XVIII.—*Reactions of Carbohydrazide. Part I.*

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As comparatively little work has been done on the aldehydic and ketonic derivatives of carbohydrazide, we decided, in conjunction with investigations on similar lines, to make a study of these compounds, particularly as regards their thermal decomposition.

The only such derivatives described so far are the dibenzylidene derivative, $CO(NH{\cdot}N{:}CHPh)_2$ (Curtius and Heidenreich, *J. pr. Chem.*, 1895, **52**, 471), and the dibenzophenone derivative, $CO(NH{\cdot}N{:}CPh_2)_2$, a compound tentatively described as such by Borsche and Merkwitz (*Ber.*, 1904, **37**, 3177; compare Wilson and Crawford, J., 1925, **127**, 103), but not synthesised. We have prepared the following carbohydrazones from carbohydrazide and the appropriate ketone: *diacetonecarbohydrazone*, $CO(NH{\cdot}N{:}CMe_2)_2$, *di*(*methyl ethyl ketone*)*carbohydrazone*, $CO(NH{\cdot}N{:}CMeEt)_2$, *diacetophenonecarbohydrazone*, $CO(NH{\cdot}N{:}CMePh)_2$, and dibenzophenonecarbohydrazone. By means of carbohydrazide, $CO(NH\cdot NH_2)_2$, we have prepared *carbohydrazones* of the type $CRR'{:}N\cdot NH\cdot CO\cdot NH\cdot NH_2$ (which we designate *δ-aminosemicarbazones*) from benzaldehyde, acetophenone, benzophenone, benzil, and diacetyl; a compound of a mixed type, *benzaldehyde acetophenone carbohydrazone*, $CHPh{:}N\cdot NH\cdot CO\cdot NH\cdot N{:}CMePh$, has also been prepared. Acetylacetone and carbohydrazide gave 3 : 5-dimethylpyrazole.

The thermal decomposition of dibenzaldehydecarbohydrazone, diacetophenonecarbohydrazone, and benzaldehyde-δ-aminosemicarbazone occurred in two stages. In boiling absolute alcoholic solution, dibenzaldehydecarbohydrazone gradually underwent decomposition, giving dibenzaldehydehydrazidicarbohydrazone, already described by Stollé (*Ber.*, 1910, **43**, 2468), and benzylideneazine : $2CO(NH\cdot N{:}CHPh)_2 =$

$$CO(NH\cdot N{:}CHPh)\cdot NH\cdot NH\cdot CO(NH\cdot N{:}CHPh) + (CHPh)_2N_2.$$

When heated at its melting point, the carbohydrazone gave 4-aminourazole and benzylideneazine, the intermediate dibenzaldehydehydrazidicarbohydrazone evidently decomposing in this way : $CO(NH\cdot N{:}CHPh)\cdot NH\cdot NH\cdot CO(NH\cdot N{:}CHPh) =$

$$\begin{array}{lcl} NH_2\cdot N & \text{——} & CO \\ \quad CO\cdot NH & \cdot & NH \end{array} + (CHPh)_2N_2.$$

Diacetophenonecarbohydrazone behaved in a similar manner, giving *diacetophenonehydrazidicarbohydrazone*, $CO(NH\cdot N{:}CMePh)\cdot NH\cdot NH\cdot CO(NH\cdot N{:}CMePh)$, and phenyl methyl ketazine in boiling alcoholic solution, and 4-aminourazole and phenyl methyl ketazine when heated without a solvent. Benzaldehyde-δ-aminosemicarbazone was scarcely affected in boiling alcohol; prolonged boiling in toluene solution gave hydrazidicarbohydrazide and benzylideneazine : $2CHPh{:}N\cdot NH\cdot CO\cdot NH\cdot NH_2 = NH_2\cdot NH\cdot CO\cdot NH\cdot NH\cdot CO\cdot NH\cdot NH_2 + (CHPh)_2N_2$. When heated a little above the melting point, the δ-aminosemicarbazone gave 4-aminourazole, hydrazine, and benzylideneazine, the former two compounds evidently resulting from the hydrazidicarbohydrazide :

$NH_2\cdot NH\cdot CO\cdot NH\cdot NH\cdot CO\cdot NH\cdot NH_2 =$

$$\begin{array}{lcl} NH_2\cdot N & \text{——} & CO \\ \quad CO\cdot NH & \cdot & NH \end{array} + N_2H_4.$$

This work will be continued.

EXPERIMENTAL.

Carbohydrazide was prepared by Kesting's method (*Ber.*, 1924, 57, 1323).

Diacetonecarbohydrazone (prisms from alcohol; m. p. 156°) was prepared by refluxing carbohydrazide with an excess of acetone for about 10 minutes and allowing the product to cool. Much heat was generated when the reactants were mixed (Found : N, 33·3. $C_7H_{14}ON_4$ requires N, 32·9%).

Di(methyl ethyl ketone)carbohydrazone (prismatic needles, m. p. 113°) was prepared in the same way, slightly more than 2 mols. of the ketone being used and the mixture being refluxed for only 5 minutes; the mixing of the reactants produced much heat. The almost solid product obtained on cooling was, after several hours, pressed on porous tile and then recrystallised from ether. The carbazone was readily soluble in acetone, alcohol, or water, and sparingly soluble in ether, and was rapidly hydrolysed by dilute mineral acids. This preparation was also carried out in aqueous solution, addition of potassium carbonate causing separation of the carbohydrazone (Found: N, 28·4. $C_9H_{18}ON_4$ requires N, 28·3%).

In the preparation of *diacetophenonecarbohydrazone*, the ease with which the derivatives decomposed in solution caused difficulties. 3 G. of carbohydrazide and 12 g. of acetophenone in 50 c.c. of absolute alcohol were gently heated for 1 hour; on cooling, the *carbohydrazone* (needles from aqueous alcohol; m. p. 204°) was deposited, but the yield was only 50% owing to decomposition during the working-up of the mother-liquor. The substance was sparingly soluble in cold solvents, but dissolved readily in hot water and in hot alcohol (Found: C, 69·2; H, 6·2; N, 19·2. $C_{17}H_{18}ON_4$ requires C, 69·4; H, 6·1; N, 19·0%).

3·2 G. of carbohydrazide and 4 g. of acetophenone in 50 c.c. of absolute alcohol gave, after being heated gently for 1 hour and then cooled, needles of carbohydrazide mixed with plates of *acetophenone-δ-aminosemicarbazone*. The latter compound (m. p. 188°) was isolated by dissolving out the carbohydrazide with cold water (Found: N, 29·0, 29·1. $C_9H_{12}ON_4$ requires N, 29·2%). The substance was readily soluble in hot water, alcohol, or pyridine and sparingly soluble or insoluble in other solvents.

Benzaldehyde acetophenone carbohydrazone (rhombic plates from alcohol; m. p. 160°) was obtained by refluxing 2 g. of the preceding compound and 1·5 g. of benzaldehyde in absolute alcohol for 1 hour and cooling the product. It dissolved in hot water, alcohol, benzene, and pyridine (Found: N, 19·3. $C_{16}H_{16}ON_4$ requires N, 20·0%).

Benzophenone reacted sluggishly. A solution of 1·8 g. of carbohydrazide and 3·64 g. of the ketone (1 mol.) in 10 c.c. of alcohol and 3 c.c. of water was refluxed for 7 hours, *benzophenone-δ-aminosemicarbazone*, $CPh_2{:}N{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}NH_2$, being gradually deposited; after being washed with cold alcohol and with warm water, this crystallised from alcohol in glistening, diamond-shaped plates (yield, 75%), m. p. 223—224° (decomp.), which were slightly soluble in alcohol and insoluble in boiling water (Found: C, 66·2; H, 5·9; N, 22·0. $C_{14}H_{14}ON_4$ requires C, 66·1; H, 5·5; N, 22·0%).

An absolute alcoholic solution (40 c.c.) of 1·27 g. of this compound and 3 g. of benzophenone (large excess) was refluxed for 40 hours; the solution gradually became yellow, but even after this time the reaction was far from complete. On cooling, plates of the δ-aminosemicarbazone appeared followed by colourless needles of dibenzophenonecarbohydrazone. The latter, after fractional crystallisation from alcohol, melted at 222—223° (yield, 0·3 g.) (Found : C, 77·1; H, 5·5; N, 13·4. Calc. for $C_{27}H_{22}ON_4$: C, 77·5; H, 5·3; N, 13·4%) and was identical with the substance described by Borsche and Merkwitz (*loc. cit.*).

Benzaldehyde-δ-aminosemicarbazone was obtained by refluxing 5 g. of carbohydrazide and 4·5 g. of benzaldehyde in absolute alcohol for 1 hour and recrystallising from alcohol the product which separated on cooling; it formed lustrous plates, m. p. 173°, soluble in alcohol or chloroform (yield, good) (Found : N, 31·5. $C_8H_{10}ON_4$ requires N, 31·5%).

Benzilmono-δ-aminosemicarbazone, $COPh{\cdot}CPh{:}N{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}NH_2$, was prepared by refluxing for ½ hour an absolute alcoholic solution of 5·8 g. of carbohydrazide and 13·5 g. (1 mol.) of benzil and then distilling off, during another ½ hour, most of the solvent. The almost solid mass obtained on cooling was washed with ether and recrystallised from absolute alcohol, white flakes, m. p. 172—174°, being obtained; these were slightly soluble in boiling alcohol and insoluble in benzene (Found : N, 19·2, 19·5. $C_{15}H_{14}O_2N_4$ requires N, 19·8%).

Diacetylmono-δ-aminosemicarbazone was prepared by heating on the water-bath molecular quantities of carbohydrazide and the diketone in absolute alcohol for 1 hour; the precipitate which gradually formed was collected hot and extracted twice with boiling absolute alcohol. The substance was a powder with a slightly yellow tinge, m. p. 260°, insoluble in all the usual solvents (Found : N, 35·3. $C_5H_{10}O_2N_4$ requires N, 35·4%).

An absolute alcoholic solution of acetylacetone (6 g.) and carbohydrazide (3 g.) was refluxed for 1 hour, and the solvent then evaporated. The residue, which slowly solidified, was dissolved in ether, recovered from the filtered solution, and dissolved in alcohol; slow evaporation then yielded a substance, m. p. 106—107°, which was identified as 3 : 5-dimethylpyrazole (Found : N, 29·1, 29·2. Calc. : N, 29·1%).

Thermal Decomposition of Carbohydrazones.

Dibenzaldehydecarbohydrazone.—An absolute alcoholic solution, on boiling for 24 hours, gradually became deep yellow. The solid deposited on cooling was collected, extracted with alcohol to dissolve out unchanged substance, and then recrystallised from much alcohol; the needles, m. p. 228°, thus obtained were shown to be dibenzaldehydehydrazidicarbohydrazone by comparison with an authentic specimen and by analysis (Found: N, 26·0. Calc.: N, 25·9%). The original solution from which this substance had been removed contained benzylideneazine and a little unchanged substance; separation was effected by means of ether, in which the former alone was soluble.

On heating at 205° for 1 hour, the carbohydrazone formed an amber-coloured liquid. The cold melt, on extraction with ether, left a white residue which was recrystallised from water and then proved to be 4-aminourazole (mixed m. p. test). The ethereal solution contained benzylideneazine.

Diacetophenonecarbohydrazone.—An alcoholic solution was boiled for 26 hours. It soon became yellow and deposited a white precipitate, which was collected when cold. The filtrate contained phenyl methyl ketazine. Recrystallisation of the precipitate from alcohol gave a colourless, crystalline powder, m. p. 239—240° (yellow melt), which became grey on keeping. It was *diacetophenonehydrazidicarbohydrazone* (Found: N, 24·2. $C_{18}H_{20}O_2N_6$ requires N, 23·9%) and was only slightly soluble in hot alcohol, readily soluble in hot pyridine, and insoluble in other solvents even when hot.

The carbohydrazone, on heating at 220° for 50 minutes, gave an orange-coloured and ultimately dark brown liquid, ammonia being evolved. Extraction of the cold powdered melt with ether left a white residue which, after recrystallisation from water, melted at 269—270° and was identified as 4-aminourazole by a mixed melting-point test and by analysis (Found: N, 48·4. Calc.: N, 48·3%): the yellow ethereal solution contained phenyl methyl ketazine. The yield of these products was almost quantitative.

Benzaldehyde-δ-aminosemicarbazone.—Scarcely any reaction occurred in boiling alcoholic or benzene solution. Boiling in toluene solution, however, for 31 hours effected decomposition. The white precipitate produced was collected when cold; after recrystallisation from absolute alcohol it melted at 197° and was identified as hydrazidicarbohydrazide (Stollé, *Ber.*, 1910, **43**, 2469). The toluene filtrate contained benzylideneazine.

The δ-aminosemicarbazone, on heating at 175° for 1½ hours, gave a deep yellow liquid, hydrazine, recognised by its reducing action, and ammonia being evolved. Extraction of the cold powdered melt with ether left a residue which, after recrystallisation from aqueous alcohol and then from water, melted at 270° and was identified as 4-aminourazole by comparison with an authentic specimen. The ethereal solution contained benzylideneazine.

Our thanks are expressed to Messrs. A. M. Munro, A. D. Neilson, B.Sc., and W. B. Stewart, B.Sc., for experimental assistance. We wish also to thank the Carnegie Trust for the Universities of Scotland for a research grant in aid of this work.

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[*Received, September 23rd,* 1926.]