43.   *Diamidides.   Part II.   2 : 4-Diaryltriazapentadienes.* *

By D. A. Peak.

A general method for the preparation of N-thiobenzoylbenzamidines (IV) has been developed and they have been shown to undergo fission by ammonia or primary amines, mainly by reaction at the amidino-carbon atom. When benzamidines are used instead of amines, the reaction gives rise to 2 : 4-diaryltriazapentadienes (III),* isolated as their relatively stable hydrated hydrochlorides.
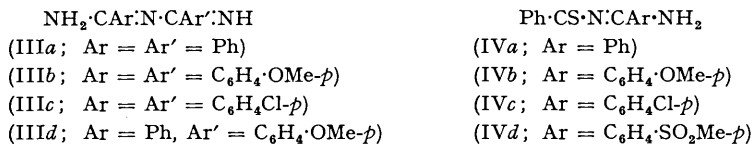
N-Benzoylbenzamidine also undergoes fission but considerably more slowly than its thio-analogue. The rate of reaction is much increased by the phenyl group on N'-benzoyl-N-phenylbenzamidine, although side-reactions occur. N-Benzoyl-N-phenylbenzamidine also reacts rapidly but probably by a different mechanism. N-2 : 4-Dinitrobenzoylbenzamidine reacts abnormally while N-benzenesulphonylbenzamidine is quite stable to ammonia. The mechanisms of these reactions are discussed.

Very small yields of 2 : 4-diphenyl-1 : 3 : 5-triazapenta-1 : 3-diene (IIIa) have been obtained by the reaction of benzamidine with ethyl benzimidate at 100° and by the pyrolysis of benzamidine in boiling benzene.

In Part I of this series * the preparation and properties were described of a number of diamidides of the types (I) and (II), in which at least one of the R, R', or R'' groups was Ph, and it was concluded that the conjugated structure of the latter type is an important

(I) NR:CPh·NR'·CPh:NR''   NRR'·CPh:N·CPh·NR''   (II)
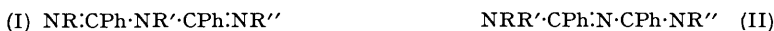
factor in stabilising the molecule or its ion. It therefore appeared probable that conjugated diamidides of the type (III), in which the nitrogen atoms carry no aryl or alkyl substituents, should be capable of existence. The present paper describes the preparation of a number of such diamidides, isolated as their fairly stable hydrated hydrochlorides.

NH$_2$·CAr:N·CAr':NH   Ph·CS·N:CAr·NH$_2$

(IIIa; Ar = Ar' = Ph)   (IVa; Ar = Ph)

(IIIb; Ar = Ar' = C$_6$H$_4$·OMe-p)   (IVb; Ar = C$_6$H$_4$·OMe-p)

(IIIc; Ar = Ar' = C$_6$H$_4$Cl-p)   (IVc; Ar = C$_6$H$_4$Cl-p)

(IIId; Ar = Ph, Ar' = C$_6$H$_4$·OMe-p)   (IVd; Ar = C$_6$H$_4$·SO$_2$Me-p)

The methods of Part I (*loc. cit.*) were not adaptable to the synthesis of the diamidides (III) owing to the instability of benzimidoyl chlorides or benzenesulphonates containing an unsubstituted imido-group. Of alternative routes, a promising one appeared to be the desulphurising amination of N-thiobenzoylbenzamidines (IV). The preparation of N-thiobenzoylbenzamidine (IVa) by condensation of thiobenzamide with phenyl cyanide in saturated ethereal hydrogen chloride was first described by Matsui (*Zentr.*, 1911, I, 982). He ascribed to it the structure of a dibenzimidoyl sulphide (NH:CPh·S·CPh:NH), but Rivier and Schneider (*Helv. Chim. Acta*, 1920, **3**, 115) preferred the structure (IV) on
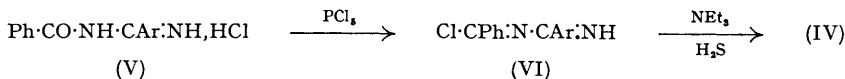
* For nomenclature see Part I, Cooper, Partridge, and Short, *J.*, 1951, 391.

physical evidence and Ishikawa (*J. Chem. Soc. Japan*, 1921, **42**, 579; *Abstr.*, 1921, **120**, 728) later provided chemical evidence for this structure. In subsequent papers (*Abstr.*, 1923, **124**, 926; *et seq.*) he extended the reaction to other thioamides and cyanides.

The preparation of *N*-thiobenzoylbenzamidine (IV*a*) itself was found to proceed smoothly by this method. The crude hydrochloride obtained from the condensation invariably contained thiobenzamide (presumably as its hydrochloride) which proved a troublesome impurity in the final product. Methods were therefore developed for the removal of the thiobenzamide by taking advantage of the greater basicity of the *N*-thiobenzoylbenzamidine. Separation by differential solubility in alkali was impracticable owing to the rapid destruction of the compound under these conditions.

When, however, the condensation was attempted with substituted thiobenzamides and phenyl cyanides, *e.g.*, *p*-methoxythiobenzamide and *p*-methoxyphenyl cyanide, it failed owing to the almost complete precipitation of the thioamide as its hydrochloride. Attempts to avoid this in model experiments with thiobenzamide and phenyl cyanide were unsuccessful. The ether could not be replaced by other compatible solvents, such as dioxan or chloroform, and the condensation also failed in anhydrous liquid hydrogen fluoride.
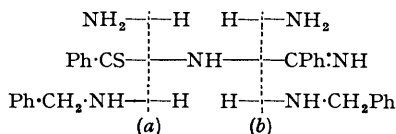
A more general method for the preparation of *N*-thiobenzoylbenzamidines was found in the following route, starting from *N*-benzoylbenzamidines which are readily available by the method of Titherley and Hughes (*J.*, 1911, **99**, 1507) :

$$\text{Ph·CO·NH·CAr:NH,HCl} \xrightarrow{\text{PCl}_5} \text{Cl·CPh:N·CAr:NH} \xrightarrow[\text{H}_2\text{S}]{\text{NEt}_3} \text{(IV)}$$

$$\text{(V)} \qquad\qquad\qquad\qquad \text{(VI)}$$

The *N*-benzoylbenzamidine was converted into its hydrochloride (V), which with phosphorus pentachloride in chloroform yielded the imidoyl chloride (VI). The latter was then converted without purification into the *N*-thiobenzoylbenzamidine by a chloroform solution of anhydrous triethylamine saturated with dry hydrogen sulphide. A somewhat similar method has been used by Kendall (B.P. 408,638) for the preparation of *N*-arylthioacylamides. This method afforded *N*-thiobenzoylbenzamidine (IV*a*), *p*-methoxy-*N*-thiobenzoylbenzamidine (IV*b*) and *p*-chloro-*N*-thiobenzoylbenzamidine (IV*c*). In the case of *p*-methylsulphonyl-*N*-thiobenzoylbenzamidine (IV*d*), although the characteristic red colour of the reaction mixture indicated its formation, the compound could not be isolated because of its rapid fission under the conditions of the experiment to *p*-methylsulphonylthiobenzamide.

With aniline and mercuric oxide, *N*-thiobenzoylbenzamidine (IV*a*) readily yielded 1 : 2 : 4-triphenyl-1 : 3 : 5-triazapenta-1 : 3-diene (II; R = R' = H, R'' = Ph). When, under the same conditions, alcoholic ammonia was used with mercuric oxide, mercuriammonium chloride, or lead hydroxide as desulphurising agent, the only products isolated were benzamidine (as picrate), thiobenzamide, cyaphenin (triphenyltriazine), an unidentified base $C_{20}H_{20}N_4S$ (as picrate), and 3 : 5-diphenyl-1 : 2 : 4-thiadiazole. The last product is a known oxidation product of thiobenzamide (Hofmann, *Ber.*, 1869, **2**, 646) and of *N*-thiobenzoylbenzamidine (Matsui, *loc. cit.*). The reason for the failure in this case was soon apparent in the rapid fission of the *N*-thiobenzoylbenzamidine with alcoholic ammonia in the absence of mercuric oxide, the red colour of the solution being discharged in a few minutes with the production of thiobenzamide and benzamidine. Under the same conditions *N*-thiobenzoylbenzamidine is stable to aniline for several days.

Thiobenzamide and benzamidine could arise by the fission of the molecule at either bond (*a*) or bond (*b*) or simultaneously at both :

$$\text{NH}_2\text{—}\!|\text{—H} \qquad \text{H—}\!|\text{—NH}_2$$
$$\text{Ph·CS—}\!|\text{——NH——}\!|\text{—CPh:NH}$$
$$\text{Ph·CH}_2\text{·NH—}\!|\text{—H} \qquad \text{H—}\!|\text{—NH·CH}_2\text{Ph}$$
$$\text{(a)} \qquad\qquad \text{(b)}$$

When the fission was carried out with benzylamine (1 mol.) the reaction proceeded rapidly at room temperature and the products isolated were thiobenzamide (58·5%), *N*-benzyl-benzamidine (78% as picrate), *N*-benzylthiobenzamide (3·5%), and benzamidine (1·2% as picrate). Under the mild conditions of the experiment it is unlikely that any substantial amount of either *N*-benzylbenzamidine or *N*-benzylthiobenzamide could have arisen as secondary product by the reaction of benzylamine with benzamidine and thiobenzamide respectively. Fission must therefore occur predominantly at (*b*).

It therefore appeared probable that fission with benzamidine instead of benzylamine would afford the required diamidide. This proved to be the case. Benzamidine (1 mol.) gradually decolourised a solution of *N*-thiobenzoylbenzamidine in ether with the formation of thiobenzamide and 2 : 4-diphenyl-1 : 3 : 5-triazapenta-1 : 3-diene (IIIa) which could be isolated from the reaction mixture either as its hydrochloride hemihydrate or as its picrate. The hydrochloride was a colourless solid of low solubility in water (*ca.* 0·4%) and of sufficient stability to be crystallised from water or ethanol without serious loss. In neutral aqueous solution it gradually deposited cyaphenin. In dilute hydrochloric acid it was rapidly converted into dibenzoylamine, a confirmation of its structure. In ethanol, the band at 247 mμ ($\varepsilon = 1\cdot73 \times 10^4$) in its ultra-violet absorption spectrum disappeared after several days, being replaced by a stronger band at 228 mμ ($\varepsilon = 2\cdot31 \times 10^4$). The curve had only a slight inflexion at *ca.* 280 mμ and the band at 330—345 mμ, associated in Part I (*loc. cit.*) with conjugation, was entirely absent. It therefore appears that both colour and this band are to be associated with the presence of at least one anilo-group in the conjugated system, since, in view of its comparative stability, the diamidide (IIIa) presumably exists in the conjugated form.
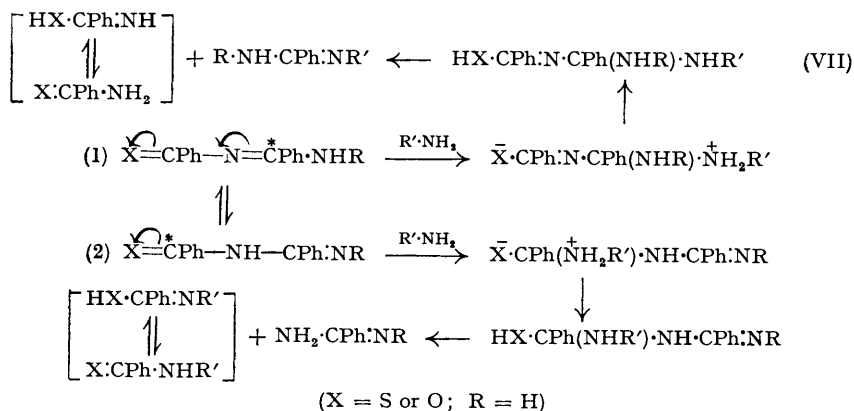
The hydrochloride melted partly at 204—206° to a turbid liquid which cleared sharply at 230°. These phenomena are due to its decomposition at its melting point into benz-amidinium chloride, phenyl cyanide, and cyaphenin, the clearing at 230° presumably being due to the melting of the cyaphenin. The picrate, similarly, partly melted at 188° to a turbid mixture of benzamidinium picrate and cyaphenin which cleared sharply at 230°. These decompositions are entirely analogous to the decomposition of 1 : 2 : 4-triphenyl-1 : 3 : 5-triazapenta-1 : 3-diene (II; R = R′ = H, R″ = Ph) to phenyl cyanide and *N*-phenylbenzamidine (Part I, *loc. cit.*). The free diamidide (IIIa) was isolated only as an oil which gradually deposited crystals of cyaphenin.

A similar procedure gave 2 : 4-di-*p*-methoxyphenyl-1 : 3 : 5-triazapenta-1 : 3-diene (IIIb) and 2 : 4-di-*p*-chlorophenyl-1 : 3 : 5-triazapenta-1 : 3-diene (IIIc) hydrochlorides as their hydrate and hemihydrate respectively. Reaction of *p*-methoxy-*N*-thiobenzoyl-benzamidine (IVb) with benzamidine gave the mixed diamidide, 2-*p*-methoxyphenyl-4-phenyl-1 : 3 : 5-triazapenta-1 : 3-diene (IIId), as its hydrochloride hydrate.

Neither *N*-phenyl- nor *N*-benzyl-benzamidine reacted with *N*-thiobenzoylbenzamidine at room temperature. In boiling benzene *N*-phenylbenzamidine reacted slowly with the formation of cyaphenin and a small yield of 1 : 2 : 4 : 5-tetraphenyl-1 : 3 : 5-triazapenta-1 : 3-diene (II; R = H, R′ = R″ = Ph) instead of the expected 1 : 2 : 4-triphenyl-1 : 3 : 5-triazapenta-1 : 3-diene (II; R = R′ = H, R″ = Ph). This could be accounted for in two ways. The triphenyldiamidide, as a mixed anhydride in the ammono-system, could disproportionate to a mixture of the tetraphenyldiamidide and the diphenyldi-amidide (IIIa), the latter being unstable under the conditions of the experiment. Altern-atively, also in its capacity as a mixed anhydride in the ammono-system, the triphenyl-diamidide could " acylate " unchanged *N*-phenylbenzamidine to the tetraphenyldiamidide with the liberation of benzamidine.

N-Benzoylbenzamidine underwent the same type of reactions as its thio-analogue but at a much slower rate. Over half was recovered unchanged after 5 days' reaction with alcoholic ammonia. After 7 days' reaction with benzylamine (1 mol.), *N*-benzyl-benzamidine (40·5% as picrate) was isolated as the major fission product. The com-plementary product, benzamide, was isolated although in poor yield. The alternative fission products, *N*-benzylbenzamide and benzamidine (as picrate), were also isolated in minor quantities. Fission thus occurs preponderatingly at the amidino-carbon–nitrogen bond as in the case of the thio-compound. The following sequences of reactions probably

occur in both cases, (1) being predominant because of the greater proportion of the conjugated tautomer :

$$\begin{bmatrix} \text{HX·CPh:NH} \\ \Updownarrow \\ \text{X:CPh·NH}_2 \end{bmatrix} + \text{R·NH·CPh:NR'} \longleftarrow \text{HX·CPh:N·CPh(NHR)·NHR'} \qquad \text{(VII)}$$

$$(1)\ \text{X=CPh—N=CPh·NHR} \xrightarrow{\text{R'·NH}_2} \bar{\text{X}}\text{·CPh:N·CPh(NHR)·}\overset{+}{\text{N}}\text{H}_2\text{R'}$$

$$\Updownarrow$$

$$(2)\ \text{X=CPh—NH—CPh:NR} \xrightarrow{\text{R'·NH}_2} \bar{\text{X}}\text{·CPh(}\overset{+}{\text{N}}\text{H}_2\text{R')·NH·CPh:NR}$$

$$\begin{bmatrix} \text{HX·CPh:NR'} \\ \Updownarrow \\ \text{X:CPh·NHR'} \end{bmatrix} + \text{NH}_2\text{·CPh:NR} \longleftarrow \text{HX·CPh(NHR')·NH·CPh:NR}$$

$$(\text{X} = \text{S or O} ;\ \text{R} = \text{H})$$

The greater reactivity of the thio-compound may be ascribed to the greater electromeric effect of the sulphur atom than of the oxygen atom.

It seemed possible that reactivity of the *N*-benzoylbenzamidines might be increased by the introduction of substituents which would promote electron deficiency at the carbon atoms marked above with an asterisk. In agreement with this, *N'*-benzoyl-*N*-phenyl-benzamidine (X = O, R = Ph above), in which the *N*-phenyl group might be expected to produce this effect by reducing the electron-donor capacity of the nitrogen atom, reacted more rapidly than *N*-benzoylbenzamidine with ammonia. *N*-Phenylbenzamidine (30% as picrate) and benzamide (19%) were isolated as fission products. In this case, however, part of the reaction takes an alternative course and one of the products of reaction was *N*-benzoylbenzamidine (32% as picrate). This could be formed by the loss of aniline instead of benzamide from the hypothetical intermediate (VII ; X = O, R = Ph, R' = H). In a similar manner, reaction with benzylamine gave *N*-phenylbenzamidine (17%) and *N'*-benzoyl-*N*-benzylbenzamidine (55·5%).

N-Benzoyl-*N*-phenylbenzamidine also reacted rapidly with alcoholic ammonia, the major product being benzanilide (68%). The reaction can scarcely be one of simple fission since the complementary fission product, benzamidine, could be isolated in only 2% yield (as picrate). Since phenyl cyanide was also identified qualitatively as a reaction product, this suggests the direct decomposition of *N*-benzoyl-*N*-phenylbenzamidine to benzanilide and phenyl cyanide in a manner exactly analogous to that postulated in Part I for the decomposition of the unstable 1 : 2 : 3 : 4-tetraphenyl-1 : 3 : 5-diazapenta-1 : 4-diene (I ; R = R' = Ph, R'' = H) :

$$\text{O=CPh—NPh—CPh=N—H} \longrightarrow [\text{HO·CPh:NPh} \rightleftharpoons \text{Ph·CO·NHPh}] + \text{Ph·CN}$$
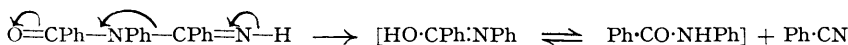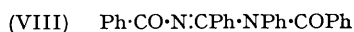
The isolation of *N*-benzoylbenzamidine (2% as picrate) indicates a certain amount of isomerisation of *N*-benzoyl-*N*-phenyl- to *N'*-benzoyl-*N*-phenyl-benzamidine during the reaction. The *N*-phenylbenzamidine isolated (5% as picrate) could arise from either isomer.

N'-Benzoyl-*N*-phenylbenzamidine used in the above experiments was prepared by the method of Wheeler, Johnson, and McFarland (*J. Amer. Chem. Soc.*, 1903, **25**, 787). Its preparation has also been reported by Beckmann and Sandel (*Annalen*, 1897, **296**, 293) by the action of aniline on *N*-benzoylbenzamidine at the boiling point of aniline. In view of the reactions of *N*-benzoylbenzamidine recorded above, this seemed an un-expected result. Repetition of this work proved it to be incorrect. No *N'*-benzoyl-*N*-phenylbenzamidine could be isolated and the products were the expected ones, *viz.*, benzamide (72%), benzanilide (3%), *N*-phenylbenzamidine (7·5%), *NN'*-diphenylbenz-

amidine (5·5%), and cyaphenin. The unexpectedly low yield of N-phenylbenzamidine and the considerable evolution of ammonia during the reaction indicate that the reaction is more complex than one of simple fission. The NN'-diphenylbenzamidine presumably arose as a secondary product from the reaction of N-phenylbenzamidine and aniline or by fission of the initially formed N'-benzoyl-N-phenylbenzamidine by aniline.

Wheeler *et al.* (*loc. cit.*) showed that the primary product of benzoylation of N-phenyl-benzamidine was N-benzoyl-N-phenylbenzamidine. So readily does this rearrange to N'-benzoyl-N-phenylbenzamidine, particularly under the catalytic influence of traces of acid, that great difficulty was experienced in the preparation of a pure sample by their method. It was ·found that benzoylation in chloroform in the presence of an excess of triethylamine readily afforded a pure product.

N-Phenylbenzamidine in ether with benzoyl chloride (1 mol.) gave NN'-dibenzoyl-N-phenylbenzamidine (VIII), the structure of which was shown by its hydrolysis to a mixture of benzanilide and dibenzoylamine. It reacted fairly rapidly with alcoholic ammonia to give benzanilide and N-benzoylbenzamidine.

(VIII) $\quad$ Ph·CO·N:CPh·NPh·COPh $\qquad$ $O_2N\langle\rangle$CO·N:CPh·NH$_2$ $\quad$ (IX)

with NO$_2$ substituent shown above the ring.

In a further attempt to increase the reactivity of the molecule by the introduction of an electrophilic group, N-2 : 4-dinitrobenzoylbenzamidine (IX) was prepared. It possessed unusual properties in that, although nearly colourless in the crystalline form, it melted to a deep red liquid, becoming colourless again on solidifying. Rapid evaporation of its pale yellow solution in ether also produced red films which quickly became colourless. Completely satisfactory analyses were not obtained. With alcoholic ammonia, purple tars were produced from which no recognisable fission products could be isolated.

N-Benzenesulphonylbenzamidine, in spite of the strong electrophilic properties of the benzenesulphonyl group, did not react with alcoholic ammonia, no benzamidine or benzene-sulphonamide being detectable after 2 days. This result, although at first sight unexpected, is in fact in accord with theoretical predictions. The electron drifts postulated above for the first stage of fission of N-benzoylbenzamidines would, if carried to completion, result in the canonical structure (X) for N-thiobenzoylbenzamidine. The corresponding structure (XI) for N-benzenesulphonylbenzamidine involves a negative charge on the central nitrogen atom which would tend to reduce the electron deficiency of the adjacent carbon atom.

PhC·N:CPh $\longleftrightarrow$ Ph·C:N·CPh $\qquad\qquad$ PhS·N:CPh $\rightleftharpoons$ PhS·N·CPh
$\quad\parallel\quad\ \ |$ $\qquad\qquad\quad\ |\qquad\ \parallel$ $\qquad\qquad\ \ \parallel\quad\ |$ $\qquad\qquad\quad\ |\qquad\parallel$
$\quad$ S $\quad$ NH$_2$ $\qquad\qquad$ S$^-$ $^+$NH$_2$ $\qquad\qquad\ $ O $\quad$ NH$_2$ $\qquad\qquad$ O$_-$ $_+$NH$_2$
$\qquad\qquad$ (X) $\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad$ (XI)

Before the work described above, an unsuccessful attempt had been made to prepare 2 : 4-diphenyl-1 : 3 : 5-triazapenta-1 : 3-diene (IIIa) by the reaction of ethyl benzimidate with benzamidine on analogy with the formation of amidines from imidic esters and ammonia :

$$\text{NH:CPh·OEt} + \text{NH}_2\text{·CPh:NH} \longrightarrow \text{NH}_2\text{·CPh:N·CPh:NH} + \text{EtOH}$$
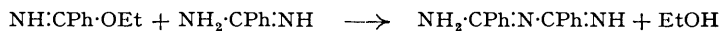
With the recognition of the low solubility of the hydrochloride of the diamidide (IIIa) and its extremely characteristic melting-point behaviour which would permit easy isolation and identification of small quantities of the compound, this reaction was reinvestigated. It was found that no appreciable reaction occurred in ether after several days either at room temperature or at the boiling point. Heating the reactants at 100° in the absence of solvent, however, gave, besides cyaphenin, a small amount (2·6%) of the diamidide (IIIa) hydrochloride. It appears certain that under these conditions a considerable proportion of the diamidide would be destroyed. To cover the possibility of an un-favourable equilibrium, the experiment was repeated in refluxing ether, the condensate being returned to the reaction mixture over sodium wire to remove ethanol continuously.

No diamidide formation was detected. A similar procedure in benzene gave a small amount (1·05%). In neither experiment was the sodium appreciably attacked. Finally, it was found possible to obtain a small amount of the diamidide (IIIa) hydrochloride (0·35%) simply by heating benzamidine in benzene solution under reflux. It is presumably formed by elimination of a molecule of ammonia from two molecules of benzamidine. The significantly lower yield in this case makes it appear probable that ethyl benzimidate, when present, plays some part in the formation of the diamidide.

EXPERIMENTAL

N-*Benzoyl*-p-*methoxybenzamidine*.—*p*-Methoxybenzamidinium chloride (28 g.) was shaken with water (28 c.c.), 5N-sodium hydroxide (56 c.c.), and chloroform (80 c.c.) until all solid had disappeared. The chloroform layer was separated and the aqueous layer re-extracted with further chloroform (3 × 80 c.c.). The combined chloroform extracts were dried (Na$_2$SO$_4$), treated with charcoal, and filtered. An aliquot was estimated by titration with 0·1N-hydrochloric acid, and the residue (290 c.c. containing 19·13 g. of *p*-methoxybenzamidine) was mixed with phenyl benzoate (25·25 g., 1 mol.). Crystalline solid separated after 30 minutes but redissolved overnight. The chloroform was then removed *in vacuo* at <50° and the residue heated at 50° for 4 hours. The mixture was cooled and dissolved in ether (300 c.c.), and the solution was extracted with ice-cold 0·67N-hydrochloric acid (900 c.c.). Basification of the aqueous acid layer at 0° with 5N-sodium hydroxide precipitated an oil which quickly solidified. Crystallisation of the crude solid (26 g.; m. p. 101—103°) from ethanol afforded N-*benzoyl*-p-*methoxybenzamidine* (19·2 g.) as square plates, m. p. 104—105° (Found : N, 10·8. C$_{15}$H$_{14}$O$_2$N$_2$ requires N, 11·0%).

N-*Benzoyl*-p-*chlorobenzamidine*.—*p*-Chlorobenzamidinium benzenesulphonate (3·13 g.) (Oxley, Partridge, Robson, and Short, *J.*, 1946, 763) was dissolved in hot water (75 c.c.), the solution was cooled, and 5N-sodium hydroxide (3 c.c.) added. The precipitated amidine was taken up in chloroform (3 × 50 c.c.), estimated by titration of an aliquot, and condensed as before with phenyl benzoate (1·1 mols.), finally at 70° for 3 hours. Crystallisation of the crude base (1·88 g.) from light petroleum (b. p. 80—100°) gave N-*benzoyl*-p-*chlorobenzamidine* (1·40 g.) as small prisms, m. p. 121—122° (Found, after drying at 100° : N, 10·8. C$_{14}$H$_{11}$ON$_2$Cl requires N, 10·8%).

N-*Benzoyl*-p-*methylsulphonylbenzamidine*.—*p*-Methylsulphonylbenzamidine (10·7 g.) and phenyl benzoate (10·0 g.) were ground together and the mixture was heated at 70—75° for 6 hours. Gradual melting and resolidification occurred during this period, and a strong smell of phenol developed. The product was dissolved in hot ethanol (110 c.c.). On cooling, N-*benzoyl*-p-*methylsulphonylbenzamidine* separated as prisms (11·2 g.), m. p. 161—162° raised to 163—164° by recrystallisation from ethanol (Found : N, 9·0. C$_{15}$H$_{14}$O$_3$N$_2$S requires N, 9·3%). Concentration of the ethanolic mother-liquor gave a second *substance*, probably NN'-dibenzoyl-*p*-methylsulphonylbenzamidine, m. p. 223—224° (Found : N, 7·0. C$_{22}$H$_{18}$O$_4$N$_2$S requires N, 6·9%).

Phenyl 2 : 4-*Dinitrobenzoate*.—A mixture of 2 : 4-dinitrobenzoic acid (27·2 g.), phenol (12·0 g.), and phosphorus oxychloride (27·2 g.) was heated slowly under reflux. Evolution of hydrogen chloride did not begin until 115° and was complete in 40 minutes. The product was poured into water, the water decanted, and the semi-solid residue dissolved in ether. The ethereal solution was washed twice with water and then with an excess of dilute sodium hydrogen carbonate solution. It was dried and concentrated to *ca.* 75 c.c. *Phenyl* 2 : 4-*dinitrobenzoate* (15·7 g.) slowly crystallised in prisms, m. p. 82—83° unchanged by further crystallisation from ether (Found : N, 9·35. C$_{13}$H$_8$O$_6$N$_2$ requires N, 9·7%).

N-(2 : 4-*Dinitrobenzoyl*)*benzamidine*.—Phenyl 2 : 4-dinitrobenzoate (11·50 g.) was added to a solution of benzamidine (4·8 g., 1 mol.) in pure chloroform (160 c.c.). A deep purple colour immediately developed. The condensation was completed as usual by heating the mixture at 60° for 3 hours in the absence of chloroform. The deep purple product was dissolved in acetone (50 c.c.) and acidified with 5N-ethanolic hydrogen chloride which precipitated a pale brown crystalline solid (11·4 g.). Recrystallisation of a small portion of this from methanol–ether afforded N-(2 : 4-*dinitrobenzoyl*)*benzamidinium chloride* as almost colourless prisms, m. p. 194—196° (Found : N, 16·5. C$_{14}$H$_{11}$O$_5$N$_4$Cl requires N, 16·0%). The remaining crude chloride was shaken with chloroform and dilute sodium hydrogen carbonate. Evaporation of the chloroform left a deep purple liquid which dissolved in ether to give a pale yellow solution. Concentration of the ether solution gave the free *base* as pale-yellow prisms, m. p.

108—110° (Found : N, 17·25, 17·1. $C_{14}H_{10}O_5N_4$ requires N, 17·8%). The compound melted to a deep red liquid and rapid evaporation of solutions produced red oils which became pale yellow on storage.

Preparation of N-*Thiobenzoylbenzamidine from Thiobenzamide and Phenyl Cyanide.*—A solution of thiobenzamide (10·28 g.) and phenyl cyanide (7·73 g.) in dry ether (350 c.c.) was saturated at 0° with dry hydrogen chloride and kept at room temperature. A red oil rapidly separated which slowly crystallised. After 5 days the orange-yellow crystals of N-thiobenzoyl-benzamidinium chloride were separated and washed by decantation. The crude product (19·1 g.), contaminated with thiobenzamide, probably in the form of its hydrochloride, was triturated with 2N-hydrochloric acid (50 c.c.) to convert the latter into free thiobenzamide, filtered, and washed on the filter with acetone. The residual solid (17·0 g.) was shaken with ether and an aqueous solution of potassium hydrogen carbonate (5 g.) until all the solid was in solution. The deep red ethereal layer was dried (Na_2SO_4) and evaporated *in vacuo*. Recrystallisation of the residue from benzene–light petroleum (b. p. 80—100°) gave the pure compound as long red needles (10·72 g., 59·5%).

Alternatively, the thiobenzamide could be removed by extracting the crude free bases into ether as above and reprecititating the N-thiobenzoylbenzamidinium chloride by the addition of ethanolic hydrogen chloride. Under these conditions, the thiobenzamide was not reprecipitated. The yield of pure material was the same by both methods.

Preparation of N-*Thiobenzoylbenzamidines from* N-*Benzoylbenzamidines.*—N-Benzoyl-benzamidine (2·0 g.) (Titherley and Hughes, *loc. cit.*) was dissolved in acetone (10 c.c.), and ethanolic hydrogen chloride was added until the solution was acid to moist Congo-red paper. Addition of ether to incipient turbidity caused the separation of the hydrochloride in small needles (2·2 g.). This was suspended in pure chloroform (10 c.c.) and heated under reflux with phosphorus pentachloride (2·4 g.). Hydrogen chloride was evolved and a clear yellow solution resulted after 15 minutes. The solution was evaporated *in vacuo* and traces of phosphorus halides were removed by evaporating twice after the addition of dry toluene. The residual yellow oil was redissolved in pure chloroform (10 c.c.) and added drop-wise at 0° to a solution of triethylamine (1·7 g., 2 mols.) in pure chloroform (20 c.c.) which had previously been saturated with dry hydrogen sulphide at 0°. An immediate red colour developed. Hydrogen sulphide was passed through the solution during the addition and subsequently for a further 3 hours. The clear red solution was kept overnight at room temperature and then washed with water. The chloroform was separated from the aqueous layer and a small interfacial layer of dark oil, dried and evaporated *in vacuo*. The residue was distributed between water and ether, and the ethereal layer was dried and acidified with ethanolic hydrogen chloride. The precipitated hydrochloride (0·91 g.) was worked up as in the previous experiment, affording N-thiobenzoyl-benzamidine (0·53 g., 25%), m. p. 73—74°, undepressed by the material prepared from thiobenzamide and phenyl cyanide.

In the same way N-benzoyl-*p*-methoxybenzamidine yielded *p-methoxy-*N-*thiobenzoyl-benzamidine* (48·5%), red leaflets (from benzene–light petroleum), m. p. 116—117° (Found : C, 66·9; H, 5·1; N, 10·4 $C_{15}H_{14}ON_2S$ requires C, 66·7; H, 5·2; N, 10·4%).

N-Benzoyl-*p*-chlorobenzamidine similarly yielded *p-chloro-*N-*thiobenzoylbenzamidine* (26%), red needles (from benzene or chloroform), m. p. 146—147° (Found : C, 61·3; H, 4·15; N, 9·9. $C_{14}H_{11}N_2ClS$ requires C, 60·8; H, 4·0; N, 10·2%).

Attempted Preparation of p-*Methylsulphonyl-*N-*thiobenzoylbenzamidine.*—N-Benzoyl-*p*-methylsulphonylbenzamidinium chloride (2·03 g.; m. p. 210—212°) appeared to react only partially with phosphorus pentachloride in chloroform. After 30 minutes, the insoluble residue (0·66 g.) was filtered off. It dissolved in water and the solution soon crystallised. The product (0·36 g.; m. p. 170—172°) crystallised from ethanol in glistening plates, m. p. 171—172° (Found : C, 59·8; H, 4·5; N, 4·7. $C_{15}H_{13}O_4NS$ requires C, 59·4; H, 4·3; N, 4·6%). It was soluble in dilute sodium hydroxide solution and was reprecipitated by acetic acid. The same material was obtained by crystallisation of N-benzoyl-*p*-methylsulphonylbenzamidinium chloride from 95% ethanol. The compound is therefore *benzoyl-*p-*methylsulphonylbenzoylamine.*

The chloroform-soluble material was processed in the usual manner. Treatment with a chloroform solution of triethylamine saturated with hydrogen sulphide caused an immediate red colouration but nothing corresponding to the desired product could be obtained by working-up the mixture after 90 minutes. When the solution was kept, the red colour changed to deep yellow and yellow crystals separated. These were *p*-methylsulphonylthiobenzamide (0·40 g.), m. p. 214—215° (decomp.) after crystallisation from butanol and undepressed by authentic material (see below). Addition of water to the chloroform mother-liquor afforded a further

quantity (0·20 g.) of *p*-methylsulphonylthiobenzamide. The chloroform layer was evaporated to dryness and the residue extracted with ether. Evaporation of the extract and crystallisation of the residue from benzene gave thiobenzamide (0·19 g.), m. p. 113—114° undepressed by authentic material.

p-*Methylsulphonylthiobenzamide.*—*p*-Methylsulphonylphenyl cyanide (0·90 g.) was dissolved in a mixture of chloroform (15 c.c.) and triethylamine (1·5 g., 3 mols.) and saturated at 0° with a stream of dry hydrogen sulphide. The solution rapidly became yellow and solid separated. After 6 hours the solid (0·96 g.; m. p. 212—214°) was isolated. Two recrystallisations from butanol furnished the pure *thioamide* as pale yellow needles, m. p. 217—218° (decomp.) (Found : N, 6·5. $C_8H_9O_2NS_2$ requires N, 6·5%).

1 : 2 : 4-*Triphenyl*-1 : 3 : 5-*triazapenta*-1 : 3-*diene* (II; R = R′ = H, R″ = Ph).—A mixture of *N*-thiobenzoylbenzamidine (0·48 g.), mercuric oxide (1·81 g.), aniline (1·0 g.), and absolute ethanol (10 c.c.) was shaken until the supernatant liquid had changed from red to pale yellow (*ca.* 1 hour) and the mercuric oxide had become dark brown. The reaction mixture was filtered and the filtrate was evaporated *in vacuo*. Trituration of the partly crystalline residue with ether–light petroleum afforded 1 : 2 : 4-triphenyl-1 : 3 : 5-triazapenta-1 : 3-diene (0·40 g.; m. p. *ca.* 145°). Recrystallisation from ether and from ethanol gave the pure product, m. p. 146—147° undepressed by material prepared from *N*-phenylbenzimidoyl chloride and benzamidine (Part I, *loc. cit.*).

Fission of N-*Thiobenzoylbenzamidine.*—(a) *With ammonia.* *N*-Thiobenzoylbenzamidine (0·12 g.) was dissolved in 2N-absolute ethanolic ammonia (3 c.c.). The red colour had been completely discharged after 30 minutes. Evaporation *in vacuo* and trituration of the residue with water (2 c.c.) gave thiobenzamide (0·06 g., 88%), m. p. and mixed m. p. 116—117°. Evaporation of the mother-liquor and treatment with picric acid in benzene afforded benzamidinium picrate (0·13 g., 74%), m. p. and mixed m. p. 238—239°.

In the presence of mercuric oxide, mercuriammonium chloride, or lead hydroxide, there were isolated in addition cyaphenin, 3 : 5-diphenyl-1 : 2 : 4-thiadiazole, needles (from methanol), m. p. 88—89° (Found : C, 70·4; H, 4·3; N, 11·9. Calc. for $C_{14}H_{10}N_2S$: C, 70·6; H, 4·2; N, 11·8%), and an unidentified sulphur-containing *picrate*, yellow needles (from ethanol), m. p. 187—188°) (Found : C, 54·1, 53·7; H, 4·1, 4·2; N, 16·9, 16·8. $C_{20}H_{20}N_4S,C_6H_3O_7N_3$ requires C, 54·0; H, 4·0; N, 17·0%).

(b) *With benzylamine.* A solution of *N*-thiobenzoylbenzamidine (3·84 g.) and benzylamine (1·71 g., 1 mol.) in dry ether (40 c.c.) became almost colourless after a few hours. A small amount of flocculent insoluble precipitate was filtered off and the filtrate shaken with N-hydrochloric acid (20 c.c.). The aqueous layer was made alkaline to Titan-yellow with lithium hydroxide, and the liberated oil (3·16 g.) isolated with ether. Treatment of this oil with ethanolic picric acid gave *N*-benzylbenzamidinium picrate (5·50 g., 78%), m. p. and mixed m. p. 168—170°. Concentration of the ethanolic mother-liquor afforded a small quantity (0·07 g.) of benzamidinium picrate, m. p. and mixed m. p. 238—239° after recrystallisation from *iso*propanol. A further quantity (0·12 g.) was obtained by addition of picric acid to the aqueous lithium hydroxide layer and acidification with acetic acid.

The original ethereal layer was evaporated and the residue extracted with boiling water (2 × 20 c.c.). The extracts on cooling afforded thiobenzamide (1·28 g., 58·5%), m. p. and mixed m. p. 115—116°. The insoluble residue, crystallised from 50% ethanol (20 c.c.), gave *N*-benzylthiobenzamide as plates (0·12 g.), m. p. and mixed m. p. 84—85°.

2 : 4-*Diphenyl*-1 : 3 : 5-*triazapenta*-1 : 3-*diene* (IIIa).—*N*-Thiobenzoylbenzamidine (4·8 g.) and benzamidine (2·4 g., 1 mol.) were dissolved in dry ether (95 c.c.), and the solution kept overnight. The red colour had almost disappeared and a white solid had separated. This was collected and identified by m. p. and mixed m. p. as cyaphenin (1·52 g.). A further small amount of cyaphenin (0·18 g.) separated on cooling the solution to −70°. 5N-Ethanolic hydrogen chloride was added to the filtrate until it was acid to moist Congo-red paper, and the precipitated solid (3·55 g.) collected. Evaporation of the filtrate and crystallisation of the residue from benzene afforded thiobenzamide (1·0 g.). The precipitated solid was triturated with water (13 c.c.) to remove benzamidinium chloride, and the undissolved solid was collected and washed with water (5 c.c.). The crude dry product (2·81 g.) was dissolved in warm absolute ethanol (40 c.c.) and filtered. Addition of acetone (80 c.c.) gave 2 : 4-*diphenyl*-1 : 3 : 5-*triazapenta*-1 : 3-*diene hydrochloride hemihydrate* as feathery needles (2·16 g.), m. p. 204—206° to a turbid liquid clearing at 230° [Found : C, 62·5; H, 5·6; N, 15·5; Cl, 13·8; H_2O (Karl Fischer), 3·4. $C_{14}H_{14}N_3Cl,0·5H_2O$ requires C, 62·5; H, 5·6; N, 15·6; Cl, 13·2; H_2O, 3·3%]. The m. p. behaviour was unaltered by further crystallisation. The compound melted completely

when placed in a bath at 215°, then became turbid, and again cleared at 230°. A portion (100 mg.), fused at 205—210°, gave a semi-solid melt which smelt strongly of phenyl cyanide. Extraction of the melt with cold methanol afforded cyaphenin (22 mg.) as insoluble residue. The methanol extract was evaporated to dryness and the residue dissolved in water. Addition of lithium picrate solution gave benzamidinium picrate (107 mg., 82%).

The hydrochloride had a low solubility in water (*ca.* 1 in 250). The neutral saturated solution slowly deposited cyaphenin as small needles. Addition of a drop of 5N-hydrochloric acid to the saturated solution caused immediate reprecipitation of the hydrochloride as fine needles. Overnight these disappeared and were replaced by stouter, opaque needles, m. p. 146—147°, identified by mixed m. p. as dibenzoylamine.

Addition of an ethereal picric acid solution instead of ethanolic hydrogen chloride to the reaction mixture afforded the *picrate* as yellow prisms, m. p. 188° to a turbid melt clearing at 230°, after crystallisation from acetone–ether (Found : C, 52·7; H, 3·6; N, 18·8. $C_{14}H_{13}N_3, C_6H_3O_7N_3$ requires C, 53·0; H, 3·55; N, 18·6%). The picrate melted completely if placed in a bath at 205°, then became turbid, and cleared at 230°. Colourless needles sublimed up the m. p. tube during heating, and sublimation of the picrate at 200°/2 mm. gave pure cyaphenin. Under the same conditions benzamidinium picrate sublimes unchanged.

The free base, prepared by shaking the hydrochloride with ether and dilute sodium hydrogen carbonate solution, was an oil which gradually deposited cyaphenin over a period of days.

2 : 4-Di-p-methoxyphenyl-1 : 3 : 5-triazapenta-1 : 3-diene (IIIb).—A solution of *p*-methoxybenzamidine (0·56 g.) and *p*-methoxy-N-thiobenzoylbenzamidine (1·0 g.) in ether (250 c.c.) became almost colourless after 40 hours. Precipitation with ethanolic hydrogen chloride afforded a hygroscopic solid (1·2 g.). This was triturated with water (7 c.c.), and then washed with acetone, and the resulting pale yellow solid (0·62 g.) crystallised from methanol–acetone. *2 : 4-Di-p-methoxyphenyl-1 : 3 : 5-triazapenta-1 : 3-diene hydrochloride monohydrate* (0·34 g.) separated in colourless prisms, m. p. 176—178° to a clear melt (Found : C, 57·15; H, 6·0; N, 12·4; Cl, 10·7. $C_{16}H_{18}O_2N_3Cl, H_2O$ requires C, 56·9; H, 5·9; N, 12·4; Cl, 10·5%).

2 : 4-Di-p-chlorophenyl-1 : 3 : 5-triazapenta-1 : 3-diene (IIIc).—In the same way *p*-chlorobenzamidine (0·47 g.) and *p*-chloro-N-thiobenzoylbenzamidine (0·82 g.) in ether (200 c.c.) afforded *2 : 4-di-p-chlorophenyl-1 : 3 : 5-triazapenta-1 : 3-diene hydrochloride hemihydrate* (0·48 g.), feathery needles (from methanol–acetone), m. p. 214—215° to a turbid melt not clearing below 260°. Repeated recrystallisation from methanol–acetone raised the m. p. to 220—221° (Found : C, 49·8; H, 3·9; N, 12·6. $C_{14}H_{12}N_3Cl_3, 0·5H_2O$ requires C, 49·7; H, 3·85; N, 12·4%)

2-p-Methoxyphenyl-4-phenyl-1 : 3 : 5-triazapenta-1 : 3-diene (IIId).—A solution of benzamidine (0·44 g.) and *p*-methoxy-N-thiobenzoylbenzamidine (1·0 g.) in ether (25 c.c.) was kept for 24 hours. The almost colourless solution was filtered from a little solid and acidified with 5N-ethanolic hydrogen chloride (1 c.c.). The sticky precipitate was separated by decantation, then triturated with water (5 c.c.), and the residual solid washed with acetone. Crystallisation from methanol–ether gave the *hydrochloride monohydrate* as fluffy needles (0·115 g.) which melted if placed in a bath at 140° but on slow heating did not melt till 163—165°, then giving a turbid liquid (Found : C, 58·9; H, 5·85; N, 13·8. $C_{15}H_{16}ON_3Cl, H_2O$ requires C, 58·5; H, 5·85; N, 13·7%).

Fission of N-*Thiobenzoylbenzamidine with* N-*Phenylbenzamidine.*—No reaction occurred between *N*-thiobenzoylbenzamidine and *N*-phenylbenzamidine in ether at room temperature over a period of several days. Accordingly, a solution of the former (0·96 g.) and the latter (0·76 g.) in benzene (8 c.c.) was heated under reflux until it was colourless (60 hours). Cyaphenin (0·45 g.) crystallised on cooling. The benzene filtrate was shaken with N-hydrochloric acid (5 c.c.), and the hydrochloride which separated was collected. This material (20 mg.; m. p. *ca.* 250°) was converted into the free base with aqueous sodium hydroxide, isolated with ether, and crystallised from methanol. It separated in needles, m. p. 181—182° not depressed by 1 : 2 : 4 : 5-tetraphenyl-1 : 3 : 5-triazapenta-1 : 3-diene (Part I; *loc. cit.*).

Fission of N-*Benzoylbenzamidine.*—(a) *With ethanol.* N-Benzoylbenzamidine (0·50 g.) was heated under reflux for 24 hours with absolute ethanol (5 c.c.). The solid which separated during heating was identified by m. p. and mixed m. p. as cyaphenin (0·10 g.). The filtrate was evaporated and the residue shaken with ether (3 c.c.) and 2N-hydrochloric acid (2 c.c.). Basification of the aqueous acid layer gave recovered *N*-benzoylbenzamidine (0·21 g.), m. p. 102—103° after crystallisation from light petroleum. Evaporation of the ethereal layer afforded a small quantity of liquid which distilled completely at 212—230° (bath-temp.) without leaving any residue of benzamide and was identified as ethyl benzoate by conversion into benzanilide, m. p. and mixed m. p. 160°.

(b) *With ammonia.* A solution of N-benzoylbenzamidine (0·50 g.) in 2N-ethanolic ammonia (5 c.c.) was kept for 7 days at room temperature and then evaporated *in vacuo*. The residue dissolved completely in 2N-hydrochloric acid (2 c.c.). Basification afforded unchanged N-benzoylbenzamidine (0·27 g.). Addition of picric acid to the mother-liquor gave a crude picrate, repeated crystallisation of which afforded benzamidinium picrate (0·13 g.), m. p. and mixed m. p. 237—238°.

(c) *With benzylamine.* A solution of N-benzoylbenzamidine (0·90 g.) in absolute ethanol (10 c.c.) and benzylamine (0·43 g., 1 mol.) was kept for 7 days at room temperature and then evaporated *in vacuo*, finally over sulphuric acid. The residue was shaken with ether and 2N-hydrochloric acid. The ethereal layer was evaporated and the residue (0·08 g.) crystallised from benzene, affording benzamide (0·03 g.), m. p. and mixed m. p. 126—127°. Evaporation of the benzene mother-liquor and crystallisation of the residue from aqueous ethanol gave N-benzylbenzamide (0·02 g.), m. p. 103—104° not depressed by authentic N-benzylbenzamide, m. p. 104—105°. The hydrochloric acid layer was made alkaline to Titan-yellow with solid lithium hydroxide, and the precipitated oil isolated with benzene. Treatment with alcoholic picric acid and recrystallisation of the crude product from ethanol gave N-benzylbenzamidinium picrate (0·71 g., 40·5%), m. p. and mixed m. p. 168—169°. The aqueous lithium hydroxide mother-liquor, neutralised with picric acid, afforded benzamidinium picrate (0·03 g.), m. p. 236—237° undepressed by authentic material.

(d) *With aniline at 180°.* A mixture of N-benzoylbenzamidine (4·5 g.) and aniline (1·9 g., 1 mol.) was heated gradually to 180°. Vigorous evolution of ammonia commenced at *ca.* 170° but soon slackened and appeared complete after 2 hours. The dark melt solidified on cooling and was extracted with ether (20 c.c.). The insoluble residue (2·41 g.) was separated by differential solubility in ethanol into cyaphenin (0·52 g.), m. p. and mixed m. p. 233—234°, and benzamide (1·75 g., 72%), m. p. and mixed m. p. 125—126°.

The ethereal extract was evaporated and the residual grey solid (1·52 g.), freed from traces of aniline *in vacuo* over sulphuric acid, was extracted with N-hydrochloric acid (10 c.c.). Crystallisation of the insoluble residue from 70% ethanol afforded benzanilide (0·12 g., 3%), m. p. and mixed m. p. 160—162°. The acid extract quickly deposited prisms (0·34 g., 5·5%), m. p. 289—292° after crystallisation from aqueous hydrochloric acid. Sachs and Bry (*Ber.*, 1901, **34**, 122) record m. p. 286° for *NN'*-diphenylbenzamidinium chloride, and the identity was confirmed by conversion into the free base, m. p. 146—147° undepressed by *NN'*-diphenyl-benzamidine. The hydrochloric acid mother-liquor, basified with aqueous sodium hydroxide, afforded a solid which after two crystallisations from light petroleum melted at 111—113° (0·30 g., 7·5%), undepressed by N-phenylbenzamidine. Its identity was confirmed by conversion into its picrate, m. p. 148—149° undepressed by N-phenylbenzamidinium picrate, m. p. 148·5°.

N-*Benzoyl*-N-*phenylbenzamidine.*—A suspension of N-phenylbenzamidine (9·8 g.) in pure chloroform (100 c.c.) and triethylamine (6·06 g., 1·02 mols.) was cooled, and redistilled benzoyl chloride (7·03 g., 1 mol.) added with stirring at 0—1°. When the solid had gone into solution, the reaction mixture was washed with an excess of ice-cold dilute sodium carbonate solution, and the chloroform layer was dried (Na₂SO₄) and evaporated *in vacuo*. The gummy residue was triturated with ether (100 c.c.), and the resulting solid (16·0 g.; m. p. 99—100°) was recrystallised by dissolving it in cold chloroform (26 c.c.) and adding ether (100 c.c.). The product separated in needles (5·55 g.), which partly melted to a turbid liquid at 102—104°, resolidified, and then remelted at 139—140°. It melted completely when placed in a bath at 110°. Repeated recrystallisation gave material melting initially to a turbid melt at 104—105° (Found : N, 9·5. Calc. for $C_{20}H_{16}ON_2$: N, 9·3%). In agreement with Wheeler *et al.* (*loc. cit.*) it gave benzanilide on hydrolysis with aqueous ethanolic hydrochloric acid and isomerised to N'-benzoyl-N-phenylbenzamidine when crystallised from ethanol.

Reaction of N'-*Benzoyl*-N-*phenylbenzamidine.*—(a) *With ammonia.* N'-Benzoyl-N-phenyl-benzamidine (0·60 g.) was shaken with 2N-ethanolic ammonia (10 c.c.) until all was in solution. After 24 hours the solution was evaporated *in vacuo*. The residue dissolved completely in ether (15 c.c.), showing the absence of more than traces of starting material. The ethereal solution was extracted with N-hydrochloric acid (3 c.c.). Evaporation of the ethereal layer and crystallisation of the residue from benzene afforded benzamide (0·045 g., 19%), m. p. and mixed m. p. 125—126°. The acid layer was basified with 5N-sodium hydroxide, and the oil (0·40 g.) isolated with ether. Conversion into the picrate by saturated ethereal picric acid solution gave an immediate precipitate (0·29 g., 32%), m. p. 198—200°, identified by mixed m. p. as N-benzoylbenzamidinium picrate. When kept, the ethereal mother-liquor deposited N-phenylbenzamidinium picrate (0·25 g., 30%).

(b) *With benzylamine.* A solution of *N'*-benzoyl-*N*-phenylbenzamidine (0·90 g.) and benzylamine (0·31 c.c.) in absolute ethanol was heated under reflux for 12 hours. The ethanol was blown off in a stream of air, and the residue triturated with 2N-acetic acid and ether (5 c.c. of each). The mixture soon deposited prisms (0·52 g., 55·5%), recrystallisation of which from ethanol afforded *N'*-benzoyl-*N*-benzylbenzamidine, m. p. 149—150° (Found : C, 80·7; H, 5·4; N, 8·9. Calc. for $C_{21}H_{18}ON_2$: C, 80·3; H, 5·7; N, 8·9%). Beckmann and Sandel (*loc. cit.*) record m. p. 147° for this compound. Basification of the aqueous acetic acid layer gave *N*-phenylbenzamidine (0·10 g., 17%), m. p. and mixed m. p. 114—115°.

The same product was formed slowly at room temperature.

Reaction of N-*Benzoyl-*N-*phenylbenzamidine with Ammonia.*—A solution of *N*-benzoyl-*N*-phenylbenzamidine (3·0 g.) in 2N-ethanolic ammonia was kept at room temperature. No unchanged material could be detected after 24 hours. The residue after evaporation *in vacuo* was shaken with ether and water. The insoluble solid (1·21 g.) was identified as benzanilide. The aqueous layer was alkaline to brilliant-yellow. Acidification with saturated ethanolic picric acid afforded benzamidinium picrate (0·10 g., 2%), m. p. 236—237° raised by authentic material. Basification of the hydrochloric acid extract of the ethereal layer gave a crude base (0·21 g.), separated by conversion by saturated ethereal picric acid into *N*-benzoylbenz-amidinium picrate (0·09 g., 2%), m. p. and mixed m. p. 199—200° after recrystallisation from ethanol, and *N*-phenylbenzamidinium picrate (0·20 g., 5%), m. p. and mixed m. p. 148—149°. The original ethereal layer on evaporation afforded an oily solid, separated by extraction with light petroleum into phenyl cyanide (0·12 g.), characterised as its *m*-nitro-derivative, and crude benzanilide (0·13 g.). The total yield of benzanilide amounted to 68%. Extraction of the combined evaporated mother-liquors with hot benzene did not yield any benzamide.

NN'-*Dibenzoyl-*N-*phenylbenzamidine.*—Benzoyl chloride (3·01 g., 1 mol.) was added to a suspension of *N*-phenylbenzamidine (4·2 g., 1 mol.) in dry ether (100 c.c.), and the mixture shaken occasionally during 1 hour. The precipitate of *N*-phenylbenzamidinium chloride was filtered off and the filtrate evaporated to dryness. Crystallisation of the residue from ethanol (15 c.c.) gave NN'-*dibenzoyl-*N-*phenylbenzamidine* (1·06 g.) as plates, m. p. 141—142°, considerably depressed by *N'*-benzoyl-*N*-phenylbenzamidine (Found : N, 6·8. $C_{27}H_{20}O_2N_2$ requires N, 6·9%).

A solution of the above compound (0·50 g.) in 5N-hydrochloric acid (10 c.c.) and ethanol (5 c.c.) was shaken overnight and the solid (0·45 g.) collected. Extraction with dilute sodium hydroxide solution gave benzanilide (0·13 g.), m. p. and mixed m. p. 160—161°. Acidification of the alkaline extract gave dibenzoylamine (0·10 g.), m. p. and mixed m. p. 145—147°.

The dibenzoyl compound (0·5 g.) was dissolved in 2N-ethanolic ammonia (10 c.c.) by shaking for 90 minutes and the solution kept overnight. Evaporation *in vacuo* and trituration of the residue with N-hydrochloric acid (5 c.c.) afforded, after crystallisation from ethanol, benzanilide (0·13 g.), m. p. and mixed m. p. 160—161°. The acid filtrate was basified with sodium hydroxide, and the resulting gummy precipitate isolated with ether. Conversion into the picrate afforded, after crystallisation from ethanol, yellow needles (0·10 g.), m. p. 202—203° identified by mixed m. p. as *N*-benzoylbenzamidinium picrate.

Attempted Reaction of N-*Benzenesulphonylbenzamidine with Ammonia.*—*N*-Benzenesulphonyl-benzamidine was satisfactorily prepared by Barber's method (*J.*, 1943, 101) for *p*-nitrobenzene-sulphonylbenzamidine. The compound (0·5 g.) was shaken with 2N-ethanolic ammonia (10 c.c.) for 3 days. Unchanged material (0·44 g.) was recovered. No trace of benzamidine or benzene-sulphonamide could be detected in the ethanolic mother-liquor.

Condensation of Benzamidine and Ethyl Benzimidate.—(*a*) Benzamidine (2·53 g.) was dissolved in dry ether (154 c.c.), and ethyl benzimidate (3·14 g., 1 mol.) added. After 5 days an aliquot (20 c.c.) was made acid to moist Congo-red paper by the addition of 5N-ethanolic hydrogen chloride (2 c.c.). The precipitate (0·85 g.) dissolved readily in cold water (2 c.c.), indicating the absence of more than traces of the diamidide (III*a*) hydrochloride.

The remaining ethereal solution was evaporated and the residue heated at 100° for 24 hours. On cooling and dilution with ether (40 c.c.), a small amount of solid (0·015 g.; m. p. 233—234°) separated and was identified as cyaphenin. The filtrate was acidified with 5N-ethanolic hydrogen chloride (4 c.c.) and the precipitated solid collected. Trituration with water (3·0 c.c.) left an insoluble residue (0·26 g.) which crystallised from ethanol–acetone in fine needles (0·13 g., 2·6%), showing the characteristic m. p. behaviour of the diamidide (III*a*) hydrochloride.

(*b*) A solution of benzamidine (2·39 g.) and ethyl benzimidate (3·26 g., 1·1 mols.) in dry ether (500 c.c.) was heated under reflux and the condensate returned to the flask through a Soxhlet extractor containing sodium wire. After 4 days the sodium remained practically

unattacked and working-up as above of an aliquot (50 c.c.) indicated the absence of more than traces of diamidide (IIIa) hydrochloride.

The ether was therefore replaced by dry benzene and heating under reflux continued for 3 days. The benzene solution was cooled, cyaphenin (0·49 g.) filtered off, and the filtrate acidified with 5N-ethanolic hydrogen chloride (4·5 c.c.). Only a slight precipitate formed. The benzene was accordingly evaporated *in vacuo* and the residue triturated with ether (30 c.c.). The residual pale-yellow solid (2·37 g.) was triturated with water (4 c.c.), and the residue extracted with cold methanol (10 c.c.). The insoluble residue (0·84 g.; m. p. 233—234°) was identified as cyaphenin. The methanol filtrate was evaporated *in vacuo*. Crystallisation of the residue from ethanol–acetone afforded the diamidide (IIIa) hydrochloride (0·05 g., 1·05%).

Pyrolysis of Benzamidine in Benzene.—A solution of benzamidine (1·27 g.) in dry benzene (270 c.c.) was heated under reflux for 3 days, ammonia being evolved throughout. Worked up as above, the reaction yielded diamidide (IIIa) hydrochloride in 0·35% yield.