CCLXXI.—*Contributions to Our Knowledge of Semicarbazones. Part IV. Action of Hydrogen Chloride.*

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IN the course of our investigations on the preparation and properties of some semicarbazones it was found that the presence of hydrochloric acid produced colorations in solutions of some of these substances. As the semicarbazones are, in part, basic compounds it occurred to us that this development of colour might be due to the formation of salts, and in fact experiments instituted to elucidate this point showed that some of these substances do form salts with acids.

The following experiments were carried out to determine under what conditions salts are formed, and to what extent their formation is influenced by the constitution of the semicarbazone. For the most part the investigations have been made on the hydrochlorides of the semicarbazones. Various methods were tried for the preparation of these salts, and it was found that special precautions had to be taken against the presence of moisture, as this tended, in the presence of hydrochloric acid, to hydrolyse the semicarbazone and give only the aldehyde or ketone and semicarbazide hydrochloride.

In many cases the salt may be prepared by dissolving the semicarbazone in dry chloroform and passing dry hydrogen chloride into the solution. The difficulty in this case is that, if the salt is unstable, exposure to air while filtering brings about decomposition, so that correct results are not obtained. The most satisfactory results were obtained by passing dry hydrogen chloride over the dry substance contained in a U-tube and estimating the quantity of acid added.

Two *piperonylideneacetonesemicarbazones* were prepared, an α - and a β -modification. These isomerides have different melting points and different properties. α -Piperonylideneacetonesemicarbazone was exposed to the action of dry hydrogen chloride, and an unstable, crystalline, vermilion *salt* containing 2.5 molecular proportions of hydrogen chloride was obtained. This salt on exposure to air loses hydrogen chloride, and finally gives a stable, orange *monohydrochloride*.

β -Piperonylideneacetonesemicarbazone gives with hydrogen chloride a stable, yellow *monohydrochloride*, and no further addition can be made to this compound even on continued passage of hydrogen chloride over the dry salt. A slight change in colour is observed, but no addition of acid.

Cinnamaldehydesemicarbazone was next prepared. This semicarbazone exhibits interesting phototropic properties after exposure to bright light. On treating this substance with hydrogen chloride it combines with 2 molecular proportions of hydrogen chloride, and gives an exceedingly unstable, deep orange *compound*. A *sulphate* of this semicarbazone was also prepared, which contained one molecular proportion of sulphuric acid. The sulphate is bright yellow, and stable in ordinary air.

Cinnamaldehydesemicarbazone, an unsaturated compound, might be expected to combine with hydrogen chloride at the double bond, or, at least, that the unsaturated nature of the substance would influence the formation of an additive compound.

The presence of a phenyl group in the semicarbazide radicle evidently influences the absorption of hydrogen chloride, for it was found that *cinnamaldehydephenylsemicarbazone* unites with only one molecular proportion of hydrogen chloride, the *monohydrochloride* thus obtained being yellow. On saturating cinnamaldehydephenylsemicarbazone with bromine a *dibromide*, $C_{16}H_{15}ON_3Br_2$, is formed, and this substance does not combine with hydrogen chloride. The addition of bromine therefore prevents salt-formation.

A *monobromo*-derivative was prepared from this dibromide by boiling with alcohol, when hydrogen bromide was evolved and *monobromocinnamaldehydephenylsemicarbazone*, $C_{16}H_{14}ON_3Br$, obtained. This compound combines rapidly with hydrogen chloride, giving a bright yellow *salt* containing one molecular proportion of hydrogen chloride. On preparing monobromocinnamaldehyde, and then forming the phenylsemicarbazone and passing hydrogen chloride over the compound, a *dihydrochloride* is obtained, which is exceedingly unstable, all the hydrogen chloride being liberated on exposure to air.

Simple semicarbazones, such as acetonesemicarbazone and acetone-phenylsemicarbazone, also absorb hydrogen chloride, but no colour is developed; the substances remain white, but lose their crystalline structure and fall to powder. Acetonesemicarbazone forms a comparatively stable *monohydrochloride*, whereas the addition of hydrogen chloride to acetonephenylsemicarbazone reaches a maximum when one and a-half molecular proportions have been taken up. This salt loses hydrogen chloride very rapidly, becoming more stable when half a molecular proportion of hydrogen chloride has been lost, that is, the *monohydrochloride* is comparatively stable. Acetophenonesemicarbazone and acetophenonephenylsemicarbazone were also examined, as these contain more phenyl groups in the molecule, and might be expected to react differently. These substances combined very readily with hydrogen chloride, giving, in each case, a yellow *dihydrochloride*, which is exceedingly unstable.

A simple aromatic aldehyde-semicarbazone, such as benzaldehyde-semicarbazone, reacts also with hydrogen chloride, giving a *monohydrochloride*, which is comparatively stable and only slightly coloured. Benzaldehydephenylsemicarbazone gives a yellow *dihydrochloride*, which is very unstable.

From the results obtained it would seem, first, that the monohydrochlorides are for the most part more stable than the dihydrochlorides, and, secondly, that the introduction of a phenyl group into the basic part of the molecule of unsaturated semicarbazones diminishes their capacity for addition of hydrogen chloride, whereas in the case of the saturated semicarbazones it increases this capacity. This is shown by a comparison of cinnamaldehydesemicarbazone dihydrochloride and cinnamaldehydephenylsemicarbazone monohydrochloride with benzaldehydesemicarbazone monohydrochloride and benzaldehydephenylsemicarbazone dihydrochloride.

We intend to extend these investigations to a larger number of semicarbazones before giving our views on the possible change of structure during addition of acids to semicarbazones, but as circumstances have arisen which render the continuation of the work impossible for the present and as it is uncertain when it can be completed it was thought advisable to record these results.

EXPERIMENTAL.

Piperonylideneacetonesemicarbazones.

Yellow piperonylideneacetone was prepared according to Haber's method (*Ber.*, 1891, **24**, 618). Haber recrystallised his product from alcohol, in which the substance is sparingly soluble, but it was found more convenient to use benzene as the solvent. The

white, stereoisomeric piperonylideneacetone was also prepared by Haber's method.

A *semicarbazone* was prepared from each ketone in the usual manner, and crystallised first from alcohol and finally from chloroform. It was found that the two stereoisomeric ketones gave one and the same semicarbazone, melting at 217° , and a mixture of the products showed no depression of the melting point:

0.2020 gave 29.15 c.c. N_2 at 16° and 766.5 mm. $N = 16.85$.

$C_{12}H_{13}O_3N_3$ requires $N_2 = 17.0$ per cent.

The semicarbazone forms white crystals, which are insoluble in water, and fairly soluble in hot alcohol or chloroform.

We designate this semicarbazone as the α -modification.

On hydrolysis with hydrochloric or acetic acid the semicarbazone yielded the yellow modification of piperonylideneacetone.

A solution of this α -semicarbazone in alcohol was exposed to ultra-violet light for thirty hours. The alcohol was then evaporated and the residue fractionally crystallised, first from water and finally from benzene and light petroleum. Besides unaltered substance there was obtained a fairly large quantity of a crystalline substance melting at 168° . The substance crystallises in creamy needles, which are more readily soluble in chloroform or alcohol than the α -semicarbazone. We designate this product the β -modification, since analysis showed it to have the same composition as the α -modification:

0.1400 gave 20.5 c.c. N_2 at 12° and 746 mm. $N = 16.94$.

$C_{12}H_{13}O_3N_3$ requires $N = 17.0$ per cent.

Addition of Hydrogen Chloride to the α -Modification.

The reaction was first carried out by passing dry hydrogen chloride into a solution of the substance in dry chloroform. A reddish-orange precipitate separated, which was collected and dried on a porous tile. This substance was very unstable, and easily decomposed by moisture. To determine the amount of hydrogen chloride with which the semicarbazone had combined the substance was warmed with excess of standard alkali, and the residual alkali titrated with standard acid. The results varied with each preparation, but approximated to a compound of the formula

Owing to the unsatisfactory nature of the results obtained by this method the following procedure was finally adopted.

A U-tube closed by means of glass stop-cocks was used. This U-tube was specially constructed so that the substance can be exposed to the action of the gas in thin layers. For this purpose instead of the ordinary tube of long limb and narrow bend the

limbs of the U-tube were 8 cm. apart and the limbs only 5 cm. in length.

The tube was first filled with dry air and weighed (weight= a). Dry hydrogen chloride was then led into the tube until the weight was constant (weight= b). The hydrogen chloride was then displaced by a current of dry air, and a quantity of the α -semicarbazone introduced into the tube (weight of tube + semicarbazone + air= c). Dry hydrogen chloride was then passed through the tube until the weight was constant; this was obtained only after several days. The tube was then closed and weighed. As there was a possibility that the hydrochloride might be unstable in air the atmosphere of hydrogen chloride was not displaced, but a correction was made for weighing in such an atmosphere.

Thus: Weight of tube + hydrochloride +
hydrogen chloride= d .

Weight of semicarbazone $= c - a$.

Weight of hydrochloride $= d - b$.

Weight of hydrogen chloride added $= d - \{c + (b - a)\}$.

0.3040 semicarbazone gave 0.4198 hydrochloride. HCl added = 27.58.

$C_{12}H_{13}O_3N_3 \cdot 2\frac{1}{2}HCl$ requires HCl = 26.93 per cent.

This salt forms bright, vermilion-coloured crystals. The melting point was indefinite, since decomposition takes place on heating; this occurs at about 125—140°.

If this salt is exposed to light for some days in the tube in which it was weighed the colour changes from vermilion to deep orange without change in weight. In order to prove that the change of colour was not due to slight loss of hydrogen chloride, hydrogen chloride was again passed over the substance, but the orange colour remained unchanged, and the weight was not altered. On prolonged exposure to light the orange-coloured salt acquired a green tint without change in weight. The vermilion colour was not restored either on warming or cooling the substance, or on keeping it in the dark. The experiment was repeated, the semicarbazone this time being subjected to the action of hydrogen chloride in the dark. The same absorption took place, and the vermilion-coloured salt was again obtained:

0.2254 semicarbazone gave 0.3114 hydrochloride. HCl added = 27.61.

$C_{12}H_{13}O_3N_3 \cdot 2\frac{1}{2}HCl$ requires HCl = 26.93 per cent.

This salt on exposure to air at the ordinary temperature rapidly evolves hydrogen chloride. A sample of the salt was exposed to the air at room temperature until, after drying in a desiccator, the weight was constant. For this several weeks were required.

The substance so obtained was orange, but not so deep in colour as the orange salt, $C_{12}H_{13}O_3N_3 \cdot 2\frac{1}{2}HCl$, just mentioned. Analysis showed the product to be a *monohydrochloride*.

The substance was warmed gently with excess of *N*/20-alkali, and the residual alkali, after filtration, titrated with *N*/20-sulphuric acid:

0.1534 required 11.4 c.c. *N*/20-NaOH. $HCl=13.52$.

$C_{12}H_{13}O_3N_3 \cdot HCl$ requires $HCl=12.83$ per cent.

This orange monohydrochloride is only partly decomposed by water, but is completely decomposed by dilute alkalis. It is apparently quite stable in ordinary air, and in a closed tube it melts and decomposes at $173-175^\circ$.

The residue obtained by treatment of the monohydrochloride with alkali was recrystallised from alcohol, and proved to be the α -semicarbazone.

Addition of Hydrogen Chloride to the β -Semicarbazone.

A solution of the β -semicarbazone in dry chloroform was saturated with dry hydrogen chloride. A yellow, crystalline precipitate separated almost immediately, which was collected, washed with chloroform and light petroleum, dried on a porous tile, and finally in a desiccator. This substance was analysed in the way already described, and proved to be a *monohydrochloride*:

0.3249 required 10.8 c.c. *N*/10-NaOH. $HCl=13.3$.

$C_{12}H_{13}O_3N_3 \cdot HCl$ requires $HCl=12.9$ per cent.

The monohydrochloride is canary-yellow, melts and decomposes at 169° , is stable in air, and fairly stable towards water. On decomposition with alkali a white substance was obtained, which on crystallisation from alcohol yielded the α -modification only, and not the β -modification. Hence in this way transformation from the β - into the α -modification can be effected. Thus:

In order to determine whether this monohydrochloride could combine with more hydrogen chloride a weighed quantity was placed in a U-tube and dry hydrogen chloride passed over it. No increase in weight took place, but the substance acquired a green tinge.

Cinnamaldehydesemicarbazone.

This compound was prepared according to Young and Witham's method (T., 1900, **77**, 230). It is white, and, if freshly prepared, undergoes no change of colour in the dark. If, however, it is first exposed to bright light, which produces no visible effect, and then placed in the dark, a yellow colour is developed. This yellow colour disappears on re-exposure of the substance to light. Evidently the freshly prepared substance must first be made active by exposure to intense light before phototropic properties are developed. Further, if either of the active forms is recrystallised, the activity disappears, and exposure to bright light is again necessary to develop phototropic properties. These three modifications all possess the same melting point, namely, 217° , which is slightly higher than that recorded in the literature. An alcoholic solution of the semicarbazone was exposed to ultra-violet light for thirty hours. The solution was then concentrated, and the residue fractionally crystallised, but unaltered substance only was obtained.

Addition of Hydrogen Chloride to the Semicarbazone.

Owing to the sparing solubility of the substance in all cold solvents the reaction could not be carried out in solution. Accordingly a weighed quantity was placed in a stoppered U-tube of the form already described, and dry hydrogen chloride passed over the semicarbazone until the weight became constant. The same precautions were taken as in the previous experiments, the substance being weighed in an atmosphere of dry hydrogen chloride and a correction made for the difference in weight of hydrochloride weighed in hydrogen chloride and hydrochloride weighed in air:

0.4148 semicarbazone gave 0.5820 hydrochloride. HCl added = 28.11.

$C_{10}H_{13}ON_3 \cdot 2HCl$ requires HCl = 27.86 per cent.

This salt of cinnamaldehydesemicarbazone, which is evidently a dihydrochloride, is deep orange, and very unstable. Moist air immediately decomposes it, with the formation of a viscid compound. During the preparation of the salt the semicarbazone, on first passing hydrogen chloride over it, partly fuses, changes colour to yellowish-orange, and finally the substance becomes powdery and assumes a deep orange colour.

As the dihydrochloride is unstable in ordinary moist air it was transferred from the U-tube to a weighing bottle in dry air in which the salt is comparatively stable. A melting-point tube was filled at the same time, sealed, and the melting point found to be 80—83°, decomposition also occurring. The apparatus used was a simple but very efficient arrangement, which enabled us to work in dry air with comparative ease.

Addition of Sulphuric Acid to Cinnamaldehydesemicarbazone.

A quantity of the semicarbazone was rubbed into a paste with concentrated sulphuric acid, when the mixture became oily and yellow. Dry ether was added, the mixture being kept cool, then just sufficient absolute alcohol to bring the whole into solution, and the mixture placed in ice. On keeping for some time yellow needles crystallised from the solution, which were collected, washed with dry light petroleum, and dried first on a porous tile and finally in a desiccator. Analysis showed the compound to be a salt of sulphuric acid. The analysis was conducted in the same way as in the case of the hydrochlorides, namely, the salt was warmed with excess of *N*/10-alkali and the residual alkali titrated with *N*/10-acid:

0.109 required 7.325 c.c. *N*/10-alkali. $\text{H}_2\text{SO}_4 = 32.92$.

$\text{C}_{10}\text{H}_{11}\text{ON}_3, \text{H}_2\text{SO}_4$ requires $\text{H}_2\text{SO}_4 = 34.1$ per cent.

Preparation of Cinnamaldehydephenylsemicarbazone.

Molecular quantities of cinnamaldehyde in alcohol and of phenyl semicarbazide hydrochloride in water were mixed. The solution became deep orange, and a precipitate immediately formed, which was collected, washed with water, and crystallised first from alcohol and finally from a mixture of chloroform and light petroleum.

The *phenylsemicarbazone* crystallises in white, felted needles, melting at 205°. It is readily soluble in chloroform or hot alcohol, and practically insoluble in light petroleum:

0.200 gave 27.2 c.c. N_2 at 12° and 751 mm. $\text{N} = 15.93$.

$\text{C}_{16}\text{H}_{15}\text{ON}_3$ requires $\text{N} = 15.84$ per cent.

The behaviour of the phenylsemicarbazone towards light is exactly the same as that of cinnamaldehydesemicarbazone. The freshly prepared substance is not affected by light or darkness, but if it is exposed to bright light and then placed in the dark a deep yellow colour is developed, which disappears on again exposing to light. Rise of temperature accelerates the conversion of the white into the yellow modification. Thus on exposing a sample of the colourless, inactive modification to light and then placing in a

closed steam-oven the yellow colour becomes apparent almost immediately. If, however, the preliminary exposure to light is omitted no change of colour is developed by heating the substance in the dark. The melting points of the three modifications were the same, namely, 205° .

A chloroform solution of the phenylsemicarbazone was exposed for thirty hours to ultra-violet light. The solution was carefully examined, but only unchanged substance was obtained.

Addition of Hydrogen Chloride to Cinnamaldehydephenylsemicarbazone.

A concentrated solution of the phenylsemicarbazone in dry chloroform was saturated with dry hydrogen chloride. A yellow, crystalline precipitate soon separated, which was collected, washed with chloroform, and dried on a porous tile. It was analysed in the usual way, and found to be a *monohydrochloride*:

0.6465 required 20.9 c.c. $N/10$ -NaOH. $HCl = 11.8$.

$C_{16}H_{15}ON_3.HCl$ requires $HCl = 12.11$ per cent.

The hydrochloride is canary-yellow, stable in air, and fairly stable towards water. It melts and decomposes at 161 – 162° . As the semicarbazone of cinnamaldehyde formed a dihydrochloride on passing dry hydrogen chloride over the dry substance it was thought that the phenylsemicarbazone might react with another molecule of hydrogen chloride if exposed to the action of dry hydrogen chloride in the dry state. Accordingly, a quantity of the monohydrochloride was placed in a U-tube and treated as already described in the preparation of other hydrochlorides. After the gas had been passed over the monohydrochloride for several days it was found that no increase in weight had taken place, the substance remaining a monohydrochloride. No change in colour was observed. Starting, however, with cinnamaldehydephenylsemicarbazone (white variety) and passing hydrogen chloride over the dry substance, the gas is rapidly taken up, and the colour becomes deep yellow. After passage of the gas for one week the percentage of hydrogen chloride absorbed was found to be 19.72; thereafter weighing at intervals the hydrogen chloride content appeared to diminish, and after passage of the gas for thirty-eight days the percentage was found to be 17.4. After this the compound continued to lose hydrogen chloride, but at a very slow rate, and with continued passage of the gas would probably approximate to 12.11 per cent. or 1 molecular proportion of hydrogen chloride.

On exposure to air this hydrochloride again gives the stable monohydrochloride:

0.2014 required 6.5 c.c. *N*/10-alkali. $\text{HCl} = 11.79$.

$\text{C}_{16}\text{H}_{15}\text{ON}_3$, HCl requires $\text{HCl} = 12.11$ per cent.

In the same way the yellow modification of cinnamaldehyde-phenylsemicarbazone was exposed to the action of dry hydrogen chloride in the dark. The yellow compound formed was slightly darker in shade than that from the white modification, and it also reached a maximum addition of hydrogen chloride. The maximum after ten days in this case was 19.46 per cent. The hydrogen chloride content diminished much more rapidly, and in thirty-eight days fell to 15.15 per cent., again an approximation to 1 molecular proportion. On exposure to air this hydrochloride gives, like that of the white modification, a stable monohydrochloride:

0.232 required 7.4 c.c. *N*/10- NaOH . $\text{HCl} = 11.59$.

$\text{C}_{16}\text{H}_{15}\text{ON}_3$, HCl requires $\text{HCl} = 12.11$ per cent.

Addition of Sulphuric Acid to Cinnamaldehydephenylsemicarbazone.

The phenylsemicarbazone was mixed with a small quantity of concentrated sulphuric acid, alcohol added until the substance dissolved, and the mixture cooled in ice. After a time yellow crystals separated, which were collected and recrystallised from glacial acetic acid. The sulphate was analysed in the usual way by heating gently with excess of standard alkali and titrating the residual alkali:

0.100 required 11.1 c.c. *N*/10- NaOH . $\text{H}_2\text{SO}_4 = 27.2$.

$\text{C}_{16}\text{H}_{15}\text{ON}_3$, H_2SO_4 requires $\text{H}_2\text{SO}_4 = 26.99$ per cent.

The sulphate is a brilliant, yellow-coloured powder, stable in air, but easily decomposed by cold water and dilute alkali with the formation of the phenylsemicarbazone and sulphuric acid.

Preparation of a Dibromide of Cinnamaldehydephenylsemicarbazone.

The theoretical quantity of dry bromine in dry chloroform was added to the phenylsemicarbazone dissolved in dry chloroform, and the mixture was allowed to remain for half-an-hour, when yellow crystals began to appear. When all the substance had crystallised out the crystals were collected, dried, and recrystallised from chloroform. The substance crystallises in canary-yellow needles, which are very sparingly soluble in chloroform, and melt at 187° . Analysis showed it to be the *dibromide* of cinnamaldehydephenylsemicarbazone:

0.200 gave 17.1 c.c. N_2 at 10° and 754 mm. $\text{N} = 10.14$.

$\text{C}_{16}\text{H}_{15}\text{ON}_3\text{Br}_2$ requires $\text{N} = 9.91$ per cent.

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This dibromide was subjected to the action of dry hydrogen chloride, but no addition took place. Evidently the dibromide does not form a hydrochloride. Also on treating cinnamaldehyde-phenylsemicarbazone monohydrochloride with bromine in chloroform solution and adding light petroleum a yellow precipitate is obtained, which consists of the dibromide of cinnamaldehydephenylsemicarbazone.

Preparation of a Monobromo-derivative of Cinnamaldehyde-phenylsemicarbazone from the Dibromide.

It was found that on recrystallisation from alcohol the dibromide was decomposed, hydrogen bromide being liberated and a white substance melting at 168° crystallising out. Some of the cinnamaldehydephenylsemicarbazone dibromide was therefore boiled in alcohol until dissolved, then diluted with water, and the product allowed to crystallise:

0.200 gave 21.05 c.c. N_2 at 12° and 739 mm. $N=12.15$.

$C_{16}H_{14}ON_3Br$ requires $N=12.20$ per cent.

The substance obtained is therefore a *monobromo-derivative* of cinnamaldehydephenylsemicarbazone. It crystallises in small, colourless, glistening needles, which after several crystallisations melt at 195° . It is readily soluble in chloroform, benzene, or boiling alcohol, but practically insoluble in light petroleum.

Addition of Hydrogen Chloride to the Monobromo-derivative of Cinnamaldehydephenylsemicarbazone.

A weighed quantity of the monobromo-derivative was placed in a U-tube and subjected to the action of hydrogen chloride in the manner already described. Reaction took place immediately, and a yellow salt was produced. Passage of the gas was continued until the weight became constant:

0.6624 monobromo-derivative gave 0.7458 hydrochloride. HCl added = 11.18.

$C_{16}H_{14}ON_3Br, HCl$ requires $HCl=9.59$ per cent.

The hydrochloride is bright canary-yellow, and fairly stable in air, gradually losing hydrogen chloride. It is partly decomposed by water and completely by dilute alkali.

Preparation of Monobromocinnamaldehydephenylsemicarbazone.

Cinnamaldehyde was first brominated according to the method described by Zincke and Hagen (*Ber.*, 1884, **17**, 1815). The brominated product separated at once, and was crystallised from

alcohol. It was mixed with the necessary quantity of phenylsemicarbazide in alcoholic solution, when the *phenylsemicarbazone* separated immediately and was crystallised from alcohol:

0.250 gave 26.2 c.c. N_2 at 12° and 745 mm. $N = 12.13$.

$C_{16}H_{14}ON_3Br$ requires $N = 12.22$ per cent.

The substance crystallises in flat, colourless prisms, melting at 197° . It is soluble in alcohol or chloroform, but more readily soluble in the latter than is the monobromo-compound derived from the dibromide. It is not identical with the latter substance, as is shown by crystalline structure, solubility, and melting point.

Addition of Hydrogen Chloride to the above Monobromocinnamaldehydephenylsemicarbazone.

Hydrogen chloride was passed over a weighed quantity of the substance until the weight became constant. The addition of hydrogen chloride took place at once, but several days elapsed before the weight became constant:

0.5922 phenylsemicarbazone gave 0.713 hydrochloride. HCl added = 16.94.

$C_{16}H_{14}ON_3Br \cdot 2HCl$ requires $HCl = 17.50$ per cent.

This *dihydrochloride* of monobromocinnamaldehydephenylsemicarbazone is bright yellow, of a slightly deeper shade than the monohydrochloride of the monobromo-compound obtained from cinnamaldehydephenylsemicarbazone dibromide. It is, however, much more unstable, and on keeping even in a stoppered weighing bottle loses hydrogen chloride, the colour at the same time disappearing. A portion of the salt was exposed to the air for some time, then dried in a desiccator, and weighed. This treatment was repeated until the weight was constant, which condition was reached at the end of three weeks, and the yellow colour had entirely disappeared. On titrating a weighed quantity of the substance with standard alkali it was found that the hydrochloride had lost the whole of the hydrogen chloride on exposure to the air.

Addition of Hydrogen Chloride to Acetonesemicarbazone.

Dry hydrogen chloride was passed over a weighed quantity of acetonesemicarbazone (m. p. 187°) in the manner previously adopted. Hydrogen chloride was absorbed at once, and the substance fused slightly, although no change in colour occurred. After some time the substance became powdery, the U-tube was weighed, and increase in weight found to have taken place. Hydrogen chloride was then passed over the substance until the weight became constant:

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1·1984 acetonesemicarbazone gave 1·5820 hydrochloride. HCl added = 24·24.

$C_4H_9ON_3$, HCl requires HCl = 24·09 per cent.

The hydrochloride is evidently a monohydrochloride, and is obtained as a white powder, melting in a closed tube at 150—151°. It is unstable in ordinary air, and hydrogen chloride is gradually evolved from it. In dry air it is comparatively stable.

Addition of Hydrogen Chloride to Acetonephenylsemicarbazone.

Dry hydrogen chloride was passed over a weighed quantity of acetonephenylsemicarbazone (m. p. 157°) as before until the weight was constant. The substance caked slightly on the first addition of hydrogen chloride, but ultimately became powdery. No colour was produced, but an addition in weight occurred, showing the formation of a salt:

1·1088 phenylsemicarbazone gave 1·4180 hydrochloride. HCl added = 21·80.

$C_{10}H_{13}ON_3$, HCl requires HCl = 16·05 per cent.

$C_{10}H_{13}ON_3$, $1\frac{1}{2}$ HCl „ HCl = 22·26 „ „

On exposure to air it rapidly loses hydrogen chloride.

Addition of Hydrogen Chloride to Acetophenonesemicarbazone.

Dry hydrogen chloride was passed over a weighed quantity of the semicarbazone (m. p. 202°) as before. The substance fused almost immediately and a yellow colour was developed. The weight increased gradually, but did not become constant, and the substance remained semi-solid, and appeared to decompose. The amount of hydrogen chloride taken up approximated to two molecular proportions, but the results could not be trusted owing to the semi-fused condition of the substance.

Addition of Hydrogen Chloride to Acetophenonephenylsemicarbazone.

This compound behaved in much the same way as the semicarbazone. Addition of hydrogen chloride takes place with fusion, and a deep yellow colour is developed. The effect of strong cooling was tried in this case, the tube being surrounded by carbon dioxide snow. Even under these conditions the substance fused although the colour developed was very much less. In the case of this phenylsemicarbazone the *hydrochloride* solidified to a hard mass adhering to the tube.

Two experiments were tried: (1) Addition of dry hydrogen chloride at room temperature:

0.5932 phenylsemicarbazone gave 0.7808 hydrochloride. HCl added = 24.02.

$C_{15}H_{15}ON_3, 2HCl$ requires HCl = 22.36 per cent.

(2) Addition of hydrogen chloride at the temperature of solid carbon dioxide:

0.3272 phenylsemicarbazone gave 0.4094 hydrochloride. HCl added = 20.05.

Addition of Hydrogen Chloride to Benzaldehydesemicarbazone.

Hydrogen chloride was passed over the semicarbazone (m. p. 222°) in the manner already described. The colour changed from white to greyish-white, and slight fusion took place on the first formation of the *monohydrochloride*:

0.8548 semicarbazone gave 1.0613 hydrochloride. HCl added = 19.45.

$C_8H_9ON_3, HCl$ requires HCl = 18.29 per cent.

The hydrochloride is greyish-white, melts at 199°, and is fairly stable in air.

Addition of Hydrogen Chloride to Benzaldehydophenylsemicarbazone.

The phenylsemicarbazone was dissolved in dry chloroform, and dry hydrogen chloride passed through the solution. The solution became yellow, and a white precipitate formed, which was collected in an atmosphere of dry air, washed with chloroform, and dried on a porous tile. A quantity of this was placed in a dry, previously weighed weighing-bottle, the bottle weighed, and the contents were shaken into excess of standard alkali; the excess of alkali after warming the mixture was titrated with standard acid:

0.2598 required 13.3 c.c. *N*/10-NaOH. HCl = 18.68.

$C_{14}H_{13}ON_3, 2HCl$ requires HCl = 23.4 per cent.

The hydrochloride evidently loses hydrogen chloride too rapidly even in dry air to allow of accurate estimation.

The substance was therefore exposed to the action of dry hydrogen chloride until the weight became constant. The substance became yellow immediately on the passage of the gas, and at the same time partly liquefied. The final product was deep yellow and semi-solid in appearance.

Owing to fusion having taken place a satisfactory result was not obtained:

0.3264 phenylsemicarbazone gave 0.4196 hydrochloride. HCl added = 22.21.

$C_{14}H_{13}ON_3, 2HCl$ requires HCl = 23.4 per cent.

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This dihydrochloride is yellow and exceedingly unstable; it decomposes immediately on exposure to air.

Annexed is a summary of the compounds examined.

Substances investigated.	Mols. HCl added.	Colour of additive product.	Stability of additive product.
α -Piperonylideneacetone-semicarbazone	2	Vermilion	Very unstable, affected by light, stable at 1 mol. HCl.
β -Piperonylideneacetone-semicarbazone	1	Canary-yellow	Stable.
Cinnamaldehydesemicarbazone	2	Deep orange	Unstable.
Cinnamaldehydephenyl-semicarbazone	1	Canary-yellow	Stable.
Cinnamaldehydephenyl-semicarbazone dibromide	No addition	—	—
Monobromo-derivative from cinnamaldehydephenylsemicarbazone dibromide	1	Yellow	Fairly stable; gradually loses HCl.
Monobromocinnamaldehydesemicarbazone	2	Bright yellow	Unstable.
Acetonesemicarbazone	1	No colour	Comparatively stable in dry air. HCl evolved slowly in ordinary air.
Acetonephenylsemicarbazone	1½	No colour	Unstable. Tends to stability at 1 mol. HCl.
Acetophenonesemicarbazone	2	Yellow	Unstable.
Acetophenonephenyl-semicarbazone	2 (indefinite)	Yellow	Unstable.
Benzaldehydesemicarbazone	1	Greyish	Fairly stable.
Benzaldehydephenyl-semicarbazone	2	Yellow	Exceedingly unstable.

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