248. *High-pressure Reactions of Carbon Monoxide. Part III. Reaction with Hydrazine.*

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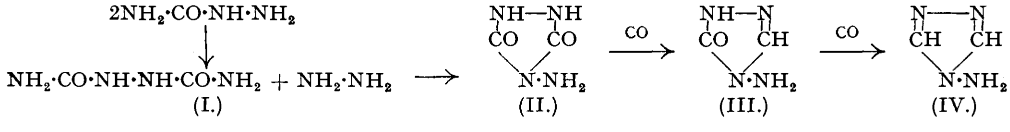
Carbon monoxide reacts with hydrazine under high pressure to give a variety of products depending upon the conditions employed. At 50° and 1000 atm., semicarbazide and ammonia are formed; at 150° and 1000 atm., 4-amino-1 : 2 : 4-triazol-3-one is produced, and at 150° and 3000 atm. the latter is reduced to 4-amino-1 : 2 : 4-triazole.

In the course of a study of the reactions of carbon monoxide under pressure, that with hydrazine has been investigated (Brit. Pat. Applns. 4720/48, 4721/48). At 150° and 1000 atm. 4-amino-1 : 2 : 4-triazol-3-one (III) was formed, and at 150° and 3000 atm. the main product was 4-amino-1 : 2 : 4-triazole (IV); in both cases ammonium carbonate was formed as a by-product. These were evidently the end products of a complex series of reactions, and in the hope of elucidating the course of the reaction by the isolation of intermediate products, carbon monoxide was caused to react with hydrazine under milder conditions. At temperatures of 20—50° and pressures of 500—1000 atm. the sole products were semicarbazide and ammonia, no carbon dioxide being formed: $CO + 2NH_2{\cdot}NH_2 \longrightarrow NH_2{\cdot}CO{\cdot}NH{\cdot}NH_2 + NH_3$. This was a surprising result. By analogy with the reaction of carbon monoxide and ammonia it might have been expected that the first step would be addition of hydrazine to carbon monoxide to give formylhydrazide, which would then react with itself to give cyclic products; the reduction of hydrazine to ammonia and semicarbazide was quite unforeseen.

The course of the subsequent reactions is fairly clear. Curtius and Heidenreich (*Ber.*, 1894, **27**, 57) have shown that semicarbazide on heating loses hydrazine to give hydrazodicarbonamide (I), which reacts with excess of hydrazine to give 4-aminourazole (II) (Thiele and Stange, *Annalen*, 1894, **283**, 41). Evidently this compound is formed in the course of the reaction of carbon monoxide with hydrazine at 150°, and its enol form must then undergo reduction by the carbon monoxide to give first (III) and then (IV).



This was confirmed by the reduction of 4-aminourazole to 4-amino-1 : 2 : 4-triazol-3-one by carbon monoxide at 150° and 1000 atm. and the reduction of the triazolone to 4-amino-1 : 2 : 4-triazole at 150° and 3000 atm. The most remarkable feature of this series of reactions is the ease with which either the triazole or the triazolone can be produced exclusively by altering the reaction pressure. This emphasises the pressure-dependence of carbon monoxide reductions, previously remarked in Part II (preceding paper).

Experimental.

(Micro-analysis by Dr. A. F. Colson. M. p.s are uncorrected.)

Reaction of Carbon Monoxide with Hydrazine.—(*a*) Hydrazine hydrate (80 c.c., 90%) was charged into a stainless-steel high-pressure autoclave of 300-c.c. capacity, fitted with a magnetically operated reciprocating stirrer. Carbon monoxide was compressed in to about 300 atm., the vessel was heated to 50°, and more gas then added until the pressure reached 500 atm.; after 20 hrs.' stirring at 50° the pressure had fallen to 470 atm. The pressure was released and the residual gas was passed through a scrubber containing dilute hydrochloric acid; the scrubbed gas contained no carbon dioxide. Evaporation of the acid washings left a crystalline residue, which was identified as ammonium chloride by analysis, by its insolubility in ethanol, by its lack of reducing properties, and by Nessler's test (Found : Cl, 66·3. Calc. for NH_4Cl : Cl, 66·4%).

The aqueous solution remaining in the vessel was filtered and evaporated under reduced pressure at 80°, and the solid residue was crystallised from alcohol, giving semicarbazide (24 g.), m. p. 96°, undepressed on admixture with an authentic specimen (Found : C, 16·2; H, 6·6; N, 55·9. Calc. for CH_5ON_3 : C, 16·0; H, 6·65; N, 56·0%).

(*b*) Hydrazine hydrate (90 c.c., 90%) was stirred with carbon monoxide at 150° and 900—1000 atm. for 20 hrs. The liquid product contained a suspended solid which was collected and found to be ammonium carbonate (5 g.). The filtrate was evaporated to dryness under reduced pressure, and the residue extracted with alcohol. The extract was concentrated to a syrup which eventually crystallised. Recrystallisation from alcohol gave 4-amino-1 : 2 : 4-triazol-3-one (15 g.), m. p. 179—180° (Found : C, 24·0; H, 3·6; N, 55·9. Calc. for $C_2H_4ON_4$: C, 24·0; H, 4·0; N, 56·0%). Curtius and Heidenreich (*Ber.*, 1894, **27**, 2685) give m. p. 181°. Reaction with benzaldehyde gave 4-benzylideneamino-1 : 2 : 4-triazol-3-one, which crystallised from alcohol in leaflets, m. p. 176—177° (Found : C, 57·3; H, 4·1; N, 29·9. Calc. for $C_9H_8ON_4$: C, 57·45; H, 4·25; N, 29·8%). Stollé (*J. pr. Chem.*, 1907, **75**, 423) gives m. p. 178°.

(*c*) Hydrazine hydrate (90 c.c., 90%) was stirred with carbon monoxide at 150° and 3000 atm. for 24 hrs.; the pressure fell to 2410 atm. The crude reaction product was filtered from ammonium carbonate (8·5 g.) and evaporated to dryness under reduced pressure. The syrupy residue was extracted with boiling ethanol (200 c.c.), and the extract was filtered and again evaporated until, on cooling to 0°, the residue crystallised. The product was recrystallised from alcohol–ether (1 : 1) to give 4-amino-1 : 2 : 4-triazole (20 g.), m. p. 80—82°, identical with an authentic specimen (prepared according to *Org. Synth.*, 1944, **24**, 12). 4-Amino-1 : 2 : 4-triazole hydrochloride crystallised from methanol, m. p. 150° (Found : C, 20·0; H, 4·2; N, 46·5; Cl, 29·5. Calc. for $C_2H_5N_4Cl$: C, 19·9; H, 4·15; N, 46·45; Cl, 29·45%). Curtius, Darapsky, and Müller (*Ber.*, 1907, **40**, 835) give m. p. 150°. Reaction with benzaldehyde gave 4-benzylideneamino-1 : 2 : 4-triazole which, crystallised from alcohol, had m. p. 169—170°, undepressed on admixture with an authentic specimen. Ruhemann and Merriman (*J.*, 1905, **87**, 1774) give m. p. 171°.

Reaction of 4-*Aminourazole with Carbon Monoxide*.—4-Aminourazole (2 g.), dissolved in water (5 c.c.), was stirred with carbon monoxide at 150° and 1000 atm. for 20 hrs.; there was no detectable pressure change, but the residual gas contained carbon dioxide. The contents of the vessel were filtered and evaporated to dryness under reduced pressure. The residue was crystallised from alcohol, giving 4-amino-1 : 2 : 4-triazol-3-one (1·0 g.), m. p. 180°, identical with the compound obtained from hydrazine.

Reaction of 4-*Amino*-1 : 2 : 4-*triazol*-3-*one with Carbon Monoxide*.—4-Amino-1 : 2 : 4-triazol-3-one (10 g.) was stirred with carbon monoxide at 15° and 3000 atm. for 15 hrs.; the residual gas contained carbon dioxide. The product was crystallised from alcohol and ether, giving 4-amino-1 : 2 : 4-triazole (7·5 g.), m. p. 80—82°, identical with the product obtained from hydrazine.

The authors are indebted to Mr. F. Bebbington and Mr. E. Wilson for assistance in carrying out the high-pressure experiments described in this and the two preceding papers.

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[*Received, October* 30*th*, 1948.]