LXXV.—*Action of Formaldehyde on Phenylhydrazine and on some Hydrazones.*

By JAMES WALLACE WALKER, M.A., Ph.D.

IN the preceding communication I have described a compound formed by the interaction of formaldehyde and phenylhydrazine, differing both in properties and in composition from that obtained from these substances by Wellington and Tollens (*Ber.*, 1885, **18**, 3300). After an extended investigation into the cause of this difference, it was found, as will be shown in this paper, that the nature of the compound produced by the interaction depends on the relative concentrations of the two reagents, as well as on other external conditions.

Preparation of the two Isomeric Substances, C₁₅H₁₆N₄.

One of these has been already described by Wellington and Tollens (*loc. cit.*), and is obtained as a crystalline precipitate when a large excess of formaldehyde is allowed to act on phenylhydrazine. When recrystallised from a mixture of alcohol and toluene, it forms rhombic tablets, melting at 183—184°. If, however, the two substances be allowed to act on each other in hydrochloric acid solution, even in presence of a large excess of formaldehyde, the substance melting at 183—184° is not the only one produced. To a solution of 10·4 grams of formaldehyde in 500 c.c. of water, containing also 3 grams of concentrated hydrochloric acid, a solution of 5 grams of phenylhydrazine hydrochloride was added. The substances are in the proportion of 10 mols. of formaldehyde to 1 of phenylhydrazine. There was an immediate white precipitate, which afterwards changed to a hard nodule. It was shaken with alcohol, to remove water from it, and then three times extracted with boiling ether. From each extract a crop of crystals was obtained on evaporation, the first melting at 123—160°, the second at about 120°, and the third at 109—115°. The residue undissolved by the ether was recrystallised from ethylic acetate, in which it was readily soluble; it then had the melting point 180—182°, and was therefore the substance discovered by Wellington and Tollens. The three crops of crystals from ether were united and dissolved in a small quantity of benzene, and some alcohol, in which they seemed much less soluble, was added; this caused no precipitation, but on evaporation in a desiccator, a small quantity of prismatic crystals separated, melting at 111—115°. This substance is the chief product when the phenylhydrazine hydrochloride is in large excess.

ACTION OF FORMALDEHYDE ON PHENYLHYDRAZINE 1281

Sixty grams of phenylhydrazine hydrochloride were dissolved in 4 litres of water, and 7 grams of a 40 per cent. solution of formaldehyde added. The substances are in the ratio of 4·5 mols. to 1. The precipitate formed slowly, and, after three days, a crystalline cake was separated and dried; it weighed 7 grams, and its melting point lay between 109—118°. It was recrystallised from methylic alcohol, in which it seemed less soluble than in ether, 1·8 gram requiring 25 grams of the boiling alcohol to dissolve it, and yielding on cooling 1·5 gram in large, slightly yellow prisms, melting at 111—113°. The melting point did not change on recrystallisation. The substance was found to contain

C = 71·35; H = 6·44; N = 22·33.

C₁₅H₁₆N₄ requires C = 71·43; H = 6·35; N = 22·22 per cent.

The new substance has therefore the same composition as the formerly known compound derived from phenylhydrazine and formaldehyde. That they are isomeric, and not polymeric with each other was shown by a determination of their molecular weights by the boiling point method. The molecular weight of the substance melting at 183—184° was found to be 277 in toluene solution, that of the substance melting at 111—113° to be 275 in benzene, instead of the calculated 252. The two are therefore isomeric with each other, but the nature of the isomerism has not yet been determined, the few experiments which have been made for this purpose having yielded no results. When heated with glacial acetic acid both are destroyed, dark brown resins being produced; both behave in the same way when dry hydrogen chloride is passed into their ethereal solutions; and phenylhydrazine and formaldehyde are both without further action on them. No compound with either could be obtained by heating with methylic iodide for half an hour on the water bath. Neither of them appeared to be reduced by dissolving sodium in its alcoholic solution, as almost the whole of the compound of higher melting point crystallised from the alcoholate solution, and no ammonia or methylic amine was given off from that melting at 111—113°.

The formula proposed by Wellington and Tollens for the first of these substances, namely,

since it contains no

doubly linked nitrogen, does not allow of stereoisomerism, so that some such structure as

the other. From a recent note on the preparation of the latter, C. Goldschmidt (*Ber.*, 1896, **29**, 1361) appears to have been unable at times to obtain it, but by using the above proportions I have never failed to obtain at least the yield quoted.

Formaldehyde and Excess of Phenylhydrazine.

As already stated under the electrolysis of sodium glycolate, a compound of formaldehyde with phenylhydrazine was obtained, whose composition corresponded to the simple formula $C_7H_8N_2$. It has been very often prepared in the course of this investigation from commercial formaldehyde by adding 2 mols. of phenylhydrazine in acetic acid solution to 1 mol. of the aldehyde, but the precipitate thus obtained was found to be very variable in melting point, different preparations having different melting points, lying between 160° and 180° . The precipitate is faintly yellow, and crystallises from benzene or ethylic acetate in pearly leaflets, which, however, have not a sharp melting point, and cannot be purified by further recrystallisation, owing probably to the sparing solubility of the substance in all solvents. For example, 5 grams of one preparation melting at 163 – 168° , whose composition was found by analysis to correspond to the formula $C_7H_8N_2$, was six times recrystallised from boiling benzene, with the following result.

Crystallisation 1.	2.	3.	4.	5.	6.
Melting point } 146 – 155° .	155 – 159°	149 – 155° .	148 – 153° .	140 – 145° .	149 – 151° .

Its composition was found to have remained unchanged, and its molecular weight determined in ethylic acetate was found to be 127; $C_7H_8N_2 = 120$. This substance would seem to be therefore, for the most part, the true hydrazone of formaldehyde. Like the two former compounds, it gives at once a brown resin when hydrogen chloride is passed into its solution in ether or ethylic acetate. The strange variation in its melting point was found to be due to the fact that it readily polymerises to a substance of much higher melting point and of double its molecular weight.

Preparation of the Polymeric Substance, $(C_7H_8N_2)_2$.

By dissolving the substance melting at 146 – 155° in a little hot aniline, and precipitating it at once by pouring into a large quantity of alcohol, crystals were obtained, similar in appearance to the original, but melting at 189 – 193° . Analysis pointed to the same formula, $C_7H_8N_2$, but a determination of the molecular weight in toluene gave a much higher value, namely, 210 instead of 120. This substance also could not be obtained with a sharp melting point by recrystallisation, but a method of obtaining it in a state of purity was finally discovered, through an attempt made to reduce the compound $C_7H_8N_2$ by adding sodium to its alcoholic solution. 2 grams of substance, melting at 158 – 165° , were heated to boiling with 100 grams of alcohol, and, although all was not dissolved, 16 grams

of sodium were rapidly added. The solid which remained after washing with alcohol weighed 0.8 gram, and melted at 210—212°. 0.5 gram of it, when dissolved in 100 c.c. of boiling alcohol, yielded on cooling 0.5 gram, melting at 210—211.5°. It was also in the form of very small leaflets. This experiment suggested the method adopted for obtaining the polymeride pure. 12 grams, melting at 145—170°, were heated for half an hour on the water bath, with 100 grams of sodium alcoholate containing 9 grams of sodium. The solid, when collected, weighed 11 grams, and melted at 205—209°. When dissolved in hot aniline and poured into alcohol, it gave a crystalline precipitate, in very fine leaflets, which weighed 9.4 grams, and melted at 210—212°.

Analysis of this substance, performed at first in an open tube, gave unaccountable results, for example,

C = 68.89, 69.09, 69.09; H = 6.76, 6.59, 6.66.

(C₇H₅N₂)₂ requires C = 70.00; H = 6.67; N = 23.33 per cent.

Those done later in a closed combustion tube gave values in agreement with the formula.

C = 69.59, 69.74; H = 6.89, 6.77; N = 23.25 per cent.

The molecular weight of the substance was determined in toluene. The constant E for toluene is calculated in the ordinary way from the equation $E = 0.02T^3/l$, where l is the heat of evaporation of 1 gram, and T the absolute boiling point. For toluene, $T = 383.8^\circ$, and $l = 83.55$, therefore $E = 3526$. It had been already observed that by long-continued boiling the substance decomposes, crystals of a lower melting point being deposited on cooling, which are most probably a mixture of the polymeric with the simple form. This was confirmed by the molecular weight determination. After each addition of fresh substance to the boiling toluene, the temperature rose rapidly for four or five minutes, and then slowly for 20 minutes, after which it remained constant for 10 minutes. The quick rise of temperature for each fresh quantity of substance, calculated separately, gives a value for the molecular weight approximating to the formula (C₇H₅N₂)₂ = 240; whilst the reading after the temperature had become constant, gives a value midway between C₇H₅N₂ and (C₇H₅N₂)₂. See Table, p. 1284.

On cooling the solution, crystals separated in leaflets melting at 155—157°. Most probably, therefore, the simple hydrazone has never been prepared free from an admixture of its polymeride. In one case, a sample was obtained which gave, on analysis, C = 69.72; H = 6.61; N = 23.25, and melted much lower than any other preparation, namely, at 126.5—128.5°. The polymeride, (C₇H₅N₂)₂, melts sharply at 210—211.5°, even when heated very slowly, turns

slightly yellow, solidifies on cooling, and melts again at 200—205°. It decomposes with slight evolution of gas when heated to 240°.

Substance.	Toluene.	Quick rise.	Entire rise.	Molecular weight calculated from	
				Quick rise.	Entire rise.
0·1670	12·565	0·220°	0·268°	260	175
0·2437	„	0·086	0·420	250	163
0·3494	„	0·108	0·549	275	179

In order to determine the relation in which these substances stand to the two isomers already described, in which all the hydrogens attached to nitrogen are replaced by CH_2 groups, they were treated with excess of formaldehyde in the expectation that one or both of the more complicated compounds, $\text{C}_{15}\text{H}_{16}\text{N}_4$, might be found. The result was negative, but the same new substance was obtained from both.

Action of Formaldehyde on Methenehydrazone.

When either the simple substance $\text{C}_7\text{H}_8\text{N}_2$, or its polymeride, $(\text{C}_7\text{H}_8\text{N}_2)_2$, is kept a few days, or is heated on the water bath for a few minutes with a large excess of formaldehyde, it is changed almost quantitatively into a new compound which is soluble in ether, and crystallises out of the solution in large, transparent prisms melting at 139—140°. It is, therefore, neither the substance prepared by Wellington and Tollens melting at 183—184°, nor its isomer melting at 111—113°. Analyses showed that it has the formula $\text{C}_{16}\text{H}_{16}\text{N}_4\text{O}$. It was found to contain

C = 67·99; H = 6·40; N = 20·25.

$\text{C}_{16}\text{H}_{16}\text{N}_4\text{O}$ requires C = 68·09; H = 6·38; N = 19·86; O = 5·67 p. c.

Its molecular weight in toluene solution was found to be 292, $\text{C}_{16}\text{H}_{16}\text{N}_4\text{O}$ = 282. The substance melts at 139—140°, is readily soluble in benzene, toluene, and ethylic acetate, less so in alcohol and ether, from all of which it crystallises in large, colourless prisms. It remains quite unchanged on exposure to air. Like all the other compounds of phenylhydrazine with formaldehyde, its ethereal solution is immediately decomposed by dry hydrogen chloride, a brown resin being produced. It remains unchanged when its alcoholic solution is acted on by sodium, the entire amount being recoverable from the solution. An attempt was made to remove the oxygen atom by dissolving the substance in hot phenylhydrazine, but it crystallised

out unaltered on cooling. The oxygen atom is, therefore, no longer present in the carbonyl condition. Assuming that the substance from which it is formed, $C_7H_5N_2$, has the constitution of an ordinary hydrazone, the only way of representing the formation of this new compound is by supposing that 3 mols. of water are eliminated from two of hydrazone and two of formaldehyde hydrate thus

C. Goldschmidt (*loc. cit.*) has prepared a substance having the same composition as the above, but finds for it the melting point 125° instead of $139-140^\circ$.

It is somewhat remarkable that, once the simple hydrazone is formed, the further action of formaldehyde should lead to the production of a substance entirely different from that directly formed from phenylhydrazine in the presence of excess of formaldehyde. This fact would seem to indicate that somehow the union between the CH_2 and the $C_6H_5 \cdot N_2H$ groups is different in $C_6H_5 \cdot N_2H : CH_2$ and in $(C_6H_5N_2)_2(CH_2)_3$, and that, when the radicles have once taken up the position peculiar to the first of these, the production of the second is no longer possible, that only the oxygen compound can then be formed. If so, one would expect to obtain always the same class of compound by the action of formaldehyde on other hydrazones, in which the combination is known to be of the form $C_6H_5 \cdot NH \cdot NR$. To test this, the hydrazones of benzaldehyde and acetophenone were employed.

Action of Formaldehyde on Benzyldenehydrazone.

The substances were allowed to remain for a long time together at the ordinary temperature, and the solid, after being dried on a porous tile, was washed with ether to free it from some benzaldehyde. It melted at $115-125^\circ$, but, after being twice recrystallised from ether, it melted at $134-135^\circ$. Analyses showed that it contained no oxygen.

C = 79.70; H = 6.11; N = 13.98.

$C_{27}H_{24}N_4$ requires C = 80.20; H = 5.94; N = 13.86 per cent.

$C_{23}H_{28}N_4O$ requires C = 77.42; H = 5.99; N = 12.90; O = 3.69 p. c.

A determination of the molecular weight in toluene gave the values 448 and 424, $C_{27}H_{24}N_4 = 404$. The only possible constitution for

$C_6H_5 \cdot N \cdot N : CH \cdot C_6H_5$

this compound is, therefore, $\begin{array}{c} CH_2 \\ | \\ C_6H_5 \cdot N \cdot N : CH \cdot C_6H_5 \end{array}$. It crystallises in

large, transparent, colourless prisms, which, unlike all the previously

1286 ACTION OF FORMALDEHYDE ON PHENYLHYDRAZINE.

described substances, is not entirely decomposed by acids, but, on heating it with strong hydrochloric acid, the solution gives off benzaldehyde.

Action of Formaldehyde on Acetophenonehydrazone.

The substances were allowed to stand as in the last experiment, but the crude product formed was much more smeary from the separation of acetophenone. After washing with ether, the residual solid was fractionally crystallised from ethylic acetate, by which means it was separated into two portions, one melting at 185° , the other at $139\text{--}140^{\circ}$. The latter, from its crystalline appearance and melting point, was evidently the oxygenated compound of methenehydrazone. The substance melting at 185° crystallises also in large, colourless prisms, which are fairly soluble in ethylic acetate, benzene, and toluene, less so in alcohol and ether. On boiling with strong hydrochloric acid solution, it gives off a strong odour of acetophenone. The values found for its molecular weight in toluene were 396, 402, 410, ($\text{C}_{23}\text{H}_{24}\text{N}_4\text{O} = 372$), and analyses showed that it had the above composition.

C = 74.22; H = 6.65; N = 15.06.

$\text{C}_{23}\text{H}_{24}\text{N}_4\text{O}$ requires C = 74.19; H = 6.45; N = 15.05; O = 4.30 p. c.

This compound, therefore, unlike that from benzylidenehydrazone, contains oxygen, and is formed from a molecule of methenehydrazone and one of acetophenonehydrazone by the action of 2 mols. of formaldehyde. Its constitution may be represented as

Since hydrazones, whose structure is known to be normal, yield both classes of compounds, there is no reason to assume that methenehydrazone has a different constitution from hydrazones in general. This is further borne out by the observation that formaldehyde can displace benzaldehyde and acetophenone, producing in the latter case at least the same oxygenated compound as is formed from methenehydrazone. But, on the other hand, unless different forms of combination be assumed, there is no explanation, first, of the existence of two substances having the composition $(\text{C}_6\text{H}_5\text{N}_2)_2(\text{CH}_2)_3$, and, secondly, why one or both of these should not be formed from $\text{C}_6\text{H}_5\cdot\text{N}_2\text{H}:\text{CH}_2$.

In one preparation of the simple hydrazone, when the ethylic acetate from which the crude precipitate had been recrystallised was evaporated to a small volume, some crystals separated in broad tables which melted sharply at $210\text{--}211^{\circ}$ with immediate decom-

position. The entire amount was only 0.4 gram. It dissolved easily in ethylic acetate and toluene, and its molecular weight in the latter solvent was found to be 250; this value points to the same formula as that of the polymeric modification of methenehydrazone, namely, $(C_7H_8N_2)_2 = 240$. It differs, however, from the latter in solubility, in that it decomposes on melting, and does not decompose on long boiling in toluene solution, but crystallises unchanged when the solution is evaporated. It was found to contain

C = 69.76; H = 5.93.

$C_{14}H_{16}N_4$ requires C = 70.00; H = 6.67; N = 23.33 per cent.

The value found for hydrogen was too low, but unfortunately there was not enough substance to repeat the analysis.

Besides these numerous crystalline compounds of formaldehyde with phenylhydrazine, the two reagents were found to give a clear oil, both in alkaline solution with excess of the aldehyde, and in neutral solution with excess of phenylhydrazine; this substance has, however, not yet been investigated.

The foregoing investigations were carried out at the suggestion and under the direction of Professor Wislicenus in his laboratory at Leipsic, and I take this opportunity of expressing to him my thanks for the continued help and advice which he has given me during the progress of the research.