CLXIII.—*Reactions of Carbohydrazide. Part II.*

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THE view expressed in Part I (J., 1927, 107) that in the thermal decomposition which carbohydrazones (or δ-aminosemicarbazones) undergo at their melting points the hydrazidicarbohydrazone (or hydrazidicarbohydrazide itself) is the intermediate product has been confirmed by investigating the thermal decomposition of dibenzaldehydehydrazidicarbohydrazone, *diacetonehydrazidicarbohydrazone*, and hydrazidicarbohydrazide. The decomposition of diacetonecarbohydrazone and *dipinacolincarbohydrazone* both in boiling alcoholic solution and at the melting point has also been found to conform to the general scheme.

The interaction of ethyl acetoacetate and carbohydrazide was next investigated. There are several possibilities :

(*a*) $COMe\cdot CH_2\cdot CO_2Et + CO(NH\cdot NH_2)_2 \xrightarrow[(-H_2O)]{} \begin{matrix} CMe\cdot CH_2\cdot CO_2Et \\ \| \\ N\cdot NH\cdot CO\cdot NH\cdot NH_2 \end{matrix}$

(I.) *Ethyl acetoacetate δ-aminosemicarbazone.*

or $\xrightarrow[(-H_2O,\ -EtOH)]{} \begin{matrix} CMe\cdot CH_2\cdot CO \\ \| \quad\quad | \\ N\text{———}N\cdot CO\cdot NH\cdot NH_2 \end{matrix}$ (II.)

(*b*) $2COMe\cdot CH_2\cdot CO_2Et + CO(NH\cdot NH_2)_2 \xrightarrow[(-2H_2O)]{}$

$CO(NH\cdot N{:}CMe\cdot CH_2\cdot CO_2Et)_2$

(III.) *Di(ethyl acetoacetate)carbohydrazone.*

or $\xrightarrow[(-2H_2O,\ -2EtOH)]{} \begin{matrix} CMe\cdot CH_2\cdot CO & CO\cdot CH_2\cdot CMe \\ \| \quad\quad | & | \quad\quad \| \\ N\text{———}N\cdot CO\cdot N\text{———}N \end{matrix}$

(IV.) *3 : 3′-Dimethyl-5 : 5′-dipyrazolonyl 1 : 1′-ketone.*

or $\xrightarrow[(-2H_2O,\ -EtOH)]{} \begin{matrix} CMe\cdot CH_2\cdot CO \\ \| \quad\quad | \\ N\text{———}N\cdot CO\cdot NH\cdot N{:}CMe\cdot CH_2\cdot CO_2Et \end{matrix}$

(V.) *3-Methyl-5-pyrazolone-1-carboxy-α-carbethoxyisopropylidenehydrazide.*

Of these substances (I), (III), (IV) and (V) were actually obtained. (I) was produced by heating the reactants in equimolecular quantities in alcoholic solution; (III) and (V) were formed together by heating 2 mols. of the ester with 1 mol. of carbohydrazide. On one occasion repetition of the latter experiment gave substances (III) and (IV), (V) not being produced.

The thermal decomposition of (I) and (III) conformed to the general scheme described in Part I: the amount of (V) did not permit of detailed investigation.

In boiling alcoholic solution (I) yielded hydrazine and *di(ethyl acetoacetate)hydrazidicarbohydrazone* (VI),

$$2CMe(:N\cdot NH\cdot CO\cdot NH\cdot NH_2)\cdot CH_2\cdot CO_2Et = N_2H_4 + [CO(NH\cdot N:CMe\cdot CH_2\cdot CO_2Et)\cdot NH\cdot]_2 \quad (VI.)$$

On heating at the melting point, (I) gave hydrazine, 4-aminourazole, and 3 : 4-dimethyl-1 : 2-pyrazo-6 : 7-pyrone (VII) (Bülow and Lobeck, *Ber.*, 1907, **40**, 708; Bülow and Schaub, *Ber.*, 1908, **41**, 1945; Wolff and Schreiner, *ibid.*, p. 550), a decomposition product of ethyl acetoacetate azine, the reaction evidently following the course :

$$2\,(I) = N_2H_4 + (VI) \longrightarrow CO\langle\begin{matrix}N(NH_2)\\NH\cdot NH\end{matrix}\rangle CO + [N(:CMe\cdot CH_2\cdot CO_2Et)]_2 \longrightarrow$$

$$2EtOH + \begin{matrix}&&NH&&O\\&\diagup&&\diagdown&\\N&&C&&CO\\\|&&&&\\MeC&-&C&&CH\\&\diagdown&&\diagup&\\&&CMe&&\end{matrix} \quad (VII.)$$

On prolonged boiling in alcoholic solution, (III) gave di(ethyl acetoacetate)hydrazidicarbohydrazone and (VII),

$$2CO(NH\cdot N:CMe\cdot CH_2\cdot CO_2Et)_2 = [CO(NH\cdot N:CMe\cdot CH_2\cdot CO_2Et)\cdot NH\cdot]_2 + (VII) + EtOH;$$

on heating at the melting point, the products were 4-aminourazole and (VII),

$$2CO(NH\cdot N:CMe\cdot CH_2\cdot CO_2Et)_2 = EtOH + (VII) + [CO(NH\cdot N:CMe\cdot CH_2\cdot CO_2Et)\cdot NH]_2 \longrightarrow CO\langle\begin{matrix}N(NH_2)\\NH\cdot NH\end{matrix}\rangle CO + (VII) + EtOH.$$

EXPERIMENTAL.

Dibenzaldehydehydrazidicarbohydrazone was heated at 250° for 3 hours. Treatment of the cooled powdered mass with ether

extracted benzylideneazine; the residue after recrystallisation from aqueous alcohol proved to be 4-aminourazole.

Hydrazidicarbohydrazide (Stollé, *Ber.*, 1910, **43**, 2468) on heating at 250° for 3 hours gave a distillate which contained hydrazine; the residue, after being washed with ether and recrystallised from aqueous alcohol, was shown to be 4-aminourazole.

Diacetonecarbohydrazone was boiled in absolute alcoholic solution for 30 hours, and the alcohol then distilled off. The residue, after being washed with ether and recrystallised from alcohol, furnished colourless crystals of *diacetonehydrazidicarbohydrazone*, m. p. 256° (Found : N, 36·8. $C_8H_{16}O_2N_6$ requires N, 36·8%). The alcoholic distillate on heating with dilute hydrochloric acid and evaporation gave hydrazine hydrochloride.

The carbohydrazone on heating at 200° for 3 hours gave a distillate of dimethylketazine (b. p. 131°); the residue after the usual treatment proved to be 4-aminourazole.

Diacetonehydrazidicarbohydrazone, identical with the specimen described above, was also obtained by refluxing acetone with hydrazidicarbohydrazide for 1 hour and recrystallising the product from alcohol. On heating at its melting point, it gave dimethylketazine and 4-aminourazole.

Dipinacolincarbohydrazone was prepared by refluxing pinacolin (9·8 g.) with carbohydrazide (4·5 g.) in absolute alcohol (20 c.c.) for 5 hours. On cooling, it separated in small plates, m. p. 188° after recrystallisation from alcohol (Found : C, 61·5; H, 10·3; N, 22·1. $C_{13}H_{26}ON_4$ requires C, 61·4; H, 10·2; N, 22·0%). An alcoholic solution, after boiling for 24 hours, deposited, on cooling, *dipinacolinhydrazidicarbohydrazone*, $(CMe_3{\cdot}CMe{:}N{\cdot}NH{\cdot}CO{\cdot}NH{\cdot})_2$, a white powder, m. p. 230° after recrystallisation from alcohol (Found : N, 26·9. $C_{14}H_{28}O_2N_6$ requires N, 26·9%). The alcoholic solution on evaporation left a resin, from which ether extracted pinacolinazine identical with the specimen previously obtained by one of us (J., 1927, 2116). The carbohydrazone was heated for 1 hour at 250° under reduced pressure. Pinacolinazine distilled over; the residue after the usual treatment was found to be 4-aminourazole.

Dipinacolinhydrazidicarbohydrazone, identical with the specimen described above, was also obtained by refluxing hydrazidicarbohydrazide with excess of pinacolin in alcohol for 10 hours. The dark brown solution after treatment with charcoal and concentration deposited plates which crystallised from alcohol and melted at 230°. The substance on heating at 250° under reduced pressure gave pinacolinazine and 4-aminourazole.

Ethyl acetoacetate δ-aminosemicarbazone (I) was obtained by refluxing 13 g. of the ester with 9 g. of carbohydrazide in 20 c.c. of

absolute alcohol for 1 hour. The powder which separated on cooling was recrystallised several times from alcohol, plates of a slightly yellowish tinge, m. p. 219°, being obtained. The compound was soluble in alcohol but insoluble in ether and chloroform (Found : C, 41·5; H, 6·9; N, 27·9. $C_7H_{14}O_3N_4$ requires C, 41·6; H, 6·9; N, 27·7%). This substance was boiled for 7 hours in absolute alcohol. On cooling, colourless plates separated. The mother-liquor was distilled and hydrazine was detected in the distillate. The plates after recrystallisation from alcohol melted at 213° and consisted of *di(ethyl acetoacetate)hydrazidicarbohydrazone* (Found : C, 45·1; H, 6·5; N, 22·6. $C_{14}H_{24}O_6N_6$ requires C, 45·1; H, 6·5; N, 22·6%).

The δ-aminosemicarbazone was heated at the melting point in a small distilling flask for 1 hour in carbon dioxide under reduced pressure. A small amount of liquid in which hydrazine was present distilled and a little unaltered substance sublimed. The residue was extracted with ether, leaving 4-aminourazole undissolved; the extract on concentration deposited 3 : 4-dimethyl-1 : 2-pyrazo-6 : 7-pyrone which, after recrystallisation from alcohol, melted at 245° and was identical with an authentic specimen (Found : C, 58·7; H, 4·9; N, 17·0. Calc. : C, 58·5; H, 4·9; N, 17·1%).

26 G. of ethyl acetoacetate were refluxed with 9 g. of carbohydrazide in 20 c.c. of absolute alcohol for 3½ hours. The deep brown solution slowly deposited a brown, crystalline mass which, after being washed with alcohol, was boiled with alcohol containing charcoal. From the filtered solution, yellow prisms of *di(ethyl acetoacetate)carbohydrazone* (III) slowly separated, m. p. 196° after recrystallisation (Found : C, 49·6; H, 7·1; N, 17·8. $C_{13}H_{22}O_5N_4$ requires C, 49·7; H, 7·0; N, 17·8%). The residue containing charcoal was extracted with boiling alcohol; the extract on cooling deposited lemon-yellow plates of *3-methyl-5-pyrazolone-1-carboxy-α-carbethoxyisopropylidenehydrazide* (V), m. p. 230° (decomp.) after recrystallisation (Found : C, 49·4; H, 6·0; N, 20·8. $C_{11}H_{16}O_4N_4$ requires C, 49·3; H, 6·0; N, 20·9%). No other substance was detected in this case. On one occasion there was obtained in addition to di(ethyl acetoacetate)carbohydrazone a substance which was sparingly soluble in alcohol and gave on recrystallisation from this solvent a white powder, m. p. 183°; this was *3 : 3′-dimethyl-5 : 5′-dipyrazolonyl 1 : 1′-ketone* (IV) (Found : C, 48·6, 48·7; H, 4·7, 4·7; N, 25·2, 25·4. $C_9H_{10}O_3N_4$ requires C, 48·6; H, 4·5; N, 25·2%).

After boiling for 12 hours an absolute-alcoholic solution of di(ethyl acetoacetate)carbohydrazone, on cooling, deposited plates, m. p. 213°, consisting of di(ethyl acetoacetate)hydrazidicarbohydrazone as shown by analysis and by comparison with the specimen previously obtained. The mother-liquor on evaporation

gave a residue, from which ether extracted 3 : 4-dimethyl-1 : 2-pyrazo-6 : 7-pyrone. The carbohydrazone was heated at its melting point for 1 hour; the cold powdered mass was extracted with ether, which dissolved 3 : 4-dimethyl-1 : 2-pyrazo-6 : 7-pyrone; the insoluble residue was found after the usual treatment to consist of 4-aminourazole.

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