CCLXXX.—*The Action of Hydrazines on Semicarbazones. Part III.*

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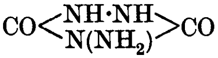
In Part II (J., 1926, 2369) it was shown that acetophenone- and benzophenone-δ-anilinosemicarbazones on heating gave the phenylhydrazones and 4-aminourazole,* the reaction probably taking place in two stages :



$$2CRR'{:}N{\cdot}NH{\cdot}CO{\cdot}NH{\cdot}NHPh = CO(NH{\cdot}N{:}CRR')_2 + CO(NH{\cdot}NHPh)_2 = 2CRR'{:}N{\cdot}NHPh + CO{<}\genfrac{}{}{0pt}{}{NH{\cdot}NH}{N(NH_2)}{>}CO$$

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* In Part II this compound was erroneously described as 1-aminourazole; the name and formula should be as now given.

From acetophenone-δ-anilinosemicarbazone, some ketazine was also produced, probably by the thermal decomposition of the intermediate carbohydrazone (compare Brown, Pickering, and Wilson, this vol., p. 107). This interpretation of the reaction has now been confirmed by heating together diacetonecarbohydrazone and diphenylcarbohydrazide, the products being acetonephenylhydrazone, 4-aminourazole and dimethylketazine. The thermal decomposition of acetone-, pinacolin-, and benzylidene-δ-anilinosemicarbazones followed the same course, no diphenylcarbohydrazide being actually isolated. In the case of acetone-δ-diphenylaminosemicarbazone, the thermal decomposition of which conformed to the general scheme, some tetraphenylcarbohydrazide, $CO(NH{\cdot}NPh_2)_2$, was actually isolated.

In the expectation of obtaining δ-anilinothiosemicarbazones, the behaviour of acetone-, acetophenone-, and dibenzyl ketone thiosemicarbazones on heating with phenylhydrazine was investigated in the usual manner. In each case, however, the phenylhydrazone and thiosemicarbazide were produced, the reaction being $CRR'{:}N{\cdot}NH{\cdot}CS{\cdot}NH_2 + NH_2{\cdot}NHPh = CRR'{:}N{\cdot}NHPh + NH_2{\cdot}NH{\cdot}CS{\cdot}NH_2$. Since acetophenone- and dibenzyl ketone semicarbazones gave excellent yields of δ-anilinosemicarbazones, the thiosemicarbazide residue is evidently more easily replaced than the semicarbazide residue.

EXPERIMENTAL.

Thermal Decomposition of δ-Anilinosemicarbazones.—In the preparation of δ-anilinosemicarbazide hydrochloride already described, it was found more advantageous to hydrolyse the acetophenone derivative (3·3 g.) by boiling under reflux for 20 minutes with 6% hydrochloric acid (75 c.c.) and to remove the acetophenone from the hot liquid by three extractions with carbon tetrachloride. The aqueous solution on cooling deposited the hydrochloride, the remainder of which was obtained by evaporating the filtrate under reduced pressure.

Acetone-δ-anilinosemicarbazone was prepared by mixing acetone with a concentrated aqueous solution of the hydrochloride and gradually adding a slight excess of solid potassium acetate with shaking. After cooling in ice for 5 hours, the product was collected (yield 94%). It crystallises in plates, not needles as formerly described (J., 1924, **125**, 2146). The m. p. varies somewhat with the rate of heating; this preparation had m. p. 170°, which was not depressed on admixture with the specimen previously described (Found: N, 27·1. Calc.: N, 27·2%). *Methyl ethyl ketone δ-anilino-*

semicarbazone (plates from alcohol, m. p. 137°) was prepared in the same way (Found : N, 25·4. $C_{11}H_{16}ON_4$ requires N, 25·4%).

Acetone-δ-anilinosemicarbazone was heated at 180° for 5 hours in a distillation flask with occasional evacuation until distillation ceased. The small quantity of distillate, after hydrolysis with dilute hydrochloric acid, yielded acetone on fractionation; the remainder of the liquid gave with benzaldehyde and potassium acetate a mixture of benzaldehydephenylhydrazone and benzalazine. The semi-resinous product remaining in the reaction flask was extracted with boiling absolute alcohol, which left a residue of 4-aminourazole. The alcoholic extract would not crystallise, but gave the usual diphenylcarbohydrazide colour reactions. Hence the products were acetonephenylhydrazone, dimethylketazine, and 4-aminourazole.

An intimate mixture of diacetonecarbohydrazone and diphenylcarbohydrazide (molecular quantities) was heated under the same conditions as before. The products were again acetonephenylhydrazone, dimethylketazine, and 4-aminourazole.

Pinacolin-δ-anilinosemicarbazone. The thermal decomposition was effected exactly as before. The distillate contained pinacolinphenylhydrazone and pinacolinazine, identified as such by hydrolysis with acid. The residue in the flask contained 4-aminourazole and gave the colour reactions of diphenylcarbohydrazide, which, however, could not be isolated.

Pinacolinazine was prepared by refluxing 11 g. of the ketone with 2·5 g. of hydrazine hydrate in 10 c.c. of absolute alcohol for 2 hours. After evaporation of the solution, the residual oil was dried over potassium carbonate and distilled; it was an almost colourless oil, b. p. 213—216°, 103°/17 mm., smelling somewhat like acetamide, insoluble in water and easily hydrolysed on boiling with acid (yield 77%) (Found : N, 14·3. $C_{12}H_{24}N_2$ requires N, 14·3%).

Benzylidene-δ-anilinosemicarbazone was heated for 1 hour at 230°. Since benzaldehydephenylhydrazone decomposes at about this temperature, the reaction was carried out under reduced pressure in a flask of the Anschütz type, in the collar of which a distillate, which soon solidified, collected. The whole reaction mass was extracted with boiling absolute alcohol; benzaldehydephenylhydrazone passed into solution whilst 4-aminourazole, the only other product, remained undissolved.

Acetone-δ-diphenylaminosemicarbazone. The reaction was carried out as usual: 4 hours' heating at 190—195°. The distillate on hydrolysis with hydrochloric acid gave acetone, diphenylhydrazine hydrochloride, and hydrazine hydrochloride. The dark residue in the flask was extracted with boiling absolute alcohol and then with boiling water; the alcoholic extract on concentration deposited small needles of tetraphenylcarbohydrazide (Acree, *Ber.*, 1903, **36**, 3157) (Found: N, 14·4, 14·3. Calc.: N, 14·2%), and evaporation of the aqueous extract left 4-aminourazole. The products were therefore acetonediphenylhydrazone, dimethylketazine, 4-aminourazole, and tetraphenylcarbohydrazide.

Action of Phenylhydrazine on Thiosemicarbazones.—Molecular quantities of the reactants were heated in toluene solution or suspension at 135°.

Acetonethiosemicarbazone (6½ hours). A little ammonia was evolved, but the only products isolated were thiosemicarbazide, acetonephenylhydrazone, and a little unaltered substance.

Acetophenonethiosemicarbazone (5 hours). This compound dissolved completely and after some time thiosemicarbazide began to separate; some hydrogen sulphide and ammonia were evolved. The substances isolated were thiosemicarbazide, acetophenonephenylhydrazone, and a small quantity of an orange-coloured *substance*, m. p. 171—172°.

Dibenzyl ketone thiosemicarbazone (which crystallises in silvery leaves, m. p. 165—166°, from alcohol or benzene), was obtained by refluxing 2·1 g. of the ketone in 15 c.c. of alcohol with 0·9 g. of thiosemicarbazide in the minimum quantity of hot water for ¾ hour (Found: N, 14·9. $C_{16}H_{17}N_3S$ requires N, 14·8%). The reaction with phenylhydrazine (4 hours) gave thiosemicarbazide, dibenzyl ketone phenylhydrazone, and some unaltered substance only.

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