CCCXV.—*The Action of Hydrazines on Semicarbazones. Part II.*

By William Baird and Forsyth James Wilson.

In Part I (J., 1924, **125**, 2145) it was shown that ketonic semicarbazones could react with phenylhydrazine in boiling toluene solution in two ways:

$$\left.\begin{array}{l} CRR'{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2 \\ \quad + NH_2{\cdot}NHPh \end{array}\right\} \begin{array}{l} \nearrow \; NH_3 + CRR'{:}N{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}NHPh \qquad (1) \\ \searrow \; NH_2{\cdot}NH{\cdot}CO{\cdot}NH_2 + CRR'{:}N{\cdot}NHPh \qquad (2) \end{array}$$

yielding either (1) a δ-anilinosemicarbazone, or (2) a phenylhydrazone and semicarbazide (or its decomposition product, hydrazodicarbonamide). Acetophenone- and benzophenone-semicarbazones reacted almost exclusively according to (1), whilst acetonesemicarbazone reacted almost exclusively according to (2).

In view of these results it was decided to make a general study of the behaviour of semicarbazones, both aldehydic and ketonic, on heating with phenylhydrazine: in all, the semicarbazones of seven aldehydes and fourteen ketones have been investigated. The semicarbazones of acetaldehyde, furfuraldehyde, benzaldehyde, anisaldehyde, cinnamaldehyde, and piperonal reacted exclusively according to scheme (2), whereas *n*-heptaldehydesemicarbazone reacted chiefly according to (2), but also to a slight extent according to (1), the yield of δ-anilinosemicarbazone being 8%.

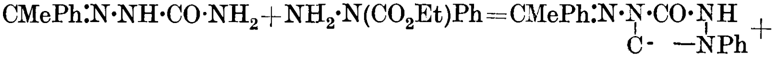
The behaviour of the ketonic semicarbazone varied in each case; in general both the δ-anilinosemicarbazone and the phenylhydrazone were formed. The approximate percentage yields of the δ-anilinosemicarbazone, indicating the extent to which reaction (1) took place, are quoted in brackets after the name of the ketone concerned : Acetone (5); methyl ethyl ketone (0, only the phenylhydrazone being produced); methyl *n*-propyl ketone (0); diethyl ketone (2); methyl *tert.*-butyl ketone (60); di-*n*-propyl ketone (13); di*iso*propyl ketone (90); *cyclo*hexanone (12); 1-methyl*cyclo*hexan-2-one (10); acetophenone (95); methyl benzyl ketone (13); benzylacetone (8); benzophenone (95); and dibenzyl ketone (90).

Examination of the schemes (1) and (2) will show that the groups R and R′ are likely to have an influence on the course of the reaction. If either or both are sufficiently bulky, then the formation of the phenylhydrazone (2) is likely to be inhibited in favour of the anilinosemicarbazone (1) since, in the production of the latter, the phenylhydrazine residue will take up a position more remote from the groups R and R′. On the whole, the experimental results seem to be in agreement with this supposition. Considering the monophenylated ketones, it will be seen that reaction (1) is most pronounced when the phenyl group is contiguous to the carbonyl group, this effect being less noticeable with methyl benzyl ketone and with benzylacetone where the phenyl group is not directly attached to the carbonyl group. In the case of the non-phenylated ketones, the yield of δ-anilinosemicarbazone is comparatively small except with methyl *tert.*-butyl ketone and di*iso*propyl ketone where there is a concentration of methyl groups on one or both of the α-carbon atoms. With the diphenylated ketones, reaction (1) is pronounced with both benzophenone and dibenzyl ketone, the attachment of a phenyl group to each α-carbon atom evidently strongly inhibiting reaction (2).

Other experiments carried out with different hydrazines support these conclusions. Whilst acetonesemicarbazone and phenylhydrazine gave a yield of only 5% of δ-anilinosemicarbazone, α-methyl-α-phenylhydrazine gave a yield of 52% of *acetone-δ-methylanilinosemicarbazone*, $CMe_2:N\cdot NH\cdot CO\cdot NH\cdot NMePh$, and αα-diphenylhydrazine gave 80% of *acetone-δ-diphenylaminosemicarbazone*, $CMe_2:N\cdot NH\cdot CO\cdot NH\cdot NPh_2$, replacement of hydrogen in the NH group of the hydrazine by methyl or phenyl evidently favouring reaction (1) at the expense of (2). On the other hand, *p*-tolylhydrazine gave only 9% of *acetone-δ-*p*-toluidinosemicarbazone*, $CMe_2:N\cdot NH\cdot CO\cdot NH\cdot NH\cdot C_7H_7$, the methyl group in this case being evidently too remote from the reactive amino-group of the hydrazine to have much effect. The same general results were obtained when α-methyl-α-phenylhydrazine or *p*-tolylhydrazine reacted with benzylacetonesemicarbazone.

Knöpfer (*Monatsh.*, 1910, **31**, 87) had already investigated the replacement of the semicarbazide residue in semicarbazones by the phenylhydrazine residue, the reaction being carried out with phenylhydrazine in boiling alcoholic or glacial acetic acid solution. No regularities were detected, and the formation of δ-anilinosemicarbazones described by us was not mentioned.

The interaction of acetophenonesemicarbazone and α-carbethoxy-α-phenylhydrazine was investigated in the expectation that the reaction would proceed according to the scheme



$$\mathrm{CMePh{:}N{\cdot}NH{\cdot}CO{\cdot}NH_2+NH_2{\cdot}N(CO_2Et)Ph=CMePh{:}N{\cdot}\underset{\underset{\displaystyle C\text{-}}{|}}{N}{\cdot}CO{\cdot}\underset{\underset{\displaystyle —NPh}{|}}{N}H}\ +$$

$\mathrm{NH_3}$+EtOH. The product, however, was *acetophenone-δ-carbethoxyanilinosemicarbazone*, $\mathrm{CMePh{:}N{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}N(CO_2Et)Ph}$, and efforts to eliminate ethyl alcohol from this compound were unsuccessful. The constitution of this substance was established by hydrolysis into acetophenone and *δ-carbethoxyanilinosemicarbazide hydrochloride*, $\mathrm{NH_2{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}N(CO_2Et)Ph,HCl}$, further hydrolysis giving hydrazine, phenylhydrazine, and alcohol.

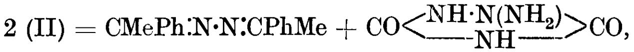
The thermal decomposition of acetophenone- and benzophenone-δ-anilinosemicarbazones was also investigated. The former gave acetophenonephenylhydrazone, 1-aminourazole and a small quantity of methyl phenyl ketazine. The probable course of the reaction is that the δ-anilinosemicarbazone (I) yields acetophenonecarbohydrazone * (II) and diphenylcarbohydrazide (III)

$$\text{(I.)}\ \mathrm{2CMePh{:}N{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}NHPh} = \text{(II.)}\ \mathrm{(CMePh{:}N{\cdot}NH)_2CO + (PhNH{\cdot}NH)_2CO}\ \text{(III.)},$$

(II) and (III) then giving acetophenonephenylhydrazone and 1-aminourazole:

$$\text{(II)} + \text{(III)} = \mathrm{2CMePh{:}N{\cdot}NHPh + CO}{<}\begin{matrix}\mathrm{NH{\cdot}N(NH_2)}\\ \mathrm{NH}\end{matrix}{>}\mathrm{CO}.$$

The methyl phenyl ketazine probably results with 1-aminourazole from the decomposition of the carbohydrazone



$$2\ \text{(II)} = \mathrm{CMePh{:}N{\cdot}N{:}CPhMe + CO}{<}\begin{matrix}\mathrm{NH{\cdot}N(NH_2)}\\ \mathrm{NH}\end{matrix}{>}\mathrm{CO},$$

(II) being known to decompose in this way on heating.

Benzophenone-δ-anilinosemicarbazone when heated to 180—190° for 7 hours gave benzophenonephenylhydrazone as the only recognisable product. Heating for a shorter time (3 hours) at 160—165° gave a different result: besides some unaltered substance, benzo-

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* Unpublished work.

phenonecarbohydrazone * was isolated; resinification occurred and diphenylcarbohydrazide could not be isolated, although various colour reactions indicated its presence. Thus the reaction apparently followed the same course as in the previous case except that no ketazine was formed. To test the supposition that the formation of the phenylhydrazone at the higher temperature was due to interaction of the carbohydrazone with diphenylcarbohydrazide, these two substances were heated together and found to yield benzophenonephenylhydrazone and, apparently, 1-aminourazole.

Work on these δ-anilinosemicarbazones will be continued.

EXPERIMENTAL.

Interaction of Semicarbazones and Phenylhydrazine.

Molecular quantities of the two reactants were heated under reflux in toluene solution or suspension at 130—135° until the evolution of ammonia had practically ceased, the time required being indicated in each case. Hydrazodicarbonamide, if formed, was filtered off and identified, and the toluene, unless otherwise stated, was then removed by distillation under reduced pressure and the residue worked up as described. The δ-anilinosemicarbazone, if formed, was characterised by analysis and by hydrolysis with hot dilute hydrochloric acid into aldehyde or ketone and δ-anilinosemicarbazide hydrochloride, previously described.

Acetaldehydesemicarbazone (6 hrs.) and *furfuraldehydesemicarbazone* (10 hrs.). Hydrazodicarbonamide and the aldehydic phenylhydrazone were the only products in each case.

n-*Heptaldehydesemicarbazone* (8 hrs.). Hydrazodicarbonamide was formed; the oily residue on cooling deposited n-*heptaldehyde-δ-anilinosemicarbazone* which, after washing with light petroleum and several recrystallisations from absolute alcohol, formed small acicular aggregates, m. p. 176° (yield 8%) (Found: N, 21·5, 21·6. $C_{14}H_{22}ON_4$ requires N, 21·4%). *n*-Heptaldehydephenylhydrazone was identified in the residue from the δ-anilinosemicarbazone by its b. p. and by hydrolysis with dilute sulphuric acid.

Benzaldehydesemicarbazone (10 hrs., 120°). About half of the substance was recovered unchanged, the products being hydrazodicarbonamide and the phenylhydrazone. In xylene solution (6 hrs. at 140—150°) the same reaction was nearly complete.

Anisaldehydesemicarbazone. This reaction, carried out as in the preceding case, gave hydrazodicarbonamide and anisaldehydephenylhydrazone; at the higher temperature, small quantities of the azine were formed.

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* Unpublished work.

Cinnamaldehyde- and piperonal-semicarbazones. These reactions, carried out as in the last two cases, gave hydrazodicarbonamide and the phenylhydrazone.

Methyl ethyl ketone semicarbazone (4 hrs., 80—90°). Hydrazodicarbonamide and semicarbazide were formed; the residual oil was identified as the phenylhydrazone by its b. p. and by hydrolysis with acid. Further experiments at higher temperatures and for longer times led to the same results, no δ-anilinosemicarbazone being detected.

Methyl propyl ketone semicarbazone (9 hrs.). Hydrazodicarbonamide was formed; the residual oil was fractioned under reduced pressure and identified as the phenylhydrazone, no δ-anilinosemicarbazone being formed.

Diethyl ketone semicarbazone (7½ hrs.). Hydrazodicarbonamide was formed; addition of 2 vols. of light petroleum to the oily residue gave, on cooling in ice, a *solid* which crystallised from alcohol in plates, m. p. 180—181°, too small in amount to identify. Further addition of light petroleum and cooling in ice deposited a solid which crystallised from alcohol, in which it was fairly soluble, in needles, m. p. 141°. This was *diethyl ketone δ-anilinosemicarbazone* (yield 2%) (Found : N, 24·2. $C_{12}H_{18}ON_4$ requires N, 23·9%). The light-petroleum solution was then evaporated, and the residue on distillation gave a fraction, b. p. 130°/6 mm., identified as diethyl ketone phenylhydrazone by hydrolysis with acid.

Methyl tert.*-butyl ketone semicarbazone* (7½ hrs.). Hydrazodicarbonamide was formed; the toluene filtrate on concentration under reduced pressure deposited crystals of the *δ-anilinosemicarbazone,* further quantities separating on addition of light petroleum and cooling in ice. This substance crystallised from absolute alcohol in silky needles, m. p. 179° (Found : N, 22·5, 22·7. $C_{13}H_{20}ON_4$ requires N, 22·6%); yield 63%. The petroleum–toluene solution was evaporated, and the ketonic phenylhydrazone remained.

cyclo*Hexanonesemicarbazone* (4 hrs.). Hydrazodicarbonamide was formed. The almost solid residue was washed with alcohol and recrystallised from methyl alcohol in plates, m. p. 192°; it was very soluble in hot pyridine and slightly soluble in boiling methyl and ethyl alcohols. It was the *δ-anilinosemicarbazone,* yield 12% (Found : N, 23·0, 22·9. $C_{13}H_{18}ON_4$ requires N, 22·8%). Concentration and freezing of the alcoholic washings deposited *cyclo*hexanonephenylhydrazone, identified by its m. p. and by conversion into tetrahydrocarbazole with sulphuric acid.

1-*Methyl*cyclo*hexan*-2-*onesemicarbazone* * (8 hrs.). Hydrazodi-

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* The ketone was prepared by the method used by Knoevenagel and Tübben for the 1 : 3-compound (*Annalen*, 1897, **297**, 154).

carbonamide was filtered off, in the heat, and the toluene filtrate on cooling in ice deposited the δ-*anilinosemicarbazone* which crystallised from alcohol in needles, m. p. 182—183° (Found : N, 21·6. $C_{14}H_{20}ON_4$ requires N, 21·5%). The toluene solution was then completely evaporated, and the oily residue solidified when cooled in ice. Extraction with hot light petroleum yielded a further quantity of the insoluble δ-anilinosemicarbazone (total yield 10%); the filtrate on evaporation in a vacuum gave a solid residue of the phenylhydrazone, which recrystallised from aqueous alcohol as nearly colourless needles, m. p. 45—46°. As the phenylhydrazone is described as an oil (Plancher, *Atti R. Accad. Lincei*, 1900, **9**, 221), it was prepared by heating the ketone for 1 hour on the water-bath with a slight excess of phenylhydrazine; the ethereal solution of the product was washed with dilute acetic acid and with water, dried and evaporated to dryness in an evacuated desiccator. The residue after crystallisation as above proved to be identical with the phenylhydrazone described by us (Found : N, 13·7. $C_{13}H_{18}N_2$ requires N, 13·9%). It quickly decomposed on exposure, giving a dark oil.

Dipropyl ketone semicarbazone (5½ hrs.). After filtration from hydrazodicarbonamide in the heat and removal of most of the toluene the ketonic δ-*anilinosemicarbazone* was deposited on cooling, the separation being assisted by addition of light petroleum; yield 13%. It crystallised from alcohol in long, silky needles, m.p. 152° (Found : N, 21·5, 21·4. $C_{14}H_{22}ON_4$ requires N, 21·4%); insoluble in light petroleum, sparingly soluble in cold alcohol, fairly soluble in other common solvents. The phenylhydrazone was obtained from the reaction mother-liquors by fractionation under reduced pressure and identified by hydrolysis with acid.

Diisopropyl ketone semicarbazone * (5½ hrs.). No hydrazodicarbonamide was formed; the toluene solution on cooling deposited the δ-*anilinosemicarbazone* which crystallised from alcohol in prismatic needles, m. p. 181° (yield 90%) (Found : N, 21·5, 21·5. $C_{14}H_{22}ON_4$ requires N, 21·4%). No other product was found.

Methyl benzyl ketone semicarbazone (7 hrs.). Hydrazodicarbonamide was formed; addition of light petroleum to the oily residue gave on cooling in ice a solid which was extracted twice with boiling light petroleum. The insoluble residue after several recrystallisations from alcohol gave colourless plates of the δ-*anilinosemicarbazone*, m.p. 181—182° (yield 13%) (Found : N, 19·9, 19·9. $C_{16}H_{18}ON_4$ requires N, 19·9%). Concentration of the petroleum mother-liquors gave crystals of the phenylhydrazone, identified by its m. p. and by hydrolysis.

* The ketone was prepared by the manganous-oxide method from *iso*butyric acid (Sabatier and Mailhe, *Compt. rend.*, 1914, **158**, 832).

Benzylacetonesemicarbazone (8 hrs.). Hydrazodicarbonamide was filtered off and most of the toluene was evaporated. On cooling, the δ-*anilinosemicarbazone* was deposited and more was obtained on addition of light petroleum and allowing to stand (yield 8%). The substance was dimorphous: it crystallised from alcohol in silky needles, m. p. 162°, but from the mother-liquors it separated in plates of the same m. p.; it was slightly soluble in cold alcohol, and easily in ether and benzene (Found: N, 19·0, 19·1. $C_{17}H_{20}ON_4$ requires N, 18·9%). The phenylhydrazone could not be obtained in the solid form from the reaction mother-liquors but was identified by hydrolysis with acid.

Dibenzyl ketone semicarbazone (4 hrs.). The solution gave a nearly solid mass of the δ-*anilinosemicarbazone*, the only product of the reaction (yield 90%). It crystallised from pyridine or glacial acetic acid in very fine needles, m. p. 205°, insoluble or nearly so in the common solvents (Found: N, 15·8, 15·8. $C_{22}H_{22}ON_4$ requires N, 15·6%).

Interaction of Semicarbazones with α-Methyl-α-phenylhydrazine, p-*Tolylhydrazine, αα-Diphenylhydrazine, and α-Carbethoxy-α-phenylhydrazine.*

With α-Methyl-α-phenylhydrazine.—Acetophenonesemicarbazone (8 hrs.). A clear solution resulted; on cooling, crystals of *acetophenone-δ-methylanilinosemicarbazone* were deposited; after concentration and addition of alcohol further quantities separated on standing (yield 85%). It was recrystallised from alcohol and was moderately soluble in cold pyridine, chloroform, and glacial acetic acid, and sparingly in cold alcohol, ether, acetone, and benzene; prisms, m. p. 196° (Found: N, 19·9, 20·0. $C_{16}H_{18}ON_4$ requires N, 19·9%). This substance, the only product of the reaction, was hydrolysed by boiling with 6% hydrochloric acid, the acetophenone was removed by ether extraction, and the aqueous solution, on evaporation under reduced pressure, gave a residue of δ-*methylanilinosemicarbazide hydrochloride*. It was purified by washing with ether, dissolving in absolute alcohol, in which it was freely soluble, and adding ether or light petroleum: it separated as an oil which solidified on being scratched, m. p. 181° (decomp.) (Found: N, 25·8; Cl, 16·3. $C_8H_{13}ON_4Cl$ requires N, 25·9; Cl, 16·4%).

Acetonesemicarbazone (8 hrs.). The hot solution was filtered from hydrazodicarbonamide; on cooling, crystals of the δ-*methylanilinosemicarbazone* were deposited, more being obtained on concentrating and adding light petroleum (yield 52%). It was sparingly soluble in cold alcohol, from which it crystallised in elongated masses of diamond-shaped plates, m. p. 194° (Found: N, 25·6, 25·5. $C_{11}H_{16}ON_4$

requires N, 25·5%). The petroleum solution contained acetonemethylphenylhydrazone, identified by its b. p. and by hydrolysis.

Benzylacetonesemicarbazone (7 hrs.). A quantity of insoluble material, too small for identification, was formed; the filtrate on evaporation left a viscous oil which solidified on dissolving in ether and evaporating in a vacuum : freezing did not effect solidification. Crystallisation from alcohol gave a sparingly soluble compound, m. p. 213°, too small in amount to identify, and the ketonic *δ-methylanilinosemicarbazone*, acicular rosettes, m. p. 113° (yield 65%) (Found : N, 18·1, 18·1. $C_{18}H_{22}ON_4$ requires N, 18·1%).

n-*Heptaldehydesemicarbazone* (7 hrs.). The toluene solution after filtration from hydrazodicarbonamide was evaporated; addition of light petroleum gave a solid too small in amount to identify. The filtrate from this was evaporated, and the ethereal solution of the residue was washed with dilute acetic acid and water, dried over potassium carbonate and evaporated; on fractionation an almost colourless oil was obtained, b. p. 169—172°/5 mm., and identified by hydrolysis as n-*heptaldehydemethylphenylhydrazone* (Found : N, 12·8. $C_{14}H_{22}N_2$ requires N, 12·8%).

With p-*Tolylhydrazine.—Acetonesemicarbazone* (9 hrs.). After filtration from hydrazodicarbonamide, the solution, on being cooled and scratched, deposited crystals which, after several recrystallisations from alcohol, had m. p. 175—176° (yield 9%). Although the analysis was not very satisfactory (Found : N, 25·0, 24·9. $C_{11}H_{16}ON_4$ requires N, 25·5%), the compound was apparently *acetone-δ-*p-*toluidinosemicarbazone*. Acetone-*p*-tolylhydrazone was identified in the toluene mother-liquors by its m. p. and by hydrolysis.

Benzylacetonesemicarbazone (8 hrs.). Hydrazodicarbonamide (yield 80%) was filtered off, the residue on crystallisation from light petroleum gave pale yellow needles, m. p. 74—78°, of *benzylacetone*-p-*tolylhydrazone* (Found : N, 11·3. $C_{17}H_{20}N_2$ requires N, 11·1%). This compound was fairly soluble in light petroleum and decomposed readily. No δ-*p*-toluidinosemicarbazone was formed.

With αα-Diphenylhydrazine.—Acetonesemicarbazone (7 hrs.). No hydrazodicarbonamide was formed; the toluene solution on cooling deposited crystals of the *δ-diphenylaminosemicarbazone*, and further quantities were obtained by evaporation and addition of a little alcohol to the residue; needles, m. p. 186—187°, from alcohol (yield 80%). The substance is dimorphous, the needles on standing in alcohol gradually changing to prisms of the same m. p., this change being accelerated by boiling; the prisms gave needles again on recrystallisation (Found : N, 20·0, 19·9. $C_{16}H_{18}ON_4$ requires N, 19·9%). It gave a pale bluish-green colour with concentrated sulphuric acid, and a very deep bluish-green colour if the sulphuric acid contained a trace of nitric acid. Aqueous-alcoholic copper sulphate solution gave a pale light-blue colour which gradually changed to a permanganate colour on standing; the colour was unaffected by boiling. Alcohol and ferric chloride gave a similar permanganate colour more rapidly; on boiling this changed to a brownish-red.

Acetophenonesemicarbazone ($8\frac{1}{2}$ hrs.). No hydrazodicarbonamide was produced, the only product being *acetophenone-δ-diphenylaminosemicarbazone* which, after extraction with boiling alcohol to remove a little unaltered semicarbazone, was recrystallised from a mixture of alcohol and pyridine; thick hexagonal plates, m. p. 236—237° (decomp.) (yield 90%); sparingly soluble in the common solvents, easily soluble in pyridine and acetic acid, and giving a bluish-green colour with concentrated sulphuric acid (Found: N, 16·3, 16·4. $C_{21}H_{20}ON_4$ requires N, 16·3%). The substance was hydrolysed by boiling for 2 hours with 12% hydrochloric acid and the aqueous portion, after removal of the acetophenone by ether, was evaporated to dryness under reduced pressure. Extraction with hot absolute alcohol left a residue of hydrazine hydrochloride; addition of dry ether to the filtrate precipitated *δ-diphenylaminosemicarbazide hydrochloride* which was converted into the *benzylidene* derivative in the usual way: long, silky needles from alcohol, m. p. 235—236° (decomp.), giving a bluish-green colour with concentrated sulphuric acid (Found: N, 17·0. $C_{20}H_{18}ON_4$ requires N, 17·0%).

Acetophenonesemicarbazone and α-Carbethoxy-α-phenylhydrazine (10 hrs.).—On cooling, *acetophenone-δ-carbethoxyanilinosemicarbazone* was collected and recrystallised from alcohol as rosettes of acicular plates, m. p. 192°. The substance was dimorphous: on standing in alcohol these crystals changed into thick plates of the same m. p., acicular plates being deposited again on recrystallisation (Found: N, 16·5, 16·5; C, 63·4; H, 5·9. $C_{18}H_{20}O_3N_4$ requires N, 16·5; C, 63·5; H, 5·9%). Decomposition took place on heating above the m. p., only methyl phenyl ketazine being isolated. The substance was hydrolysed by boiling for 5 minutes with dilute hydrochloric acid, and the aqueous portion, after removal of the acetophenone with ether, was evaporated to dryness under reduced pressure. The residual *δ-carbethoxyanilinosemicarbazide hydrochloride* was obtained as a microcrystalline mass by precipitating the absolute-alcoholic solution with ether, m. p. 190° (Found: Cl, 12·9, 12·9. $C_{10}H_{15}O_3N_4Cl$ requires Cl, 12·9%). The *benzylidene* derivative crystallised from alcohol as needles, m. p. 158° (decomp.) (Found: N, 17·0, 17·1. $C_{17}H_{18}O_3N_4$ requires N, 17·2%). The hydrochloride was hydrolysed with difficulty by slow distillation with 50% sulphuric acid, alcohol being detected in the distillate and hydrazine and phenylhydrazine in the residue.

Action of Heat on δ-Anilinosemicarbazones.

Benzophenone-δ-anilinosemicarbazone.—This gave, after 7 hours' heating at 180—190° and cooling, a clear, hard resin which was extracted with ether. The extract was evaporated to dryness in a vacuum and the residue, after being recrystallised from alcohol (charcoal), was found to be benzophenonephenylhydrazone. No other substance was isolated except a small quantity of a *compound*, m. p. 213°. The experiment was repeated (3 hrs. at 160—165°) and the melt when cold was broken up with ether. The crystals which gradually formed were collected, washed with ether and extracted with boiling alcohol, leaving a minute residue. The extract on cooling deposited a solid which was fractionally crystallised from alcohol. Benzophenonecarbohydrazone, m. p. 223—225°, was first obtained and identified by comparison with an authentic specimen (Found : N, 13·2. Calc. : N, 13·4%); unaltered δ-anilinosemicarbazone was also obtained. Many of the crops turned pink on standing, the mother-liquors gave colour reactions which are also given by diphenylcarbohydrazide, but this substance could not be isolated, only resinous products being obtained.

Acetophenone-δ-anilinosemicarbazone.—The substance was heated at 220—225° for 2 hours, a little ammonia being evolved after that time. The cold melt was extracted twice with ether to remove acetophenonephenylhydrazone. The residue was extracted with a little hot alcohol which dissolved methyl phenyl ketazine; the insoluble solid after recrystallisation from water melted at 273—274° (decomp.), and was identified as 1-aminourazole (Found : N, 48·3. Calc. : N, 48·3%).

Action of Diphenylcarbohydrazide on Benzophenonecarbohydrazone.—Molecular quantities of the two reactants were heated to 185° for 8 hours. The cold mass was extracted with ether and ultimately solidified after being scratched. The solid was extracted with boiling absolute alcohol; the residue was very small, but dissolved in water with an acid reaction and appeared to be 1-aminourazole; the alcoholic extract contained benzophenonephenylhydrazone.

In conclusion, we wish to thank the Carnegie Trust for the Universities of Scotland for a research grant which has partly defrayed the expenses of this work. We wish also to thank the Governors of this College for a research assistantship which has enabled one of us (W. B.) to share in this investigation, during part of which he was also holder of the "Nobel Industries Prize," for which thanks are now expressed to Nobel Industries, Ltd.

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