247. *High-pressure Reactions of Carbon Monoxide. Part II. Reducing Action.*

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Many organic compounds are reduced by carbon monoxide under anhydrous conditions at high temperatures and pressures. In absence of catalyst at 150—250° and 3000 atm., nitro-, nitroso-, and azoxy-benzene are reduced to azobenzene, *N*-phenylhydroxylamine to aniline, and *N*-phenylbenzaldoxime to benzylideneaniline. In presence of Raney cobalt, benzyl alcohol, phenylmethylcarbinol, and benzhydrol are reduced to the corresponding hydrocarbons, benzilic acid gives a mixture of benzophenone and diphenylacetic acid, and benzaldehyde gives a mixture of toluene and benzoic acid. Phenols, ethers, esters, amides, ketones, and purely aliphatic alcohols are not reduced by anhydrous carbon monoxide.

In the course of work on the reaction of carbon monoxide with arylamines (Part I, preceding paper) evidence was obtained that diarylcarbinols could be reduced to diarylmethanes by the action of carbon monoxide at high temperatures and pressures. Since carbon monoxide can only remove oxygen and cannot supply hydrogen, it seemed likely that novel effects might be achieved by using it as a reducing agent. The effect of carbon monoxide on a range of organic compounds containing typical reducible groups both in presence and in absence of hydrogenation catalysts was therefore investigated.

Nitrobenzene was reduced to azobenzene in high yield at 250° and 3000 atm. with formation of carbon dioxide. Little reduction occurred at 200° or at pressures below 2500 atm., and nickel and cobalt catalysts had no effect on the reaction. It was not found possible to reduce aliphatic nitro-compounds at temperatures below their decomposition points. Nitrosobenzene and azoxybenzene were reduced to azobenzene, *N*-phenylhydroxylamine to aniline, and *N*-phenylbenzaldoxime to benzylideneaniline at lower temperatures, but even in these cases it was essential to maintain a pressure of at least 2500 atm. Although the main product of the reduction of phenylhydroxylamine was aniline, a small amount of azobenzene was also produced. This presumably arose from condensation of aniline with phenylhydroxylamine to give azoxybenzene which then underwent reduction to azobenzene.

Alcohols showed somewhat different behaviour. Benzyl alcohol and benzhydrol underwent little reduction with carbon monoxide at 250° and 3000 atm., but were largely dehydrated to ethers. However, in presence of Raney cobalt they were reduced to toluene and diphenylmethane, respectively; Raney nickel was somewhat less effective. Phenylmethylcarbinol similarly gave ethylbenzene, and benzilic acid was reduced to diphenylacetic acid accompanied by a considerable quantity of benzophenone. All attempts to reduce purely aliphatic alcohols were unsuccessful, and it was evident that primary aromatic alcohols were reduced much less readily than secondary by carbon monoxide, since benzyl alcohol invariably yielded considerable amounts of dibenzyl ether in addition to toluene, whereas phenylmethylcarbinol gave only the hydrocarbon.

A surprising result was obtained with benzaldehyde. Reaction with carbon monoxide at 250° and 3000 atm. in presence of Raney cobalt gave a mixture of toluene and benzoic acid, and it seems probable that the catalyst induced a Cannizzaro reaction to give benzoic acid and benzyl alcohol, which was then reduced by the carbon monoxide.

Diphenyl ether, dibenzhydryl ether, benzoic acid, ethyl benzoate, acetanilide, benzophenone, benzil, phenol, quinol, β-naphthol, and diacetone alcohol did not react with carbon monoxide in presence or absence of catalysts at 250° and 3000 atm.

EXPERIMENTAL.

(Microanalyses by Dr. A. F. Colson. All m. p.s are uncorrected.)

High-pressure experiments were carried out essentially by the same method and in the same equipment as described in Part I. In no case was there any marked pressure drop during the reaction.

Nitrobenzene. Nitrobenzene (40 g.) was treated with carbon monoxide at 250° and 3000 atm. for 24 hrs. The residual gas contained carbon dioxide. The crude product was distilled with steam; unchanged nitrobenzene (2 g.) distilled over initially, followed by a red solid which was collected, dried, and crystallised from light petroleum (b. p. 100—120°), giving azobenzene (29 g.), m. p. 66—67°, undepressed on admixture with an authentic specimen.

Nitrosobenzene. Nitrosobenzene (10 g.) was treated with carbon monoxide at 150° and 3000 atm. for 18 hrs. The residual gas contained 6·8% of carbon dioxide. The crude tarry product was dissolved in light petroleum (b. p. 100—120°), adsorbed on a column of alumina, and eluted with light petroleum (b. p. 60—80°). Evaporation of the elutriate left azobenzene (7 g.), m. p. 66—67°.

Azoxybenzene. Azoxybenzene (15 g.) was treated with carbon monoxide at 200° and 3000 atm. for 20 hrs. The residual gas contained carbon dioxide. The crude product crystallised from light petroleum (b. p. 100—120°) to give azobenzene (13 g.), m. p. 66—67°.

N-*Phenylhydroxylamine.* *N*-Phenylhydroxylamine (36 g.) was treated with carbon monoxide at 200° and 3000 atm. for 24 hrs. The residual gas contained carbon dioxide. The crude product was distilled with steam, and the distillate was acidified with hydrochloric acid and extracted with ether. The ethereal extract was evaporated, and the residue crystallised from light petroleum, giving azobenzene (1·25 g.), m. p. 66—67°. The acid solution was treated with excess of sodium hydroxide and extracted with ether, and the extract was dried over sodium hydroxide and distilled. This gave aniline (11·3 g.), b. p. 182°. Reaction with acetic anhydride gave the acetyl derivative, m. p. 117—118°, undepressed on admixture with authentic acetanilide.

N-*Phenylbenzaldoxime.* *N*-Phenylbenzaldoxime (21 g.) was treated with carbon monoxide at 150° and 3000 atm. for 20 hrs. The residual gas contained carbon dioxide. The product was distilled under reduced pressure, giving benzaldehyde (5·4 g.), b. p. 56—60°/9 mm. (2 : 4-dinitrophenylhydrazone, m. p. 231—232°, undepressed on admixture with an authentic specimen), and benzylideneaniline (12·3 g.), b. p. 150°/9 mm., m. p. 53—54°, undepressed on admixture with an authentic specimen (Found : C, 86·4; H, 5·9; N, 8·0. Calc. for $C_{13}H_{11}N$: C, 86·2; H, 6·1; N, 7·75%).

Benzyl alcohol. Benzyl alcohol (30 g.) and Raney cobalt (0·5 g.) were treated with carbon monoxide at 200° and 3000 atm. for 21 hrs. The residual gas contained carbon dioxide. The product was distilled with steam, and the distillate extracted with ether. The extract was dried (K_2CO_3) and fractionally distilled, giving toluene (10 g.), b. p. 110—111° (dinitro-derivative, m. p. 69—70°, undepressed on admixture with 2 : 4-dinitrotoluene), and unchanged benzyl alcohol (5 g.), b. p. 205—207°. The steam-distillation residue was extracted with ether, and the extract dried (K_2CO_3) and distilled, giving dibenzyl ether (14 g.), b. p. 168—170°/15 mm. (Found : C, 84·7; H, 7·1; *M*, 196. Calc. for $C_{14}H_{14}O$: C, 84·85; H, 7·05%; *M*, 198).

Phenylmethylcarbinol. The carbinol (40 g.) and Raney cobalt (0·5 g.) were treated with carbon monoxide at 250° and 3000 atm. for 24 hrs. The residual gas contained carbon dioxide. The crude product was filtered from catalyst and distilled, giving ethylbenzene (30·7 g.), b. p. 134—136°, $d_{4^\circ}^{20^\circ}$ 0·8670, $n_D^{20^\circ}$ 1·4980 (Found : C, 90·6; H, 9·3. Calc. for C_8H_{10} : C, 90·55; H, 9·45%).

Benzhydrol. Benzhydrol (50 g.) and Raney cobalt (0·5 g.) were treated with carbon monoxide at 200° and 3000 atm. for 20 hrs. The residual gas contained 9·4% of carbon dioxide. The product was filtered from catalyst and fractionally distilled, giving a small amount of unchanged benzhydrol, together with diphenylmethane (23 g.), b. p. 121—122°/9 mm., m. p. and mixed m. p. 23°. There remained a high-boiling residue which was crystallised from light petroleum (b. p. 60—80°), giving *s*-tetraphenylethane (5 g.), m. p. 209°, undepressed on admixture with an authentic specimen.

Benzilic acid. Benzilic acid (30 g.) and Raney cobalt (0·5 g.) were treated with carbon monoxide at 200° and 3000 atm. for 20 hrs. The product was treated with dilute sodium carbonate solution and extracted with ether. Evaporation of the extract gave benzophenone (8·5 g.) (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 236—237°). The sodium carbonate solution was acidified with dilute hydrochloric acid and the precipitate was collected and crystallised from ethanol, giving diphenylacetic acid (11 g.), m. p. 144—145° (Found : C, 79·5; H, 5·6; equiv., 213. Calc. for $C_{14}H_{12}O_2$: C, 79·25; H, 5·65%; equiv., 212).

Benzaldehyde. Benzaldehyde (40 g.) and Raney cobalt (0·5 g.) were treated with carbon monoxide at 250° and 3000 atm. for 20 hrs. The residual gas contained carbon dioxide. The crude product was washed with an aqueous solution of sodium hydrogen sulphite to remove unchanged aldehyde, and the residual oil was distilled with steam. The distillate contained a colourless oil, which was separated and fractionally distilled to give toluene (9 g.), b. p. 110—112° (2 : 4-dinitro-derivative, m. p. 66°, undepressed on admixture with authentic 2 : 4-dinitrotoluene). The residue from the steam-distillation was extracted with boiling water. On cooling the extract, crystals of benzoic acid (10 g.), m. p. 122°, separated (Found : C, 68·8; H, 4·9; equiv., 124. Calc. for $C_7H_6O_2$: C, 68·5; H, 4·9%; equiv., 122).

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