Price, Re. 1] [*Vol. 7, Part X, pp. 205 to 223.*

JOURNAL

OF THE

Indian Institute of Science.

CONTENTS.

DR. M. O. FORSTER, F.R.S., CHAIRMAN OF EDITORIAL BOARD.

CONDENSATION OF AROMATIC AMINES WITH CHLOROFORM OR CARBON TETRACHLORIDE IN THE PRESENCE OF FINELY DIVIDED COPPER.

By R. C. Shah.

In 1904, Ullmann[1] was able to show that finely divided copper (Natur-kupfer C, copper-bronze) readily eliminates the iodine from aromatic iodo-compounds yielding cuprous iodide and derivatives of diphenyl. A few years later[2] it was shown that the reagent acts catalytically in condensing halogenated benzenes with metallic phenoxides, thus providing a simple method for preparing substituted diphenyl oxides; still later[3] Ullmann showed that the copper reacts catalytically in removing hydrogen halides from aromatic amines and halogenated benzenes, yielding substituted diphenylamines. Thus aniline and *p*-chloronitrobenzene yield *p*-nitrodiphenylamine. The yields are quite good when potassium carbonate is added, as this not only neutralises the hydrogen halide formed during the reaction, but also stabilises any carboxylic acids by converting them into potassium salts, and the method is a general one for preparing arylanthranilic acids.[4] With halogen or methoxy-substituted amines the addition of amyl alcohol is advisable. In a similar manner 2-chloro-4-nitrobenzoic acid condenses at 180° with sodium phenoxide yielding 5-nitrodiphenylether-2-carboxylic acid.[5] In some cases a mixture of copper and potassium iodide or even cuprous iodide gives good results.[6]

The replacement of halogen in aromatic halides by hydroxyl is readily effected by heating the compound with sodium acetate at 140–150° in the presence of a little copper powder. By this process salicylic acid is readily obtained from *o*-chlorobenzoic acid; and halogen can be replaced by carboxyl by heating the halogenated benzene with aqueous alcoholic potassium cyanide and cuprous cyanide at 200°.[7]

So far no systematic study appears to have been made of reactions between aromatic amines and simple aliphatic halogen derivatives in the presence of finely divided copper. Two isolated observations on such reactions have been noticed in the literature. Tchichibabin and Ryumshin[8] used copper powder in the preparation of ethyl-and

[1] *Annalen*, 1904, **332**, 38.
[2] Ullmann and Spangel, *ibid.*, 1906, **350**, 83.
[3] *Ibid.*, 1907, **355**, 312.
[4] Goldberg, *Ber.*, 1906, **39**, 1691; 1907, **40**, 2448.
[5] Ullmann and Wagner, *Annalen*, 1907, **355**, 361.
[6] Goldberg, *Ber.*, 1907, **40**, 4541.
[7] Rosemund and Struck, *Ber.*, 1919, **52**, 1749.
[8] *J. Russ. Phys. Chem. Soc.*, 1915, **47**, 1247.

benzyl-pyridines from pyridine and the alkyl halides, and Hartung[1] has shown that aniline and carbon tetrachloride condense much more readily in the presence of a copper-mercury couple than in its absence, yielding diphenyl-*p*-aminobenzamidine.

The experiments recorded in this paper prove conclusively that copper-bronze has a marked catalytic effect on condensations between chloroform or carbon tetrachloride and bases of the type of aniline, *p*-toluidine or *p*-anisidine. The following seven reactions have been examined in the presence of finely divided copper.

1. Aniline and carbon tetrachloride.
2. *p*-Toluidine and carbon tetrachloride.
3. *m*-Toluidine and carbon tetrachloride.
4. *p*-Aminophenol and carbon tetrachloride.
5. *p*-Anisidine and carbon tetrachloride.
6. Aniline and bromoform.
7. Diphenylamine and chloroform.

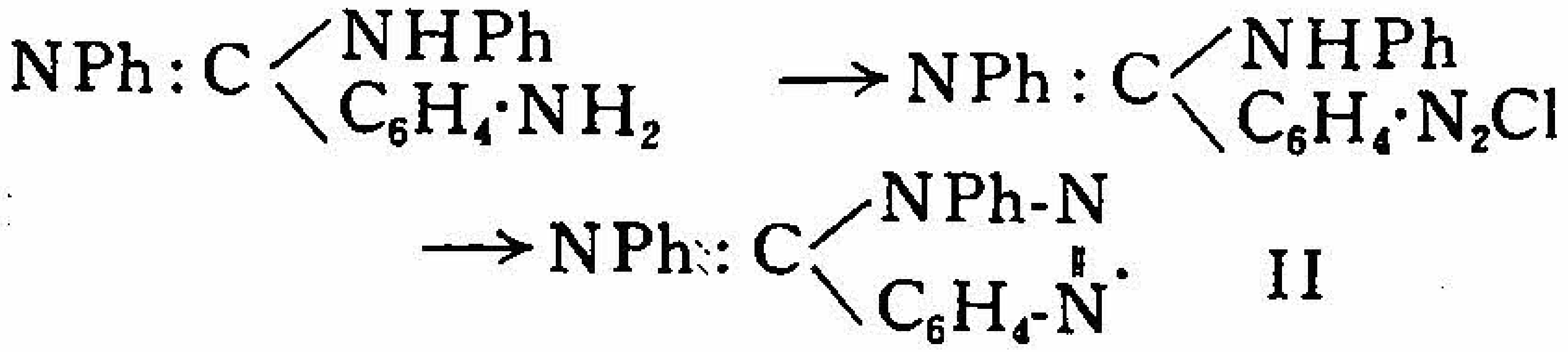
I. Aniline and Carbon Tetrachloride.

By heating the components during 30 hours at 170° Hofmann[2] obtained diphenyl-*p*-aminobenzamidine, $PhN : C \begin{cases} NHPh \\ C_6H_4{\cdot}NH_2 \end{cases}$, but no mention is made of the yield. By the addition of 0·1 per cent. of copper-bronze it has been found possible to carry out the reaction at 60–75° and to obtain a 45 per cent. yield of the para-compound, together with a 10 to 12 per cent. yield of the isomeric diphenyl-*o*-aminobenzamidine, a compound not hitherto isolated. The latter compound crystallises from alcohol in colourless needles melting at 115–116°, forms a picrate, a yellow crystalline monohydrochloride and a colourless crystalline dihydrochloride as well as acetyl and benzoyl derivatives, which however could not be obtained in a crystalline form.

The constitution of the ortho-compound is based upon the following :—

(*a*) Its reaction with nitrous acid and ready conversion into a 1 : 2 : 3-phentriazine derivative

I



$$NPh : C \begin{cases} NHPh \\ C_6H_4{\cdot}NH_2 \end{cases} \longrightarrow NPh : C \begin{cases} NHPh \\ C_6H_4{\cdot}N_2Cl \end{cases} \longrightarrow NPh : C \begin{cases} NPh\text{-}N \\ C_6H_4\text{-}N \end{cases} \quad II$$

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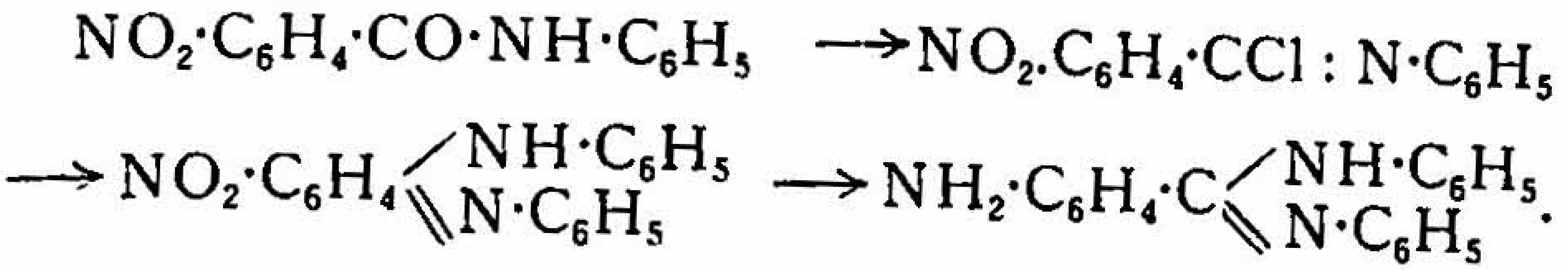
[1] *J. Chem. Soc.*, 1918, 113, 183.

[2] *Proc. Roy. Soc.*, 1858, 9, 284.

(*b*) Its hydrolysis with a mixture of glacial acetic and hydrochloric acids when the products formed are anthranilic acid and a base melting at 143° and identical with Korner's 2-methyl-3-phenyl-4-quinazolone.[1]

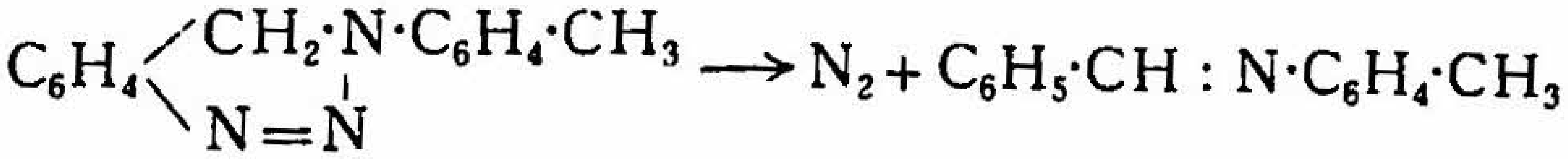
(*c*) Its synthesis from *o*-nitrobenzanilide by the following series of reactions :—



$$NO_2{\cdot}C_6H_4{\cdot}CO{\cdot}NH{\cdot}C_6H_5 \longrightarrow NO_2.C_6H_4{\cdot}CCl : N{\cdot}C_6H_5$$

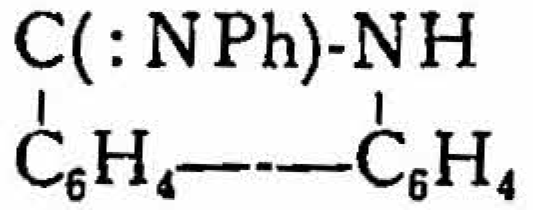
$$\longrightarrow NO_2{\cdot}C_6H_4\left\langle\begin{matrix}NH{\cdot}C_6H_5\\ N{\cdot}C_6H_5\end{matrix}\right. \longrightarrow NH_2{\cdot}C_6H_4{\cdot}C\left\langle\begin{matrix}NH{\cdot}C_6H_5\\ N{\cdot}C_6H_5\end{matrix}\right. .$$

The phentriazine melting at 145°, when heated alone or under reduced pressure, evolves nitrogen, and if the reaction is analogous to that described by Busch,[2]



$$C_6H_4\left\langle\begin{matrix}CH_2{\cdot}N{\cdot}C_6H_4{\cdot}CH_3\\ N{=}N\end{matrix}\right. \longrightarrow N_2 + C_6H_5{\cdot}CH : N{\cdot}C_6H_4{\cdot}CH_3$$

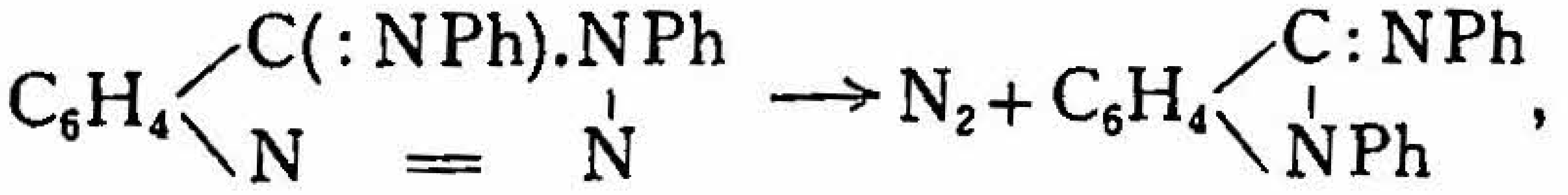
the product should be



$$\begin{matrix}C(:NPh)\text{-}NH\\ | \qquad\quad |\\ C_6H_4\text{———}C_6H_4\end{matrix}$$

which on hydrolysis would give phenanthridone.[3]

It is possible, however, that elimination of nitrogen proceeds as follows :—



$$C_6H_4\left\langle\begin{matrix}C(:NPh).NPh\\ N \quad = \quad N\end{matrix}\right. \longrightarrow N_2 + C_6H_4\left\langle\begin{matrix}C:NPh\\ NPh\end{matrix}\right. ,$$

and this product on hydrolysis should give phenyl-anthranil.

When the triazine derivative is warmed with hydrochloric acid and copper powder nitrogen is evolved and an uncrystallisable powder melting at 55–60° is obtained.

The identity of the quinazolone derivative with Körner's compound was proved by synthesis of the latter from *o*-aminobenzanilide[4] and determining the mixed melting point. Kolbe, and also Pictet and Gouset describe the *o*-aminobenzanilide as crystallising in glistening needles and melting at 131–132°. The compound, however, exists in two forms; when crystallised from benzene it forms colourless glistening needles melting at 117–118°, but if the temperature is maintained at 117–120° it resolidifies and then melts at the tempera-

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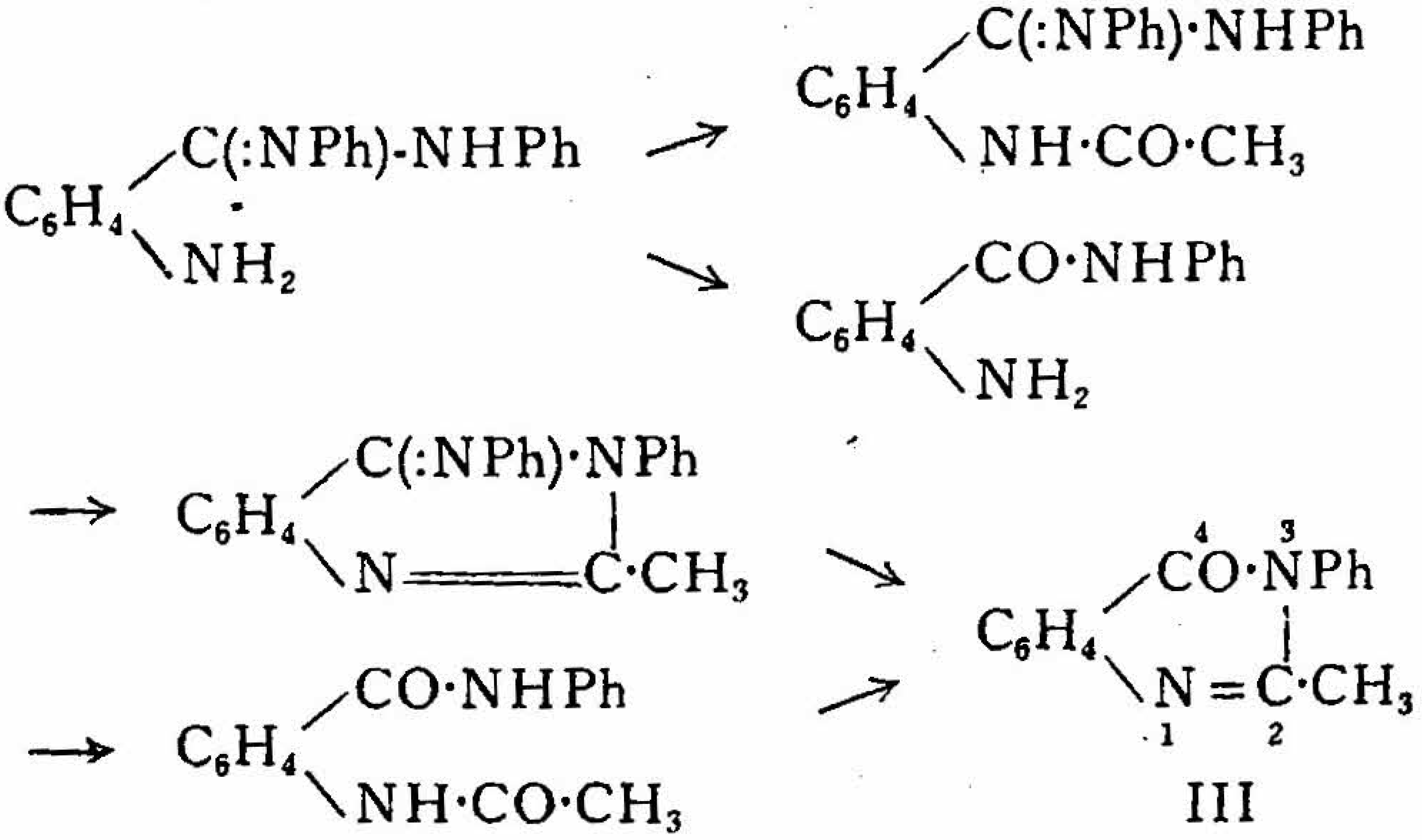
[1] *J. Pr. Chem.*, 1887, [II], **36**, 155.

[2] *Ibid.*, 1895, [II], **51**, 269.

[3] Graebe and Wander, *Annalen*, 1893, **276**, 249.

[4] Kolbe, *J. Pr. Chem.*, [II], **30**, 477; Pictet and Gouset, *Arch. Sci. Phys.*, 1897, [IV], **3**, 37.

ture given by Kolbe. The corresponding acetyl derivative melts at 177–178°, whereas Körner gives the melting point at 167–168°. When the acetyl derivative is heated for an hour at 200–210° it yields the quinazolone derivative, which crystallises from alcohol in colourless cubes melting at 143° as compared with the yellow crystals melting at 146–147° described by Körner. A more convenient method of converting *o*-acetamino-benzanilide into the quinazolone derivative is to boil it with concentrated hydrochloric acid or merely to dissolve in a solution of hydrogen chloride in absolute alcohol and leave overnight; similar treatment converts diphenyl-*o*-aminobenzamidine into the quinazolone compound. The formation of this compound from the *o*-aminobenzamidine may be explained in either of the following ways:—



III

It is interesting to note that whereas carbon tetrachloride and aniline yield a mixture of diphenyl-*p*- and diphenyl-*o*-aminobenzamidine, the product formed from aniline and trichloronitromethane is α-triphenylguanidine[1], $NPh:C(NHPh)_2$.

II. Carbon Tetrachloride with *p*-Toluidine, *p*-Anisidine or *p*-Aminophenol.

The reaction between *p*-toluidine and carbon tetrachloride proceeds at 60–75° in the presence of 0·1 per cent. of copper-bronze; a 50 per cent. yield of a compound melting at 149–150° is obtained, together with a small amount of di-*p*-tolylcarbamide.

The main product cannot be the *p*-aminobenzamidine as the para-position is already occupied and it is presumably di-*p*-tolyl-*o*-amino-*p*-methylbenzamidine.

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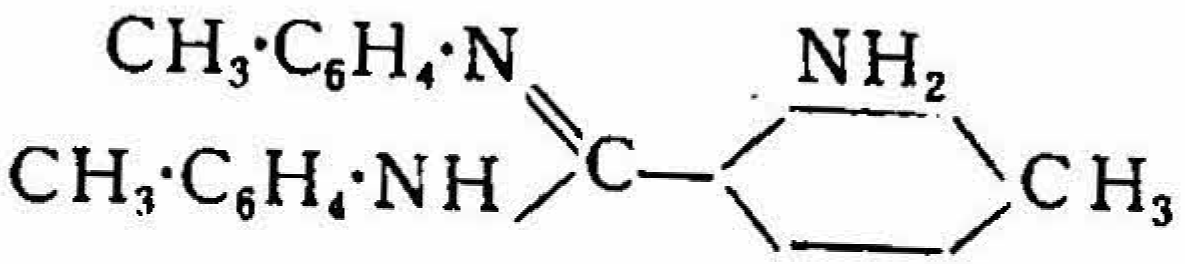
[1] Basset, *Annalen*, 1866, 138, 255.

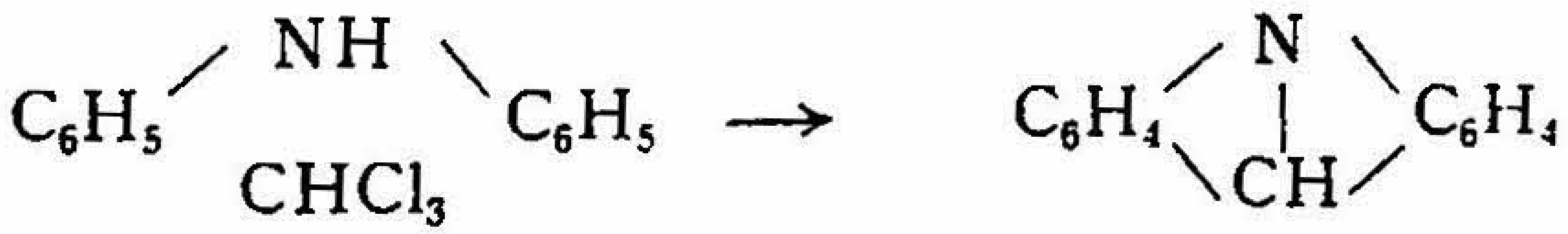


A similar reaction takes place with *p*-anisidine, and a 40 per cent. yield of a compound melting at 139–140° is obtained. The *o*-amino-structures of the products from *p*-toluidine and *p*-anisidine is supported by the ease which they yield 1:2:3-phentriazine derivatives. With *p*-aminophenol and *m*-toluidine no definite products have so far been isolated.

III. Aniline and Bromoform: Diphenylamine and Chloroform.

From the products of the reaction of aniline and bromoform at 125–130° for 9 hours in the presence of 0·1 per cent. of finely divided copper, a 4 per cent. yield of paraleucaniline and a 5 per cent. yield of pararosaniline hydrochloride could be isolated, indicating that condensation occurs between the carbon atom of the bromoform and carbon atoms of the aniline molecules.

At 200° in the presence of 1 per cent. of copper, diphenylamine and chloroform give a 15 per cent. yield of triphenylparaleucaniline, whereas in the presence of zinc chloride the main product is acridine[1] and not the paraleucaniline derivative.



EXPERIMENTAL.

I. Condensation of aniline with carbon tetrachloride.

The pure materials were dried and freshly distilled before use. The copper-bronze was washed with ether to remove grease.

After several trials, it was found that the best yields were obtained by the following process:—27 grams of aniline, 6 grams of carbon tetrachloride and 0·04 gram of copper powder are heated in a round-bottom flask provided with a reflux condenser for 5 hours at 70° and subsequently for 2 hours at 80–85°. The mass is then made alkaline with sodium hydroxide and steam distilled to remove aniline. The non-volatile resin is dried carefully and then extracted with light petroleum (b.p. 70–80°) in a soxhlet extractor during 10 hours. The

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[1] Fischer and Körner, *Ber.*, 1884, 17, 101.

residue (7·2 grams) is ground to a powder, washed first with 40 cc. of cold benzene and then with 15 cc. of cold alcohol on a Buchner funnel. The product is crude diphenyl-*p*-aminobenzamidine, melts at 193–194° and after one crystallisation from boiling alcohol gives pure white crystals melting at 198–199° and corresponding with 43 per cent. of the theoretical yield.

The hot light petroleum extract is poured into a flask and allowed to stand for two hours when a red sticky product is deposited. The clear liquid is decanted into a beaker and on standing over-night crystals of the pure diphenyl-*o*-aminobenzamidine are deposited. The red tarry matter contains a certain amount of the same compound and this can be recovered as picrate by adding a hot alcoholic solution of picric acid to the hot alcoholic solution of the red resin. The crystals so attained can be crystallised from glacial acetic acid and are then decomposed by warming with fairly concentrated sulphuric acid and making alkaline with ammonia. The base so obtained is crystallised from boiling alcohol with the addition of a little animal charcoal and the total yield of the ortho-compound is 1·2 grams, or 11 per cent. of the theoretical.[1]

Diphenyl-*p*-aminobenzamidine is only moderately soluble in benzene, but dissolves fairly readily in hot alchohol and quite readily in hot acetone, chloroform or pyridine. Its *acetyl* derivative, $C_{21}H_{19}ON_3$ separates from 50 per cent. alcohol in cubical crystals melting at 182–183°. 0·1120 gave 14·0 cc. of nitrogen at 23° and 684 mm. $N = 12{\cdot}7$; $C_{21}H_{19}ON_3$ requires 12·8 per cent.

The *benzoyl* derivative, $C_{26}H_{21}ON_3$, prepared by the action of benzoic anhydride on the base at 100°, crystallises from dilute acetic acid in colourless prisms melting at 223–224°. It is only sparingly soluble in hot alcohol.

The base reacts with phenyl *iso*thiocyanate yielding a compound, which crystallises from a mixture of pyridine and water in yellow needles melting at 174–176°, and sparingly soluble in most solvents.

Definite compounds with picric acid or *s*-trinitrobenzene could not be isolated. The solution of the base in hydrochloric acid is readily diazotised and then couples with β-naphthol.

Diphenyl-o-aminobenzamidine,

$$\left.\begin{array}{l} C_6H_5\cdot N \\ C_6H_5\cdot NH \end{array}\right\rangle C\cdot C_6H_4\cdot NH_2,$$

crystallises from alcohol in colourless needles melting at 115–116°, and dissolves readily in cold acetone, chloroform or ether.

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[1] i.e., calculated on the theoretical yield from the amount of carbon tetrachloride used.

Analyses

1. 0·1636 gave 0·4714 of carbon dioxide and 0·0925 of water.
2. 0·1480 gave 0·4257 of carbon dioxide and 0·0849 of water.
3. 0·1510 gave 0·4385 of carbon dioxide and 0·0850 of water.
4. 0·0956 gave 14·0 cc. of nitrogen at 22° and 676 mm.
5. 0·1243 gave 17·9 cc. of nitrogen at 22° and 676 mm.

	Found					Calculated for
	1.	2.	3.	4.	5.	$C_{19}H_{17}N_3$
C	78·60	78·45	79·20	....	....	79·44
H	6·28	6·37	6·25	....	....	5·92
N	....	....	....	15·0	14·8	14·63

6. 1·92 gram of the base requires 16·3 cc. of a 0·83 N. solution of sodium nitrite for diazotisation, = 0·467 gram as compared with 0·462, the theoretical value for one amino-group.

Molecular Weight.—0·193 gram dissolved in 17·4 grams of benzene produced a depression of 0·21°, and 0·382 gram dissolved in the same weight of solvent produced a depression of 0·39°.

	Found		Calculated
	1.	2.	
M	264	282	287.

The base forms a colourless *dihydrochloride*, $C_{19}H_{17}N_3$, 2HCl, which is transformed at 110° into a yellow *monohydrochloride*, $C_{19}H_{17}N_3$, HCl. The yellow monohydrochloride is also formed by the partial hydrolysis of the dihydrochloride in faintly acidic solutions. The *picrate* crystallises from chloroform or glacial acetic acid in orange yellow prisms melting and decomposing at 225–230°.

The base also forms with *s*-trinitrobenzene a definite compound obtained by mixing hot alcoholic solutions of the components, and crystallises in orange red needles melting at 128–129°.

The acetyl and benzoyl derivatives have been obtained as resins but when left in contact with alcoholic hydrogen chloride or boiled with concentrated hydrochloric acid are converted into quinazolone derivatives (cf. p. 214).

Formation of the 1:2:3*-phentriazine derivative*, II.

3*-Phenyl-*3:4*-dihydro-phen-*1:2:3*-triazine-*4*-ketoanil*, $C_{19}H_{14}N_4$, is readily prepared by diazotising at 0° a solution of the base in dilute sulphuric acid, the end-point being determined by potassium iodide-starch paper. The solution is immediately made alkaline with ammonia and the yellow precipitate extracted with ether, and after drying and removal of the ether is crystallised from alcohol. The yield is 90 per cent. of the theoretical and the substance forms yellow rhombohedra melting at 139–140°.

0·1157 gave 21·4 cc. of nitrogen measured at 25° and 671 mm.
N = 18·7. $C_{19}H_{14}N_4$ requires 18·8 per cent.

When the phentriazine compound is heated above its melting point it begins to evolve nitrogen at 180°. Under diminished pressure it decomposes at a lower temperature but after heating 1 gram for 10 hours at 175° under diminished pressure, 0·4 gram of crude or 0·2 gram of pure unaltered phentriazine was isolated without any definite product of decomposition.

When dissolved in dilute hydrochloric acid and treated at room-temperature with small amounts of copper-bronze the triazine derivative is decomposed. To obtain the product the addition of copper-powder is continued until nitrogen ceases to be evolved. The copper is removed by filtration, washed with methyl alcohol, the washings added to the acid filtrate, the whole made alkaline with ammonia and extracted with ether. After removal of ether a viscous film is left which on drying in a vacuum forms a dry powder melting at 55–60° and readily soluble in all solvents.

0·211 gave 0·0944 of silver chloride: Cl = 11·1, $C_{19}H_{15}N_2Cl$ requires 11·6 per cent.

*Hydrolysis of the diphenyl-*o*-aminobenzamidine.*

From the experiments in which the base was hydrolysed with 15 per cent. alcoholic potash and with 50 per cent. sulphuric acid, only unaltered base and aniline could be isolated. By boiling with a mixture of alcohol and concentrated hydrochloric acid, aniline and a base melting at 165–168° were obtained. When the base (0·5 gram) was boiled for three hours with 10 cc. of a mixture of equal volumes of glacial acetic and concentrated hydrochloric acids anthranilic acid and Körner's 2-methyl-3-phenyl-4-quinazolone could be isolated from the products by the following process: After hydrolysis the mixture is evaporated nearly to dryness, then extracted with water, filtered and the clear filtrate precipitated with ammonia. The precipitate consists of Körner's compound, and after crystallisation from alcohol forms colourless cubical crystals melting at 143°. The ammoniacal filtrate when acidified with acetic acid and extracted four times with ether yields flat, colourless plates of anthranilic acid melting at 145°.

2-Methyl-3-phenyl-4-quinazolone, III. The base crystallises from alcohol in colourless cubical crystals melting at 143°. (Found C = 75·3, H = 5·5, N = 11·8. Calculated C = 76·3, H = 5·1 and N = 11·9 per cent). When the base is dissolved in warm dilute hydrochloric acid and allowed to cool it yields pearly leaflets of a *monohydrochloride*, $C_{15}H_{12}ON_2$, HCl, (Cl = 13·0. Theory requires 13·0 per cent). When boiled for five hours with concentrated hydrochloric acid part of the base is recovered unaltered, but a portion is converted into an acid, which crystallises from water in colourless plates melting at 165–167° and which has not, so far, been further investigated.

Synthesis of Körner's quinazolone derivative.

As the quinazolone obtained from diphenyl-*o*-aminobenzamidine did not correspond completely with Körner's description of the compound prepared from *o*-acetaminobenzanilide it was considered advisable to prepare it from this source, and the following points are of interest.

(*a*) In converting *o*-nitrobenzoyl chloride [1] into the anilide the pyridine method gives a 60 per cent. yield and the Schotten-Baumann method a 70 per cent. yield of the pure anilide.

(*b*) Three methods were tried for reducing the nitro-compound to *o*-aminobenzanilide, viz., ammonium sulphide, [2] zinc dust and glacial acetic acid below 30° and iron powder with dilute acetic acid at 60°. The first method gives a 40 per cent. yield and the other two 30 per cent. yields of the amino-compound.

(*c*) *o*-Acetaminobenzanilide is readily prepared by the action of acetic anhydride on the base. It crystallises from hot alcohol in colourless, prismatic needles melting at 177–178°; [3] when heated in a hard glass test tube in an oil bath at 200–210° as recommended by Körner and the product crystallised repeatedly from alcohol, a small yield of colourless, cubical crystals melting at 142–143° is obtained and a mixed melting point indicated the identity of this product with that obtained from the diphenyl-*o*-aminobenzamidine. A better yield of the quinazolone, viz., 70 per cent. of the theoretical, is obtained

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[1] Cohen and Arms, *J. Chem. Soc.*, 1905, 87, 1190.
[2] Pictet and Gouset.
[3] Körner 166–167°.

when the *o*-acetaminobenzanilide is boiled for six hours with concentrated hydrochloric acid. Diphenyl-*o*-acetaminobenzamidine readily yields the quinazolone when boiled for five hours with concentrated hydrochloric acid, or left at the ordinary temperature with a solution of hydrogen chloride in absolute (99 per cent.) alcohol.

When the diphenyl-*o*-aminobenzamidine is benzoylated and the crude pasty benzoyl derivative is left in contact with a solution of hydrogen chloride in absolute alcohol, a product is formed which crystallises from alcohol in colourless needles melting at 150–151° and presumably consists of 2 : 3-*diphenyl*-4-*quinazolone*, $C_{20}H_{14}ON_2$.

Synthesis of diphenyl-o-aminobenzamidine from o-nitrobenzanilide.

In converting the *o*-nitrobenzanilide into the imide chloride, care is needed in removing the phosphorus oxychloride, as otherwise decomposition of the imide chloride occurs.[1] It is most readily accomplished by heating the reaction mixture at 70° under diminished pressure and finally washing away the last traces by means of petroleum ether (b. p. 70–80°). The *imide chloride*, $NO_2\cdot C_6H_4\cdot CCl : N\cdot C_6H_5$, is a liquid which does not solidify when kept in a freezing mixture. It reacts readily with water giving the original anilide. The corresponding amidine, *diphenyl-o-nitrobenzamidine*,  $NO_2\cdot C_6H_4\cdot C\begin{smallmatrix}\nearrow N\cdot C_6H_5 \\ \searrow NH\cdot C_6H_5\end{smallmatrix}$, is readily obtained by dissolving the imide chloride in 20 times its weight of boiling light petroleum (b. p. 80–90°), slowly adding the requisite amount of aniline and heating on the water bath for an hour. After removal of the solvent an excess of alkali is added to the viscous mass and the aniline is removed by distillation in steam. As it was not found possible to obtain the nitro-amidine in a crystalline form owing to the readiness with which it dissolves in all organic solvents with the exception of light petroleum, the crude, dark-coloured product was reduced with zinc dust and glacial acetic acid at the room-temperature. At the end of 12 hours unaltered zinc and zinc acetate were removed by filtration and the clear solution evaporated nearly to dryness on the water bath. The product was digested with dilute sulphuric acid, filtered from tarry matter and the filtrate boiled with a little animal charcoal, again filtered and finally made alkaline with ammonia and extracted with ether. After removal of the ether, the product was pressed on a porous plate and finally recrystallised from boiling alcohol with the addition of a little animal charcoal. The crystals (0·3 gram) so obtained melted at 114–115° and proved to be identical with the diphenyl-*o*-aminobenzamidine obtained by condensing aniline and carbon tetrachloride in the presence of copper-

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[1] It was not found possible to prepare the imide chloride by means of thionyl chloride.

bronze, as proved by mixed melting-point determination, the formation of the picrate melting at 220–225° and of the phentriazine derivative melting at 140–141°.

Synthesis of diphenyl-m-*aminobenzamidine.*

For purposes of comparison it was decided to prepare the isomeric diphenyl-*m*-aminobenzamide from *m*-nitrobenzanilide by a series of reactions similar to that adopted for the synthesis of the *o*-compound. *m*-nitrobenzanilide has been previously prepared by heating together the acid and aniline.[1] A good yield can be obtained by gradually adding the acid chloride (22 grams) to a mixture of aniline (13 grams) and diethylaniline (23 grams) and finally heating for half an hour on the water bath. The cold mass is extracted with dilute acid and the residue crystallised from alcohol when it forms colourless plates melting at 153–154°.

The *imide chloride*, $NO_2\cdot C_6H_4\cdot CCl : N\cdot C_6H_5$, is a pale coloured oil readily soluble in most organic solvents with the exception of light petroleum, and does not solidify when placed in a freezing-mixture. It is much more stable than the isomeric ortho-compound and in its preparation the phosphorus oxychloride may be removed by heating to 100–110° under 30 mm. pressure. *Diphenyl*-m-*nitrobenzamidine*, $NO_2\cdot C_6H_4\cdot C(NH\cdot C_6H_5) : N\cdot C_6H_5$, is obtained in an 88 per cent. yield by the action of aniline on the imide chloride in the presence of diethylaniline[2] and crystallises from alcohol in flat, yellow needles melting at 151–152°.

0·1175 gave 15·7 cc. of nitrogen at 23·5° and 670 mm. N = 13·5; $C_{19}H_{15}O_2N_3$ requires 13·3 per cent.

The *hydrochloride* crystallises from hot glacial acetic acid in colourless prisms melting and decomposing at 225–227°. It is only sparingly soluble in cold alcohol.

Diphenyl-m-*aminobenzamidine*, is obtained by reducing the nitro-compound with iron powder and dilute acetic acid at 80–85° during one hour, and finally for 60 minutes at 95°. The product is made alkaline with sodium carbonate and the precipitate is filtered hot, washed with water, dried and extracted with boiling alcohol. The alcoholic solution after treatment with animal charcoal is concentrated, when unaltered nitro-base, if present, separates, as it is only sparingly

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[1] Engler and Volkhausen, *Ber.*, 1875, 8, 35.

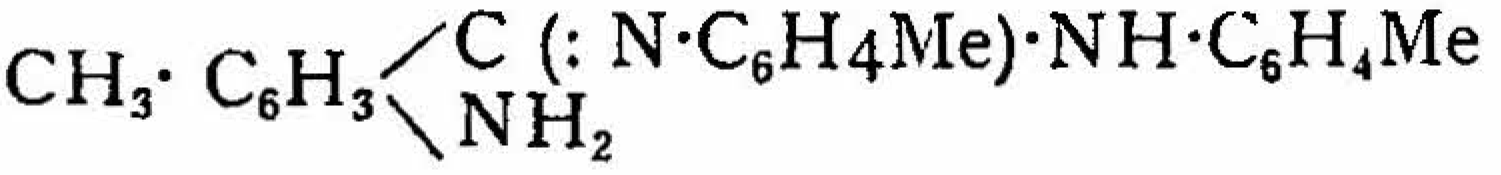
[2] The use of diethylaniline in the condensation of imide chlorides with arylamines appears to be a distinct improvement on the usual method of boiling the components in light petroleum solution.

soluble in cold alcohol. The alcoholic solution is evaporated to dryness and the residue extracted with dilute sulphuric acid (7–8 per cent.), the extract boiled with animal charcoal and then made alkaline with ammonia, filtered, washed and dried. The crude base, 30 per cent. yield, forms a grey powder melting at 80–90° and so far has not been obtained in a crystalline form. It dissolves readily in most organic solvents with the exception of light petroleum and from hot solutions in this solvent it separates as a thick syrup. It is readily diazotised and then couples with β-naphthol yielding a red dye. It forms a colourless *dihydrochloride*, $C_{19}H_{17}N_3$, 2HCl (Cl = 18·9. Theory 19·7 per cent.), and a yellow *monohydrochloride*, $C_{19}H_{17}N_3$, HCl. So far it has not been possible to isolate a crystalline acetyl derivative.

II. Condensation of p-toluidine with carbon tetrachloride.

22 grams of *p*-toluidine, 4 grams of carbon tetrachloride and 0·1 per cent. of catalyst were heated for two hours at 60–65°, the solid product being made alkaline with an excess of sodium hydroxide and then submitted to steam distillation. The dark brown, non-volatile residue weighed 4 grams and was extracted with dilute sulphuric acid (7 per cent.) when a small amount of residue was left. The acid extract was boiled with animal charcoal and then made alkaline with ammonia. The crude product melted at 120–135° and after crystallisation from light petroleum formed colourless needles melting at 149–150°.

The portion of the product insoluble in acid separated from its alcoholic solution in fine silky needles melting at 253–255° and was identified as s-di-*p*-tolylcarbamide. A subsequent experiment was made with the addition of absolute alcohol (7cc.) to the original mixture, but the yield of condensation product was much the same. *Di*-p-*tolyl*-o-*amino*-p-*methyl benzamidine*,



$$CH_3\cdot C_6H_3\begin{cases} C(:N\cdot C_6H4Me)\cdot NH\cdot C_6H_4Me \\ NH_2 \end{cases}$$

dissolves readily in most organic solvents, crystallises most readily from light petroleum (b.p. 70–80°) and melts at 149–150°. It dissolves in acids yielding yellow solutions.

(1) 0·1230 gave 0·3580 of carbon dioxide and 0·0830 of water.

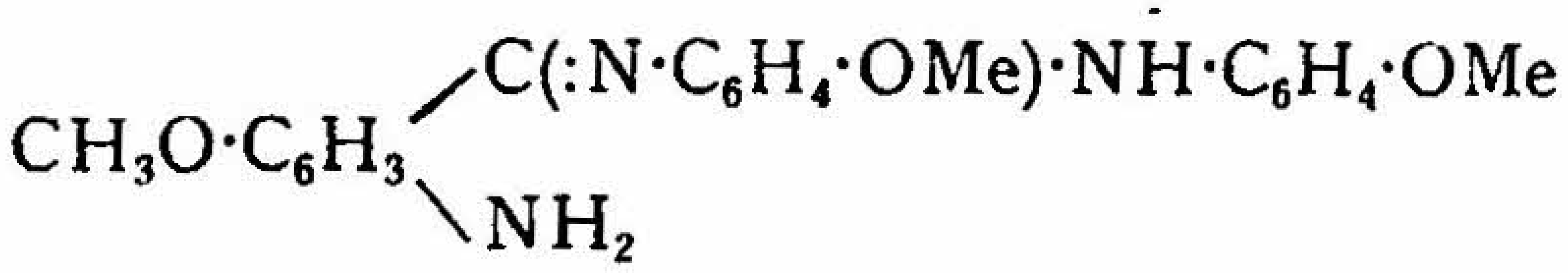
(2) 0·0888 gave 11·3 cc. of nitrogen at 24° and 670 mm.

Found.		Calculated for $C_{22}H_{23}N_3$
C	79·4	80·2 per cent.
H	7·5	7·0 per cent.
N	12·9	12·8 per cent.

The base is readily diazotised in acid solution, but the product does not couple with β-naphthol. The amount of sodium nitrite required corresponds with the presence of one amino-group in the compound diazotised and when the resulting solution is made alkaline and immediately extracted with ether a compound is obtained which crystallises in rectangular laminae melting at 145°, and possessing all the properties of a 1:2:3-phentriazine derivative. 0·0776 gram gave 13·1 cc. of nitrogen at 24° and 670 mm. $N = 17{\cdot}1$; $C_{22}H_{20}N_4$ requires 16·5 per cent.

Condensation of p-*anisidine with carbon tetrachloride.*

The condensation was carried out in the same manner as already described with *p*-toluidine and with the addition of absolute alcohol, first for four hours at 70-80° and subsequently for four hours at 85°. The free base, 2·85 grams from 5 grams of carbon tetrachloride, crystallises from boiling alcohol in colourless needles melting at 139–140°. It appears to be *di*-p-*anisyl*-o-*amino*-p-*methoxybenzamidine.*



$$CH_3O{\cdot}C_6H_3\begin{cases}C(:N{\cdot}C_6H_4{\cdot}OMe){\cdot}NH{\cdot}C_6H_4{\cdot}OMe\\ NH_2\end{cases}$$

(1) 0·1522 gave 0·3890 of carbon dioxide and 0·0882 of water.

(2) 0·1451 gave 16·1 cc. of nitrogen at 23·5° and 670 mm.

		Found.	Calculated for $C_{22}H_{23}O_3N_3$.
C	....	69·70	70·03.
H	....	6·44	6·10.
N	....	11·25	11·14.

When treated with nitrous acid it yields a phentriazine derivative melting at 122–123°. 0·0975 gave 14·1 cc. of nitrogen at 24° and 670 mm. $N = 14{\cdot}6$; $C_{22}H_{20}O_3N_4$ requires $N = 14{\cdot}4$ per cent.

III. Condensation of Aniline with Bromoform.

50 grams of aniline, 25 grams of freshly distilled bromoform and 0·057 gram of copper-bronze were heated at 125–130° during eight hours; at the end of this time it had formed a thick viscid mass, whereas in a similar experiment made without the addition of the catalyst the components remained practically unaltered.

The viscid mass was extracted with alcoholic hydrogen chloride, the extract diluted with water, made alkaline with sodium hydroxide and shaken repeatedly with ether. Three grams of a solid insoluble in ether were obtained. After removal of the solvent from the ethereal solution and steam distillation of the residue to remove aniline a further 5·7 grams of solid were obtained which was mixed with the previous 3 grams.

After removal of the ether and before steam distillation the liquor was left over-night and deposited on the sides of the flask 0·65 gram of needle-shaped crystals which proved to be paraleucaniline.

The 8·7 gram of solid was extracted repeatedly with benzene when a dark red residue of 2 grams was obtained. This proved to be impure pararosaniline, and from it paraleucaniline was prepared by reduction with zinc and hydrochloric acid;[1] this crystallised from ether in long needles melting at 146–147°. The percentage of pararosaniline in the crude red product was estimated by Knecht and Hibbert's titanous chloride method and found to be 46.

The percentages of paraleucaniline and pararosaniline obtained in the condensation are respectively 4 and 5 calculated on the theoretical yield from the weight of bromoform taken. No definite products could be isolated from the benzene extract.

IV. Condensation of Diphenylamine with Chloroform.

15 grams of diphenylamine, 10 grams of chloroform, 20 grams of anhydrous sodium acetate and 0·16 gram of copper-powder were heated in a sealed tube for 12 hours at 180–200°. The semi-solid product was extracted first with water and then with concentrated hydrochloric acid in order to remove unaltered diphenylamine. From these extracts no acridine could be isolated, only diphenylamine. The presence of triphenylparaleucaniline in the residue was indicated by its turning blue in contact with the air. The triphenylparaleucaniline was not isolated as such but oxidised by means of chloranil, in a solution of alcohol and glacial acetic acid, to triphenylpararosaniline and the crude dye extracted in a Soxhlet for 10 hours with benzene and then crystallised from hot alcohol. The yield was 15 per cent. of the theoretical.

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[1] Fischer, *Annalen*, 1878, **194**, 268.

APPENDIX.

A. Dimorphism of o-Aminobenzanilide.

As already stated (p. 207) the melting point of *o*-aminobenzanilide was found to be 117–118°, whereas previous workers, Kolbe and also Pictet and Gouset, have given the melting point as 131°. The compound melting at 117–118° is *o*-aminobenzanilide, as it yields aniline and anthranilic acid when hydrolysed with concentrated hydrochloric acid. The lower melting is termed the *α*- and the higher melting the *β*-compound. When the freshly prepared compound is heated in a melting point tube it fuses to a clear liquid at 117–118°, if however the temperature is maintained at 117–120° for a few minutes the mass solidifies and then melts at 131° to a clear liquid.

The *β*-form when melted in a narrow test-tube and allowed to solidify forms a crystalline mass melting at 117–118°; but if the *β*-form is melted and cooled to 125° and then a crystal of the *β*-form is added and the mass allowed to solidify the product melts at 131° and not 117–180°. In these respects the two forms are similar to the dimorphous forms of benzophenone.[1]

When crystallised from chloroform the main product is the *β*-form but a small amount of the α-form is also obtained. By cautiously cooling a hot benzene solution, glistening transparent needles of the α-form are obtained together with a small amount of the *β*-form, occasionally the α-form alone is obtained, and even when such a solution is seeded with the *β*-form the main product consists of α-crystals.

Neither compound dissolves in alkali, and neither when dissolved in alcohol gives a colouration with ferric chloride. They both yield the same acetyl derivative melting at 177–178°.

B. Salts of Diphenyl-*o*-, *m*-, and *p*-aminobenzamidines.

As already pointed out (p. 211) the *ortho*-compound yields a colourless dihydrochloride and a yellow monohydrochloride. The *meta*-and *para*-compounds behave similarly and not only hydrochlorides but sulphates also have been prepared. The fact that the *meta*-compound also yields a yellow monohydrochloride indicates that in all probability the yellow colour is not due to the formation of a quinonoid structure.[2]

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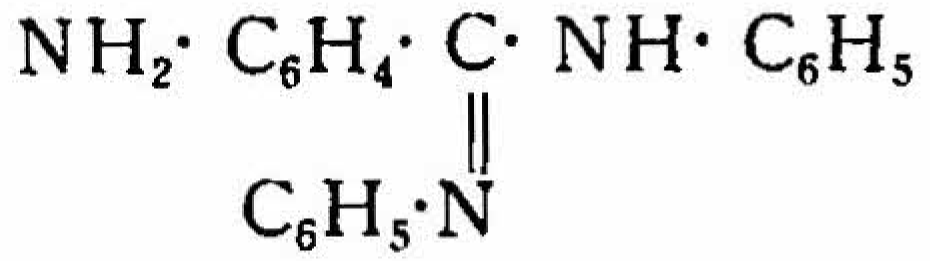
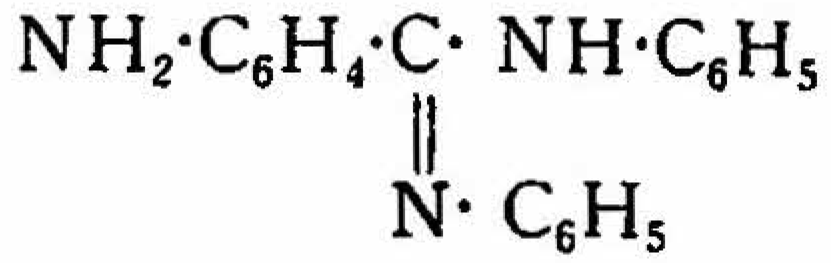
[1] Zincke, *Annalen*, 1871, 159, 377.
[2] Compare however R. Ciusa, *Alti R. Accad. Lincei*, 1919, [v] 28, ii, 366.

In the case of the *para*-compound it has been found possible to prepare two monohydrochlorides, one yellow (α) and the other colourless (β), which are mutually interconvertible.

The nature of the isomerism has not been established. It is probably not due to benzenoid-quinonoid isomerism as the *meta*-compound also yields yellow and colourless salts. Theoretically, the base itself can exist in *cis* and *trans* modifications.



$$\begin{array}{l} NH_2\cdot C_6H_4\cdot C\cdot NH\cdot C_6H_5 \\ \qquad\qquad\qquad\; \| \\ \qquad\quad C_6H_5\cdot N \end{array}$$



$$\begin{array}{l} NH_2\cdot C_6H_4\cdot C\cdot NH\cdot C_6H_5 \\ \qquad\qquad\quad\;\; \| \\ \qquad\qquad\quad\;\; N\cdot C_6H_5 \end{array}$$

and it is possible that the two monohydrochlorides correspond with these two forms. In this case the hydrochlorides are derived from two stereoisomeric bases and attempts have been made to show the existence of the base itself in colourless and yellow forms.

*Salts of diphenyl-*o*-aminobenzamidine.*

The *dihydrochloride*, $C_{19}H_{17}N_3$, 2 HCl, is formed when concentrated hydrochloric acid is added to the hot alcoholic solution of the base, the mixture heated for 15 minutes and allowed to cool. It forms colourless plates, and after washing with alcoholic hydrogen chloride and keeping for two days in a vacuum desiccator over caustic potash gave the following result on analysis.

0·2916 gave 0·244 of silver chloride. Cl = 20·7; theory requires 19·7 per cent.

When heated in the air at 110° hydrogen chloride is evolved and the yellow monohydrochloride is formed.

The *monohydrochloride*, $C_{19}H_{17}N_3$, HCl, is most readily prepared by adding 1·5 times the theoretical amount of alcoholic hydrogen chloride to a cold alcoholic solution of the base when yellow prismatic crystals of the salt quickly separate. When obtained by heating the dihydrochloride at 110° for 40 hours it appears amorphous.

0·5306 gave 0·227 silver chloride. Cl = 10·6; theory requires 10·9 per cent.

Both salts are sparingly soluble in water and when the dihydrochloride is warmed with only slightly acidic solutions it turns yellow.

*Salts of Diphenyl-*m*-aminobenzamidine.*

The *dihydrochloride*.—When dry hydrogen chloride is passed into a benzene solution of the base a yellow precipitate is first obtained but this turns colourless as more of the gas is passed. The mixture is not readily filtered as it absorbs moisture from the air, but is best poured on to a porous plate, which is placed in a desiccator over caustic potash and evacuated.

0·235 gave 0·178 of silver chloride. Cl = 18·9; theory requires 19·7.

The *monohydrochloride*, obtained by heating the dihydrochloride in a current of dry air at 200–210° for 10 hours has a yellow colour.

0·373 gave 0·185 of silver chloride. Cl = 12·3; theory requires 10·9.

*Salts of diphenyl-*p*-aminobenzamidine.*

The *disulphate*, $C_{19}H_{17}N_3$, H_2SO_4, is obtained by adding the base gradually to a boiling 10–15 per cent. solution of sulphuric acid so long as the base dissolves, filtering and allowing to stand over-night, again filtering and washing with dilute sulphuric acid and then with alcohol, as water produces a yellow coloration. After drying at 110–115° it gave the following result on analysis.

0·407 gave 0·257 of barium sulphate. SO_4 = 26·0; theory requires 24·94 per cent.

The *dihydrochloride*, $C_{19}H_{17}N_3$, 2HCl. The base is dissolved in moderately concentrated hydrochloric acid and the clear solution concentrated. It forms colourless needles which, after washing with dilute hydrochloric acid and drying in a vacuum desiccator over caustic potash, gave the following result; 0·3665 gave 0·289 of silver chloride. Cl = 19·5; theory requires 19·7 per cent.

The salt turns pale yellow at 200°, deep yellow at 220—240° and melts with decomposition at 265–275°.

The yellow *monosulphate*, $2C_{19}H_{17}N_3$, H_2SO_4. Very dilute sulphuric acid is added cautiously to a suspension of the base in boiling water, the pale yellow solution filtered and allowed to stand, when deep yellow needles separate. After washing with water and drying at 110°, 0·4006 gave 0·1425 of barium sulphate, SO_4 = 14·6; theory requires 14·3 per cent.

The yellow *monohydrochloride* (*a*) is obtained by crystallising the colourles monohydrochloride from boiling glacial acetic acid. It forms yellow rhombohedral plates.

0·259 gave 0·116 of silver chloride; Cl = 11·1; theory requires 10·9 per cent.

The white *monohydrochloride* (β), obtained by gradually adding dilute hydrochloric acid to a suspension of the base in boiling water until the base dissolves, crystallises in slender, snow-white needles. After drying at 110°, 0·472 gave 0·216 of silver chloride; Cl = 11·3; theory requires 10·9 per cent.

As the dihydrochloride of the *ortho*-base readily loses hydrogen chloride yielding the yellow monohydrochloride the action of heat on the *para*-dihydrochloride was studied. At 135° for 6 hours the loss of hydrogen chloride is practically negligible, and even after three hours at 170° the percentage of chlorine is 15·4 as compared with 11·1 required for the monohydrochloride. It is thus clear that the *para*-dihydrochloride is much more stable at 170° than the isomeric *ortho*-compound.

The β-monohydrochloride can be crystallised from alcohol without undergoing change; when crystallised from acetone it yields a mixture of α-and β-compounds and when crystallised from glacial acetic acid is completely converted into the α-isomeride.

When the β-compound is heated in a test-tube at 150–160° for six hours it shows no change. When heated in a melting-point tube it begins to turn yellow at about 200°, is completely yellow at 230° and melts and decomposes at 260–270°. The β-compound is not altered by exposure to sunlight, but when triturated in a mortar turns bright yellow. The α-hydrochloride when exposed to air at the ordinary temperature gradually passes over into the white compound and the change is more rapid in the absence of light and at 110°. Exposure to bright sunlight for four hours does not bring about this change and the change from α- to β-compound is accomplished without any noticeable change in weight.

When the free base is heated at 110° for an hour it assumes a pale yellow colour, but turns colourless again on cooling. At 180–190° the yellow colour is more intense and the change more rapid. At 198° the yellow solid melts to a clear yellow liquid. If placed in a tube and heated to 200° the crystals turn yellow and melt to a yellow liquid and if the tube is then maintained at 180–185° for some time crystallisation sets in and the whole solidifies to a mass of yellow crystals, which however become colourless on cooling to the ordinary temperature.

It is impossible to say at present whether the colourless and yellow salts and bases represent two stereoisomeric forms.

In conclusion it is my pleasing duty to express my sincere gratitude to Dr. J. J. Sudborough for his keen interest in the work and for his encouragement and able guidance. I have also pleasure in thanking Dr. M. O. Forster for advice connected with my work.

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PRINTED AND PUBLISHED
BY GEORGE KENNETH AT THE DIOCESAN PRESS
POST BOX 455, MADRAS—1924. C6204