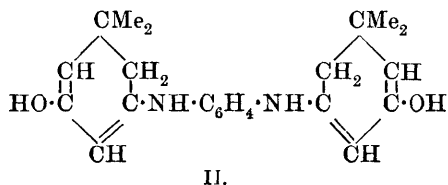
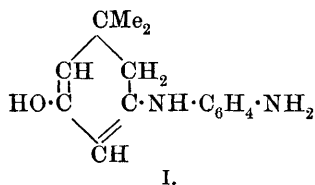


XLIII.—*The Condensation of Dimethyldihydroresorcin and of Chloroketodimethyltetrahydrobenzene with Primary Amines. Part II. Diamines.—m- and p-Phenylenediamine.*

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

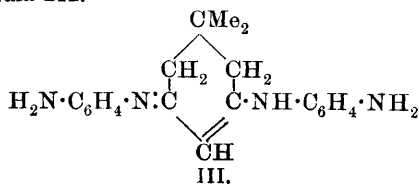
IN a previous communication (this vol., p. 187), the condensation of dimethyldihydroresorcin and of chloroketodimethyltetrahydrobenzene with primary monamines was described, and it was there shown that these two substances condensed directly with 1 and 2 molecules respectively of a monamine. When molecular proportions of the resorcin and a primary diamine are heated together in alcoholic solution they interact to give an 80 per cent. yield of the simple condensation product (I) formed from 1 molecule of each constituent.



In addition to this there is, however, also formed a small amount of the compound II, resulting from the condensation of 2 molecules of the resorcin with 1 of the diamine. The compounds of the formula I, which will be referred to as the monometa- or monopara-compounds, are, unlike the original diamines, quite stable substances; they are both colourless when pure, but the para-compound slowly assumes a reddish-yellow tint on exposure to daylight; they function as di-acid bases, giving rise to dihydrochlorides which react with one molecular proportion of platinic chloride to form platinum salts. The latter tenaciously retain a certain amount of alcohol even when dried in a vacuum, and only part with it completely when heated to 120°. The bases are insoluble in water, but dissolve in alcohol to form neutral solutions which produce with ferric chloride a reddish-brown coloration; on acetylation by means of acetic anhydride, they yield monoacetyl derivatives only, which still give a colour reaction with ferric chloride. In the previous communication, it was shown that the introduction of an acetyl group into a monoamino-derivative destroyed the ferric chloride colour reaction of the free base by causing the originally hydroxylic oxygen atom in the compound to become ketonic; in the case of these substances, however, the acetyl group is not able to exert the same influence on the oxygen atom, since it is the free amino-nitrogen which is acetylated and not the nitrogen atom directly attached to the resorcin complex; this fact was proved in the case of the monopara-compound by showing that its acetyl derivative could also be prepared by the condensation of dimethyldihydroresorcin with *p*-aminoacetanilide.

When either the monometa- or the monopara-compound is boiled with hydrochloric acid, it is hydrolysed, giving rise to the hydrochloride of the corresponding *m*- or *p*-phenylenediamine and *s*-bisresorecyl-*m*- or -*p*-phenylenediamine (II); the latter substance may also be prepared by the condensation of the mono-derivative with a second molecule of the resorcin. These di-substituted phenylenediamines are also di-acid bases having a neutral reaction; they are not acetylated by boiling with acetic anhydride and may be recrystallised without change from glacial acetic acid; in alcoholic solution they give with ferric chloride a reddish-yellow colour.

Chloroketodimethyltetrahydrobenzene condenses at once with 2 molecules of *m*-phenylenediamine to give the hydrochloride of a base having the formula III.



This hydrochloride is only very slightly soluble in boiling water, giving a neutral solution from which the free base is precipitated in a crystalline form on the addition of potassium hydroxide; the base, which may be referred to as the dimeta-compound, is insoluble in water, and dissolves readily in alcohol, forming a strongly alkaline solution. On mixing the latter with an alcoholic solution of dimethyldihydroresorcin, a buff-coloured precipitate is at once formed which is a molecular combination of the base with the resorcin; it has the same percentage composition, but twice the molecular weight of the monometa-compound; it dissolves readily in glacial acetic acid and on treatment with potassium hydroxide gives a precipitate of the dimeta-base, thus showing that it is a salt; it is insoluble in ordinary organic solvents except boiling methyl alcohol, and even in this case the process of solution is accompanied by decomposition. It was not found possible to convert this salt into a true condensation product by elimination of the elements of water.

EXPERIMENTAL.

Action of Dimethyldihydroresorcin on m-Phenylenediamine.

A solution of 14 grams of dimethyldihydroresorcin (1 mol.) and 10 grams of freshly distilled *m*-phenylenediamine (1 mol.) in absolute alcohol was boiled for two hours on the water-bath; a portion of the alcohol was then distilled off and the brown solution *A* set aside to crystallise; 16.5 grams of a yellowish-pink solid separated, which, after washing with cold alcohol and powdering in a mortar, were recrystallised from alcohol.

0.1249 gave 0.3348 CO₂ and 0.0954 H₂O. C = 73.10; H = 8.48.

0.1302 „ 14.1 c.c. moist nitrogen at 18.5° and 747 mm. N = 12.28.

C₁₄H₁₈ON₂ requires C = 73.05; H = 7.83; N = 12.18 per cent.

5-Hydroxy-3-m-aminophenylamino-1:1-dimethyl-Δ^{3:5}-dihydrobenzene,

$$\text{CMe}_2 \left\langle \begin{array}{c} \text{CH}_2 \cdot \text{C}(\text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2) \\ \text{CH} \text{---} \text{C}(\text{OH}) \end{array} \right\rangle \text{CH}$$
 (monometa-compound), prepared as above, is a pink substance which crystallises from alcohol in flattened needles, or more commonly in hard, dome-shaped aggregates, and melts at 234—234.5°; it dissolves only with difficulty in hot methyl or ethyl alcohol, although the solubility is somewhat increased by first powdering the crystals; when, however, it is dissolved, it does not separate out again without considerably concentrating the solution; it dissolves also in boiling acetone or pyridine, but is insoluble in ethyl acetate, chloroform, ether, or benzene. The crystals after prolonged boiling in alcoholic solution with animal charcoal lose their pink colour, but still retain a faint yellow coloration, which can only be removed by

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dissolving the base in hydrochloric acid and precipitating it from solution by the addition of potassium hydroxide. An alcoholic solution of the base, which is neutral to litmus, gives a reddish-brown coloration with ferric chloride.

Mr. A. J. Ewins very kindly undertook the determination of the molecular weight of this substance according to the method recently described by Barger and Ewins (Trans., 1905, 88, 1756); using pyridine as the solvent and benzil as the standard, he obtained the value 217; $C_{14}H_{18}ON_2$ requires M.W. = 230.

The brown alcoholic mother liquors and washings from the pink crystals after boiling with animal charcoal and filtering became somewhat lighter in colour; on precipitation with water, they yielded 5.5 grams of a yellow solid melting at $210-220^\circ$, which proved to be a mixture of the above-mentioned pink crystals with a small amount of the *s*-bisresorcy-*m*-phenylenediamine (m. p. 268—269.5°) described on p. 392.

The *hydrochloride*, $C_{14}H_{18}ON_2 \cdot 2HCl$, was prepared by dissolving the base in the least quantity of absolute alcohol and saturating in the cold with dry hydrogen chloride. On addition of ether, a pinkish-white solid was deposited which gave the following numbers on titration of its aqueous solution.

0.1251 required 8.26 c.c. *N*/10 NaOH. $HCl = 24.06$.

0.1206 gave 0.1145 AgCl. $HCl = 24.17$.

$C_{14}H_{20}ON_2Cl_2$ requires $HCl = 24.09$ per cent.

The *platinichloride*, $C_{14}H_{18}ON_2 \cdot H_2PtCl_6$, obtained by adding an alcoholic solution of platinic chloride to a warm alcoholic solution of the hydrochloride, separates from the solution on cooling in needles. The substance tenaciously retains alcohol, as shown by the low values 26.03 and 26.43 obtained on estimating the platinum in the substance when dried in a vacuum. On heating to constant weight at 120° , the following numbers were obtained:

0.2822 gave 0.0856 Pt. $Pt = 30.33$.

$C_{14}H_{20}O_2N_2Cl_6Pt$ requires $Pt = 30.66$ per cent.

The *acetyl* derivative, $C_8H_{11}O \cdot NH \cdot C_6H_4 \cdot NHAc$, was obtained by heating 1 gram of the base for ten minutes over a water-bath with 3 grams of acetic anhydride and 2 grams of glacial acetic acid. On pouring the mixture into water, an oily substance separated; the latter, on solidifying, was crystallised from a mixture of alcohol and ethyl acetate, from which it separated in faintly yellow plates melting at $210.5-211.5^\circ$.

0.1202 gave 10.7 c.c. moist nitrogen at 18° and 758 mm. $N = 10.27$.

$C_{16}H_{20}O_2N_2$ requires $N = 10.29$ per cent.

The substance is readily soluble in cold ethyl alcohol, but is insoluble in ethyl acetate, chloroform, ether, light petroleum, or benzene. In alcoholic solution, it gives with ferric chloride a reddish-brown coloration.

Action of Hydrochloric Acid on the Monometa-compound.

(a) *Under Atmospheric Pressure.*—Four grams of the pink monometa-compound were boiled in a reflux apparatus for twenty minutes with 7 grams of concentrated hydrochloric acid and 3 c.c. of water; the solution was then largely diluted with water and neutralised with potassium hydroxide, and the yellowish-brown precipitate thus obtained was filtered off and repeatedly extracted with hot water until the washings were practically colourless. The residue *A*, which weighed 2.5 grams and did not give a sharp melting point, was purified by boiling with animal charcoal and recrystallising several times from aqueous alcohol, when it melted at 268–269° and was found by means of a mixed melting point to be identical with the *s*-diorsorcy-*m*-phenylenediamine described on p. 392.

The aqueous filtrate from *A* was made alkaline and extracted with ether; the residue from the ethereal extract was found to distil without decomposition, giving a light yellow oil, which solidified on sowing with a crystal of *m*-phenylenediamine, and then melted at 60–63°; this substance was further identified as *m*-phenylenediamine by condensing it in alcoholic solution with chloroketodimethyltetrahydrobenzene, when it gave the hydrochloride described on p. 393; the latter was further converted into the corresponding base (m. p. 118°, with evolution of gas), as described on p. 393.

(b) *Under Increased Pressure.*—Three grams of the base were heated in a sealed tube with 12 grams of concentrated hydrochloric acid for three hours at 180°; the contents of the tube, consisting of a brown liquid and some prismatic crystals, were dissolved in water and made alkaline with solid sodium carbonate; a small quantity of a brown oil separated, which was filtered off and rejected. The filtrate was then evaporated to dryness, acidified with hydrochloric acid, and extracted with ether; the ethereal extract on evaporation yielded 0.5 gram of a yellowish-brown oil which slowly solidified, and was identified as $\beta\beta$ -dimethylglutaric acid by the fact that when mixed with a pure specimen of this acid it did not depress its melting point.

Condensation of Dimethyldihydroresorcin with the Monometa-compound.

Five grams of the monometa-compound (p. 389) and 4 grams of dimethyldihydroresorcin were heated together in boiling alcoholic solution for twelve hours; on evaporating off the major portion of the

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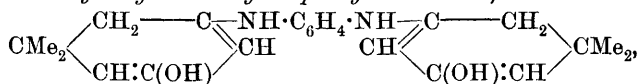
alcohol, the solution deposited 7 grams of a yellow, crystalline solid which, after being decolorised by means of animal charcoal, was recrystallised from aqueous alcohol.

0.113 gave 0.3104 CO₂ and 0.0871 H₂O. C = 74.91; H = 8.56.

0.1126 gave 7.7 c.c. moist nitrogen at 19° and 775 mm. N = 8.02.

C₂₂H₂₈O₂N₂ requires C = 75.00; H = 7.95; N = 7.95 per cent.

s-Bisdimethyldihydroresorcyl-*m*-phenylenediamine,



separates from aqueous alcohol in colourless plates which melt at 268—269.5°; it dissolves readily in cold glacial acetic or formic acid, but is insoluble in all other organic solvents; its alcoholic solution, which is neutral to litmus, gives a marked reddish-brown colour with ferric chloride. The substance was recovered unchanged after boiling for three hours in alcoholic solution with one molecular proportion of *m*-phenylenediamine, showing that it would not condense any further.

The *hydrochloride*, C₂₂H₂₈O₂N₂·2HCl, was prepared by suspending the base in alcohol and saturating the solution in the cold with dry hydrogen chloride; on evaporating the clear yellow solution so obtained to dryness in a vacuum, a white solid remained which could not be recrystallised without undergoing decomposition; it was therefore analysed without further purification.

0.1256 gave 0.0856 AgCl. HCl = 17.32.

C₂₂H₃₀O₂N₂Cl₂ requires HCl = 17.17 per cent.

The substance is readily soluble in cold alcohol; when this solution is diluted with water, the free base is precipitated, whilst the hydrochloric acid is quantitatively liberated and may be estimated by titration.

0.1303 required 6.08 c.c. *N*/10 NaOH. HCl = 17.09.

0.128 „ 5.94 c.c. *N*/10 NaOH. HCl = 16.93.

Action of Chloroketodimethyltetrahydrobenzene on m-Phenylenediamine.

Seven grams (1 mol.) of chloroketodimethyltetrahydrobenzene and 9 grams (2 mols.) of *m*-phenylenediamine dissolved in alcohol were heated over a water-bath; a yellow, crystalline precipitate of the hydrochloride (p. 393) began to separate almost immediately; after heating for one and a half hours, the precipitate was filtered off, washed with alcohol, and dried on a porous tile; its weight was 12.7 grams. When dissolved in a large volume of boiling water and poured in a thin stream into a dilute solution of potassium hydroxide,

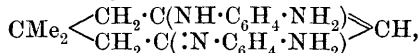
a buff-coloured, crystalline precipitate was produced, which, after washing free from alkali and drying on a porous tile, was recrystallised from aqueous alcohol. The following numbers were obtained on analysis of the substance heated to constant weight at 105—110°.

0.138 gave 0.378 CO₂ and 0.1012 H₂O. C = 74.70 ; H = 8.14.

0.1122 „ 17 c.c. moist nitrogen at 18° and 748 mm. N = 17.19.

C₂₀H₂₄N₄ requires C = 75.00 ; H = 7.50 ; N = 17.50 per cent.

5-*m*-Aminophenylimino-3-*m*-aminophenylamino-1 : 1-dimethyl-Δ³-tetrahydrobenzene (dimeta-compound),



is an extremely hygroscopic substance, which crystallises from dilute alcohol in buff-coloured, flat needles which melt at 118—120° with evolution of gas. The substance when dried in a vacuum still retained a considerable amount of moisture; for analysis it was weighed in a boat contained in a weighing bottle and heated to constant weight at 105°; when thus dried, the residue melts at 148—150°, but on exposure to air it recovers its original melting point of 118°; it is readily soluble in cold ethyl alcohol, acetone, or ethyl acetate, sparingly so in hot ether, chloroform, or benzene, and is insoluble in water; in alcoholic solution, the substance has a strongly alkaline reaction; it yields an oily picrate and an amorphous platinum salt, neither of which was analysed.

The *hydrochloride*, C₂₀H₂₄N₄·HCl, obtained by the condensation of chloroketodimethyltetrahydrobenzene with *m*-phenylenediamine as above described, was crystallised from alcohol.

0.1306 gave 0.0504 AgCl. Cl = 9.49.

C₂₀H₂₅N₄Cl requires Cl = 9.95 per cent.

The salt is very slightly soluble in a large volume of boiling alcohol and separates from this solution in oblong plates; it dissolves with difficulty in a large volume of boiling water to give a neutral solution.

Reaction of the Dimeta-compound with Dimethyldihydroresorcin.

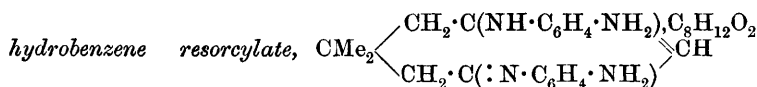
On mixing together alcoholic solutions containing equal weights of the dimeta-compound and dimethyldihydroresorcin, a yellow, crystalline precipitate was at once formed; this substance, when washed with alcohol, was dried in a vacuum.

0.1164 gave 0.3119 CO₂ and 0.0895 H₂O. C = 73.08 ; H = 8.54.

0.1324 „ 13.9 c.c. moist nitrogen at 17° and 769 mm. N = 12.33.

C₂₈H₃₆O₂N₄ requires C = 73.05 ; H = 7.83 ; N = 12.18 per cent.

5-*m*-Aminophenylimino-3-*m*-aminophenylamino-1 : 1-dimethyl-Δ³-tetra-



prepared as above, forms fine, yellow needles, which darken at 258° and melt with evolution of gas at $260\text{--}261^\circ$; it is insoluble in ethyl acetate, acetone, chloroform, light petroleum, or benzene, is slightly soluble with decomposition in boiling methyl or ethyl alcohol, and readily dissolves in cold glacial acetic or formic acid. A solution in glacial acetic acid, on making alkaline with potassium hydroxide, gave a precipitate of the dimeta-compound, which was characterised by its melting point (118°) and by the fact that when mixed with a sample of the pure substance it did not depress its melting point.

Action of Dimethyldihydroresorcin on p-Phenylenediamine.

Ten grams of dimethyldihydroresorcin and 7 grams of *p*-phenylenediamine were boiled together in alcoholic solution for three hours; after distilling off some of the alcohol, the solution was allowed to cool, when it deposited a mass of light yellow crystals, which, when filtered off and dried, weighed 13 grams; these crystals were boiled with alcohol and filtered from about 1 gram of a yellow, insoluble solid *A*; the filtrate, on addition of light petroleum, deposited a mass of faintly yellow, flat needles.

0.1253 gave 0.3358 CO_2 and 0.0904 H_2O . $\text{C} = 73.09$; $\text{H} = 8.01$.

0.1096 ,, 11.5 c.c. moist nitrogen at 19° and 758 mm. $\text{N} = 12.03$.

$\text{C}_{14}\text{H}_{18}\text{ON}_2$ requires $\text{C} = 73.05$; $\text{H} = 7.83$; $\text{N} = 12.18$ per cent.

5-Hydroxy-3-*p*-aminophenylamino-1:1-dimethyl- $\Delta^{3:5}$ -dihydrobenzene, $\text{CMe}_2 \begin{array}{l} \text{CH}_2 \cdot \text{C}(\text{NH} \cdot \text{C}_6\text{H}_4 \cdot \text{NH}_2) \\ \text{CH} \text{---} \text{C}(\text{OH}) \end{array} \text{CH}$ (monopara-compound), crystallises from aqueous alcohol or a mixture of alcohol and ligroin in colourless needles and melts at $209\text{--}210^\circ$; it dissolves readily in cold alcohol, is fairly soluble in hot acetone, ethyl acetate, or chloroform, and is slightly soluble in boiling water; its solution in alcohol is neutral and gives with ferric chloride a reddish-brown colour. Although colourless when quite pure, the substance slowly assumes a reddish-yellow colour on exposure to light.

A determination of the molecular weight by the freezing point method, using diphenylamine as solvent, gave the following result:

0.304, in 26.3596 diphenylamine, gave $\Delta t = 0.41$. M.W. = 247.

$\text{C}_{14}\text{H}_{18}\text{ON}_2$ requires M.W. = 230.

The yellow, insoluble substance *A*, mentioned above, proved to be identical with the *s*-bisresorcyl-*p*-phenylenediamine described on p. 396.

The *hydrochloride*, $C_{14}H_{18}ON_2 \cdot 2HCl$, obtained as a white, crystalline precipitate on saturating an alcoholic solution of the base with dry hydrogen chloride, gave the following numbers on titration in aqueous solution:

0.1258 required 8.1 c.c. $N/10$ NaOH. $HCl = 23.50$.

$C_{14}H_{20}ON_2Cl_2$ requires $HCl = 24.09$ per cent.

The *platinichloride*, $C_{14}H_{18}ON_2 \cdot H_2PtCl_6$, is obtained in the form of golden-yellow, glistening plates on mixing warm alcoholic solutions of the foregoing hydrochloride and platinic chloride. The crystals were analysed after heating to constant weight at 110° .

0.1751 gave 0.0524 Pt. $Pt = 29.92$.

$C_{14}H_{20}ON_2Cl_6Pt$ requires $Pt = 30.66$ per cent.

The *acetyl* derivative, $C_8H_{11}O \cdot NH \cdot C_6H_4 \cdot NHAc$, was prepared by heating 2 grams of the base with 6 grams of acetic anhydride and 4 grams of glacial acetic acid for ten minutes over a water-bath. On pouring into water, a light yellow solid was precipitated, which crystallised from a mixture of alcohol and acetone in oblong plates melting at $255-256^\circ$.

0.1219 gave 10.8 c.c. moist nitrogen at 19° and 757 mm. $N = 10.15$.

$C_{16}H_{20}O_2N_2$ requires $N = 10.29$ per cent.

The compound is fairly soluble in hot alcohol, acetone, or chloroform, and is insoluble in ethyl acetate, benzene, or ether; it gives a reddish-yellow colour with ferric chloride in alcoholic solution. The same substance was also obtained by condensing dimethyldihydroresorcin in alcoholic solution with *p*-aminoacetanilide, showing that in the monopara-compound it was the nitrogen in the para-position to the resorcin complex which had been acetylated.

The monopara-compound did not yield a diacetyl derivative even on boiling with acetic anhydride and acetic acid.

Action of Hydrochloric Acid on the Monopara-compound.

A solution of 4 grams of the monopara-compound in 9 grams of concentrated hydrochloric acid and 10 c.c. of water was boiled in a reflux apparatus for a quarter of an hour; on diluting the solution and making it faintly alkaline, a yellow solid was precipitated; this substance, after extraction with boiling water and drying, weighed 2 grams; it was identified as the *s*-bisresorcyl-*p*-phenylenediamine described on p. 396 by the fact that it did not melt at 300° and by its insolubility in all ordinary organic solvents.

The alkaline filtrate from this substance slowly deposited 0.8 gram of unchanged monopara-base; the mother liquors were thereupon

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made strongly alkaline with potassium hydroxide and extracted with ether; the ethereal extract on evaporation yielded 0.3 gram of a solid which melted between 130° and 140° and was proved to be *p*-phenylenediamine by the following tests for this substance: (*a*) it dissolved in hydrochloric acid to give a brown solution, which was turned violet by ferric chloride, and (*b*) on heating with potassium dichromate and sulphuric acid it gave *p*-benzoquinone.

Condensation of Dimethyldihydroresorcin with the Monopara-compound.

A solution of 2 grams of the monopara-base and 1.5 grams of dimethyldihydroresorcin in alcohol was boiled over a water-bath for twelve hours; the solution was then filtered from a yellow, crystalline precipitate, which on drying weighed only 0.6 gram; on further heating, the solution deposited more of this precipitate, but the reaction was very slow. The substance, which was insoluble in nearly all ordinary organic solvents, was purified by dissolving in a large volume of boiling glacial acetic acid and precipitating it by means of water.

0.1100 gave 0.3005 CO_2 and 0.0833 H_2O . $\text{C} = 74.50$; $\text{H} = 8.41$.

0.1112 „ 7.6 c.c. moist nitrogen at 17° and 761 mm. $\text{N} = 7.94$.

$\text{C}_{22}\text{H}_{28}\text{O}_2\text{N}_2$ requires $\text{C} = 75.00$; $\text{H} = 7.95$; $\text{N} = 7.95$ per cent.

s-Bisdimethyldihydroresorcyl-p-phenylenediamine (for formula, compare the corresponding meta-compound described on p. 392), prepared as above, forms light yellow needles which do not melt below 300° ; it is insoluble in all ordinary organic solvents.

The *hydrochloride*, $\text{C}_{22}\text{H}_{28}\text{O}_2\text{N}_2 \cdot 2\text{HCl}$, was obtained in a manner similar to the one employed in preparing the corresponding meta-derivative described on p. 392; it cannot be recrystallised without undergoing hydrolysis and yielding the free base. Dissolved in aqueous alcohol and titrated by means of sodium hydroxide, using phenolphthalein as indicator, it gave the following numbers:

0.1274 required 6.02 c.c. *N*/10 NaOH . $\text{HCl} = 17.26$.

0.1303 „ 6.18 c.c. *N*/10 NaOH . $\text{HCl} = 17.32$.

$\text{C}_{22}\text{H}_{30}\text{O}_2\text{N}_2\text{Cl}_2$ requires $\text{HCl} = 17.17$ per cent.

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