

88. *Diamidides. Part I. Derivatives of Triazapentadiene and Tetra-azaheptatriene.*

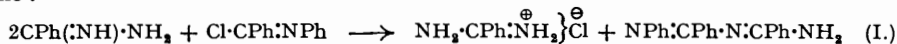
By F. C. COOPER, M. W. PARTRIDGE, and W. F. SHORT.

Numerous diamidides $\text{NR}'\cdot\text{CPh}\cdot\text{NR}''\cdot\text{CPh}\cdot\text{NR}''$ and $\text{NRR}'\cdot\text{CPh}\cdot\text{N}\cdot\text{CPh}\cdot\text{NR}''$ have been prepared from the appropriate imidochloride and amidine (Ley and Müller, *Ber.*, 1907, **40**, 2950). *N*-Phenylbenzamidine and *N*-phenylbenzimidochloride afford decomposition products of the diamidide $\text{NH}\cdot\text{CPh}\cdot\text{NPh}\cdot\text{CPh}\cdot\text{NPh}$ (VII) and, as minor product, the diamidide $\text{NHPH}\cdot\text{CPh}\cdot\text{N}\cdot\text{CPh}\cdot\text{NPh}$ (VIII), the structure of which is proved by methylation to $\text{NPhMe}\cdot\text{CPh}\cdot\text{N}\cdot\text{CPh}\cdot\text{NPh}$, and by unambiguous synthesis. The triamidide $\text{NPh}\cdot\text{CPh}\cdot\text{N}\cdot\text{CPh}\cdot\text{NPh}\cdot\text{CPh}\cdot\text{NPh}$, a by-product in the preparation of the diamidide (VIII), is also obtained from *NN'*-diphenylbenzamidine and the imidochloride, $\text{NPh}\cdot\text{CPh}\cdot\text{N}\cdot\text{CPh}\cdot\text{Cl}$. The nascent imidosulphonate $\text{NPh}\cdot\text{CPh}\cdot\text{O}\cdot\text{SO}_2\text{Ph}$, obtained by rearrangement of benzophenone oxime benzenesulphonate, and *N*-phenylbenzamidine afford the diamidide (VIII) (30%) and *NN'*-diphenylbenzamidine (38%), a decomposition product of the unstable diamidide (VII). The diamidide (VIII) is also obtained from *N*-phenylbenzamidine, benzanilide, benzenesulphonyl chloride, and pyridine, and the formation of by-products is explained by 1 : 4-addition of a phenylammonium ion to the system $\text{NRR}'\cdot\text{CPh}\cdot\text{N}\cdot\text{CPh}\cdot\text{NR}''$ or by interaction of the reciprocal pair. Diamidides $\text{NRR}'\cdot\text{CPh}\cdot\text{N}\cdot\text{CPh}\cdot\text{NR}''$ yield normal salts but di- and tri-amidides derived from $\text{NR}'\cdot\text{CPh}\cdot\text{NR}''\cdot\text{CPh}\cdot\text{NR}''$ are readily decomposed by acids (HX) to $\text{NHR}\cdot\text{CPh}\cdot\text{NR}'$ and $\text{X}\cdot\text{CPh}\cdot\text{NR}''$. The bond structures of the diamidides are discussed in the light of their ultraviolet absorption spectra.

THE work of Barnes and Schoenheimer (*J. Biol. Chem.*, 1943, **151**, 123) and of Plentl and Schoenheimer (*ibid.*, 1944, **153**, 203) indicates that the primary source of nitrogen in the

pyrimidine and purine components of nucleic acids is ammonia, and that it is unlikely that their biosynthesis involves amidine-nitrogen. Nevertheless, the resemblance of the amidine group to the N-C-N system in pyrimidines and purines has provided a basis for a useful working hypothesis in the development of amidines having chemotherapeutic activity (Andrewes, King, and Walker, *Proc. Roy. Soc.*, 1946, **133**, B, 28). The extension of the amidine group to N-C-N-C-N appeared to us to be a subject of interest, since this system exhibits a closer formal resemblance to the carbon-nitrogen system in cytidine, cytosine, adenine, guanine, pteridines, isalloxazines, and 4-aminoglyoxaline-5-carboxamide, which has been suggested as an intermediate metabolite of purines by Shive, Ackermann, Gordon, Gretzenander, and Eakin (*J. Amer. Chem. Soc.*, 1947, **69**, 725).

Few compounds possessing the open-chain N-C-N-C-N system have hitherto been described, apart from diguanide and biuret derivatives. Ley and Müller (*Ber.*, 1907, **40**, 2950) prepared "2 : 4 : 5-triphenylbiamidid" * (I) by interaction of *N*-phenylbenzimidochloride with benzamidine :

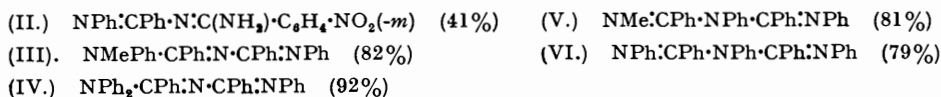


These authors did not fulfil their promise of a further communication on the preparation of compounds of this type by the reaction of substituted imino-ethers with amidines. The direct addition of benzylamine to ethyl cyanotrionate was found by Curtiss and Nickell (*J. Amer. Chem. Soc.*, 1913, **35**, 887) to afford a very unstable compound, $\text{C}_{23}\text{H}_{31}\text{O}_{10}\text{N}_3$, to which they assigned the structure $\text{C}(\text{OH})(\text{CO}_2\text{Et})_2\cdot\text{C}(\text{:NH})\cdot\text{N}(\text{CH}_2\text{Ph})\cdot\text{C}(\text{:NH})\cdot\text{C}(\text{OH})(\text{CO}_2\text{Et})_2$. Analogous compounds were not obtained from *isobutylamine* or ethylamine; diethylamine and dipropylamine afforded amidines, and aniline did not react. "Dibenzimidine" $\text{NH}\cdot\text{CPh}\cdot\text{NH}\cdot\text{CPh}\cdot\text{NH}$ (Pinner and Klein, *Ber.*, 1878, **11**, 4) and analogues obtained respectively from *p*-toluamidine (Glock, *Ber.*, 1888, **21**, 2650) and β -naphthamidine (Pinner, *Ber.*, 1892, **25**, 1434) and acetic anhydride were shown by Pinner (*Ber.*, 1892, **25**, 1624) to be triazines.

A number of new methods for the preparation of diamidides will be described in this series of memoirs, and we now record the preparation of aryltriazapentadienes by interaction of amidines with imidochlorides, ketoxime sulphonates, or imidosulphonates.

Apart from the example reported by Curtiss and Nickell (*loc. cit.*), there appears to be no record of the production of a diamidide by the addition of an amidine or an amidinium ion to a cyanide. The possible similarity of this reaction to some of the recently developed methods for the preparation of amidines led us to examine the reaction of phenylammonium benzene-sulphonate with two equivalents of phenyl cyanide (cf. Oxley and Short, *J.*, 1946, **147**) and of *N*-phenylbenzamidine and 4-methylsulphonylphenyl cyanide (cf. Oxley, Partridge, and Short, *J.*, 1948, **303**). No evidence was found of the formation of a diamidide.

We have confirmed the production of 1 : 2 : 4-triphenyl-1 : 3 : 5-triazapenta-1 : 3-diene (I) in 72% yield by the method of Ley and Müller (*loc. cit.*), and have prepared 4-*m*-nitrophenyl-1 : 2-diphenyl-1 : 3 : 5-triazapenta-1 : 3-diene (II) from *m*-nitrobenzamidine (2 mols.) and *N*-phenylbenzimidochloride in ether. The fully substituted diamidides (III)—(VI) were obtained by prolonged (9—12 days) reaction of an *NN*- or *NN'*-disubstituted amidine (2 mols.) and the appropriate imidochloride in benzene, the yields being indicated in parentheses :

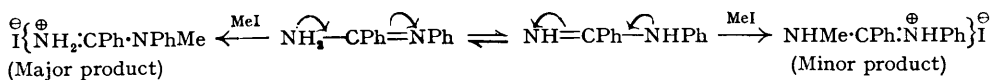


N-Methyl-*N*-phenylbenzamidine and *N*-phenylbenzimidochloride (1 mol.) in pyridine afforded only 17% of the diamidide (III), whereas *NN'*-diphenylbenzamidine and *N*-methylbenzimidochloride under these conditions gave 73% of the diamidide (V).

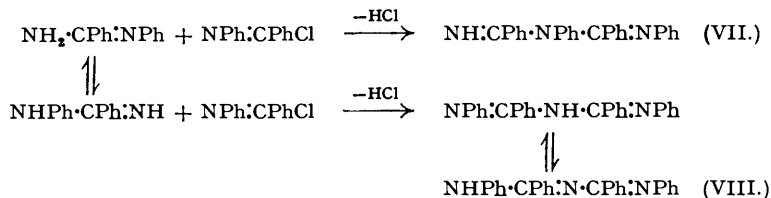
Methylation of *N*-phenylbenzamidine affords *N*-methyl-*N*-phenylbenzamidine and *N'*-methyl-*N*-phenylbenzamidine in the ratio 150 : 1 (Pyman, *J.*, 1923, **123**, 3359) and the

* The compound (I) was regarded by Ley and Müller as a derivative of the hypothetical substance "biformamidid" ($\overset{1}{\text{NH}}\cdot\overset{2}{\text{CH}}\cdot\overset{3}{\text{NH}}\cdot\overset{4}{\text{CH}}\cdot\overset{5}{\text{NH}}$) and was named "2 : 4 : 5-triphenylbiamidid." The name given to this compound in Beilstein's "Handbuch der organischen Chemie," 4th edn., XII, 266, is "*N*-phenyl-*N'*-(α -iminobenzyl)-benzamidin." The Editor has suggested the generic term "diamidide" for this class of compound and that individual examples should be named as derivatives of 1 : 3 : 5-triazapentadiene. Certain diamidides in which the position of the double bonds is ambiguous are arbitrarily named as derivatives of the 1 : 3-diene ($\overset{1}{\text{NH}}\cdot\overset{2}{\text{CH}}\cdot\overset{3}{\text{N}}\cdot\overset{4}{\text{CH}}\cdot\overset{5}{\text{NH}_2}$); on this system (I) becomes 1 : 2 : 4-triphenyl-1 : 3 : 5-triazapenta-1 : 3-diene. Compounds containing the chain N-C-N-C-N-C-N are similarly termed "triamidides" and are regarded as derivatives of 1 : 3 : 5 : 7-tetra-azaheptatriene.—W. F. S.

predominating *N*-methylation may be attributed to stabilisation of the anilo-form by the operation of the "Thiele factor" (Lapworth and Manske, *J.*, 1928, 2535).



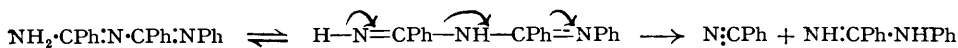
Similarly, benzoylation affords *N*-benzoyl-*N*-phenylbenzamidine, although this is rearranged to *N'*-benzoyl-*N*-phenylbenzamidine on being heated (Wheeler, Johnson, and McFarland, *J. Amer. Chem. Soc.*, 1903, 25, 787). In so far as an imidochloride may be regarded as an "alkylating agent" (cf. Oxley and Short, *J.*, 1948, 1514), it might therefore be expected that *N*-phenylbenzamidine and *N*-phenylbenzimidochloride would yield 1:2:3:4-tetra-phenyl-1:3:5-triazapenta-1:4-diene (VII) as main product, 1:2:4:5-tetraphenyl-1:3:5-triazapenta-1:3-diene (VIII) being formed in smaller quantity:



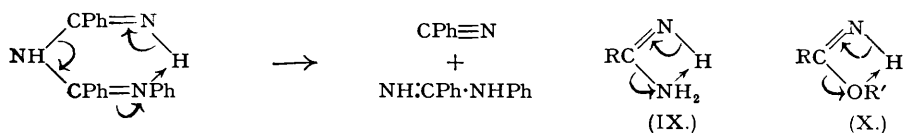
This expectation has been fulfilled to the extent that, whilst up to 16% of a diamidide has been isolated and shown to have the structure (VIII), the major products of the reaction were decomposition products of the diamidide (VII), which is therefore presumably formed in preponderating quantity but rapidly decomposed: $\text{NH} \cdot \text{CPh} \cdot \text{NPh} \cdot \text{CPh} \cdot \text{NPh} \longrightarrow \text{PhCN} + \text{NPh} \cdot \text{CPh} \cdot \text{NHPPh}$. This instability appears to be characteristic of many diamidides containing the group $\cdot \text{NR} \cdot \text{CPh} \cdot \text{NH}$ (see below).

The products obtained from *N*-phenylbenzamidine (2 mols.) and *N*-phenylbenzimidochloride vary with the solvent; e.g., in benzene solution 6% of the diamidide (VIII), 62% of *NN'*-diphenylbenzamidine, and 79% of *N*-phenylbenzamidine were obtained after 5 days; after 4 days 7% of a compound $\text{C}_{39}\text{H}_{30}\text{N}_4$, shown to be a triamidide (XV), was obtained in addition to 5% of the diamidide (VIII) and 38% of *NN'*-diphenylbenzamidine. The isolation of approximately equivalent quantities of *NN'*-diphenylbenzamidine (11%) and phenyl cyanide (13%) from the same reactants after 2 days in ether is consistent with the decomposition of the diamidide (VII), and those products could not be formed by a simple decomposition of the isomeric diamidide (VIII). *NN'*-Diphenylbenzamidine (19%) and the triamidide (16%) were obtained from *N*-phenylbenzamidine, *N*-phenylbenzimidochloride, and potassium carbonate in boiling acetone.

Evidence for the structure of the diamidide (VIII) was first sought by hydrolysis, but the compound was resistant to acids, 84% of unchanged diamidide and a little benzoic acid being recovered after 4 hours' boiling with concentrated hydrochloric acid. Boiling alcoholic potassium hydroxide hydrolysed the diamidide to *N*-phenylbenzamidine in agreement with the structure (VIII). The absence of the group $\cdot \text{NPh} \cdot \text{CPh} \cdot \text{NH}$ in this diamidide is indicated by the recovery of 90% of the compound after an hour's heating at 190–200°, whereas under these conditions 1:2:4-triphenyl-1:3:5-triazapenta-1:3-diene (I) afforded *N*-phenylbenzamidine (83%). This decomposition is probably due to attraction of electrons by the anilo-nitrogen atom and, although the effect may be transmitted through the chain:

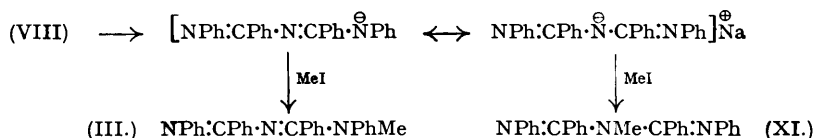


the process may be initiated by the formation of a hydrogen bond which determines the direction of the subsequent electronic displacements:

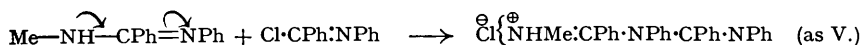


This interpretation brings the process into line with the production of cyanides by the decomposition of amidines (IX), imino-ethers (X; R' = Alk), and imidosulphonates (X; R' = SO_2Ar), represented for simplicity as taking place intramolecularly.

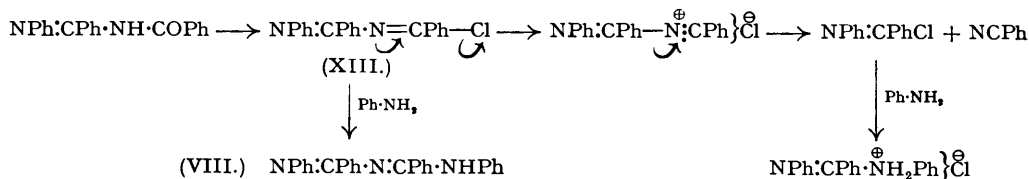
Conclusive evidence for the structure (VIII) was obtained by converting the diamide by successive action of sodamide and methyl iodide into 5-methyl-1 : 2 : 4 : 5-tetraphenyl-1 : 3 : 5-triazapenta-1 : 3-diene (III), which was also synthesised by an unequivocal method :



The alternative methylation product (XI) was not detected, and the isomeric diamide (V) was the sole product isolated (94%) when an attempt was made to obtain (XI) from *N'*-methyl-*N*-phenylbenzamidine and *N*-phenylbenzimidochloride. It is evident that the introduction of a *N'*-methyl group into *N*-phenylbenzamidine, by increasing the affinity of the *N'*-nitrogen atom for a proton, favours the anilo-form, so that the process, unlike the alkylation of *N*-phenylbenzamidine (above), becomes substantially unidirectional :



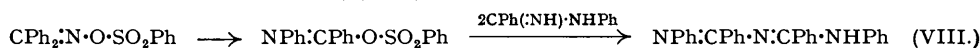
The preparation of 5-methyl-1 : 2 : 4 : 5-tetraphenyl-1 : 3 : 5-triazapenta-1 : 3-diene (III) (48%) from *N*-benzoyl-*N'*-phenylbenzamidine, phosphorus pentachloride, and methylaniline was undertaken as a model experiment for the unequivocal synthesis of the diamide (VIII). 1-*p*-Chlorophenyl-2 : 4 : 5-triphenyl-1 : 3 : 5-triazapenta-1 : 3-diene (XII) (10%) was prepared similarly by using thionyl chloride and *p*-chloroaniline. Attempts to isolate the unstable intermediate *N*-(*N'*-phenylbenzimidyl)benzimidochloride (XIII) in analytically pure condition were unsuccessful, but the slightly impure material remaining after the removal of phosphoryl chloride afforded the diamide (VIII) (30%) on reaction with aniline. *N*-Benzoyl-*N'*-phenylbenzamidine, phosphorus pentachloride, and aniline gave 12% of this diamide in boiling benzene or 17% in cold chloroform, small quantities of *NN'*-diphenylbenzamidine and phenyl cyanide being also produced in each case. When the reaction was carried out in pyridine, the diamide (5%), *NN'*-diphenylbenzamidine (77%), and phenyl cyanide (27%) were obtained, and the formation of these products can be accounted for by the following sequence of reactions :



The production of *NN'*-diphenylbenzamidine in this reaction cannot be explained by 1 : 2- or 1 : 4-addition of a phenylammonium ion to the diamide (VIII), since fission of the resulting complex would also give *N*-phenylbenzamidine, a readily detected compound which was not present in the reaction product. *N*-Phenylbenzamidine is, however, produced in analogous transformations carried out at a higher temperature with the imidosulphonate corresponding to the imidochloride (XIII) and addition of a phenylammonium ion is therefore probably involved (see below).

N-Benzoyl-*NN'*-diphenylbenzamidine, phosphorus pentachloride, and ammonia afforded *NN'*-diphenylbenzamidine but no 1 : 2 : 3 : 4-tetraphenyl-1 : 3 : 5-triazapenta-1 : 4-diene (VII), confirming the conclusion that this diamide is unstable. No 1 : 2 : 4 : 5-tetraphenyl-1 : 3 : 5-triazapenta-1 : 3-diene (VIII) was detected in the product, and this provides evidence against the assumption that when this diamide is formed from *N*-phenylbenzamidine and *N*-phenylbenzimidochloride it is produced by rearrangement of the isomeric 1 : 4-diene (VII).

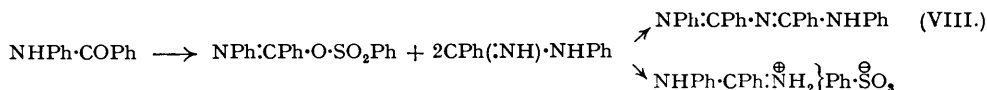
The method of preparing substituted amidines from ketoxime sulphonates and amines (Oxley and Short, *J.*, 1948, 1514) has now been extended to the production of 1 : 2 : 4 : 5-tetraphenyl-1 : 3 : 5-triazapenta-1 : 3-diene (VIII) (30%) :



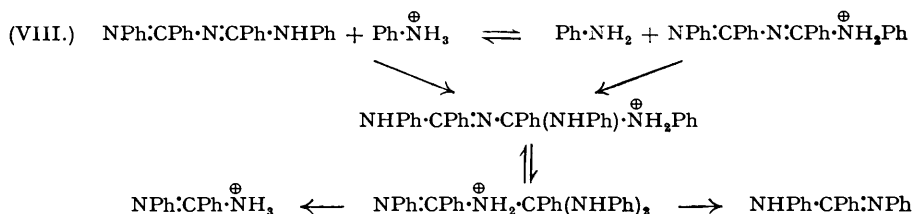
On account of the mesohydric tautomerism of *N*-phenylbenzamidine, the isomeric tetraphenyl-triazapentadiene (VII) would be expected as a second product of this reaction; the *NN'*-di-

phenylbenzamidine (38%) obtained as a by-product was apparently formed by decomposition of this diamidide.

Since *N*-substituted imidosulphonates, formed by the action of sulphonyl chlorides on *N*-substituted amides, are sufficiently stable in the presence of pyridine to yield amidines on the subsequent addition of amines (Oxley, Peak, and Short, *J.*, 1948, 1618), it appeared likely that this series of reactions could be extended to the preparation of diamidides. In agreement with this, benzanilide, treated with benzenesulphonyl chloride in the presence of pyridine and then with *N*-phenylbenzamidine, afforded 1 : 2 : 4 : 5-tetraphenyl-1 : 3 : 5-triazapenta-1 : 3-diene (VIII) (17—23%) :



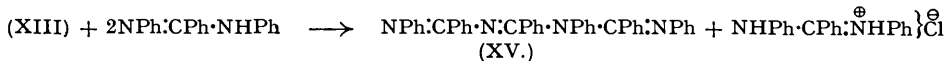
The possibility of a further unambiguous synthesis of the diamidide (VIII) from the imidosulphonate of *N*-benzoyl-*N'*-phenylbenzamidine and aniline was examined. With 1 mol. of aniline, the products isolated from the reaction mixture were *N*-phenylbenzamidine (18%), *NN'*-diphenylbenzamidine (46%), benzanilide (8%), and 1 : 2 : 4 : 5-tetraphenyl-1 : 3 : 5-triazapenta-1 : 3-diene (VIII) (0.5%); with 2 moles of aniline, the reaction mixture afforded *N*-phenylbenzamidine (32%), *NN'*-diphenylbenzamidine (46%), benzanilide (7%), and phenyl cyanide (31%). We suggest that these reactions involve the formation of an imidosulphonate $\text{NPh}\cdot\text{CPh}\cdot\text{N}\cdot\text{CPh}\cdot\text{O}\cdot\text{SO}_2\text{Ph}$ which behaves in exactly the same way as the imidochloride (XIII) in the scheme formulated above and yields benzanilide by hydrolysis during the working of the reaction mixture. The isolation of *N*-phenylbenzamidine in addition to *NN'*-diphenylbenzamidine suggests decomposition of the diamidide by addition of a phenylammonium ion :



Evidence for the participation of the imidosulphonate was obtained by heating *N*-benzoyl-*N'*-phenylbenzamidine, benzenesulphonyl chloride, and pyridine and treating the resulting mixture with water. The products obtained were phenyl cyanide (28%), benzanilide (54%), benzenesulphonic acid (77%), and the diamidide (VIII) (1.6%). The mode of formation of (VIII) in this reaction is uncertain, but in view of its formation in this experiment, the synthesis of this diamidide from the imidosulphonate (XIV) can no longer be regarded as unambiguous.

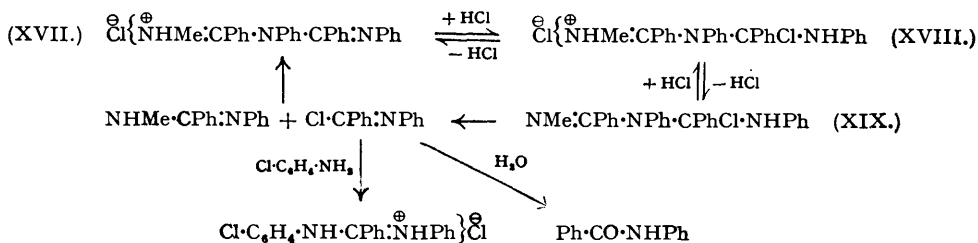
Evidence for the postulated fission of 1 : 2 : 4 : 5-tetraphenyl-1 : 3 : 5-triazapenta-1 : 3-diene (VIII) to give *N*-phenylbenzamidine and *NN'*-diphenylbenzamidine was sought by heating the diamidide with bases and their salts. The diamidide (84, 90, and 92% respectively) was recovered when heated for 90 minutes at 100° with aniline (2 mols.), aniline (2 mols.) and pyridine, or with pyridinium benzenesulphonate (1 mol.), but under the same conditions phenylammonium benzenesulphonate (2 mols.) in pyridine caused fission to *N*-phenylbenzamidine (92%) and *NN'*-diphenylbenzamidine (80%). This breakdown can be formulated as addition of a phenylammonium ion to $\text{>C}\cdot\text{N}\cdot$ in the diamidide, but occurs more readily than analogous additions to the $\text{>C}\cdot\text{N}\cdot$ group in amidines (Oxley and Short, *J.*, 1949, 449) or to the cyano-group in cyanides (Partridge and Short, *J.*, 1947, 390; Oxley, Partridge, and Short, *J.*, 1948, 303). Hickinbottom (*J.*, 1934, 1981) has shown that butadiene does not combine with aniline alone but reaction occurs in presence of phenylammonium chloride giving, *inter alia*, 1-anilinobut-2-ene by 1 : 4-addition of the elements of aniline. We therefore suggest that fission of the diamidide involves 1 : 4-addition of phenylammonium ion to the conjugated system of double bonds in the diamidide or of aniline to the diamidide ion as illustrated above. Similar additions of a phenylammonium ion to a conjugated system provide simpler explanations than those hitherto suggested for the decomposition of *N*¹-phenyldiguanide (Sugino, *J. Chem. Soc. Japan*, 1939, 60, 411) and of dibenzoylamine, $(\text{PhCO})_2\text{NH}$ (Brunner, Seeger, and Dittrich, *Monatsh.*, 1924, 45, 69), by phenylammonium chloride.

Ghadiali and Shah (*J. Univ. Bombay*, 1937, 6, ii, 127) obtained a compound $C_{39}H_{30}N_4$ by the interaction of *N*-phenylbenzamidine and *N*-phenylbenzimidochloride in methanol-ether and, solely on the evidence of its nitrogen content and mode of formation, assigned to it the formula $NPh:CPh:N:CPh:NPh:CPh:NPh$ (XV) in preference to the symmetrical structure $N(CPh:NPh)_3$ (XVI). The properties of this compound were in satisfactory agreement with those of the by-product which we obtained in the preparation of the diamidide (VIII), and an unambiguous synthesis showed that it is 1 : 2 : 4 : 5 : 6 : 7-hexaphenyl-1 : 3 : 5 : 7-tetraazahepta-1 : 3 : 6-triene (XV) :

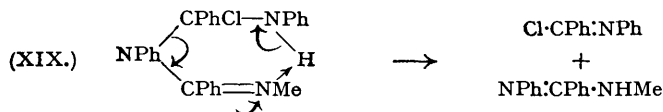


The triamidide (7%) produced in this way was accompanied by the diamidide (VIII) (9%), and repetition of Ghadiali and Shah's experiment afforded *N*-phenylbenzamidine (54%) and the triamidide (23%) and, in addition, the diamidide (VIII) (21%). The triamidide exhibited thermal stability and resistance to alkaline hydrolysis similar to that shown by the diamidide (VIII).

The diamidides (I), (III), and (VIII) afforded hydrochlorides and picrates but attempts to prepare the corresponding salts from the diamidide (V) and from the triamidide (XV) afforded decomposition products of these compounds. When the diamidide (V) was treated with hydrogen chloride in anhydrous benzene an oil separated, and the supernatant benzene solution afforded only *p*-chlorophenylammonium chloride and the unchanged diamidide (17%) on treatment with *p*-chloroaniline. Free hydrogen chloride and solvent were removed from the oil, and the residual gum when dissolved in benzene and treated successively with *p*-chloroaniline and water afforded benzanilide (30%), *N*-methyl-*N'*-phenylbenzamidine (36%), *N*-*p*-chlorophenyl-*N'*-phenylbenzamidine (7%), and unchanged diamidide (17%). The following scheme accounts for the formation of these products if it is assumed that (a) the diamidide hydrochloride (XVII) is somewhat soluble in benzene and (b) the precipitated oil consists of the salt of the chloride (XVIII), which partially dissociates when excess of hydrogen chloride is removed, giving the chloride (XIX) (compare Hantzsch, *Ber.*, 1931, 64, 667; Work, *J.*, 1942, 429), which then decomposes into *N*-methyl-*N'*-phenylbenzamidine and *N*-phenylbenzimidochloride :



The following mechanism for the fission of the chloride (XIX) is analogous to that postulated for the thermal decomposition of the diamidide (I) :

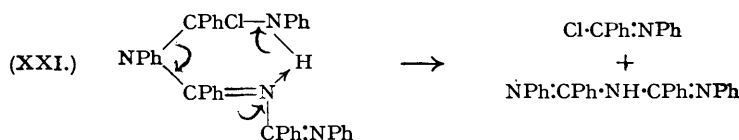


No *N*-*p*-chlorophenyl-*N'*-methylbenzamidine was detected in the product, and this appears to preclude the formation and decomposition of the alternative chloride, $NHMe:CPhCl:NPh:CPh:NPh$ (XX).

A solution of 1-methyl-2 : 3 : 4 : 5-tetraphenyl-1 : 3 : 5-triazapenta-1 : 4-diene (V) in ethanolic lactic acid yielded, on the addition of aqueous sodium picrate, *NN'*-diphenylbenzamidinium picrate (65%); the base and picric acid in benzene afforded *NN'*-diphenylbenzamidinium picrate (44%) and *N*-methyl-*N'*-phenylbenzamidinium picrate (14%). The diamidide (V) and hydrochloric acid in aqueous ethanol afforded benzanilide (25%), *N*-methyl-*N'*-phenylbenzamidine (46%), and unchanged diamidide (25%). Benzanilide (91%) and *N*-methyl-*N'*-phenylbenzamidine (86%) were isolated from the mixture produced when the base (V) was treated successively with hydrogen chloride in chloroform and with water. It is

suggested that these decompositions occur by the mechanism illustrated above, although some of them could be interpreted by postulating direct hydrolysis of the diamidide. The isolation of both *NN'*-diphenylbenzamidinium picrate and *N*-methyl-*N'*-phenylbenzamidinium picrate indicates the formation of two addition compounds corresponding to the isomeric chlorides (XIX) and (XX).

The triamidide (XV) and ethanolic picric acid afforded the picrate of the diamidide (VIII) (59%), and the hydrochloride of this diamidide (67%) was precipitated by hydrogen chloride from a chloroform solution of the triamidide. The same hydrochloride (81%) was precipitated from a benzene solution of the triamidide, and *N*-*p*-chlorophenyl-*N'*-phenylbenzamidide (12%) was obtained when *p*-chloroaniline was added to the solution remaining after removal of the precipitated hydrochloride. The decomposition of the triamidide appears to be similar to that of the diamidide, but with the difference that the addition compound (XXI) is more readily decomposed than the corresponding chloride (XIX), so that *N*-phenylbenzimidochloride passes immediately into the benzene solution :



The isolation of the diamidide hydrochloride in these experiments with the triamidide is at variance with the results of Ghadiali and Shah (*loc. cit.*), who describe the preparation of the triamidide hydrochloride from the base and hydrogen chloride in benzene. Their hydro-

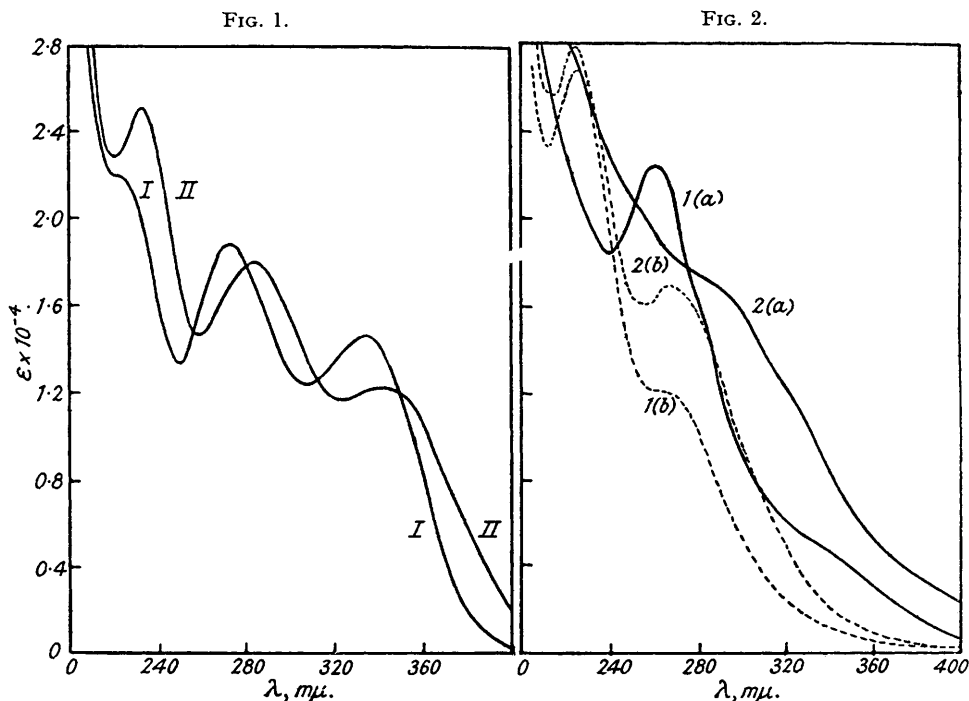


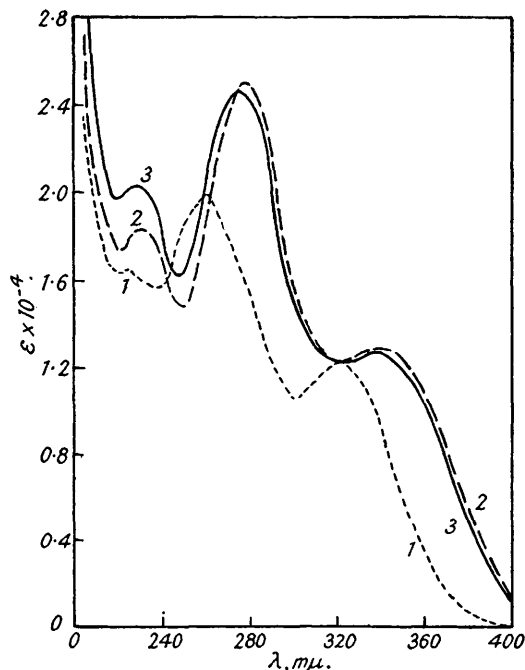
FIG. 1.—(I) 5-Methyl-1:2:4:5-tetraphenyl-1:3:5-triazapenta-1:3-diene (III). (II) 1:2:4:5:5-Pentaphenyl-1:3:5-triazapenta-1:3-diene (IV) in 0.1N-ethanolic hydrochloric acid.

FIG. 2.—(1) 1-Methyl-2:3:4:5-tetraphenyl-1:3:5-triazapenta-1:4-diene (V). (2) 1:2:3:4:5-Pentaphenyl-1:3:5-triazapenta-1:4-diene (VI); a, with freshly prepared solution in 0.1N-ethanolic hydrochloric acid; b, after 5 days' keeping.

chloride melted at approximately the same temperature as the first m. p. of the diamidide hydrochloride, and the proportion of nitrogen found in their hydrochloride does not permit a clear distinction to be made between the diamidide and the triamidide hydrochlorides. The

ease with which the triamidide undergoes decomposition in the presence of hydrogen chloride accounts for the formation of the diamidide as a by-product in the previously described unambiguous synthesis of the triamidide from *N*-benzoyl-*N'*-phenylbenzamidine. Indeed, in other syntheses of this diamidide where the triamidide is formed simultaneously from the

FIG. 3.



- (1) 1 : 2 : 4-Triphenyl-1 : 3 : 5-triazapenta-1 : 3-diene (I). (2) 1-*p*-Chlorophenyl-2 : 4 : 5-triphenyl-1 : 3 : 5-triazapenta-1 : 3-diene (XII). (3) 1 : 2 : 4 : 5-Tetraphenyl-1 : 3 : 5-triazapenta-1 : 3-diene (VIII) in 0.1*N*-ethanolic hydrochloric acid.

structures already arbitrarily assigned to these compounds in preference to the tautomeric non-conjugated structures are correct. Further evidence of conjugation is provided by the colour of the diamidides; all unconjugated bases are colourless, whereas all bases for which the ions show spectroscopic evidence of conjugation are yellow.

Compound.	$\lambda_{\max.}$, m μ .	$\epsilon_{\max.} \times 10^{-4}$.	$\lambda_{\max.}$, m μ .	$\epsilon_{\max.} \times 10^{-4}$.
NH:CPh·NHPh	234	1.81	275 *	0.78
NMe:CPh·NHPh	—	—	270	0.88
NPh:CPh·NHPh	—	—	273	1.29
NH:CPh·NPh ₂	225	1.73	270	0.629
NPh:CPh·N:CPh·NPh·CPh·NPh	235	3.33	272	2.66

* Figures in italics refer to inflexions or bends.

Solvent: 0.1*N*-ethanolic hydrochloric acid.

The significance of the bands in the regions of 230 and 270 m μ . is not clear. From the data summarised in the Table, it can be seen that these bands may also occur in the spectra of substituted amidines and in the triamidide. The band at 220—235 m μ . may possibly be assigned to the absorption of a C=N group, intensified and displaced, whereas benzenoid absorption may be responsible for the band in the region of 270 m μ . (cf. Barany, Braude, and Pianka, *J.*, 1949, 1898). In the spectrum of the triamidide there is some indication of a submerged maximum at 340—360 m μ . ($\epsilon = 1.3 \times 10^4$).

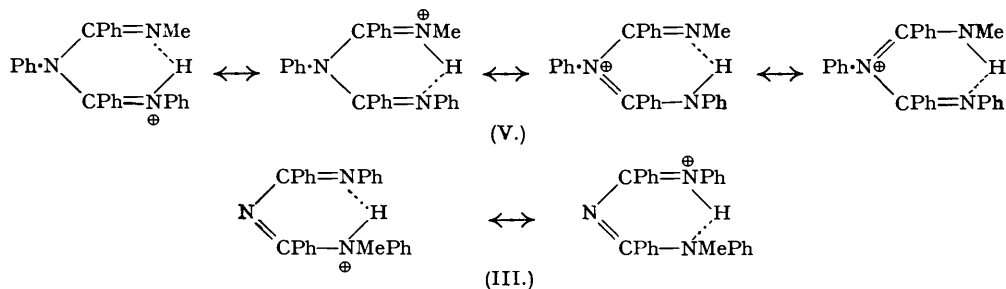
That the curves 1(*a*) and 2(*a*) given in Fig. 2 may refer to the spectra of the ions of these diamidides and not to decomposition products was demonstrated by observations on the change of these spectra with time. The results summarised in curves 1(*a*) and 2(*a*) were obtained

the reaction between *N*-phenylbenzamidine and *N*-phenylbenzimidochloride, no evidence is available to exclude the possible formation of the diamidide *via* the triamidide.

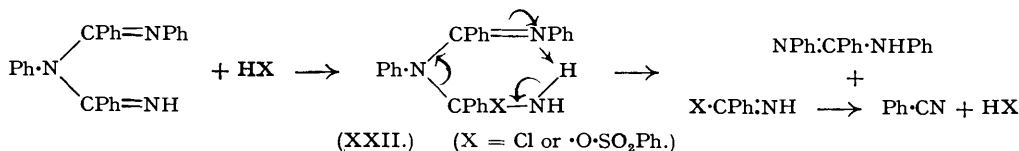
Evidence for the bond structure of the diamidides capable of exhibiting tautomerism was sought from their ultra-violet absorption spectra. In the spectra of the ions of the necessarily conjugated diamidides, 5-methyl-1 : 2 : 4 : 5-tetraphenyl-1 : 3 : 5-triazapenta-1 : 3-diene (III) and 1 : 2 : 4 : 5 : 5-pentaphenyl-1 : 3 : 5-triazapenta-1 : 3-diene (IV), three bands of decreasing intensity, at 220—235 m μ ., 270—285 m μ ., and 330—345 m μ ., can be distinguished (Fig. 1). The last band is absent from the spectra of the ions of the isomeric unconjugated diamidides, 1-methyl-2 : 3 : 4 : 5-tetraphenyl-1 : 3 : 5-triazapenta-1 : 4-diene (V) and 1 : 2 : 3 : 4 : 5-pentaphenyl-1 : 3 : 5-triazapenta-1 : 4-diene (VI); a band at 262 m μ . is present in the unconjugated methyltetraphenyltriazapentadiene but the other bands are retained only as inflexions or bends [Fig. 2; curves 1(*a*), 2(*a*)]. The band at 330—345 m μ . is apparently characteristic of the conjugated diamidides. Absorption maxima at 220—230, 260—280, and 320—345 m μ . in the spectra of the ions of 1 : 2 : 4-triphenyl-1 : 3 : 5-triazapenta-1 : 3-diene (I), 1 : 2 : 4 : 5-tetraphenyl-1 : 3 : 5-triazapenta-1 : 3-diene (VIII), and 1-*p*-chlorophenyl-2 : 4 : 5-triphenyl-1 : 3 : 5-triazapenta-1 : 3-diene (XII) (see Fig. 3) indicate that the conjugated

within 15 minutes of the preparation of the solution; a slight modification of both curves was apparent after 40 minutes. After 20 hours, the curve for 1 : 2 : 3 : 4 : 5-pentaphenyl-1 : 3 : 5-triazapenta-1 : 4-diene was identical with the curve 2(b) obtained when the spectroscopic solutions had been kept for 5 days. The change in 1-methyl-2 : 3 : 4 : 5-tetraphenyl-1 : 3 : 5-triazapenta-1 : 4-diene was slower.

A number of speculative suggestions may be made with regard to the remarkable differences in stability of certain diamidides. Conjugation appears to be a more important factor in stabilising these molecules or their ions than the formation of mesomeric cyclic hydrogen-bonded structures analogous to those put forward by Hunter and Roberts (*J.*, 1941, 820) for certain formazyl derivatives, since similar cyclic structures can be assigned to the unstable ion of 1-methyl-2 : 3 : 4 : 5-tetraphenyl-1 : 3 : 5-triazapenta-1 : 4-diene (V) and the stable ion of 5-methyl-1 : 2 : 4 : 5-tetraphenyl-1 : 3 : 5-triazapenta-1 : 3-diene (III) :



Our failure to obtain 1 : 2 : 3 : 4-tetraphenyl-1 : 3 : 5-triazapenta-1 : 4-diene (VII) may be ascribed to instability owing to the absence of conjugation, and its decomposition may be formulated in a manner analogous to the thermal decomposition of 1 : 2 : 4-triphenyl-1 : 3 : 5-triazapenta-1 : 3-diene (I). In the reactions in which its formation could have been expected, it may have undergone rapid decomposition *via* an unstable addition compound (XXII) similar to those (XIX and XXI) postulated in the decomposition of 1-methyl-2 : 3 : 4 : 5-tetraphenyl-1 : 3 : 5-triazapenta-1 : 4-diene and of the triamidide :



EXPERIMENTAL.

Phenyl Cyanide and Phenylammonium Benzenesulphonate.—Phenylammonium benzenesulphonate and phenyl cyanide (2 mols.) when heated together at 200—220° for 1 hour afforded *N*-phenylbenzamidine (91%). Since the mother-liquors from the isolation of the amidine were colourless when alkaline and afforded no yellow material on extraction with ethyl acetate, it was unlikely that a diamidide was a minor constituent of the product of the reaction.

N-Phenylbenzamidine and p-Cyanophenyl Methyl Sulphone.—When equimolecular quantities of these reagents were heated together at 180° for 4 hours, unchanged amidine (90%) and cyanide (93%) were recovered.

1 : 2 : 4-Triphenyl-1 : 3 : 5-triazapenta-1 : 3-diene (I) was obtained (72% yield) by interaction of *N*-phenylbenzimidochloride and benzamidine (2 mols.) in ether (Ley and Müller, *loc. cit.*) for 90 minutes; it had m. p. 146—147° (Ley and Müller record m. p. 152°) (Found : N, 14.0. Calc. for C₂₀H₁₇N₃ : N, 14.0%). The hydrochloride had m. p. 245—247° (decomp.); Ley and Müller record m. p. 250° (decomp.) (Found : N, 12.3. Calc. for C₂₀H₁₇N₃·HCl : N, 12.5%). The *picrate* separated as needles from aqueous acetic acid, m. p. 167—168° with resolidification on further heating (Found : loss at 100°/vac., 1.75. Found, on dried material : N, 16.05. C₂₆H₂₀O₇N₆·½H₂O requires H₂O, 1.7%. C₂₆H₂₀O₇N₆ requires N, 15.9%). The *benzenesulphonate* crystallised from aqueous ethanol in prisms, m. p. 207—207.5° (decomp.) (Found : N, 9.0. C₂₆H₂₃O₃N₃S requires N, 9.2%).

This base (1 g.) when heated at 190—200° for 1 hour yielded a gum which smelt strongly of phenyl cyanide; *N*-phenylbenzamidine (0.55 g., 83%), m. p. and mixed m. p. 115—116°, was recovered from this material.

4-*m*-Nitrophenyl-1 : 2-diphenyl-1 : 3 : 5-triazapenta-1 : 3-diene (II).—To a solution of *N*-phenylbenzimidochloride (4.3 g.) in anhydrous ether (30 c.c.), a suspension of *m*-nitrobenzamidine (6.6 g., 2 mols.) in anhydrous ether (100 c.c.) was added. After 1 day's shaking, the solvent was evaporated and

m-nitrobenzamidinium chloride was extracted with hot water (20 c.c.). The residue, dissolved in hot ethanol (50 c.c.) and acidified with dilute hydrochloric acid, afforded 4-*m*-nitrophenyl-1 : 2-diphenyl-1 : 3 : 5-triazapenta-1 : 3-diene hydrochloride (3.14 g., 41%), m. p. 216—218° (decomp.), raised by recrystallisation from ethanol to 219—221° (decomp.) (Found : N, 14.5. $C_{20}H_{16}O_2N_4$, HCl requires N, 14.7%). When the reactants were boiled in dry benzene for 1 hour, the yield was 47%.

5-Methyl-1 : 2 : 4 : 5-tetraphenyl-1 : 3 : 5-triazapenta-1 : 3-diene (III).—(i) A solution of *N*-phenylbenzimidochloride (4.3 g.) and *N*-methyl-*N*-phenylbenzamidine (8.4 g., 2 mols.) in dry benzene (90 c.c.) was kept for 11 days and filtered from the solid which slowly separated. The benzene was evaporated, and the residue, after crystallisation from aqueous ethanol, yielded 5-methyl-1 : 2 : 4 : 5-tetraphenyl-1 : 3 : 5-triazapenta-1 : 3-diene (6.4 g., 82%) as yellow prisms, m. p. 104.5—105°, unchanged on recrystallisation from light petroleum [Found : N, 10.95%; *M* (Rast), 396. $C_{27}H_{23}N_3$ requires N, 10.8%; *M*, 389.5]. The benzene-insoluble solid consisted of *N*-methyl-*N*-phenylbenzamidinium chloride (3.9 g., 80%) which with alkali afforded the amidine, m. p. and mixed m. p. 85—86°. The hydrochloride of 5-methyl-1 : 2 : 4 : 5-tetraphenyl-1 : 3 : 5-triazapenta-1 : 3-diene separated very slowly as colourless prisms when hydrochloric acid was added to an aqueous ethanolic solution of the base, and had m. p. 234—234.5° (decomp.) (Found : N, 10.0. $C_{27}H_{23}N_3$, HCl requires N, 9.8%). The colloidal precipitate obtained on adding aqueous sodium picrate to a solution of the base in aqueous-ethanolic lactic acid crystallised when kept, and on recrystallisation from ethanol the pure picrate was obtained as orange-yellow prisms, m. p. 159.5—160.5° (Found : N, 13.45; $C_6H_5O_7N_3$, 36.95. $C_{27}H_{23}N_3$, $C_6H_5O_7N_3$ requires N, 13.6; $C_6H_5O_7N_3$, 37.05%).

Equimolecular quantities of *N*-phenylbenzimidochloride and *N*-methyl-*N*-phenylbenzamidine when brought into reaction in dry pyridine (15 mols.) afforded 5-methyl-1 : 2 : 4 : 5-tetraphenyl-1 : 3 : 5-triazapenta-1 : 3-diene (17%), m. p. and mixed m. p. 104.5—105°.

(ii) 1 : 2 : 4 : 5-Tetraphenyl-1 : 3 : 5-triazapenta-1 : 3-diene (VIII) (1.9 g.; see below), dissolved in dry benzene (40 c.c.), was boiled with a suspension of finely powdered sodamide (0.205 g., 1.05 mols.) in benzene (10 c.c.) until no more ammonia was evolved (2½ hours). Methyl iodide (1.4 g., 2 mols.) in dry benzene (10 c.c.) was added to the clear solution and the mixture was boiled for 90 minutes. The solvent was evaporated, and the residue, after extraction of sodium iodide with water, afforded on fractional crystallisation from ethanol 1 : 2 : 4 : 5-tetraphenyl-1 : 3 : 5-triazapenta-1 : 3-diene (0.75 g., 39%), m. p. and mixed m. p. 182—184°, and 5-methyl-1 : 2 : 4 : 5-tetraphenyl-1 : 3 : 5-triazapenta-1 : 3-diene (0.7 g., 36%), m. p. 104—105°, undepressed on admixture with the compound prepared by the foregoing procedure. Only unchanged 1 : 2 : 4 : 5-tetraphenyl-1 : 3 : 5-triazapenta-1 : 3-diene was recovered when attempts were made to carry out this methylation with methyl iodide in the presence of anhydrous potassium carbonate, or by heating the diene with a large excess of methyl iodide under pressure at 100° for 17 hours.

(iii) A solution of *N*-benzoyl-*N'*-phenylbenzamidine (7.5 g.) and phosphorus pentachloride (5.45 g., 1.05 mols.) in dry chloroform was kept at 20° for 5 hours, methylaniline (9.4 g., 3.5 mols.) was added, and, after being kept for 7 days, the solution was boiled for 90 minutes and evaporated to dryness under reduced pressure. The residue, after extraction with water, was crystallised from dilute aqueous ethanolic sodium hydroxide (charcoal) and gave 5-methyl-1 : 2 : 4 : 5-tetraphenyl-1 : 3 : 5-triazapenta-1 : 3-diene (4.2 g., 43%), m. p. and mixed m. p. 104.5—105°. The aqueous extract slowly deposited 5-methyl-1 : 2 : 4 : 5-tetraphenyl-1 : 3 : 5-triazapenta-1 : 3-diene hydrochloride (0.6 g., 5%), m. p. and mixed m. p. 233—234° (decomp.).

N-Benzoyl-*N'*-phenylbenzamidine.—The following procedure gave consistently better yields than the method of Wheeler, Johnson, and McFarland (*J. Amer. Chem. Soc.*, 1903, 25, 787). Benzoyl chloride (11.7 g.) in dry, alcohol-free chloroform (50 c.c.) was added dropwise during one hour to a mechanically stirred solution of *N*-phenylbenzamidine (32.7 g., 2 mols.) in chloroform (170 c.c.). After being kept for 2 days, the suspension was filtered and evaporated; crystallisation of the residue from ethanol afforded *N*-benzoyl-*N'*-phenylbenzamidine (17—19.5 g., 68—78%), m. p. 143—144°. Wheeler *et al.* record m. p. 143° (Found : N, 9.35. Calc. for $C_{20}H_{16}ON_2$: N, 9.35%).

N-Methylbenzimidochloride was obtained from *N*-methylbenzamide and thionyl chloride in 39% yield, b. p. 65—67°/2.8 mm.; von Braun and Pinkernelle (*Ber.*, 1934, 67, 1218) record b. p. 90—92°/13 mm. (Found : Cl, 22.95, 23.2. Calc. for C_8H_8NCl : Cl, 23.1%). Von Pechmann's method (*Ber.*, 1895, 28, 2362) failed to give any of the desired product.

1-Methyl-2 : 3 : 4 : 5-tetraphenyl-1 : 3 : 5-triazapenta-1 : 4-diene (V).—*N*-Methylbenzimidochloride (3.1 g.) and *NN'*-diphenylbenzamidine (10.9 g., 2 mols.), dissolved in dry benzene (150 c.c.), were kept for 9 days and filtered. The yellow gum remaining after evaporation of the solvent afforded on crystallisation from ethanol 1-methyl-2 : 3 : 4 : 5-tetraphenyl-1 : 3 : 5-triazapenta-1 : 4-diene (6.3 g., 81%), m. p. 147—148°; the pure compound was obtained as clusters of pale yellow needles, m. p. 148.5—149.5°, from light petroleum (b. p. 100—120°) [Found : C, 83.65; H, 5.75; N, 10.75; *M* (Rast), 384. $C_{27}H_{23}N_3$ requires C, 83.25; H, 5.95; N, 10.8%; *M*, 389.5]. On admixture with *NN'*-diphenylbenzamidine the m. p. was depressed to 123—125°. The benzene-insoluble material yielded *NN'*-diphenylbenzamidine (4.4 g., 41%), m. p. and mixed m. p. 146.5—147°, when dissolved in alcohol and treated with sodium hydroxide solution.

The yield was 73% when equimolecular quantities of *N*-methylbenzimidochloride and *NN'*-diphenylbenzamidine interacted in pyridine for 1 day. Unchanged *NN'*-diphenylbenzamidine (98%) was recovered when an attempt was made to carry out the reaction in acetone in the presence of anhydrous potassium carbonate.

A solution of *N*-phenylbenzimidochloride (4.3 g.) and *N*-methyl-*N'*-phenylbenzamidine (8.4 g., 2 mols.) in dry benzene (300 c.c.) was kept for 9 days and filtered. Solvent was evaporated from the filtrate, and

the residue, on crystallisation from ethanol, afforded 1-methyl-2 : 3 : 4 : 5-tetraphenyl-1 : 3 : 5-triazapenta-1 : 4-diene (7.35 g., 94%), m. p. and mixed m. p. 148—149°. The benzene-insoluble solid, when dissolved in water and added to excess of aqueous ammonia, afforded *N*-methyl-*N'*-phenylbenzamidinium (3.2 g., 78%).

Double decomposition of an aqueous-ethanolic lactic acid solution of the triazapentadiene and aqueous sodium picrate yielded *NN'*-diphenylbenzamidinium picrate (65%), m. p. and mixed m. p. 217° (decomp.) (Found : N, 14.2; $C_8H_5O_7N_3$, 45.6. Calc. for $C_{19}H_{16}N_2, C_8H_5O_7N_3$: N, 13.95; $C_8H_5O_7N_3$, 45.7%). Equivalent quantities of the diamide and picric acid in benzene afforded yellow needles, m. p. 200—208°, after sintering at 160°; fractional crystallisation of this material from benzene yielded *NN'*-diphenylbenzamidinium picrate (44%), m. p. and mixed m. p. 216.5—217° (decomp.), and *N*-methyl-*N'*-phenylbenzamidinium picrate (14%), m. p. 165—167°, undepressed on admixture with the authentic compound.

1 : 2 : 3 : 4 : 5-*Pentaphenyl-1 : 3 : 5-triazapenta-1 : 4-diene* (VI).—A solution of *N*-phenylbenzimidochloride (5.4 g.) and *NN'*-diphenylbenzamidinium chloride (13.6 g., 2 mols.) in dry benzene (200 c.c.) was kept for 13 days, filtered from precipitated *NN'*-diphenylbenzamidinium chloride (7.2 g.), and evaporated under reduced pressure; the residue, on crystallisation from ethanol, afforded 1 : 2 : 3 : 4 : 5-*pentaphenyl-1 : 3 : 5-triazapenta-1 : 4-diene* (8.9 g., 79%) as pale yellow needles, m. p. 146.5—148°, raised by further crystallisation from ethanol to 149—150°, depressed to 130—133° on admixture with *NN'*-diphenylbenzamidinium chloride (Found : N, 9.15. $C_{32}H_{25}N_3$ requires N, 9.3%).

NN-Diphenylbenzamidinium was obtained in 34% yield by the aluminium chloride method (cf. Oxley, Partridge, and Short, *J.*, 1947, 1110) when the reactants were heated at 190—200° for 1 hour (cf. Oxley and Short, *J.*, 1949, 449).

1 : 2 : 4 : 5 : 5-*Pentaphenyl-1 : 3 : 5-triazapenta-1 : 3-diene* (IV).—The suspension obtained by interaction of *N*-phenylbenzimidochloride (2.7 g.) and *NN*-diphenylbenzamidinium chloride (6.8 g., 2 mols.) in benzene for 12 days was filtered and evaporated *in vacuo*. The residue, on being dissolved in ethanol and made alkaline with sodium hydroxide, slowly deposited dense clusters of yellow needles (5.2 g., 92%), m. p. 135—137°; recrystallisation from ethanol afforded 1 : 2 : 4 : 5 : 5-*pentaphenyl-1 : 3 : 5-triazapenta-1 : 3-diene*, m. p. 137.5—138° (Found : C, 85.3; H, 5.5; N, 9.3. $C_{32}H_{25}N_3$ requires C, 85.1; H, 5.5; N, 9.3%). The *picrate* crystallised as yellow prisms (from ethanol), m. p. 167—168° after sintering at 141° (Found : N, 12.1. $C_{32}H_{25}N_3, C_8H_5O_7N_3$ requires N, 12.4%).

1-*p*-*Chlorophenyl-2 : 4 : 5-triphenyl-1 : 3 : 5-triazapenta-1 : 3-diene* (XII).—A mixture of *N*-benzoyl-*N*-phenylbenzamidinium (7.5 g.) and thionyl chloride (3.3 g., 1.1 mols.) was kept at 20° for 5 days and then heated at 100° for 2 hours; *p*-chloroaniline (6.4 g., 2 mols.), dissolved in dry benzene (30 c.c.), was added, and the mixture kept for 4 days. The solid (5.6 g.) which separated, after crystallisation from dilute ethanolic sodium hydroxide and repeated recrystallisation from benzene-light petroleum (b. p. 80—100°), yielded 1-*p*-*chlorophenyl-2 : 4 : 5-triphenyl-1 : 3 : 5-triazapenta-1 : 3-diene* (1 g., 10%), m. p. 177—179°, as pale yellow needles (Found : N, 10.05; Cl, 8.5. $C_{26}H_{20}N_3Cl$ requires N, 10.25; Cl, 8.7%).

1 : 2 : 4 : 5-*Tetraphenyl-1 : 3 : 5-triazapenta-1 : 3-diene* (VIII).—(i) *N*-Benzoyl-*N'*-phenylbenzamidinium (7.5 g.) and phosphorus pentachloride (5.2 g., 1 mol.) reacted exothermally when mixed in dry, alcohol-free chloroform (40 c.c.). After 1 day, chloroform (25 c.c.) and ether (150 c.c.) were added, and the mixture rapidly extracted with water (3 × 50 c.c.) and dried ($MgSO_4$); on concentration under reduced pressure to about half its volume, the solution slowly yielded colourless prisms (2.1 g., 26%) which gradually decomposed above 160° (Found : labile Cl, 9.4. $C_{20}H_{15}N_2Cl$ requires Cl, 11.1%). A mixture of this substance (1 g.) with aniline (5 g., 17.5 mols.) dissolved in dry benzene (30 c.c.) was kept for 6 days; the precipitate which formed, after being dissolved in hot ethanol and treated with a slight excess of aqueous sodium hydroxide, afforded 1 : 2 : 4 : 5-*tetraphenyl-1 : 3 : 5-triazapenta-1 : 3-diene* (0.35 g., 30%) as pale yellow needles, m. p. 183.5—184° (Found : C, 83.1; H, 4.8; N, 11.3; *M* (Rast), 352. $C_{26}H_{21}N_3$ requires C, 83.15; H, 5.65; N, 11.2%; *M*, 375).

A solution of the base in ethanol, on the addition of aqueous hydrochloric acid, afforded the *hydrochloride*, colourless plates (from glacial acetic acid) which melted with effervescence at 250—254°, resolidified, and melted again at 300—306° (Found : N, 10.45. $C_{26}H_{22}N_3Cl$ requires N, 10.2%). The *picrate* crystallised as clusters of yellow needles from ethanol and had m. p. 190—191° (Found : N, 14.05. $C_{32}H_{24}O_7N_6$ requires N, 13.9%).

(ii) *N*-Benzoyl-*N'*-phenylbenzamidinium (6.85 g.), phosphorus pentachloride (5 g., 1.05 mols.), and aniline (2.35 g., 1.1 mols.) were boiled together in dry benzene for 4 hours. The precipitate (1.2 g.) was crystallised from dilute ethanolic sodium hydroxide; these crystals afforded a dilute lactic-acid-soluble fraction from which *NN'*-diphenylbenzamidinium (0.25 g., 4%) was isolated, and a dilute lactic-acid-insoluble fraction which after being crystallised from ethyl acetate-light petroleum (b. p. 80—100°) afforded 1 : 2 : 4 : 5-*tetraphenyl-1 : 3 : 5-triazapenta-1 : 3-diene* (0.25 g., 3%), m. p. and mixed m. p. 183—184°. The benzene mother-liquors after being evaporated *in vacuo* yielded a gum which smelt strongly of phenyl cyanide and from which a further quantity of the diamide (0.8 g., 9%), m. p. and mixed m. p. 183—184°, was obtained by crystallisation from dilute ethanolic sodium hydroxide.

(iii) *N*-Benzoyl-*N'*-phenylbenzamidinium (7.5 g.) and phosphorus pentachloride (5.45 g., 1.05 mols.), suspended in dry, alcohol-free chloroform (50 c.c.), gradually dissolved when kept at 20° for 1 hour; a solution of aniline (8.2 g., 3.5 mols.) in pure chloroform (50 c.c.) was added, and the mixture kept for 6 days. After removal of the phenylammonium chloride (5.85 g.) which crystallised, the solvent was evaporated under reduced pressure and the yellow gum which remained was crystallised from ethanol. Phenyl cyanide (1.4 g., 54%), b. p. 190—198°, was recovered from the mother-liquors by adding water and extracting with ether; it was characterised by conversion into *m*-nitrophenyl cyanide, m. p. and mixed m. p. 116—117°. The crystals (3.05 g.) from ethanol, when crystallised from dilute ethanolic sodium hydroxide and fractionally crystallised from ethanol, yielded 1 : 2 : 4 : 5-*tetraphenyl-1 : 3 : 5-*

triazapenta-1 : 3-diene (1.65 g., 17%), m. p. and mixed m. p. 182—183°, and *NN'*-diphenylbenzamidino (0.8 g., 12%).

(iv) A mixture of *N*-benzoyl-*N'*-phenylbenzamidino (7.5 g.), phosphorus pentachloride (5.45 g., 1.05 mols.), and anhydrous pyridine (5.95 g., 3 mols.) was heated at 100° for 135 minutes; aniline (4.65 g., 2 mols.) was added, and the heating continued for a further 90 minutes. The resulting semi-solid mass was extracted with hot water (150 c.c.), and the extract, which would have contained *N*-phenylbenzamidinium chloride had this been formed in the reaction, was made alkaline with aqueous ammonia; the precipitate (0.25 g.; m. p. 136—141°) afforded pure *NN'*-diphenylbenzamidino (0.15 g., 2%), m. p. and mixed m. p. 146—147°, on crystallisation from ethanol. Phenyl cyanide (1.5 g., 58%) was recovered from the ammoniacal mother-liquors by extraction with ether; no *N*-phenylbenzamidino was detected in this ethereal extract. The hot water-insoluble material when worked up in the usual way afforded *NN'*-diphenylbenzamidino (5.1 g., 75%) and 1 : 2 : 4 : 5-tetraphenyl-1 : 3 : 5-triazapenta-1 : 3-diene (0.5 g., 5%).

Attempted Synthesis of 1 : 2 : 3 : 4-Tetraphenyl-1 : 3 : 5-triazapenta-1 : 4-diene (VII).—A solution of *N*-benzoyl-*NN'*-diphenylbenzamidino (6.25 g.) and phosphorus pentachloride (3.8 g., 1.1 mols.) in dry benzene (150 c.c.) was boiled for 90 minutes. The solvent was evaporated at below 40° and the residue was shaken with saturated ethanolic ammonia (20 c.c.) for 20 hours. After removal of ammonium chloride, the filtrate was concentrated, and *NN'*-diphenylbenzamidino (2.8 g., 61%) crystallised.

Reaction of N-Phenylbenzimidochloride with N-Phenylbenzamidino.—(i) A solution of *N*-phenylbenzimidochloride (4.3 g.) and *N*-phenylbenzamidino (7.85 g., 2 mols.) in dry benzene (120 c.c.) was kept for 5 days. The solvent was evaporated, and the residue extracted with warm water (50 c.c.). Addition of aqueous ammonia to the aqueous extract afforded *N*-phenylbenzamidino (3.1 g., 79%), m. p. and mixed m. p. 112—113°. The water-insoluble material, which smelt strongly of phenyl cyanide, was dissolved in ethanol, made alkaline with aqueous sodium hydroxide, and poured into water. *NN'*-Diphenylbenzamidino was extracted from the precipitate by cold aqueous lactic acid and recovered as the base, m. p. and mixed m. p. 144—146° (3.35 g., 62%). Crystallisation from ethanol of the material insoluble in lactic acid afforded 1 : 2 : 4 : 5-tetraphenyl-1 : 3 : 5-triazapenta-1 : 3-diene (0.45 g., 6%), m. p. 183—184°, not depressed by authentic material (Found : N, 11.4. Calc. for C₂₆H₂₁N₃ : N, 11.2%).

(ii) After 1 day the yield of 1 : 2 : 4 : 5-tetraphenyl-1 : 3 : 5-triazapenta-1 : 3-diene was 3%.

(iii) In a repetition of this experiment in which the period of reaction was 4 days, the basic material which was sparingly soluble in lactic acid was fractionally crystallised from ethanol and eventually separated into 1 : 2 : 4 : 5-tetraphenyl-1 : 3 : 5-triazapenta-1 : 3-diene (5%), m. p. 181—183° not depressed by the authentic compound, and 1 : 2 : 4 : 5 : 6 : 7-hexaphenyl-1 : 3 : 5 : 7-tetra-azahepta-1 : 3 : 6-triene (0.7 g., 7%), m. p. 178—179° not depressed on admixture with the authentic compound (see below).

(iv) *N*-Phenylbenzimidochloride (6.5 g.) and *N*-phenylbenzamidino (11.8 g., 2 mols.) were allowed to react in anhydrous ether for 2 days and the solvent was evaporated at room temperature. *N*-Phenylbenzamidinium chloride (56%) was extracted from the residue with warm water; the insoluble material on fractional crystallisation from ethanol afforded 1 : 2 : 4 : 5 : 6 : 7-hexaphenyl-1 : 3 : 5 : 7-tetra-azahepta-1 : 3 : 6-triene (2.8 g., 17%), m. p. and mixed m. p. 178.5—179.5°, and *NN'*-diphenylbenzamidino (0.9 g., 11%). Benzanilide (0.35 g., 6%) and phenyl cyanide (0.4 g., 13%), which was characterised by conversion into its *m*-nitro-derivative, were recovered from the mother-liquors.

(v) When the reaction was conducted in dry, alcohol-free chloroform, the products isolated were *N*-phenylbenzamidino (48%), *NN'*-diphenylbenzamidino (24%), 1 : 2 : 4 : 5-tetraphenyl-1 : 3 : 5-triazapenta-1 : 3-diene (16%), and 1 : 2 : 4 : 5 : 6 : 7-hexaphenyl-1 : 3 : 5 : 7-tetra-azahepta-1 : 3 : 6-triene (9%).

(vi) *N*-Phenylbenzimidochloride (4.3 g.) and *N*-phenylbenzamidino (3.9 g., 1 mol.), when boiled for 2 hours in dry acetone in the presence of anhydrous potassium carbonate, yielded 1 : 2 : 4 : 5 : 6 : 7-hexaphenyl-1 : 3 : 5 : 7-tetra-azahepta-1 : 3 : 6-triene (1.8 g., 16%) and *NN'*-diphenylbenzamidino (1.2 g., 19%).

Reaction of Benzophenone Oxime Benzenesulphonate with N-Phenylbenzamidino.—A solution of the benzenesulphonate (Oxley and Short, *J.*, 1948, 1514) (27 g.) and *N*-phenylbenzamidino (31.4 g., 2 mols.) in dry, alcohol-free chloroform (300 c.c.) was warmed gently till the exothermic reaction had subsided, and then boiled for 30 minutes. The solvent was evaporated under reduced pressure; a hot aqueous extract (2 × 100 c.c.) of the residue afforded *N*-phenylbenzamidino (11.5 g., 73%) when made alkaline with aqueous ammonia. The water-insoluble gum was crystallised from ethanolic hydrochloric acid. A hot ethanolic solution of the crystals was made alkaline with aqueous sodium hydroxide, and a mixture of colourless and yellow needles (17.1 g.) separated on cooling. *NN'*-Diphenylbenzamidino was extracted from this mixture by heating with lactic acid (10 c.c.) and water (100 c.c.), filtering, and adding aqueous ammonia; the yield was 8.1 g. (38%). Crude lactic-acid-insoluble 1 : 2 : 4 : 5-tetraphenyl-1 : 3 : 5-triazapenta-1 : 3-diene (9 g., 30%), m. p. 179—182°, afforded the pure compound (6.6 g., 22%), m. p. and mixed m. p. 183.5—184°, after crystallisation from ethanol. The diamide prepared in this way was further characterised as its picrate, m. p. 190—191°, undepressed on admixture with the authentic compound.

Interaction of Benzanilide, Benzenesulphonyl Chloride, and N-Phenylbenzamidino.—A solution of benzanilide (4.9 g.) and benzenesulphonyl chloride (4.5 g., 1.03 mols.) in anhydrous pyridine (6 c.c., 3 mols.) was heated at 100° for 90 minutes; *N*-phenylbenzamidino (9.5 g., 1.95 mols.), dissolved in anhydrous pyridine (8 c.c.), was added, and the mixture heated for a further 3 hours. The residue left after evaporation of the pyridine under reduced pressure yielded, after crystallisation first from ethanol and then from dilute ethanolic sodium hydroxide, 1 : 2 : 4 : 5-tetraphenyl-1 : 3 : 5-triazapenta-1 : 3-diene

(VIII) (2.15 g., 23%), m. p. and mixed m. p. 183.5—184°. In another experiment, where the period of heating with *N*-phenylbenzamidide was 90 minutes, the yield was 17%.

Interaction of N-Benzoyl-N'-phenylbenzamidide, Benzenesulphonyl Chloride, and Aniline.—(i) A mixture of the benzamidide (7.5 g.), benzenesulphonyl chloride (4.4 g., 1 mol.), and anhydrous pyridine (6 g., 3 mols.) was heated at 100° for 2½ hours; aniline (4.65 g., 2 mols.) was added, and the mixture heated for a further 90 minutes. Next day the product was poured into water (250 c.c.) and concentrated hydrochloric acid (15 c.c.); the solid (4.3 g.) which separated gave *NN'*-diphenylbenzamidide (3.1 g., 46%), m. p. and mixed m. p. 146—147°, after being washed with ethanol and ether and crystallised from dilute ethanolic sodium hydroxide. The precipitate (0.55 g.) obtained on mixing the ethanol washings with the aqueous mother-liquors yielded benzanilide (0.35 g., 7%) after crystallisation from ethanol. From the remaining acid aqueous-alcoholic mother-liquors, phenyl cyanide (0.8 g., 31%), b. p. 189—193°, was isolated by extraction with ether and characterised as its *m*-nitro-derivative; *N*-phenylbenzamidide (1.6 g., 32%) was recovered by adding alkali.

(ii) The foregoing experiment was repeated with aniline (2.3 g., 1 mol.). The solid (5.2 g.) which separated when the reaction mixture was poured into water and hydrochloric acid afforded on crystallisation from dilute ethanolic sodium hydroxide and fractional crystallisation from ethanol *NN'*-diphenylbenzamidide (2.5 g., 37%) and 1 : 2 : 4 : 5-tetraphenyl-1 : 3 : 5-triazapenta-1 : 3-diene (VIII), m. p. and mixed m. p. 182—183° (0.05 g., 0.5%). Further fractional crystallisation from ethanol of the material in the first ethanol mother-liquors yielded benzanilide (0.4 g., 8%) and further *NN'*-diphenylbenzamidide (0.6 g., 9%). The aqueous hydrochloric acid mother-liquors gave crude *N*-phenylbenzamidide, m. p. 98—102° (1.15 g., 23%), on treatment with excess of aqueous ammonia; the pure compound (0.9 g., 18%) was obtained by crystallisation from light petroleum.

Interaction of N-Benzoyl-N'-phenylbenzamidide and Benzenesulphonyl Chloride.—A mixture of the benzamidide (7.5 g.), benzenesulphonyl chloride (4.4 g., 1 mol.), and anhydrous pyridine (6 g., 3 mols.) was heated at 100° for 2½ hours and poured into concentrated hydrochloric acid (15 c.c.) diluted with water (100 c.c.). Benzanilide (2.65 g., 54%) and phenyl cyanide (0.65 g., 28%) were recovered from an ethereal extract of the liquid. When dissolved ether was removed from the acid aqueous liquid, a solid (0.2 g.) separated; after crystallisation from dilute ethanolic sodium hydroxide this had m. p. 182.5—183.5°, undepressed on admixture with authentic 1 : 2 : 4 : 5-tetraphenyl-1 : 3 : 5-triazapenta-1 : 3-diene (VIII); the yield was 0.15 g. (1.6%). From the acid aqueous mother-liquor, benzenesulphonic acid was isolated as *S*-benzylthiuronium benzenesulphonate (77%), m. p. 147.5—148° (Chambers and Watt, *J. Org. Chem.*, 1941, 6, 376, record m. p. 147.5—148.5°).

Decomposition of 1 : 2 : 4 : 5-Tetraphenyl-1 : 3 : 5-triazapenta-1 : 3-diene (VIII).—(i) After the pure base (1 g.) had been heated at 190—200° for 1 hour, its m. p. had fallen to 178—180°; crystallisation from alcohol afforded the pure compound (0.9 g.), m. p. and mixed m. p. 182.5—183.5°. (ii) A mixture of the base (1.9 g.), phenylammonium benzenesulphonate (2.5 g., 2 mols.), and anhydrous pyridine (1.6 g., 4 mols.) was heated at 100° for 90 minutes, poured into water (100 c.c.), and acidified with hydrochloric acid. From the precipitate, *NN'*-diphenylbenzamidide (1.1 g., 80%), m. p. 138—142°, was obtained by dissolution in dilute ethanolic sodium hydroxide and dilution with water; recrystallisation from ethanol yielded the pure compound (0.85 g., 62%), m. p. and mixed m. p. 146—147°. On the addition of aqueous ammonia the acid solution yielded *N*-phenylbenzamidide (0.9 g., 92%), m. p. and mixed m. p. 115—116°, after recrystallisation from benzene-light petroleum. (iii) The base (1.9 g.) did not dissolve completely when heated at 100° with aniline (0.95 g., 2 mols.) for 90 minutes; unchanged diamidide (1.6 g., 84%) was recovered from the reaction mixture. (iv) A mixture of the base (1.9 g.), aniline (0.95 g., 2 mols.), and pyridine (1.2 g., 3 mols.) formed a homogeneous solution when heated at 100° for 90 minutes; the precipitate obtained on addition of dilute hydrochloric acid afforded unchanged diamidide (1.7 g., 90%), m. p. and mixed m. p. 183—184°, on crystallisation from dilute ethanolic sodium hydroxide. (v) The diamidide (1.9 g.), pyridinium benzenesulphonate (1.2 g., 1 mol.), and pyridine (1.6 g., 4 mols.), after being heated together at 100° for 90 minutes, yielded unchanged diamidide (1.75 g., 92%). (vi) A solution of the diamidide (1.9 g.) in ethylene glycol (65 c.c.), water (3 c.c.), and potassium hydroxide (4 g.) was boiled (160—162°) for 3 hours; the yellow solution became almost colourless. After removal of the solvent, the residue yielded benzoic acid (0.9 g., 74%). (vii) After being boiled for 4 hours with concentrated hydrochloric acid, the diamidide was largely (84%) recovered unchanged; extraction of the hydrochloric acid with ether afforded benzoic acid (10%). (viii) When 1 : 2 : 4 : 5-tetraphenyl-1 : 3 : 5-triazapenta-1 : 3-diene (1.9 g.) was boiled with potassium hydroxide (4 g.) in water (4 c.c.) and ethanol (20 c.c.) for 25 hours, unchanged diamidide (1.45 g., 76%), m. p. 183—184°, crystallised on cooling. The solid (0.25 g.), m. p. 95—102°, which separated on pouring of the mother-liquors into water afforded *N*-phenylbenzamidide (0.15 g., 15%), m. p. and mixed m. p. 112—114°, after crystallisation from light petroleum.

1-Methyl-2 : 3 : 4 : 5-tetraphenyl-1 : 3 : 5-triazapenta-1 : 4-diene (V) and *Hydrogen Chloride.*—(i) On addition of hydrochloric acid to a solution of the diene in ethanol and dilution with water, benzanilide (25%) was obtained; the mother-liquors afforded *N*-methyl-*N'*-phenylbenzamidide (46%), m. p. and mixed m. p. 131—133°, and unchanged diamidide (25%) on addition of aqueous ammonia and fractional crystallisation of the precipitate from ethanol. (ii) From a solution of the base in chloroform which had been saturated with hydrogen chloride and kept for 2 days, benzanilide (91%) and *N*-methyl-*N'*-phenylbenzamidide (86%) were isolated. (iii) On saturation with dry hydrogen chloride of a solution of 1-methyl-2 : 3 : 4 : 5-tetraphenyl-1 : 3 : 5-triazapenta-1 : 4-diene (15 g.) in dry benzene (250 c.c.), a heavy, orange oil separated. The mixture was kept for 4 hours, and the benzene layer decanted and evaporated to dryness under reduced pressure. *p*-Chloroaniline (1.3 g.), dissolved in benzene (100 c.c.), was added to the residue, and the mixture kept for 4 days. *p*-Chlorophenylammonium chloride (1.6 g.) which crystallised was separated, and the solid (2.5 g., 17%), m. p. 140—144°, which was obtained by evaporating the filtrate afforded on crystallisation from ethanol unchanged diamidide (2.1 g., 14%), m. p. and mixed m. p. 148.5—149.5°.

Free hydrogen chloride was removed from the precipitated oil at 0.5 mm. over sodium hydroxide, and the resulting gum (15 g.) was dissolved in dry benzene (200 c.c.) containing *p*-chloroaniline (4.6 g.). The precipitate (11.25 g.) which formed during 5 days was separated into water-soluble and water-insoluble fractions; the former afforded *N*-methyl-*N'*-phenylbenzamidide (2.4 g., 30%), m. p. and mixed m. p. 131—133°, by precipitation with aqueous ammonia; and the latter, on fractional crystallisation first from dilute ethanolic sodium hydroxide and then from light petroleum (b. p. 80—100°), yielded benzanilide (0.4 g., 5%), m. p. and mixed m. p. 162—163°, and *N*-*p*-chlorophenyl-*N'*-phenylbenzamidide (0.8 g., 7%), m. p. 120—121°, undepressed on admixture with an authentic specimen. The benzene solution was evaporated, and the residue separated by means of dilute aqueous lactic acid into soluble and insoluble fractions. *N*-Methyl-*N'*-phenylbenzamidide (0.5 g., 6%) was recovered from the soluble fraction. By fractional crystallisation of the insoluble fraction from ethanol, benzanilide (1.9 g., 25%) and unchanged diamidide (2.6 g., 17%), m. p. and mixed m. p. 148—149°, were recovered.

N-*p*-Chlorophenyl-*N'*-methylbenzamidide.—*N*-Methylbenzamidide (2.25 g.) was heated with thionyl chloride (2.4 g., 1.2 mols.) at 100° for 1 hour; excess of thionyl chloride was evaporated under reduced pressure at room temperature, and *p*-chloroaniline (4.25 g., 2 mols.), dissolved in dry benzene (50 c.c.), was added. The solid which separated during 4 days, after being basified with aqueous ammonia, yielded *N*-*p*-chlorophenyl-*N'*-methylbenzamidide (2.6 g., 63%), which crystallised as needles from light petroleum (b. p. 100—120°), and had m. p. 129—130° (Found: N, 11.25. $C_{14}H_{13}N_2Cl$ requires N, 11.45%). The picrate, needles from ethanol, had m. p. 179—180° (Found: N, 14.8. $C_{20}H_{16}O_7N_5Cl$ requires N, 14.8%).

1 : 2 : 4 : 5 : 6 : 7-Hexaphenyl-1 : 3 : 5 : 7-tetra-azahepta-1 : 3 : 6-triene (XV).—(i) A solution of *N*-benzoyl-*N'*-phenylbenzamidide (7.5 g.) and phosphorus pentachloride (5.45 g., 1.05 mols.) in dry, alcohol-free chloroform (50 c.c.) was shaken occasionally during 4 hours, and was then added dropwise at 0° to a solution of *NN'*-diphenylbenzamidide (23.8 g., 3.5 mols.) in pure chloroform (120 c.c.). *NN'*-Diphenylbenzamidinium chloride (18.9 g.) which had separated after 2 days was removed, and the yellow filtrate evaporated. The residue was stirred with dilute aqueous sodium hydroxide and then fractionally crystallised from ethanol to recover *NN'*-diphenylbenzamidide (4.65 g.) and a crop of yellow crystals (2.05 g.), m. p. 140—170°, which was separated into two fractions by means of hot aqueous lactic acid. The insoluble fraction (1.05 g.), m. p. 174—176°, afforded on crystallisation from ethanol 1 : 2 : 4 : 5 : 6 : 7-hexaphenyl-1 : 3 : 5 : 7-tetra-azahepta-1 : 3 : 6-triene (0.95 g., 7%) as yellow prisms, m. p. 178.5—179.5°, depressed to 160—165° on admixture with 1 : 2 : 4 : 5-tetraphenyl-1 : 3 : 5-triazapenta-1 : 3-diene [Found: C, 84.65; H, 5.85; N, 10.35%; *M* (Rast), 520. $C_{39}H_{30}N_4$ requires C, 84.45; H, 5.45; N, 10.1%; *M*, 554]. The lactic-acid-soluble fraction, after being basified with aqueous ammonia and crystallised from ethanol, gave 1 : 2 : 4 : 5-tetraphenyl-1 : 3 : 5-triazapenta-1 : 3-diene (0.8 g., 9%), m. p. and mixed m. p. 182—183°.

(ii) (cf. Ghadiali and Shah, *loc. cit.*) A solution of *N*-phenylbenzimidochloride (4.3 g.) in anhydrous ether was added slowly to a dry methanolic solution of *N*-phenylbenzamidide (7.85 g., 2 mols.), and the mixture kept for 5 days. The 1 : 2 : 4 : 5 : 6 : 7-hexaphenyl-1 : 3 : 5 : 7-tetra-azahepta-1 : 3 : 6-triene (2.6 g., 23%), m. p. and mixed m. p. 176—178°, which separated was collected. Evaporation of the filtrate and crystallisation of the water-insoluble fraction of the residue from ethanol afforded 1 : 2 : 4 : 5-tetraphenyl-1 : 3 : 5-triazapenta-1 : 3-diene (1.6 g., 21%), m. p. and mixed m. p. 182—183°. *N*-Phenylbenzamidide (4.25 g., 54%) was recovered from the water-soluble fraction.

1 : 2 : 4 : 5 : 6 : 7-Hexaphenyl-1 : 3 : 5 : 7-tetra-azahepta-1 : 3 : 6-triene (1 g.) was heated at 190—200° for 2 hours; the solid product was crystallised from ethanol and afforded the unchanged compound (0.85 g.), m. p. and mixed m. p. 178—179°. A solution of the triamidide (0.2 g.) in ethanol (15 c.c.), sodium hydroxide (0.1 g.), and water (0.5 c.c.) was boiled for 30 minutes and poured into water; the solid (0.19 g.) which was precipitated had m. p. 177—179°, undepressed on admixture with the triamidide. When equimolecular quantities of picric acid and the triamidide were mixed in ethanol and the solution was concentrated, 1 : 2 : 4 : 5-tetraphenyl-1 : 3 : 5-triazapenta-1 : 3-diene picrate (78%), m. p. 187—189°, crystallised; recrystallisation from ethanol afforded the pure picrate, m. p. and mixed m. p. 190—191°, in 59% yield. When a solution of the triamidide in ethanol was acidified with concentrated hydrochloric acid and poured into water, unchanged triamidide (63%), m. p. and mixed m. p. 176—178°, was precipitated.

An oil which slowly solidified was precipitated on saturating with hydrogen chloride a solution of the triamidide (0.75 g.) in benzene (30 c.c.). The benzene-insoluble solid, m. p. 245—250° (efferv.; second m. p. 295—300°), was crystallised from glacial acetic acid and gave 1 : 2 : 4 : 5-tetraphenyl-1 : 3 : 5-triazapenta-1 : 3-diene hydrochloride (0.45 g., 81%), m. p. 250—254° (efferv.; second m. p. 300—306°) (Found: N, 10.0. Calc. for $C_{28}H_{22}N_3Cl$: N, 10.2%). This hydrochloride was converted into the base, m. p. 182—183°, undepressed by authentic 1 : 2 : 4 : 5-tetraphenyl-1 : 3 : 5-triazapenta-1 : 3-diene. The benzene solution was evaporated to dryness under reduced pressure and the residue was dissolved in a solution of *p*-chloroaniline (0.35 g.) in benzene (25 c.c.). Next day, the solvent was evaporated; a solution of the resultant solid in water after being made alkaline with aqueous ammonia afforded *N*-*p*-chlorophenyl-*N'*-phenylbenzamidide (0.05 g., 12%), m. p. and mixed m. p. 121—122° after crystallisation from light petroleum.

Treatment of a solution of the triamidide in chloroform with hydrogen chloride afforded 1 : 2 : 4 : 5-tetraphenyl-1 : 3 : 5-triazapenta-1 : 3-diene hydrochloride in 67% yield.

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