed by fission into an imidoyl chloride and an amidine, which then react to give (XIII), a series of reactions already exemplified by Cooper, Partridge, and Short (*loc. cit.*).



Cyclic thia-dioxides could not be obtained from *p*-nitro-*N*-(2-phenylsulphonylphenyl)benzamidine and the corresponding *p*-methylsulphonylbenzamidine, and the failure of both methods is doubtless associated with the deactivation of the *ortho*-positions by the sulphonyl group.

Oxidation of the thia-compounds (IV; R = H, H, NO₂; R' = H, NO₂, NO₂; Ar = Ph, *p*-NO₂·C₆H₄, Ph respectively) with hydrogen peroxide or chromic anhydride gave 5-phenyl-2 : 3-6 : 7-dibenzo-1-thia-4-azacyclohepta-2 : 4 : 6-triene-1 : 1-dioxide (XV) and its dinitro-derivatives.



EXPERIMENTAL

Preparation of Intermediates.

2-Benzamidodiphenyl Sulphide.—2-Aminodiphenyl sulphide hydrochloride (25 g.), m. p. 206—208°, prepared in 87% yield by the method of Roberts and Turner (*J.*, 1926, 1208), was added to a stirred mixture of benzene (75 c.c.) and water (170 c.c.), containing sodium hydroxide (4.2 g.), and the liberated amine was benzoylated by the simultaneous addition of aqueous sodium hydroxide (1.5 mols.) and benzoyl chloride (1 mol.) at 0—5°. The crude product (29 g.), isolated by extraction with benzene, crystallised from benzene–light petroleum and then from ethanol, giving 2-benzamidodiphenyl sulphide as colourless needles, m. p. 66—67.5° (54%) (Found: N, 4.7. $C_{19}H_{15}ONS$ requires N, 4.6%).

4'-Nitro-2-p-nitrobenzamidodiphenyl Sulphide.—2-Amino-4'-nitrodiphenyl sulphide (20 g.), prepared as described by the Soc. Anon. des Mat. Col. et Prod. Chim. de St. Denis (B.P. 376,961), and *p*-nitrobenzoyl chloride (14.9 g.) were heated at 170° for 7 hr., and then at 225° until evolution of hydrogen chloride ceased. The crude product (29 g.), obtained by successive triturations with hot dilute alkali, dilute acid, and water, crystallised from 2-ethoxyethanol, giving 4'-nitro-2-p-nitrobenzamidodiphenyl sulphide as yellowish-brown plates, m. p. 214—215° (Found: N, 10.8. $C_{19}H_{13}O_5N_3S$ requires N, 10.6%).

2-Benzamido-4 : 4'-dinitrodiphenyl Sulphide.—Nitration of *o*-chloroaniline in excess of sulphuric acid (de Bruyn, *Rec. Trav. chim.*, 1916, 36, 126) gave 2-chloro-5-nitroaniline, m. p. 117—118° (86%), and this is the best method for the preparation of this amine (cf. Buchanan and Graham, *J.*, 1949, 3435). The chloro-amine (143 g.), sodium sulphide nonahydrate (292 g.), sodium hydrogen carbonate (102 g.), water (1650 c.c.), and alcohol (2400 c.c.) were refluxed for 90 min. A mixture of sodium hydrogen carbonate (102 g.), water (820 c.c.), and alcohol (820 c.c.) was then added, followed, after refluxing for 5 min., by *p*-chloronitrobenzene (140 g.) in alcohol (1650 c.c.). Refluxing was continued for 3 hr., and, after cooling overnight, the precipitated solid was filtered off, triturated successively with warm water and alcohol, dried, and extracted with hot ethyl acetate. Concentration of the extract gave 2-amino-4 : 4'-dinitrodiphenyl sulphide as an orange-brown solid (77 g.; m. p. 171—172.5°), which on recrystallisation from ethyl acetate formed orange-yellow, prismatic needles, m. p. 174—175.5° (Found: C, 49.3; H, 3.15; N, 14.05. $C_{12}H_9O_4N_3S$ requires C, 49.5; H, 3.1; N, 14.4%). 2-Benzamido-4 : 4'-dinitrodiphenyl sulphide, obtained from the amine and benzoyl chloride in pyridine below 10°, crystallised from 2-ethoxyethanol in pale yellow needles, m. p. 200.5—201.5° (Found: N, 10.35. $C_{19}H_{13}O_5N_3S$ requires N, 10.6%).

4 : 4'-Dinitro-2-p-nitrobenzamidodiphenyl sulphide (63%), prepared similarly, separated from 2-ethoxyethanol in small pale yellow needles, m. p. 210—211° (Found: N, 12.35. $C_{19}H_{12}O_7N_4S$ requires N, 12.7%). When heated just below its m. p. this compound changes into a polymorphic form, m. p. 224—224.5°, so that the m. p. observed depends upon the rate of heating.

2-Benzamido-4 : 4'-dibromodiphenyl Sulphide.—4-Bromobenzenethiol (75.6 g.), 2 : 5-dibromonitrobenzene (112.4 g.), potassium hydroxide (25.6 g.), copper bronze (8 g.), and water (100 c.c.), heated at 175° for 7½ hr. gave, after extraction with benzene, the sulphide, m. p. 171—173° (67.5%), and crystallisation from benzene afforded 4 : 4'-dibromo-2-nitrodiphenyl sulphide as yellow prisms, m. p. 172—173.5° (Found: C, 37.1; H, 2.0; N, 3.8. $C_{12}H_7O_2NBr_2S$ requires C, 37.0; H, 1.8; N, 3.6%). The nitro-compound (36 g.), reduced iron powder (120 g.), alcohol (510 c.c.), concentrated hydrochloric acid (1.5 c.c.), and water (720 c.c.) were refluxed for 22 hr. and gave the crude amine, m. p. 79.5—82° (90%). Crystallisation from ethyl acetate–light petroleum afforded colourless prisms of 2-amino-4 : 4'-dibromodiphenyl sulphide, m. p. 80—82° (Found: C, 40.4; H, 2.7; N, 4.2. $C_{12}H_9NBr_2S$ requires C, 40.1; H, 2.5; N, 3.9%). Benzoylation afforded the benzoyl derivative (86%) in colourless, prismatic needles, m. p. 119—120.5° (Found: C, 49.1; H, 2.8; N, 3.4. $C_{19}H_{13}ONBr_2S$ requires C, 49.2; H, 2.8; N, 3.0%).

2 : 4-Dibenzamidodiphenyl Sulphide.—2 : 4-Dinitrodiphenyl sulphide was obtained in 66% yield by a modification of the method of Bogert and Evans (*Ind. Eng. Chem.*, 1926, 18, 301) in which the reactants were heated at 150° for 6 hr. Attempts to reduce the 2-nitro-group by Raney nickel and hydrogen or stannous chloride in hydrochloric acid or acetic acid were unsuccessful. With sodium sulphide and sodium hydrogen carbonate in methanol, the only substance isolated was diphenyl disulphide, m. p. and mixed m. p. 59—60° (Found: C, 65.55; H, 4.6. Calc. for $C_{12}H_{10}S_2$: C, 66.0; H, 4.6%). The same compound was obtained in the attempted partial reduction of 2 : 4 : 4'-trinitrodiphenyl sulphide (Hodgson, *J.*, 1948, 2022) with sodium disulphide in aqueous alcohol. A mixture of the dinitro-compound (22 g.) and reduced

iron powder (32 g.), added to alcohol (300 c.c.), concentrated hydrochloric acid (5 c.c.), and water (480 c.c.) and refluxed with stirring for 3 hr., gave the crude base, m. p. 101—104° (13 g.). Crystallisation from aqueous alcohol gave 2 : 4-diaminodiphenyl sulphide, as buff needles, m. p. 106—108° (Found: N, 13.2. Calc. for $C_{12}H_{12}N_2S$: N, 13.0%). Bogert and Evans (*loc. cit.*) record m. p. 107°. The NN'-dibenzoyl derivative separated from methanol-acetone in solvated crystals, m. p. 120°, which after being dried at 80°/1 mm. had m. p. 169—169.5° (Found: N, 6.75. $C_{26}H_{20}O_2N_2S$ requires N, 6.6%). The di-p-nitrobenzoyl derivative crystallised from 2-ethoxyethanol in yellow, prismatic needles, m. p. 206—206.5° (Found: N, 10.7. $C_{26}H_{18}O_6N_4S$ requires N, 10.9%).

2-Benzamido-5'-chloro-2'-methylthiophenyl Sulphide.—5-Chloro-2-methylbenzenethiol (6.32 g.) (Sharp, J., 1951, 2961; Archer and Suter, *J. Amer. Chem. Soc.*, 1952, 74, 4296) and o-chloronitrobenzene (6.28 g.) were added, in that order, to a solution of sodium (1.3 g.) in alcohol (100 c.c.). The mixture was refluxed for 4 hr., cooled, and poured into water, and the precipitated solid was extracted with ether. Evaporation of the washed and dried extract to a small volume gave 5'-chloro-2'-methyl-2-nitrothiophenyl sulphide as bright yellow prisms, m. p. 79.5—81° (61%) (Found: C, 55.9; H, 3.5; N, 4.7. $C_{13}H_{10}O_2NCIS$ requires C, 55.8; H, 3.6; N, 5.0%). The nitro-compound (31 g.) reduced iron powder (110 g.), alcohol (600 c.c.), water (900 c.c.), and concentrated hydrochloric acid (0.5 c.c.) were stirred and refluxed for 19 hr. Extraction with chloroform gave the amine as an oil (28 g.) which readily solidified, crystallisation from light petroleum (b. p. 40—60°) giving buff prisms, m. p. 59.5—61° (Found: N, 5.7. $C_{13}H_{12}NCIS$ requires N, 5.6%). The benzoyl derivative (yield, 92%; m. p. 70—72.5°) crystallised from alcohol in colourless, feathery needles, m. p. 74—75.5° (Found: N, 4.3. $C_{20}H_{16}ONCIS$ requires N, 4.0%).

2-Benzamidodiphenyl Sulphone.—2-Aminodiphenyl sulphone (1 g.; Ullmann, *Ber.*, 1901, 34, 1153), pyridine (8 c.c.), and benzoyl chloride (0.7 g.) were kept at room temperature for 3 hr. and heated under reflux for $\frac{1}{2}$ hr. The mixture was poured into dilute sulphuric acid, and the solid which separated was recrystallised from a little methanol giving the crude benzoyl derivative, m. p. 107—109° (75%). Recrystallisation from methanol gave 2-benzamidodiphenyl sulphone as colourless prisms, m. p. 111—112.5° (Found: N, 4.6. $C_{18}H_{15}O_3NS$ requires N, 4.15%).

N-(2-Phenylthiophenyl)benzamidine.—A mixture of 2-aminodiphenyl sulphide benzenesulphonate (5.38 g.), m. p. 225—226° (Found: N, 4.0. $C_{18}H_{17}O_3NS_2$ requires N, 3.9%), and phenyl cyanide (1.55 g.) was heated at 200° for 2 hr. The cooled melt was extracted with a large volume of hot water and the crude amidine (62%) was isolated by basification and extraction with chloroform. It crystallised from benzene-light petroleum in colourless plates, m. p. 103—104.5° (Found: N, 9.5. $C_{19}H_{16}N_2S$ requires N, 9.2%).

p-Nitro-N-(2-phenylthiophenyl)benzamidine, prepared similarly (47% yield), crystallised from benzene-light petroleum in fine yellow needles which were dried at 55°/1 mm. for 6 hr. and then had m. p. 108—109.5° (Found: N, 12.0. $C_{19}H_{15}O_2N_3S$ requires N, 12.0%). *p-Methylsulphonyl-N-(2-phenylthiophenyl)benzamidine* (yield, 70%) crystallised from chloroform-light petroleum in pale yellow cubes, m. p. 183—184° (Found: N, 7.3. $C_{20}H_{18}O_2N_2S_2$ requires N, 7.3%).

p-Nitro-N-(2-p-nitrophenylthiophenyl)benzamidine.—2-Amino-4'-nitrodiphenyl sulphide benzenesulphonate, prepared from its constituents, had m. p. 250—251° (Found: N, 7.2. $C_{18}H_{16}O_5N_2S_2$ requires N, 6.9%). This salt (8.1 g.) and p-nitrophenyl cyanide (3.35 g.) were heated at 200° for 2 hr. and the crude amidine was liberated by alkali, collected in ether, and recrystallised from benzene (2.26 g.; m. p. 140—143°). A second recrystallisation gave p-nitro-N-(2-p-nitrophenylthiophenyl)benzamidine as yellow prismatic needles, m. p. 156—157° (Found: N, 14.0. $C_{19}H_{14}O_4N_4S$ requires N, 14.2%).

N-(2-Phenylsulphonylphenyl)benzamidine.—2-Aminodiphenyl sulphone (5 g.) was converted into its benzenesulphonate (7.5 g.; m. p. 170°) with excess of benzenesulphonic acid in absolute alcohol. This salt (7.2 g.) and phenyl cyanide (1.8 g.) were heated at 210° for 4 hr., and the resulting glass was dissolved in warm alcohol and diluted with excess of 0.5N-hydrochloric acid before extraction of unchanged 2-aminodiphenyl sulphone with ether. The aqueous solution was basified with 2N-sodium hydroxide, and the crude amidine (3.55 g., m. p. 165°) was washed with water and crystallised from methanol, giving N-(2-phenylsulphonylphenyl)benzamidine as colourless prisms, m. p. 165—166.5° (Found: C, 67.6; H, 4.8; N, 8.5. $C_{19}H_{16}O_2N_2S$ requires C, 67.85; H, 4.8; N, 8.3%).

p-Nitro-N-(2-phenylsulphonylphenyl)benzamidine, prepared similarly in 33% yield, crystallised from 2-ethoxyethanol in pale yellow prisms, m. p. 254° (decomp.) (Found: N, 11.0. $C_{19}H_{15}O_4N_3S$ requires N, 11.0%).

p-Methylsulphonyl-*N*-(2-phenylsulphonylphenyl)benzamidine (53.5%) crystallised from 2-ethoxyethanol in colourless prisms, m. p. 248—250° (Found: N, 7.2. C₂₀H₁₈O₄N₂S₂ requires N, 6.8%).

5-Aryl-2 : 3-6 : 7-dibenzo-1-thia-4-azacyclohepta-2 : 4 : 6-trienes from 2-Benzamidodiphenyl Sulphides.

5-Phenyl-2 : 3-6 : 7-dibenzo-1-thia-4-azacyclohepta-2 : 4 : 6-triene.—2-Benzamidodiphenyl sulphide (18 g.), phosphoryl chloride (30 c.c.), and nitrobenzene (80 c.c.) were boiled under reflux for 4 hr. and then distilled under reduced pressure to remove the solvent. The residue was triturated with warm 5*N*-sodium hydroxide, and the crude thia-aza-compound was collected in benzene. Recrystallisation from methanol gave 5-phenyl-2 : 3-6 : 7-dibenzo-1-thia-4-azacyclohepta-2 : 4 : 6-triene (65%) as pale yellow needles, m. p. 117—118° (Found: C, 79.6; H, 4.4; N, 4.9; S, 11.0. C₁₉H₁₃NS requires C, 79.4; H, 4.5; N, 4.9; S, 11.15%).

2''-Nitro-5-*p*-nitrophenyl-2 : 3-6 : 7-dibenzo-1-thia-4-azacyclohepta-2 : 4 : 6-triene.—(1) 4'-Nitro-2-*p*-nitrobenzamidodiphenyl sulphide (29 g.), phosphoryl chloride (68 c.c.), and nitrobenzene (200 c.c.), boiled for 5 hr. and worked up as in the preceding experiment, afforded a 69% yield of 2''-nitro-5-*p*-nitrophenyl-2 : 3-6 : 7-dibenzo-1-thia-4-azacyclohepta-2 : 4 : 6-triene, flocculent yellow needles, m. p. 229.5° (Found: C, 59.8; H, 2.9; N, 11.5. C₁₉H₁₁O₄N₃S requires C, 60.5; H, 2.9; N, 11.1%).

(2) The amide (14.5 g.), phosphorus pentachloride (7.6 g.), and chlorobenzene (150 c.c.) were boiled under reflux for 2 hr., then treated with charcoal and filtered. The solvent was removed from the filtrate under reduced pressure, the residue was dissolved in ethyl acetate, and the solution concentrated and diluted whilst hot with light petroleum. The yellow prismatic needles which separated on cooling were recrystallised in the same way and gave *p*-nitro-*N*-(2-*p*-nitrophenylthiophenyl)benzimidoyl chloride (68%), m. p. 124—125° (Found: C, 55.2; H, 2.9; N, 10.4. C₁₉H₁₂O₄N₃ClS requires C, 55.1; H, 2.9; N, 10.15%). When this imidoyl chloride was boiled with phosphoryl chloride and nitrobenzene it gave the thia-aza-compound, m. p. and mixed m. p. 229.5°.

2'' : 3'-Dinitro-5-phenyl-2 : 3-6 : 7-dibenzo-1-thia-4-azacyclohepta-2 : 4 : 6-triene.—(1) 2-Benzamido-4 : 4'-dinitrodiphenyl sulphide (17 g.), phosphoryl chloride (8.3 c.c., 2.1 mols.), and nitrobenzene (300 c.c.) were boiled under reflux for 4 hr. at 220° (oil-bath); the product, isolated as described in the previous examples, was recrystallised from ethyl acetate-chloroform, giving 2'' : 3'-dinitro-5-phenyl-2 : 3-6 : 7-dibenzo-1-thia-4-azacyclohepta-2 : 4 : 6-triene as pale yellow needles, m. p. 202—204° (63.5%) (Found: C, 61.05; H, 3.1; N, 11.2; S, 8.8. C₁₉H₁₁O₄N₃S requires C, 60.5; H, 2.9; N, 11.1; S, 8.5%). When the amide (9.4 g.), phosphoryl chloride (36 c.c., 16.5 mols.), and nitrobenzene (145 c.c.) were refluxed at 200° for 4 hr. and worked up as in the cyclodehydration experiment, the concentrated chloroform solution gave a solid (7.46 g.), m. p. 125—130°, by addition of light petroleum. Two crystallisations from benzene gave *N*-(5-nitro-2-*p*-nitrophenylthiophenyl)benzimidoyl chloride as yellow needles, m. p. 130.5—132° (Found: C, 54.7; H, 3.15; N, 10.0. C₁₉H₁₂O₄N₃ClS requires C, 55.1; H, 2.9; N, 10.15%). The imidoyl chloride (1.65 g.), m. p. and mixed m. p. 130.5—132°, was also obtained by boiling the amide (2 g.), phosphorus pentachloride (0.9 g.), and chlorobenzene (25 c.c.) for 2 hr. When the imidoyl chloride (0.5 g.) and formic acid (10 c.c.) were boiled for 1½ hr., a solid separated progressively and precipitation was completed by the addition of water (yield, 0.43 g.; m. p. 200.5—202°). Recrystallisation from ethyl acetate gave 2-benzamido-4 : 4'-dinitrodiphenyl sulphide, m. p. and mixed m. p. 201—202°. The imidoyl chloride (0.5 g.), fused sodium acetate (0.5 g.), and acetic anhydride (12 c.c.) were refluxed for 12 hr. and then evaporated to dryness under reduced pressure, and the residue was shaken with sodium hydrogen carbonate solution and extracted with chloroform. The residue from the washed and dried (MgSO₄) chloroform solution was recrystallised twice from ethyl acetate, giving colourless prisms of 2-diacetyl-amino-4 : 4'-dinitrodiphenyl sulphide, m. p. 165—166.5° (Found: N, 11.45. C₁₆H₁₃O₆N₃S requires N, 11.2%). The same diacetyl-amine was obtained from *p*-nitro-*N*-(5-nitro-2-*p*-nitrophenylthiophenyl)benzimidoyl chloride (below), acetic anhydride, and sodium acetate. (2) The imidoyl chloride (1 g.), phosphoryl chloride (0.5 c.c., 2.2 mols.), and nitrobenzene (18 c.c.) gave the thia-aza-compound, m. p. and mixed m. p. 199.5—201°, when boiled under reflux for 5 hr. at 220° (oil-bath).

2'' : 3'-Dinitro-5-*p*-nitrophenyl-2 : 3-6 : 7-dibenzo-1-thia-4-azacyclohepta-2 : 4 : 6-triene.—(1) 4 : 4'-Dinitro-2-*p*-nitrobenzamidodiphenyl sulphide (1 g.), phosphoryl chloride (0.5 c.c., 2.4 mols.), and nitrobenzene (18 c.c.) were refluxed for 4 hr. at 220°, cooled, and decomposed as in previous experiments, a large volume of chloroform being necessary for the extraction of the

product. Successive crystallisations from 2-ethoxyethanol and from ethyl acetate (by concentration of the dilute solution) gave bright yellow 2'' : 3'-dinitro-5-p-nitrophenyl-2 : 3-6 : 7-dibenzo-1-thia-4-azacyclohepta-2 : 4 : 6-triene (40%), m. p. 277—279° (Found : C, 54.4 ; H, 2.3 ; N, 13.5. $C_{19}H_{10}O_6N_4S$ requires C, 54.0 ; H, 2.4 ; N, 13.3%). When the amide (10 g.), phosphoryl chloride (35 c.c., 16.8 mols.), and nitrobenzene (180 c.c.) were refluxed at 200° for 5 hr., the crude product (7.84 g.), m. p. 197—199°, isolated as in previous cases, was purified by dissolution in boiling ethyl acetate (1 l.) (charcoal) and concentration to 150 c.c., giving bright yellow needles of p-nitro-N-(5-nitro-2-p-nitrophenylthiophenyl)benzimidoyl chloride, m. p. 205—205.5° (Found : C, 49.5 ; H, 2.7 ; N, 12.5. $C_{19}H_{11}O_6N_4ClS$ requires C, 49.7 ; H, 2.4 ; N, 12.2%). The same imidoyl chloride (1.25 g.) was obtained from the amide (2.2 g.), phosphorus pentachloride, and chlorobenzene under the conditions described for the dinitro-compound. When the imidoyl chloride was boiled with formic acid for 1 hr., 4 : 4'-dinitro-2-p-nitrobenzamidodiphenyl sulphide, m. p. and mixed m. p. 211—211.5°, was regenerated and was converted into the form of m. p. 224—224.5° by heating just below the m. p. 2-Amino-4 : 4'-dinitrodiphenyl sulphide, m. p. and mixed m. p. 175—176°, was obtained by boiling the imidoyl chloride (0.4 g.) with concentrated hydrochloric acid (10 c.c.) and alcohol (40 c.c.) for 17 hr. Boiling acetic anhydride and sodium acetate converted the imidoyl chloride into 2-diacetyl-amino-4 : 4'-dinitrodiphenyl sulphide, m. p. and mixed m. p. 163—166°.

(2) The imidoyl chloride (0.4 g.), phosphoryl chloride (0.25 c.c., 3.1 mols.), and nitrobenzene (10 c.c.) were boiled for 2 hr. and gave the thia-aza-compound, m. p. and mixed m. p. 274—276°.

2'' : 3'-Dibromo-5-phenyl-2 : 3-6 : 7-dibenzo-1-thia-4-azacyclohepta-2 : 4 : 6-triene.—2-Benzamido-4 : 4'-dibromodiphenyl sulphide (30 g.), phosphoryl chloride (60 c.c.), and nitrobenzene (360 c.c.) were refluxed for 2 hr. and worked up as in previous experiments. The residue from the evaporated chloroform extract was crystallised from benzene—light petroleum and gave the cyclic compound, the first crop (68%) having m. p. 154—155° and the second (10%) m. p. 152.5—154°. Recrystallisation of the first crop from the same solvent gave lemon-yellow prisms of unchanged m. p. (Found : C, 51.2 ; H, 2.7 ; N, 3.05 ; Br, 35.9. $C_{19}H_{11}NBr_2S$ requires C, 51.2 ; H, 2.5 ; N, 3.1 ; Br, 35.95%).

1''-Chloro-4'-methyl-5-phenyl-2 : 3-6 : 7-dibenzo-1-thia-4-azacyclohepta-2 : 4 : 6-triene, yellow hexagonal prisms from ethyl acetate, m. p. 165.5—166.5° (Found : C, 71.9 ; H, 4.15 ; N, 4.1. $C_{20}H_{14}NClS$ requires C, 71.5 ; H, 4.2 ; N, 4.2%), was obtained from 2-benzamido-5'-chloro-2'-methyl-diphenyl sulphide (1.37 g.) and phosphoryl chloride (9 c.c.) in 3½ hr. The yield was 89% when an old sample of phosphoryl chloride was employed, but much starting material was recovered when freshly distilled phosphoryl chloride was used.

5-Aryl-2 : 3-6 : 7-dibenzo-1-thia-4-azacyclohepta-2 : 4 : 6-trienes from
N-(2-Arylthioaryl)benzamidines.

A mixture of the amidine, nitrobenzene (15 c.c. per g.), and phosphoryl chloride (7—9 mols.) was boiled under reflux for 4—5 hr., liquids were removed by distillation under reduced pressure, and the residue was triturated with 5N-sodium hydroxide before being extracted with chloroform. The chloroform solution was concentrated, and the thia-aza-compound was precipitated by the addition of light petroleum and recrystallised from benzene—light petroleum.

5-Phenyl- and 2''-nitro-5-p-nitrophenyl-2 : 3-6 : 7-dibenzo-1-thia-4-azacyclohepta-2 : 4 : 6-trienes, prepared by this method in 70% and 44% yield respectively, were identical (mixed m. p.s) with specimens prepared from the amides (above). 5-p-Nitrophenyl-2 : 3-6 : 7-dibenzo-1-thia-4-azacyclohepta-2 : 4 : 6-triene (28%) crystallised in yellow prisms, m. p. 141—142° (Found : C, 69.5 ; H, 3.6 ; N, 8.5. $C_{19}H_{12}O_2N_2S$ requires C, 68.65 ; H, 3.6 ; N, 8.4%). 5-p-Methylsulphonylphenyl-2 : 3-6 : 7-dibenzo-1-thia-4-azacyclohepta-2 : 4 : 6-triene was obtained in 61% yield as yellow prismatic needles, m. p. 191—191.5° (Found : C, 65.6 ; H, 4.0 ; N, 4.2. $C_{20}H_{16}O_2NS_2$ requires C, 65.75 ; H, 4.1 ; N, 3.8%).

Miscellaneous Reactions.

2''-Nitro-5-p-nitrophenyl-2 : 3-6 : 7-dibenzo-1-thia-4-azacyclohepta-2 : 4 : 6-triene and Methyl Sulphate (Experiments by Dr. A. E. S. FAIRFULL).—The nitro-compound (3 g.) and methyl sulphate (4.5 c.c.) were boiled for 4 min., cooled, and diluted with ether. The gum which separated was washed with methanol, giving a grey solid (4.1 g.). A solution of this solid (0.4 g.) in methanol (100 c.c.) was evaporated to give orange needles (0.25 g.), m. p. 148—152°, and the change was hastened by adding a few drops of water to the methanol. Crystallisation from ethanol gave 2-o-methylaminophenylthio-4' : 5-dinitrobenzophenone, m. p. 154—155° (Found : C, 58.6 ; H, 3.8 ; N, 10.2. $C_{20}H_{15}O_5N_3S$ requires C, 58.7 ; H, 3.7 ; N, 10.3%), converted by

48% hydrobromic acid into an unstable *hydrobromide*, m. p. 185—187° (decomp.), which reverted to its progenitors with alcohol or water (Found: N, 8.2. $C_{20}H_{16}O_5N_3BrS$ requires N, 8.6%). The amino-ketone (0.6 g.), methyl iodide (10 c.c.), and potassium carbonate (1 g.) were stirred and boiled under reflux for 100 hr., and the filtered solution was then evaporated and the residue (0.41 g., m. p. 128—133°) crystallised successively from ethanol and benzene-light petroleum, giving 2-*o*-dimethylaminophenylthio-4':5-dinitrobenzophenone as red prisms, m. p. 141—142° (Found: C, 59.5; H, 4.3; N, 9.7, 9.9. $C_{21}H_{17}O_5N_3S$ requires C, 59.6; H, 4.0; N, 9.9%). On admixture with the monomethyl compound the m. p. was depressed to 122—124°.

2''-Amino-5-*p*-aminophenyl-2:3-6:7-dibenzo-1-thia-4-azacyclohepta-2:4:6-triene (With Dr. T. I. WATKINS).—The dinitro-compound (11.4 g.), stannous chloride dihydrate (61.5 g.), concentrated hydrochloric acid (90 c.c.), and alcohol (150 c.c.) were stirred and heated under reflux for 1.5 hr. The alcohol was evaporated under reduced pressure and the cooled residual solution was poured slowly into 30% aqueous sodium hydroxide (300 c.c.) with stirring, the temperature being kept below 10°. The precipitated *diamine* was isolated and crystallised from a large volume of alcohol in pale yellow rhombs, m. p. 216—217° (57%) (Found: C, 72.0; H, 4.85; N, 13.45. $C_{19}H_{15}N_3S$ requires C, 71.9; H, 4.75; N, 13.25%). The *diacetyl* derivative separated from alcohol in small, yellow needles, m. p. 288—289° (Found: N, 10.7. $C_{23}H_{19}O_2N_3S$ requires N, 10.5%). The *diethoxycarbonyl* derivative, prepared in 74% yield by treating the diamine in alcohol with ethyl chloroformate (2 mols.) in presence of excess of diethylaniline, formed colourless plates (from alcohol), m. p. 187—188° (Found: N, 9.4. $C_{25}H_{23}O_4N_3S$ requires N, 9.1%). When an excess of ethyl chloroformate was used the product was the tetraethoxycarbonyl derivative, yellow needles, m. p. 234—236° (Found: N, 6.5. $C_{31}H_{31}O_8N_3S$ requires N, 6.8%).

2''': 3'-Dicyano-5-phenyl-2:3-6:7-dibenzo-1-thia-4-azacyclohepta-2:4:6-triene.—The corresponding dibromo-compound (4.45 g.) and cuprous cyanide (3.6 g., 4 mols.) were ground together and added during 30 min. to boiling quinoline (30 c.c.). The mixture was refluxed for a further 30 min., cooled, and poured into 5*N*-hydrochloric acid (300 c.c.), and water (1 l.) was added. The precipitated solid was filtered off, washed with water, dried, and exhaustively extracted with hot chloroform. Evaporation of the combined extracts gave a residue which was treated with hot ethyl acetate (30 c.c.). The insoluble material (0.4 g.; m. p. 313—315°), which recrystallised from 2-ethoxyethanol as colourless needles, m. p. 317—318°, was identified as 2:7-dicyano-9-phenylphenanthridine by analysis (Found: C, 82.9; H, 3.8; N, 13.9. Calc. for $C_{21}H_{11}N_3$: C, 82.6; H, 3.6; N, 13.8%) and comparison with an authentic specimen, m. p. 314—316°, prepared by the method of Libman and Slack (*J.*, 1951, 2588) who record m. p. 302°. Concentration of the ethyl acetate filtrate (above) and addition of light petroleum gave the *dicyanide* (60%), m. p. 216—219°, which was obtained as fine, pale yellow needles, m. p. 224—225° (Found: C, 74.6; H, 2.9; N, 12.8. $C_{21}H_{11}N_3S$ requires C, 74.75; H, 3.25; N, 12.5%), after two crystallisations from ethyl acetate and one from benzene. The dicyanide was unchanged on further treatment with cuprous cyanide under the conditions used for its preparation, but with cuprous bromide, after 1.5 hr., 2:7-dicyano-9-phenylphenanthridine was formed in *ca.* 0.5% yield.

Action of Cuprous Bromide on 2''': 3'-Dibromo-5-phenyl-2:3-6:7-dibenzo-1-thia-4-azacyclohepta-2:4:6-triene.—The dibromo-compound (4.4 g.), cuprous bromide (5.7 g.), and quinoline (40 c.c.) were refluxed for 3 hr. and the dark mixture was worked up as described in the similar experiment using cuprous cyanide. The chloroform-soluble extract was crystallised from ethyl acetate to give a mixture of yellow prisms (0.5 g.), m. p. 146—149°, raised to 156—157° by recrystallisation from ethyl acetate and identified as starting material by a mixed m. p. determination, and almost colourless needles (1.12 g.), m. p. 197.5—199°. The latter, after two crystallisations from ethyl acetate, had m. p. 200.5—201.5° (Found: C, 55.5; H, 2.7; N, 3.4; Br, 38.1. Calc. for $C_{19}H_{11}NBr_2$: C, 55.2; H, 2.7; N, 3.4; Br, 38.7%), undepressed on admixture with 2:7-dibromo-9-phenylphenanthridine, m. p. 200—201°, prepared according to Ritchie (*J. Proc. Roy. Soc. N.S.W.*, 1945, 78, 141) who records m. p. 201°.

5-Phenyl-2''': 3'-bis-*N*-phenylamidino-2:3-6:7-dibenzo-1-thia-4-azacyclohepta-2:4:6-triene.—A powdered, intimate mixture of the dicyanide (5.8 g.) and anilinium benzenesulphonate (8.5 g.) was heated at 210° for 2½ hr. with occasional stirring. After being cooled, the melt was dissolved in alcohol (charcoal) and basified with aqueous ammonia. The yellow precipitate was filtered off, washed with water, and dissolved in dilute acetic acid. This solution was boiled with charcoal for a few minutes, filtered, and again basified with ammonia. The precipitated diamidine, which could not be obtained crystalline, was purified by two treatments of its benzene solution with charcoal and reprecipitation with light petroleum, to give a yellow solid (4.6 g.), m. p. 144—148°, which was still partly hydrated after being dried at 100° [Found: C, 74.3; H, 4.6;

N, 12.95; H₂O (Karl Fischer), 1.15. C₃₃H₂₅N₅S_{0.33}H₂O requires C, 74.8; H, 4.85; N, 13.2; H₂O, 1.1%].

NN'-Di-(2-phenylsulphonylphenyl)benzamidine.—(1) *N*-(2-Phenylsulphonylphenyl)benzamidine (2.5 g.), phosphoryl chloride (15 c.c.), and nitrobenzene (35 c.c.) were boiled under reflux for 4 hr. and liquids were then removed at 100° under reduced pressure. The residue was dissolved in a small volume of warm methanol, the solution was diluted with 5*N*-hydrochloric acid, and the precipitated oil was collected in chloroform. Evaporation of the solvent afforded a solid (0.5 g.) which was recrystallised successively from methanol and ethyl acetate, giving NN'-di-(2-phenylsulphonylphenyl)benzamidine as large rods, m. p. 214—215° (Found : C, 67.25; 67.2; H, 4.6, 4.95; N, 5.4, 5.5. C₃₁H₂₄O₄N₂S₂ requires C, 67.4; H, 4.35; N, 5.1%).

(2) 2-Benzamidodiphenyl sulphone (2 g.), phosphorus pentachloride (1.4 g.), and dry benzene (10 c.c.) were refluxed for 30 min., then freed from liquids by distillation finally at 100°/1 mm., and the residue crystallised from benzene–light petroleum (b. p. 60—80°), giving crude *N*-(2-phenylsulphonylphenyl)benzimidoyl chloride (1.7 g.), m. p. 118—120°. Recrystallisation from the same solvent gave cream-coloured rods, m. p. 126—129°, but the crude material was used in subsequent experiments. The imidoyl chloride (1 g.), 2-aminodiphenyl sulphone (0.86 g.), and nitrobenzene (10 c.c.) were heated at 200° for 3 hr. and the crude amidine (1.37 g.), isolated as described in (1), was crystallised from acetic acid, giving the pure amidine (61%), m. p. 213—214°, undepressed on admixture with the sample prepared as above.

(3) The imidoyl chloride (1 g.), *N*-(2-phenylsulphonylphenyl)benzamidine (1.9 g.), and nitrobenzene (10 c.c.), heated at 200—210° for 3 hr., gave the crude amidine (1.5 g.), which on crystallisation from acetic acid gave the pure compound (46%), m. p. and mixed m. p. 212—214° (Found : C, 67.5; H, 4.4; N, 4.8%).

(4) 2-Benzamidodiphenyl sulphone (1 g.), phosphoryl chloride (2 c.c.), and nitrobenzene (10 c.c.) were refluxed for 4 hr., nitrobenzene was then removed under reduced pressure, and the residue crystallised from methanol. The first crystals to separate (0.3 g.) consisted of 2-aminodiphenyl sulphone, m. p. and mixed m. p. 119—120°, and NN'-di-(2-phenylsulphonylphenyl)benzamidine (0.02 g.) was then deposited and had m. p. and mixed m. p. 213—214°.

5-Phenyl-2 : 3-6 : 7-dibenzo-1-thia-4-azacyclohepta-2 : 4 : 6-triene 1 : 1-Dioxide.—(1) Chromic anhydride (1.3 g.) was added to a solution of the thia-aza-compound (1 g.) in acetic acid (30 c.c.), the mixture was warmed cautiously, refluxed for 15 min., and poured into water. The yellow amorphous precipitate was crystallised from methanol, giving the crude dioxide (36%), m. p. 183—185°, raised by two further crystallisations to 188—189° (Found : C, 72.3, 72.1; H, 4.0, 4.15; N, 4.4. C₁₉H₁₃O₂NS requires C, 71.5; H, 4.1; N, 4.4%). (2) 27% Hydrogen peroxide (1 c.c.) was added to a solution of the thia-aza-compound (0.2 g.) in acetic acid (8 c.c.); the mixture was kept at room temperature for 2 hr. and then at 50° for 2 hr. More hydrogen peroxide (0.5 c.c.) was then added, and, after the temperature had been kept at 75° for 1 hr. and at 90° for 1 hr., the mixture was poured into water. The solid was collected and recrystallised from methanol, giving the crude dioxide (45%), m. p. 186—188°, raised to 188—189° by a further crystallisation.

2'' : 3'-Dinitro-5-phenyl-2 : 3-6 : 7-dibenzo-1-thia-4-azacyclohepta-2 : 4 : 6-triene 1 : 1-Dioxide.—27% Hydrogen peroxide (32 c.c.) was added in 4 portions during 5 hr. to a solution of the thia-aza-compound (4 g.) in acetic acid (800 c.c.) at 90°. The mixture was kept at 90° for another 12 hr., cooled, filtered, and diluted with water. The solid was crystallised from acetic acid, giving the dioxide as yellow prisms (41.5%), m. p. 256—259°, raised to 259—259.5° by further crystallisation (Found : C, 55.9; H, 2.7; N, 10.3. C₁₉H₁₁O₆N₃S requires C, 55.75; H, 2.7; N, 10.3%).

2''-Nitro-5-*p*-nitrophenyl-2 : 3-6 : 7-dibenzo-1-thia-4-azacyclohepta-2 : 4 : 6-triene 1 : 1-dioxide, obtained in 62% yield by the method used for the preparation of its isomer, crystallised from acetic acid in yellow prisms, m. p. 252—254° (Found : C, 55.3; H, 2.7; N, 10.65. C₁₉H₁₁O₆N₃S requires C, 55.75; H, 2.7; N, 10.3%).

2'' : 3'-Diamino-5-phenyl-2 : 3-6 : 7-dibenzo-1-thia-4-azacyclohepta-2 : 4 : 6-triene 1 : 1-Dioxide.—(1) The corresponding nitro-compound (5.15 g.) was added during ½ hr. to a solution of stannous chloride dihydrate (51 g.) in absolute ethanol (65 c.c.), and the resulting red solution was refluxed for 1 hr., acidified with concentrated hydrochloric acid (50 c.c.), and distilled under reduced pressure to remove the alcohol. The residue was poured into excess of 5*N*-sodium hydroxide at 0°, the solid which separated was washed with water and dissolved in hot methanol, and the solution concentrated to a small volume, giving the crude product (63%), m. p. 283—284°. Recrystallisation from methanol gave the diamine as yellow prisms, m. p. 285—287° (Found : C, 64.8; H, 4.4; N, 11.6. C₁₉H₁₅O₂N₃S requires C, 65.3; H, 4.3; N, 12.0%). (2) A solution

of the nitro-compound (1 g.) in ethyl acetate (200 c.c.) was shaken with Raney nickel (2 g.) and hydrogen under atmospheric conditions for 24 hr., and gave a somewhat lower yield of the diamine.

2''-Amino-5-p-aminophenyl-2:3-6:7-dibenzo-1-thia-4-azacyclohepta-2:4:6-triene 1:1-dioxide, prepared similarly, was obtained in 76% yield by stannous chloride reduction and in 37% yield by catalytic reduction of the dinitro-compound. The *diamine* separated from ethyl acetate in solvated form, m. p. 160° (decomp.), which lost solvent on crystallisation from methanol which gave yellow prisms, m. p. 213—215° (Found : C, 64·8; H, 4·8; N, 12·2. $C_{19}H_{15}O_2N_3S$ requires C, 65·3; H, 4·3; N, 12·0%).

The authors are indebted to Mr. R. J. Kemp for experimental assistance.

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[Received, June 25th, 1954.]
