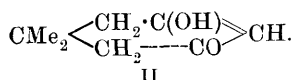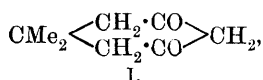XXVI.—*The Condensation of Dimethyldihydroresorcin and of Chloroketodimethyltetrahydrobenzene with Primary Amines. Part I. Monamines.—Ammonia, Aniline, and* p-*Toluidine.*

By PAUL HAAS, B.Sc., Ph.D.

THE constitution of dimethyldihydroresorcin may be expressed by either of the two formulæ:

$$CMe_2 \underset{CH_2 \cdot CO}{\overset{CH_2 \cdot CO}{<}} > CH_2, \qquad CMe_2 \underset{CH_2 ---- CO}{\overset{CH_2 \cdot C(OH)}{<}} \gg CH.$$
$$\text{I.} \qquad\qquad\qquad\qquad \text{II.}$$

Although dimethyldihydroresorcin behaves towards hydroxylamine (Vorländer and Erig, *Annalen*, 1897, **294**, 316) and semicarbazide (compare p. 198) as a diketone, the fact of its giving with ferric chloride in aqueous solution a violet-red colour and of its reacting with phosphorus trichloride (Crossley and Le Sueur, Trans., 1903, **83**, 110) to give 5-chloro-3-keto-1 : 1-dimethyl-$\Delta^4$-tetrahydrobenzene points to the presence of a hydroxyl group as indicated by formula II. It is this hydroxyl group which is responsible for the acid reaction of the substance, as well as its solubility in sodium or potassium hydroxide and in sodium hydrogen carbonate; so acidic is this hydroxyl that it may even be esterified by means of alcohol and strong sulphuric acid (Vorländer, *loc. cit.*) after the manner of a carboxylic acid; whereas, however, carboxylic acids produce in a naphthalene solution a bimolecular depression of freezing point, dimethyldihydroresorcin exhibits no such abnormality, although its molecular conductivity $K = 0.00071$ is no less than one-third of that of $\gamma$-acetylbutyric acid, which has the value $K = 0.0022$ (*v.* Schilling and Vorländer, *Annalen*, 1899, **308**, 184).

The replacement of the hydroxyl group by chlorine gives rise to chloroketodimethyltetrahydrobenzene; this substance forms a semicarbazone, showing that it still contains a carbonyl oxygen, and its constitution must therefore be represented by the following formula:

$$CMe_2 \underset{CH_2 - CO}{\overset{CH_2 \cdot CCl}{<}} \gg CH.$$
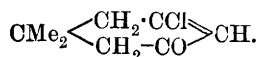
The disappearance of the hydroxyl group is accompanied by a loss of acid properties, the substance being insoluble in cold potassium hydroxide and dissolving only on warming with the formation of the potassium salt of dimethyldihydroresorcin. On the whole, then, this hydroxyl group is more phenolic than alcoholic in nature, and it was

therefore thought to be of interest to determine whether the chlorine atom in chloroketodimethyltetrahydrobenzene resembles the chlorine in an aromatic or an aliphatic compound. With this object in view, the behaviour of chloroketodimethyltetrahydrobenzene towards amines has been studied. In every case investigated, it was found to react in one molecular proportion with two molecules of the base, giving rise to a type of compound which Vorländer (*loc. cit.*, p. 305) states he was unable to prepare by the direct condensation of alkyldihydroresorcins with *p*-toluidine; it became necessary, therefore, to include in this investigation the condensation of dimethyldihydroresorcin with amines, and it was found that here, in every case, the two constituents reacted together in molecular proportions only, although the condensation products so obtained could be made to react with a second molecule of the base in the presence of zinc chloride.

### Condensations of Dimethyldihydroresorcin.

(a) *Ammonia.*   5-*Hydroxy*-3-*amino*-1 : 1-*dimethyl*-$\Delta^4$-*tetrahydrobenzene* (*Monoamine*).—Dimethyldihydroresorcin dissolves in aqueous ammonia to a colourless solution which probably contains the ammonium salt, since it gives with silver nitrate a precipitate of the corresponding silver salt; when, however, the solution is evaporated to dryness, the resulting solid is not an ammonium salt, but an amine derived from this substance by the loss of water; this amine, which may be referred to briefly as the monoamine, gives no precipitate with silver nitrate in aqueous solution.

(b) p-*Toluidine.*   5-*Hydroxy*-3-p-*tolylamino*-1 : 1-*dimethyl*-$\Delta^{3:5}$-*dihydrobenzene* (*Monotoluidide*), page 196, has already been described by Vorländer (*loc. cit.*).

(c) *Aniline.*   5-*Hydroxy*-3-*phenylamino*-1 : 1-*dimethyl*-$\Delta^{3:5}$-*dihydrobenzene* (*Monoanilide*), page 202.

### Condensations of Chloroketodimethyltetrahydrobenzene.

(a) *Ammonia.*   5-*Imino*-3-*amino*-1 : 1-*dimethyl*-$\Delta^3$-*tetrahydrobenzene* (*Diamine*) *Hydrochloride.*—In spite of repeated attempts, it was not found possible to isolate the free base in a state of purity, since it breaks up at once, evolving ammonia.
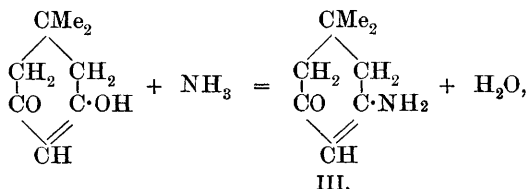
(b) p-*Toluidine.* 5-p-*Tolylimino*-3-p-*tolylamino*-1 : 1-*dimethyl*-$\Delta^3$-*tetrahydrobenzene* (*Ditoluidide*) *Hydrochloride* and

(c) *Aniline.*   5-*Phenylimino*-3-*phenylamino*-1 : 1-*dimethyl*-$\Delta^3$-*tetrahydrobenzene* (*Dianilide*) *Hydrochloride.*—The two latter substances, when dissolved in a large volume of boiling water, give on treatment with caustic alkalis the corresponding bases, which are very stable substances; they are not hydrolysed by heating with concentrated hydro-
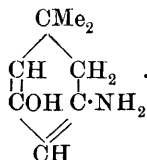
chloric acid in sealed tubes at 125°; if, however, they are heated with the same acid for three hours at 150—200°, they undergo a curious change, yielding $p$-toluidine hydrochloride and $\beta\beta$-dimethylglutaric acid.

The formation of this acid was explained by a separate experiment, in which it was found that a 35 per cent. yield of $\beta\beta$-dimethylglutaric acid may be obtained from dimethyldihydroresorcin by heating it under pressure with concentrated hydrochloric acid.
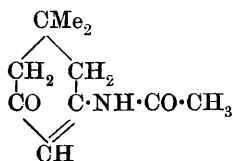
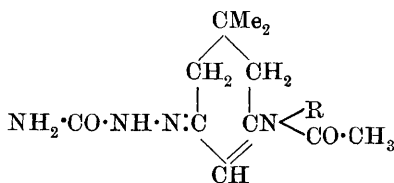The formation of the monoamine from dimethyldihydroresorcin should be expressed by the equation :

$$
\begin{array}{c}
\text{CMe}_2 \\
\diagup \diagdown \\
\text{CH}_2 \quad \text{CH}_2 \\
\mid \qquad \mid \\
\text{CO} \quad \text{C·OH} \\
\diagdown \diagup \diagup \\
\text{CH}
\end{array}
+ \text{NH}_3 =
\begin{array}{c}
\text{CMe}_2 \\
\diagup \diagdown \\
\text{CH}_2 \quad \text{CH}_2 \\
\mid \qquad \mid \\
\text{CO} \quad \text{C·NH}_2 \\
\diagdown \diagup \diagup \\
\text{CH} \\
\text{III.}
\end{array}
+ \text{H}_2\text{O},
$$

but the chemical behaviour of the amine is not in agreement with formula III ; no evidence of a carbonyl group can be obtained by means of either hydroxylamine, semicarbazide, or $p$-bromophenylhydrazine, whilst the substance gives a deep cherry-red colour with ferric chloride ; from these facts, it would appear that the constitution is better represented by the formula

$$
\begin{array}{c}
\text{CMe}_2 \\
\diagup \diagdown \\
\text{CH} \quad \text{CH}_2 \\
\parallel \qquad \mid \\
\text{COH} \ \text{C·NH}_2 \\
\diagdown \diagup \diagup \\
\text{CH}
\end{array}
.
$$

When this monoamine is heated with an excess of acetic anhydride, a monoacetyl derivative is formed, which no longer gives any colour with ferric chloride ; it must therefore be concluded either that the introduction of the acetyl group into the molecule has caused the hydroxylic oxygen to become ketonic or that the hydroxyl group has been acetylated ; seeing, however, that the substance gives a semi-carbazone, the former alternative is the more likely and the formula accordingly becomes

$$
\begin{array}{c}
\text{CMe}_2 \\
\diagup \diagdown \\
\text{CH}_2 \quad \text{CH}_2 \\
\mid \qquad \mid \\
\text{CO} \quad \text{C·NH·CO·CH}_3 \\
\diagdown \diagup \diagup \\
\text{CH}
\end{array}
$$

The monoanilide and monotoluidide, just like the monoamine, also produce colour reactions with ferric chloride and do not give oximes or semicarbazones; when, however, they are heated with semicarbazide in alcoholic solution, they undergo hydrolysis, liberating aniline and toluidine respectively, and both give the disemicarbazone of dimethyl-dihydroresorcin. On acetylation, both the monotoluidide and the monoanilide give rise to substances which no longer give colour reactions with ferric chloride, but which condense readily with semicarbazide, giving compounds having the general formula

$$\begin{array}{c} CMe_2 \\ \diagup\diagdown \\ CH_2 \quad CH_2 \\ | \qquad | \\ NH_2\cdot CO\cdot NH\cdot N\!:\!C \qquad CN\!\!<\!\!\begin{array}{c}R\\CO\cdot CH_3\end{array} \\ \diagdown\diagup \\ CH \end{array}$$

With a view to obtaining evidence of the hydroxyl group in the monotoluidide, this substance was treated in chloroform solution with phosphorus trichloride; a violent reaction at once set in, resulting in the formation of the above-mentioned ditoluidide hydrochloride. Phosphorus pentachloride produced a similar decomposition, giving the ditoluidide hydrochloride and chloroketodimethyltetrahydro-benzene; this reaction may be explained by assuming the hydroxyl group in the monotoluidide to be replaced by chlorine with the formation of an intermediate compound,
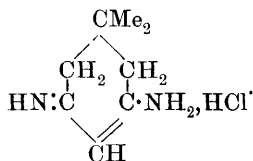
$$CMe_2\!\!<\!\!\begin{array}{c}CH_2\cdot C(NHC_7H_7)\\CH\!=\!=\!=\!=\!CCl\end{array}\!\!>\!\!CH,$$
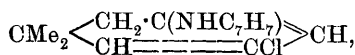
which then condenses with a second molecule of $p$-toluidine, set free from the monotoluidide by the hydrolytic action of the liberated hydrochloric acid; the dimethyldihydroresorcin which is thereby set free is then converted by the remaining phosphorus haloid into chloro-ketodimethyltetrahydrobenzene. The formulæ for the dianilide and ditoluidide are taken to be of the type

$$\begin{array}{cc} \begin{array}{c} CMe_2 \\ \diagup\diagdown \\ CH_2 \quad CH_2 \\ | \qquad | \\ RN\!:\!C \qquad C\cdot NHR \\ \diagdown\diagup \\ CH \end{array} & \text{and not} \quad \begin{array}{c} CMe_2 \\ \diagup\diagdown \\ CH \quad CH_2 \\ | \qquad | \\ RNH\cdot C \qquad C\cdot NHR' \\ \diagdown\diagup \\ CH \end{array} \end{array}$$

inasmuch as both substances are mono-acid bases, giving rise to monohydrochlorides only; moreover, the dianilide gives a mono-

acetyl, and the ditoluidide a monobenzoyl derivative ; the formula of the diamine hydrochloride would accordingly by analogy be

$$
\begin{array}{c}
\mathrm{CMe_2} \\
\diagup \diagdown \\
\mathrm{CH_2} \quad \mathrm{CH_2} \\
| \qquad | \\
\mathrm{HN\!:\!C} \qquad \mathrm{C\cdot NH_2, HCl^{\cdot}} \\
\diagdown \diagup\diagup \\
\mathrm{CH}
\end{array}
$$

The action of nitrous acid on these substances is still under investigation.

## Summary.

1. 5-Chloro-3-keto-1 : 1-dimethyl-$\Delta^4$-tetrahydrobenzene reacts directly with two molecules of a primary base, yielding a compound of the type $RN\!:\!C_8H_{12}\cdot NHR, HCl$.

2. Dimethyldihydroresorcin condenses with one molecule only of a primary base, yielding a compound of the type $C_8H_{10}NHR$, the elements of water being eliminated between the hydroxyl group of the resorcin and a hydrogen from the amino-group.

3. Neither chloroketodimethyltetrahydrobenzene nor dimethyldihydroresorcin reacts with secondary amines.

4. The replacement of the hydroxyl group in dimethyldihydroresorcin by a basic group such as $-NH_2$, $-NH\cdot C_6H_5$, or $-NH\cdot C_7H_7$, causes the remaining ketonic oxygen atom of the resorcin to become hydroxylic, as shown by the behaviour of the resulting substance towards ferric chloride and phosphorus trichloride. If, however, the substituting group is rendered more acidic by the introduction of an acetyl group, this second oxygen atom becomes ketonic and is able to condense with semicarbazide.

5. The mono-derivatives obtained from dimethyldihydroresorcin can be converted into di-derivatives either by condensation with a second molecule of the primary base in presence of zinc chloride or by the action of the phosphorus haloids.

6. An attempt to prepare an unsymmetrical di-derivative from the monoamine and $p$-toluidine in the presence of zinc chloride resulted in the displacement of ammonia by $p$-toluidine and the formation of the monotoluidide.

## Experimental.

### Action of Ammonia on Dimethyldihydroresorcin.

A solution of 20 grams of dimethyldihydroresorcin in 15 c.c. of concentrated ammonia was evaporated to small bulk over a water-bath ; after drying in a vacuum, there remained a light yellow solid

residue, which was purified by crystallisation from chloroform. A further quantity of material was obtained from the chloroform mother liquors by evaporating them to dryness and crystallising the residue from water, when some unchanged dimethyldihydroresorcin separated; the aqueous solution on evaporation left almost pure material.

0·1260 gave 0·3184 $CO_2$ and 0·1112 $H_2O$. C = 68·93; H = 9·86.

0·1304 ,, 11·6 c.c. moist nitrogen at 18° and 760·5 mm. N = 10·28.

$C_8H_{13}ON$ requires C = 69·06; H = 9·36; N = 10·07 per cent.

*5-Hydroxy-3-amino-1 : 1-dimethyl-Δ³⁵-dihydrobenzene* (monoamine), $CMe_2{<}^{CH_2 \cdot C(NH_2)}_{CH=C(OH)}{>}CH_2$, crystallises from chloroform or benzene in colourless, flattened needles melting at 163·5—164°; it is readily soluble in cold water, acetone, ether, or alcohol, is very sparingly soluble in cold chloroform or benzene, and is insoluble in light petroleum; it dissolves readily in hydrochloric acid, giving a hydrochloride, and is insoluble in strong caustic potash. Its solution in water which is neutral to litmus gives no precipitate with silver nitrate, showing that it is not an ammonium salt. Dissolved in alcohol and boiled with strong potassium hydroxide solution and a few drops of chloroform, it develops a faint but distinct odour of carbylamine. It does not yield an oxime, a *p*-bromophenylhydrazone, or a semicarbazone, and its aqueous solution gives a cherry-red colour with ferric chloride.

The *hydrochloride*, $C_8H_{13}ON,HCl$, is obtained by evaporating a hydrochloric acid solution of the base to small bulk over a water-bath; on standing in a desiccator over caustic potash, the solution deposits large, transparent, lozenge-shaped slabs which melt at 186—188°; the crystals are readily soluble in alcohol or water, giving an acid solution.

0·1176 required 6·75 c.c. $N$/10 NaOH = 0·0246 HCl.    HCl = 20·92.

$C_8H_{13}ON,HCl$ requires HCl = 20·77 per cent.

The *platinichloride*, $(C_8H_{13}ON)_2,H_2PtCl_6$, was obtained by dissolving the base in the least quantity of alcohol, acidifying the solution with a little hydrochloric acid, and adding to it the calculated amount of platinic chloride dissolved in alcohol. It separates from the solution in orange-coloured plates which melt with decomposition at 197—198° and are readily soluble in alcohol and in water.

0·1978 gave 0·0551 Pt.    Pt = 27·86.

$C_{16}H_{28}O_2N_2Cl_6Pt$ requires Pt = 28·32 per cent.

The *picrate*, $C_8H_{13}ON,C_6H_2(NO_2)_3 \cdot OH$, separates from a chloroform solution of the two constituents as a yellow oil which, after warming

on the water-bath, solidifies to a mass of deep canary-yellow crystals which melt at 135°.

0·1217 gave 16 c.c. moist nitrogen at 16° and 757 mm.    N = 15·26.
$C_{14}H_{16}O_8N_4$ requires N = 15·21 per cent.

The *acetyl* derivative was prepared by heating 10 grams of the monoamine with 15 grams of acetic anhydride for half an hour on the water-bath.    After removing the excess of the anhydride by boiling the solution with methyl alcohol, the resulting solid was crystallised from benzene.

0·1207 gave 8·5 c.c. moist nitrogen at 17° and 758 mm.    N = 7·76.
$C_{10}H_{15}O_2N$ requires N = 7·73 per cent.

5-*Keto*-3-*acetylamino*-1 : 1-*dimethyl*-$\Delta^3$-*tetrahydrobenzene*,
$$CMe_2\!\!<^{CH_2 \cdot C \cdot NH \cdot Ac}_{CH_2\!\!-\!\!-\!\!-\!\!-CO}\!\!>\!CH,$$
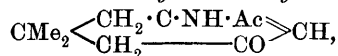
crystallises from benzene in oblong plates and melts at 157°; it is readily soluble in cold chloroform, alcohol, or water, sparingly so in benzene, and insoluble in ligroin.    Treated in aqueous solution with bromine water, it is converted into dibromodimethyldihydroresorcin. The substance gives no colour with ferric chloride in aqueous solution.    When evaporated on the water-bath with dilute hydrochloric acid, it loses acetic acid, giving the hydrochloride of the monoamine.

The *semicarbazone*, $NH_2 \cdot CO \cdot NH \cdot N\!:\!C_8H_{11} \cdot NH \cdot Ac$, of the above acetyl derivative was obtained by dissolving 1 gram of this substance in an alcoholic solution of 1·2 grams of semicarbazide hydrochloride and 1·2 grams of potassium acetate, from which the precipitated potassium chloride had been removed by filtration.    After heating for one and a half hours on the water-bath, the major portion of the alcohol was evaporated off ; the solution on standing deposited 0·8 gram of a white, crystalline solid, which was analysed after recrystallisation from water.

0·1275 gave 25·6 c.c. moist nitrogen at 20° and 762 mm.  N = 22·93.
$C_{11}H_{18}O_2N_4$ requires N = 23·53 per cent.

The substance is readily soluble in cold methyl or ethyl alcohol and is fairly soluble in warm ethyl acetate or acetone, but is insoluble in light petroleum ; it crystallises from water or from a mixture of alcohol and light petroleum in rhombic plates melting at 208·5—209·5°.

### Action of Bromine Water on the Monoamine.

Bromine water added to an aqueous solution of the monoamine produced at once a white, crystalline precipitate of dibromodimethyl-

dihydroresorcin, which crystallised from dilute alcohol in flattened needles melting at 144—146°.

0·1028 gave 0·1295 AgBr.    Br = 53·62.

$C_8H_{10}O_2Br_2$ requires Br = 53·68 per cent.

The aqueous mother liquors on evaporation yielded ammonium bromide.   An aqueous solution of dimethyldihydroresorcin treated as above with bromine water yielded the same dibromide (m. p. 144—146°).

### Action of Potassium Hydroxide on the Monoamine.

A solution of 1 gram of the monoamine and 1 gram of potassium hydroxide in 6 grams of water was boiled for six hours; on acidifying the solution with hydrochloric acid, 0·6 gram of dimethyldihydro-resorcin was precipitated.

### Action of p-Toluidine on the Monoamine.

A solution of 4 grams o the monoamine and 3 grams of p-toluidine in 10 grams of alcohol was heated with 1 gram of zinc chloride in a sealed tube for six hours at 150—160°.   The contents of the tube were then filtered and evaporated to dryness; the residue, after extracting with boiling water, was crystallised from acetic acid, from which it separated in hexagonal plates melting at 199—200°.   This substance had all the properties of the monotoluidide described on page 196, and when mixed with it did not depress its melting point.

### Action of Ammonia on Chloroketodimethyltetrahydrobenzene.

A mixture of 8 grams of chloroketodimethyltetrahydrobenzene with 35 c.c. of alcoholic ammonia was heated in a sealed tube for three hours at 100°; the yellow alcoholic solution was then filtered from some crystals of ammonium chloride formed during the reaction, and evaporated to dryness.   The yellowish-brown, solid residue, after decolorising by extraction with chloroform, was purified by crystal-lisation from a mixture of alcohol and ether.

0·1237 gave 0·2611 $CO_2$ and 0·1064 $H_2O$.   C = 55·33; H = 9·18.

0·1494   ,,   21 c.c. moist nitrogen at 764 mm. and 21·5°.  N = 16·05.

0·1256   ,,   0·1059 AgCl.   Cl = 20·85.

$C_8H_{14}N_2$,HCl requires  C = 55·01;  H = 8·60;  N = 16·05;  Cl = 20·34 per cent.

5-Imino-3-amino-1 : 1-dimethyl-Δ³-tetrahydrobenzene (diamine) hydro-

*chloride*, $CH_2 {<} {CMe_2-CH_2 \atop C(:NH)\cdot CH} {>} C \cdot NH_2, HCl$, is readily soluble in cold alcohol, giving a greenish-yellow solution, from which it is precipitated by ether in fine, silken-white needles which, on standing, change to stout prisms melting at $257-258°$; it is very soluble in methyl alcohol, formic acid, or water, but is insoluble in acetone, chloroform, ether, or light petroleum. The aqueous solution has a blue fluorescence which is changed to greenish-yellow by the addition of caustic potash in the cold; on gently warming, however, ammonia is readily evolved.

The *platinichloride*, $(C_8H_{14}N_2)_2, H_2PtCl_6$ separates from the solution in orange-yellow, hexagonal plates on mixing an alcoholic solution of the hydrochloride with one of platinic chloride; it melts with decompositon at $215°$.

$0 \cdot 1765$ gave $0 \cdot 0499$ Pt. Pt $= 28 \cdot 27$.
$\qquad C_{16}H_{30}N_4Cl_6Pt$ requires Pt $= 28 \cdot 40$ per cent.

### *Attempts to prepare 5-Imino-3-amino-1 : 1-dimethyl-$\Delta^3$-tetrahydrobenzene (the Diamine Base) from its Hydrochloride.*

(1) *With Silver Oxide.*—An aqueous solution of the hydrochloride was thoroughly shaken with freshly precipitated silver oxide and filtered; the strongly alkaline filtrate, after evaporation to dryness over a water-bath, left a syrupy residue; the latter was extracted with benzene, but during the process there was a considerable evolution of ammonia, and the benzene solution on cooling deposited crystals of the monoamine.

(2) *With Silver Sulphate and Barium Hydroxide.*—The diamine hydrochloride dissolved in water was treated with a solution of silver sulphate until no further precipitate of silver chloride was formed; the filtered solution was then warmed with a slight excess of barium hydroxide, the excess being subsequently precipitated by means of a current of carbon dioxide. After filtering off the precipitated barium salts, the aqueous solution was evaporated to dryness; the syrupy alkaline residue so obtained was then boiled with benzene, but a considerable evolution of ammonia was noticed during the process; the benzene solution on cooling deposited silken needles which melted between $95°$ and $105°$. This substance, which appeared only to be decomposed by further crystallisation, gave numbers on analysis which showed it to be a mixture of the diamine base with the monoamine.

The *picrate* of the diamine, $C_8H_{14}N_2, C_6H_2(NO_2)_3 \cdot OH$, was prepared by heating some of the syrupy residue, obtained from the diamine hydrochloride as described in the previous experiment, with a chloroform solution of picric acid; after heating for an hour, the precipitated

yellow solid was filtered off and crystallised from a mixture of acetone and light petroleum ; it forms orange-yellow, flattened needles and melts at 175°.

0·1128 gave 18·5 c.c. moist nitrogen at 18° and 768·5 mm.  N = 19·14.
$C_{14}H_{17}O_7N_5$ requires N = 19·07 per cent.

### Conversion of the Diamine into the Monoamine.

Two grams of the diamine hydrochloride dissolved in a small amount of water were warmed on the water-bath for half an hour with a solution of 1·2 grams (2 mols.) of caustic potash in 10 c.c. of water.   On cooling the mixture, a mass of yellow needles separated out which, when purified by recrystallisation from benzene, melted at 164—165° and in every way resembled the monoamine ; the substance was further characterised by conversion into its hydrochloride melting at 183—185°.

### Conversion of the Monoamine into the Diamine Hydrochloride.

Two and a half grams of the monoamine dissolved in 10 c.c. of alcoholic ammonia were heated in a sealed tube with 2 grams of fused and powdered zinc chloride for three hours at 160° ; the tube now contained an alcoholic solution and some well-formed prismatic crystals attached to the sides of the tube ; the crystals collected from a number of experiments were found to be insoluble in all organic solvents ; when treated with water, they were decomposed with the liberation of zinc hydroxide, giving a green, fluorescent solution ; the latter on evaporation yielded a solid residue which crystallised from a mixture of alcohol and ether in tabular prisms melting at 258° and had all the properties of the hydrochloride of the diamine described on page 195.

### Action of p-Toluidine on Dimethyldihydroresorcin.

The monotoluidide which results from the condensation in alcoholic solution of *p*-toluidine with dimethyldihydroresorcin has already been described by Vorländer and Erig (*Annalen*, 1897, **294**, 315).

4-*Hydroxy*-3-*tolylamino*-1 : 1-*dimethyl*-$\Delta^{3:5}$-*dihydrobenzene*      (mono-toluidide),   $CMe_2\underset{CH=\!=\!=\!=C(OH)}{\overset{CH_2 \cdot C(NH \cdot C_7H_7)}{\diagdown \diagup}}CH$, when perfectly pure is colourless and melts at 202° and not at 200°, as stated by the above-mentioned authors : it gives with ferric chloride in alcoholic solution a cherry-red colour and does not yield a semicarbazone.

The *hydrochloride* of the monotoluidide, $C_{15}H_{19}ON,HCl$, was obtained by saturating a chloroform solution of the base with dry hydrogen
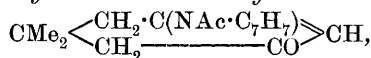
chloride. The residue left on evaporating the solution to dryness in a vacuum crystallised from a mixture of alcohol and ether in prisms which melted with decomposition at 208—212° after contracting some degrees below that temperature. The substance dissolves readily in water, giving an acid solution.

0·1269 required 4·7 c.c. $N/10$ NaOH = 0·0171 HCl.   HCl = 13·52.
$C_{15}H_{19}ON$,HCl requires HCl = 13·74 per cent.

The *acetyl* derivative was prepared by boiling a solution of 10 grams of the monotoluidide with 12 grams of acetic anhydride for two hours over an iron gauze ; after evaporating down the mixture several times with methyl alcohol, it was placed in a vacuum over caustic potash, when it solidified after about a week. The brown solid was then purified by boiling in chloroform solution with animal charcoal and crystallising from a mixture of chloroform and light petroleum (b. p. 60—80°).

0·1247 gave 0·3426 $CO_2$ and 0·0902 $H_2O$.   C = 74·93 ; H = 8·03.
0·134    ,,    6·2 c.c. moist nitrogen at 22·5° and 774 mm.   N = 5·32.
$C_{17}H_{21}O_2N$ requires C = 75·27 ; H = 7·75 ; N = 5·15 per cent.

5-*Keto*-3-*acetyl*-p-*tolylamino*-1 : 1-*dimethyl*-$\Delta^3$-*tetrahydrobenzene*,
$$CMe_2 \begin{matrix} CH_2 \cdot C(NAc \cdot C_7H_7) \\ CH_2 \underline{\qquad\qquad} CO \end{matrix} CH,$$
crystallises from light petroleum in long, colourless, transparent prisms which melt at 95—97° ; it is readily soluble in cold chloroform, alcohol, or ether, and fairly soluble in boiling light petroleum (b. p. 40—60°) ; its solution in alcohol gives no colour with ferric chloride.

The *semicarbazone*, $NH_2 \cdot CO \cdot NH \cdot N \colon C_8H_{11}NAc \cdot C_7H_7$, of the acetyl derivative of the monotoluidide, was prepared without the application of heat by allowing the acetyl derivative to stand with two molecular proportions of semicarbazide acetate ; it crystallises from alcohol in stellar aggregates of oblong plates and melts with evolution of gas at 216° or 221° according to the rate at which it is heated ; it is very slightly soluble in cold alcohol and is insoluble in acetone.

0·1102 gave 16 c.c. moist nitrogen at 19° and 769 mm.   N = 16·84.
$C_{18}H_{24}O_2N_4$ requires N = 17·07 per cent.

### Action of Semicarbazide on the Monotoluidide.

One gram of the monotoluidide was heated on the water-bath for two hours with an alcoholic solution of semicarbazide acetate obtained by mixing 1 gram of semicarbazide hydrochloride, dissolved in the least quantity of water, with an alcoholic solution of 1 gram of

potassium acetate and filtering off the precipitated potassium chloride. On cooling the mixture, an odour of $p$-toluidine was observed, and the solution deposited 0·4 gram of a crystalline solid which, when washed with alcohol, melted with decomposition at 213—216°; this substance was identified as the semicarbazone of dimethyldihydroresorcin both by its melting point and by its insolubility in ordinary organic solvents.

0·1014 gave 27 c.c. moist nitrogen at 10·5° and 784 mm.   N = 32·88.
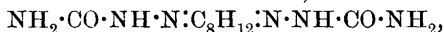$C_{10}H_{18}O_2N_6$ requires N = 33·07 per cent.

The alcoholic mother liquors on further concentration yielded unchanged monotoluidide.

### Semicarbazone of Dimethyldihydroresorcin.

One gram of dimethyldihydroresorcin dissolved in alcohol was added to an alcoholic solution containing two molecular proportions of semicarbazide acetate obtained in the manner described above.    On warming the mixture for five minutes on the water-bath, a copious white precipitate was formed, which, after filtering, was thoroughly washed with hot alcohol and dried in a vacuum.

0·1059 gave 29·8 c.c. moist nitrogen at 16° and 771 mm.   N = 33·31.
$C_{10}H_{18}O_2N_6$ requires N = 33·07 per cent.

*Dimethyldihydroresorcin disemicarbazone,*
$$NH_2 \cdot CO \cdot NH \cdot N \colon C_8H_{12} \colon N \cdot NH \cdot CO \cdot NH_2,$$
melts with evolution of gas at 213—216°; it is very slightly soluble in boiling ethyl alcohol and is insoluble in all ordinary organic solvents.

### Action of p-Toluidine on Chloroketodimethyltetrahydrobenzene.

When chloroketodimethyltetrahydrobenzene (1 mol.) and $p$-toluidine (2 mols.) are heated together, they react with considerable violence; in alcohol or benzene solution, the reaction takes place quite gently in the cold on standing for some hours, or more rapidly on heating, with the formation of a mass of yellow crystals; the latter, dissolved in a large volume of boiling water and treated with dilute potassium hydroxide, gave a light yellow, curdy precipitate which, after washing with water, was purified by crystallisation from alcohol.

0·1257 gave 0·3826 $CO_2$ and 0·0966 $H_2O$.    C = 83·01 ;  H = 8·54.
0·1262   „   0·3842 $CO_2$   „   0·0967 $H_2O$.    C = 83·10;  H = 8·51.
0·1346   „    10·4 c.c. moist nitrogen at 21·5° and 770 mm.   N = 8·89.
$C_{22}H_{26}N_2$ requires C = 83·02 ;  H = 8·17 ;  N = 8·80 per cent.

5-p-*Tolylimino*-3-p-*tolylamino*-1 : 1-*dimethyl*-$\Delta^3$-*tetrahydrobenzene* (di-toluidide), $CMe_2 \begin{smallmatrix} CH_2 \cdot C(NH \cdot C_7H_7) \\ CH_2 - C(:N \cdot C_7H_7) \end{smallmatrix} \!\!\! > \!\! CH$, is a light yellow solid which persistently retains its colour even after boiling in alcoholic solution with animal charcoal ; it crystallises from alcohol in light yellow plates melting at 208—210° ; it is readily soluble in cold chloroform and slightly so in hot ether ; it dissolves readily in glacial acetic acid, but with difficulty in hot dilute hydrochloric or sulphuric acid, and is insoluble in water. A solution of the base in alcohol has a strongly alkaline reaction to litmus. The substance is unaffected by boiling with alcoholic potash.

The *hydrochloride*, $C_{22}H_{26}N_2,HCl$, is formed directly in practically theoretical yield by the condensation of *p*-toluidine with chloroketo-dimethyltetrahydrobenzene, as described above ; it crystallises from formic acid in canary-yellow, hexagonal plates which contain a molecule of formic acid and melt with decomposition at 320°.

0·1248 gave 0·3170 $CO_2$ and 0·0838 $H_2O$.   C = 69·27 ; H = 7·46.
0·1307   ,,   8·2 c.c. moist nitrogen at 21° and 775·6 mm.   N = 7·28.
0·1283   ,,   0·0463 AgCl.   Cl = 8·92.
0·2660 on heating to 130° lost 0·0276.   $H_2CO_2$ = 11·58.
$C_{22}H_{27}N_2Cl,H_2CO_2$ requires C = 68·91 ; H = 7·24 ; N = 6·99 ; Cl = 8·86.
$H_2CO_2$ = 11·48 per cent.

It is sparingly soluble in hot alcohol and dissolves only in a very large volume of boiling water, giving a neutral solution ; it is insoluble in all ordinary organic solvents except formic and acetic acids. It may also be prepared by dissolving the base in alcohol and adding hydro-chloric acid to the boiling solution ; on cooling, yellow, hexagonal plates separate out, which do not contain a molecule of the solvent.

0·1208 gave 0·0500 AgCl.   Cl = 10·23.
$C_{22}H_{26}N_2,HCl$ requires Cl = 10·02 per cent.

The *platinichloride*, $(C_{22}H_{26}N_2)_2,H_2PtCl_6$, is formed as an immediate yellow precipitate on mixing an alcoholic solution of the base acidified with hydrochloric acid with the calculated amount of platinic chloride dissolved in alcohol ; it decomposes at 253°.

0·2016 gave 0·0377 Pt.   Pt = 18·70.
$C_{44}H_{54}N_4Cl_6Pt$ requires Pt = 18·62 per cent.

The *benzoyl* derivative, $C_{22}H_{25}N_2 \cdot CO \cdot C_6H_5$, was prepared by vigor-ously shaking a suspension of the base in aqueous caustic potash with an ethereal solution of benzoyl chloride ; a white, crystalline solid was formed, which was purified by crystallisation from dilute alcohol.

0·1222 gave 0·3702 $CO_2$ and 0·0845 $H_2O$.   C = 82·62 ; H = 7·68.

0·1269   ,,   7·5 c.c. moist nitrogen at 18·5° and 760·7 mm.   N = 6·82.

$C_{29}H_{30}ON_2$ requires C = 82·46 ; H = 7·11 ; N = 6·63 per cent.

It crystallises from dilute alcohol in needles which melt with decomposition between 144° and 149° ; it is very soluble in cold alcohol, chloroform, acetone, or ether.

### Action of Fuming Hydrochloric Acid on the Ditoluidide.

Two and a half grams of the ditoluidide hydrochloride heated with 12 grams of fuming hydrochloric acid in a sealed tube at 125° for two hours remained practically unchanged.

The same proportions as above were therefore heated for two hours at 250° ; the contents of the tube, consisting of a brown liquid in which were suspended crystals of *p*-toluidine hydrochloride, were poured into water, and the acid solution A thus obtained was extracted with ether. The ethereal extract on evaporation yielded 0·8 gram of a brown, viscous oil, which solidified after some days ; the solid was purified by crystallisation from a mixture of alcohol and light petroleum, when a well-defined, crystalline substance was obtained which melted at 101°. This was identified as $\beta\beta$-dimethylglutaric acid by conversion into the anhydride (m. p. 124·5°), anilic acid (m. p. 134—135°), and anil (m. p. 156°), all these melting points agreeing closely with those given by Perkin (Trans., 1896, **69**, 1473). The acid solution A, when rendered alkaline and extracted with ether, gave 1 gram of *p*-toluidine, which was identified by its crystalline form and characteristic odour and melting point (45°).

### Action of Fuming Hydrochloric Acid on Dimethyldihydroresorcin.

Two grams of dimethyldihydroresorcin and 8 grams (16 mols.) of fuming hydrochloric acid were heated in a sealed tube fo two hours at 230° ; the brown, resinous mass contained in the tube was then extracted with water ; on evaporating the aqueous solution to dryness, there remained 0·8 gram of white crystals which melted at 94—100° ; they were converted without further purification into the anhydride, melting after crystallisation at 125°, and the latter into the anilic acid (m. p. 134·5°), which was analysed.

0·1236 gave 6·8 c.c. moist nitrogen at 9·5° and 776 mm.   N = 6·72.

$C_{11}H_{17}O_3N$ requires N = 6·63 per cent.

The amount of $\beta\beta$-dimethylglutaric acid obtained in this experiment corresponds to a yield of about 35 per cent.

## Conversion of the Monotoluidide into the Ditoluidide.

To a mixture of 5·5 grams of the monotoluidide with 2·5 grams of *p*-toluidine heated to 200° were added, in portions, 1·5 grams of freshly fused and powdered zinc chloride, the heating being continued for about one hour. On cooling, the contents of the flask solidified; they were broken up, extracted with dilute hydrochloric acid to remove any unchanged *p*-toluidine, filtered, washed, and dried, 7·5 grams of solid being thus obtained. On dissolving this substance in a large volume of boiling water and pouring the filtered solution into dilute caustic potash, a yellow precipitate was at once formed which, after crystallising from alcohol, had the melting point of the ditoluidide base.

0·1223 gave 0·3720 $CO_2$ and 0·0950 $H_2O$.    $C = 82·95$; $H = 8·63$.
0·1271    ,,    10·6 c.c. moist nitrogen at 22° and 761 mm.    $N = 9·46$.
   $C_{22}H_{26}N_2$ requires $C = 83·02$; $H = 8·17$; $N = 8·80$ per cent.

## Action of Phosphorus Trichloride on the Monotoluidide.

Fifteen grams (3 mols.) of the monotoluidide, dissolved in 70 grams of chloroform, were treated with 3 grams (1 mol.) of phosphorus trichloride; a fairly violent reaction at once set in, and the solution assumed a claret-red colour. After heating for three hours over a water-bath, the chloroform was distilled off; on extracting the red resin so obtained with ether, a yellow, solid residue was obtained, which was identified as the hydrochloride of the ditoluidide by crystallisation from formic acid, from which it separated in yellow, hexagonal plates.

0·1253 gave 0·0458 AgCl.    $Cl = 9·04$.
   $C_{22}H_{27}N_2Cl,H_2CO_2$ requires $Cl = 8·86$ per cent.

## Action of Phosphorus Pentachloride on the Monotoluidide.

To a solution of 10 grams of the monotoluidide dissolved in 50 grams of chloroform were added, in portions, 10 grams of phosphorus pentachloride, the whole being heated on the water-bath for one and a half hours, by which time the evolution of hydrochloric acid had considerably diminished; the brown chloroform solution was then poured into water and extracted with ether. After some minutes, a yellow solid began to separate from the ethereal solution; this substance, which weighed 3·6 grams, was identified as the hydrochloride of the ditoluidide; when dissolved in a large volume of boiling water and precipitated with caustic potash, it gave the free base

melting at 206—208°. The ethereal solution, on evaporation, gave
6·5 grams of a brown liquid, which, on distillation in steam,
yielded 2·2 grams of a light yellow oil ; the latter was identified as
chloroketodimethyltetrahydrobenzene  by conversion into its semi-
carbazone, which melted at 196—197° with evolution of gas ; another
portion of the oil was converted into the ditoluidide hydrochloride by
condensing it with $p$-toluidine ; the hydrochloride was then converted
into the base and found to give the melting point characteristic of
this substance. The residue left in the flask after submitting the
above-mentioned brown oil to steam distillation was crystallised from
benzene ; it separated from this solvent in short, flat needles melting
at 183—184°.

$$0\cdot1042 \text{ gave } 0\cdot1360 \text{ AgCl.} \quad Cl = 32\cdot29.$$

This substance, which was soluble in ether, alcohol, or chloroform,
but insoluble in light petroleum, was not further investigated.

### Action of Aniline on Dimethyldihydroresorcin.

Four grams of dimethyldihydroresorcin and 3 grams of aniline
were heated in alcoholic solution for three hours over a water-bath.
The yellow solid remaining after evaporation of the alcohol was
crystallised once from acetic acid to remove any free aniline and then
from benzene until it was obtained colourless.

$0\cdot1302$ gave $0\cdot3722$ $CO_2$ and $0\cdot1004$ $H_2O$.   $C = 77\cdot96$ ; $H = 8\cdot57$.
$0\cdot1391$   ,,   $8\cdot2$ c.c. moist nitrogen at $21°$ and $758$ mm. $N = 6\cdot79$.
   $C_{14}H_{17}ON$ requires $C = 78\cdot14$ ; $H = 7\cdot90$ ; $N = 6\cdot51$ per cent.

$5$-$Hydroxy$-$3$-$phenylamino$-$1 : 1$-$dimethyl$-$\Delta^{3:5}$-$dihydrobenzene$   (mono-
anilide), $CMe_2\!\!<^{CH_2\cdot C(NH\cdot C_6H_5)}_{CH\!=\!=\!=\!C(OH)}\!\!>CH$, crystallises from acetic acid
in rhombic plates and from benzene in clusters of oblong plates
which melt at 180°. It is readily soluble in cold alcohol or chloroform,
but is insoluble in cold ether. Its alcoholic solution is neutral to
litmus and gives with ferric chloride a cherry-red colour.

The *hydrochloride*, $C_{14}H_{17}ON,HCl$, was prepared by saturating a
chloroform solution of the base with dry hydrogen chloride. The
solution on standing deposited silken-white needles which were
recrystallised from a mixture of alcohol and ether.

$0\cdot1327$ required $5\cdot24$ c.c. $N/10$ NaOH $= 0\cdot0191$ HCl.   HCl $= 14\cdot41$.
   $C_{14}H_{18}ONCl$ requires HCl $= 14\cdot51$ per cent.

The substance melts with decomposition at 184—186°.

The *acetyl* derivative was prepared by boiling 4 grams of the mono-
anilide with 7 grams of acetic anhydride for one and a half hours over a

wire gauze. The mixture was then evaporated with methyl alcohol and left in a vacuum for some days; as it still showed no signs of solidifying, it was dissolved in a mixture of chloroform and light petroleum; the solution, on being allowed to evaporate slowly, deposited well-formed amber-coloured plates with truncated angles.

0·1226 gave 0·3374 $CO_2$ and 0·0845 $H_2O$. $C = 75·05$; $H = 7·65$.

0·1750 „ 9 c.c. moist nitrogen at 25° and 767 mm. $N = 5·79$.

$C_{16}H_{19}O_2N$ requires $C = 74·70$; $H = 7·39$; $N = 5·45$ per cent.

*5-Keto-3-acetylphenylamino-1 : 1-dimethyl-$\Delta^3$-tetrahydrobenzene,*

$$CMe_2 \genfrac{<}{>}{0pt}{}{CH_2 \cdot C(NAc \cdot C_6H_5)}{CH_2\text{———}CO} CH,$$
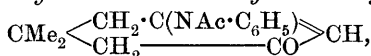
melts at 65·5—66·5°; it is readily soluble in cold alcohol, ether, chloroform, ethyl acetate, or benzene, but is only slightly soluble in boiling light petroleum. An alcoholic solution of the substance gives no colour with ferric chloride.

The *semicarbazone* of this acetyl derivative,

$$NH_2 \cdot CO \cdot NH \cdot N \colon C_8H_{11}NAc \cdot C_6H_5,$$
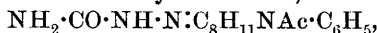
which was prepared in a manner similar to the one described for the corresponding toluidine derivative on p. 197, crystallises from alcohol in hexagonal plates and melts with evolution of gas at 210·5°. It is fairly soluble in hot alcohol, but only slightly so in hot acetone or ethyl acetate.

0·1046 gave 16·2 c.c. moist nitrogen at 15·5° and 762 mm. $N = 18·15$.

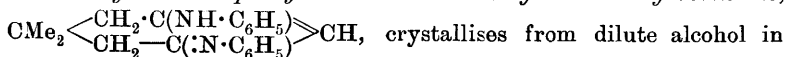$C_{17}H_{22}O_2N_4$ requires $N = 17·83$ per cent.

### Action of Aniline on Chloroketodimethyltetrahydrobenzene.

As in the case of *p*-toluidine, when aniline is heated with chloroketodimethyltetrahydrobenzene, a violent reaction takes place with the formation of a yellow solid. This substance is, however, best prepared by heating one molecular proportion of the chloro-compound with two of aniline in benzene solution. The yellow crystals so obtained are the hydrochloride of the dianilide; they are dissolved in a large volume of boiling water and filtered hot into a solution of caustic potash; the light yellow, curdy precipitate which is at once formed is filtered, washed free from alkali, and crystallised from dilute alcohol.

0·1248 gave 0·3782 $CO_2$ and 0·0910 $H_2O$. $C = 82·65$; $H = 7·97$.

$C_{20}H_{22}N_2$ requires $C = 82·76$; $H = 7·60$ per cent.

*5 - Phenylimino - 3 - phenylamino - 1 : 1 - dimethyl - $\Delta^3$ - tetrahydrobenzene,*

$CMe_2 \genfrac{<}{>}{0pt}{}{CH_2 \cdot C(NH \cdot C_6H_5)}{CH_2\text{—}C(\colon N \cdot C_6H_5)} CH$, crystallises from dilute alcohol in

204    THE CONDENSATION OF DIMETHYLDIHYDRORESORCIN.

light yellow, oblong plates and melts at 193—195°; it is readily soluble in cold chloroform, alcohol, or glacial acetic acid, and in hot benzene, but it is only sparingly so in ether, and is insoluble in water. The solution in alcohol has a strongly alkaline reaction.    Boiling alcoholic potash has no action on the substance.

The *hydrochloride* may be obtained either as described above, by condensation of aniline with chloroketodimethyltetrahydrobenzene, or by crystallising the base from alcohol acidified with hydrochloric acid. Prepared in the former way by condensation and recrystallised from formic acid, the substance gave on analysis the following numbers :

0·1273 gave 0·0518 AgCl.    Cl = 10·06.

0·1600 heated to 150° lost 0·0186.    $H_2CO_2 = 11·55$.

$C_{20}H_{23}N_2Cl,H_2CO_2$ requires Cl = 9·79 ; $H_2CO_2 = 12·34$ per cent.

It crystallises from formic acid in stellar aggregates of stout, flat needles, which contain 1 molecule of the solvent ; the crystals slowly lose this formic acid and change their form to stout, rhombic slabs resembling sulphur.

The *platinichloride*, $(C_{20}H_{22}N_2)_2,H_2PtCl_6$, was prepared by adding to an alcoholic solution of the hydrochloride the calculated amount of platinic chloride dissolved in alcohol.    A crystalline precipitate of orange-yellow needles was at once formed, which, after washing with alcohol and drying, gave the following numbers on analysis :

0·2029 gave 0·0396 Pt.    Pt = 19·51.

$C_{40}H_{46}N_4Cl_6Pt$ requires Pt = 19·68 per cent.

The salt is insoluble in alcohol and in water.

The *acetyl* derivative, $C_{20}H_{21}N_2 \cdot CO \cdot CH_3$, was prepared from two grams of the dianilide base by heating it over a water-bath for two hours with excess of acetic anhydride ; after evaporating the solution several times with methyl alcohol in order to remove the excess of the anhydride, the brown, syrupy residue was crystallised from a mixture of chloroform and light petroleum and subsequently from dilute alcohol.

0·1341 gave 9 c.c. moist nitrogen at 13° and 767·5 mm.    N = 8·01.

$C_{22}H_{24}ON_2$ requires N = 8·43 per cent.

The substance separates from dilute alcohol in stellar aggregates of prisms melting at 161—162° ; it is readily soluble in cold alcohol, acetone, ethyl acetate, or chloroform, but is insoluble in ether, light petroleum, or water.

### *Conversion of the Monoanilide into the Dianilide.*

Two and a half grams of the monoanilide, when heated with 2 grams of aniline and 1 gram of zinc chloride for one hour at $200-220°$, gave an olive-brown, viscous liquid, which, after extraction with dilute hydrochloric acid, solidified to a yellow mass ; the latter dissolved in a large volume of boiling water to a clear solution, which, on treatment with caustic potash, gave a canary-yellow precipitate ; this substance, which crystallised from dilute alcohol in plates melting at $193-195°$, had all the properties of the dianilide.

### *Behaviour of Chloroketodimethyltetrahydrobenzene and of Dimethyl-dihydroresorcin towards Methylaniline.*

Three grams (1 mol.) of chloroketodimethyltetrahydrobenzene and 2 grams (1 mol.) of methylaniline were heated together in alcoholic solution for four hours ; the solution was then acidified and distilled in steam, when some unchanged chloro-compound was recovered ; the major portion of this substance had, however, been hydrolysed by the acid solution and was recovered therefrom in the form of a crystalline precipitate of dimethyldihydroresorcin weighing 2 grams. The acid mother liquors, when made alkaline and extracted with ether, yielded 2 grams of dimethylaniline unchanged.

Molecular proportions of dimethyldihydroresorcin and methylaniline heated together in alcoholic solution for three hours also did not react, the unchanged materials being recovered from the mixture.

CHEMICAL LABORATORY,
ST. THOMAS'S HOSPITAL,
LONDON, S.E.