## 246. *High-pressure Reactions of Carbon Monoxide. Part I. Reaction with Primary Arylamines.*

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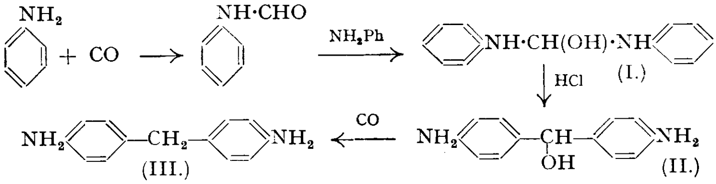
Carbon monoxide reacts with aniline in the presence of a trace of hydrogen chloride at 250° and 2500—3000 atm. to give a polymeric product consisting of aniline residues linked by methylene and/or carbinol groups in the *o*- and *p*-positions. The probable course of this reaction has been determined. The introduction of substituents into the reactive *o*- and *p*-positions of the aniline molecule affects the nature of the products; amines having one such substituent (*e.g.*, *o*-toluidine, *p*-bromoaniline) give products similar to the products from aniline; amines having two such substituents (*e.g.*, the *m*-xylidines) give diformamidodiarylmethanes; 2 : 4 : 6-trisubstituted anilines (*e.g.*, mesidine) are merely converted into their *N*-formyl derivatives. Under similar conditions methylaniline yields *N*-methylformanilide, and dimethylaniline fails to react.

Some 15 years ago it was observed in these laboratories that carbon monoxide reacted with aniline in presence of an acid catalyst at high temperature and pressure to give a basic product of high molecular weight. The observation was not pursued at that time, but we have recently studied the reaction in some detail and determined the nature of the products.

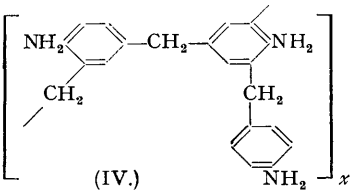
It was found that, when aniline containing a small amount of aniline hydrochloride was heated to 250° with carbon monoxide at 3000 atm. pressure, a reaction took place giving carbon dioxide and a brown amorphous solid, the pressure falling sharply. Little reaction occurred at 200° or at 2000 atm. or in absence of the hydrochloride. The solid product contained varying amounts of oxygen, and the whole of the nitrogen was present in the form of primary amino-groups, which were determined by diazotisation. It was separable into two fractions. The one, soluble in N- but insoluble in 3N-hydrochloric acid, was oxygen-free and had the empirical formula $C_7H_7N$; it therefore seemed probable that it consisted of aniline residues linked by methylene groups, presumably in the *o*- and *p*-positions. The other fraction, soluble in 0·1N- but not in N-hydrochloric acid, appeared to be a substance of similar structure, in which some of the methylene groups were replaced by carbinol; although the whole of the nitrogen was present as primary amino-groups, the material contained oxygen ranging from 4·4 to 14·5% in different samples. Further data on the reaction were obtained by carrying out experiments in which the pressure was maintained at 2700—3000 atm. by the continual introduction of fresh carbon monoxide, and the reaction was stopped and samples withdrawn for examination at regular intervals. After 10 hours the reaction mixture was still liquid and completely soluble in 3N-hydrochloric acid; at this stage it contained 25% of unchanged aniline, and *pp*′-diaminodiphenylmethane was identified among the reaction products. During the next 5 hours it was largely converted into the mixture of acid-soluble polymers described above, and during the following 10 hours this slowly reacted further to form an infusible, insoluble, cross-linked



material having no basic properties. It is considered likely that the initial step in the reaction is the interaction of aniline and carbon monoxide to give formanilide, which, it is postulated, may then react with more aniline to give the unstable intermediate (I) which undergoes rearrangement to *pp'*-diaminodiphenylcarbinol (II) under the influence of the acid catalyst; the carbinol is then reduced by carbon monoxide to *pp'*-diaminodiphenylmethane (III).

Both the diarylmethane and the carbinol contain unsubstituted positions ortho- to the amino-groups, and can therefore react further with more carbon monoxide to give polymeric *products* of types (IV) and (V) and ultimately a completely cross-linked structure.

The behaviour of substituted anilines was consistent with this interpretation. Dimethylaniline failed to react with carbon monoxide under the conditions used for aniline, and methylaniline gave only *N*-methylformanilide. Primary amines having one substituent in the *o*- or *p*-position (*o*-toluidine, *p*-toluidine, *p*-bromoaniline, ethyl anthranilate) gave products closely resembling those obtained from aniline, but no evidence of cross-linking was observed. *vic.*-*m*-Xylidine, having only one reactive position, gave 4 : *4'-diformamido-*3 : 3' : 5 : *5'-tetramethyldiphenylmethane* (VI) as the sole product, and *as*-*m*-xylidine similarly gave 2 : *2'-diformamido-*3 : 3' : 5 : *5'-tetramethyldiphenylmethane* (VII); in the latter case, however, a considerable amount of formo-*as*-*m*-xylidide was also produced, presumably owing to the lower reactivity of the *o*- compared with the *p*-position. Mesidine, having no free *o*- or *p*-positions, gave only formomesidide (VIII).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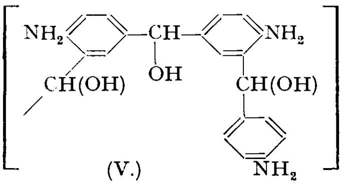
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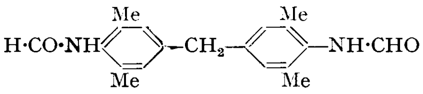
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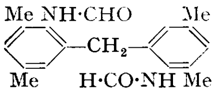
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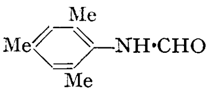
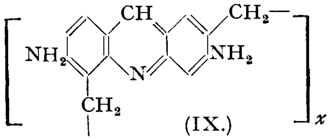

(VIII.)

A curious feature is the isolation of free amines only from aniline and the monosubstituted anilines even when the reaction was stopped at the diaminodiphenylmethane stage, whereas mesidine and the xylidines gave exclusively formamido-compounds. This indicates that the initial formylation step in the reaction cycle is slow and that the two following steps to give the diaminodiarylcarbinol are relatively rapid. The final step in the cycle, reduction of carbinol to methylene, must also be slow since oxygen-containing compounds of high molecular weight were invariably present, sometimes in high proportion, in the products from aniline and monosubstituted anilines.

The reaction has been applied to two diamines, both of which showed somewhat different behaviour. *m*-Phenylenediamine yielded an acid-soluble product very similar in general properties to the products from aniline, but only half of the total nitrogen was present as primary amino-groups; it is possible that the polymer in this case is built up of 2 : 8-diaminoacridine residues linked by methylene groups (IX), since Albert (*J.*, 1941, 121, 484; 1947, 244) has shown that *m*-phenylenediamine reacts with formic acid to give 2 : 8-diaminoacridine.


(IX.)

Benzidine reacted with carbon monoxide at 250° and 3000 atm. to give an infusible, acid-insoluble product which was clearly highly cross-linked, but apparently contained free amino-groups since it absorbed mineral acids from dilute solution and could be acetylated.

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## EXPERIMENTAL.

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

*Reaction of Aniline with Carbon Monoxide.*—(a) *Acid-soluble products.* Aniline (40 g.) and hydrochloric acid (0·2 c.c., 35%) were charged into a stainless-steel, high-pressure autoclave of 80 c.c. capacity, fitted with a magnetically operated reciprocating stirrer. Carbon monoxide was compressed in to a pressure of 1000 atm. and the temperature was raised to 250°. The pressure was then raised to 3000 atm. by introduction of more carbon monoxide, and the mixture was stirred at 250° for 23 hours during which time the pressure slowly fell to 2200 atm. The residual gas contained 12·65% of carbon dioxide. After cooling, and releasing the pressure there remained 50 g. of a pale brown solid, completely soluble in 0·2N-hydrochloric acid (Found : C, 75·6; H, 6·1; N, 11·6%; acetyl value 269 mg. KOH/g.; titration with 0·1N-sodium nitrite gave $NH_2$, 13·35%). In subsequent experiments the products contained less oxygen.

The crude product (130 g.) was stirred with 3N-hydrochloric acid (500 c.c.) at 20° to remove low-molecular-weight bases, and the residue (125 g.) was then extracted four times with cold N-hydrochloric acid (4 × 1 l.). The extracts were made alkaline by addition of dilute sodium hydroxide solution, and the precipitate was collected, washed with water, and dried at 60°, giving a fawn powder (81 g.), m. p. 110—120° [Found: C, 79·9; H, 6·2; N, 13·3 $(C_7H_7N)_n$ (IV) requires C, 80·0; H, 6·65; N, 13·35%]. The residue insoluble in N-hydrochloric acid was extracted four times with cold 0·1N-hydrochloric acid (4 × 1 l.), leaving a dark brown powder (9 g.) insoluble in all concentrations of acid. The base, isolated from the extract as described above, was a fawn powder (35 g.), m. p. 160—170° (Found : C, 78·0; H, 5·6; N, 12·0%). A fraction similarly obtained from a product of higher initial oxygen content had C, 68·9; H, 5·9; N, 11·6%. Both the acid-soluble fractions were diazotised on treatment with nitrous acid, and the diazonium salts gave red lakes with alkaline β-naphthol.

(b) *Acid-insoluble products.* Aniline (40 g.) and hydrochloric acid (0·2 c.c., 35%) were caused to react with carbon monoxide at 250° as described above, but the pressure was held at 2700—3000 atm. by continual addition of fresh carbon monoxide, and at 5-hourly intervals the vessel was cooled and the pressure released and samples were removed for examination, with the following results :

| Time, hrs. | Appearance. | % Soluble in 3N-HCl. | % Insoluble in 3N-HCl, soluble in N-HCl. | % Insoluble in N-HCl, soluble in 0·1N-HCl. | % Acid-insoluble. |
|---|---|---|---|---|---|
| 5 | Mobile liquid | 100 | | | |
| 10 | Viscous liquid | 100 | | | |
| 15 | Solid | 6·8 | 67·5 | 6·0 | 20 |
| 20 | Solid | 0 | 3·3 | 6·6 | 86·5 |
| 25 | Solid | 0 | 0 | 0 | 100 |

The acid-insoluble product was a dark brown powder insoluble in organic solvents. It was unattacked by boiling concentrated hydrochloric acid or alcoholic potassium hydroxide, had no detectable basic properties, and on heating decomposed without melting (Found: C, 73·4; H, 6·5; N, 10·3. $C_{17}H_{14}O_2N_2$ requires C, 73·4; H, 5·05; N, 10·1%).

(c) 4 : 4′-*Diaminodiphenylmethane.* Aniline (40 g.) and hydrochloric acid (0·2 c.c., 35%) were treated with carbon monoxide at 250° and 3000 atm. pressure for 10 hours, during which the pressure fell to 2410 atm. The product, a viscous liquid, was distilled under reduced pressure, giving unchanged aniline (10 g.) and a fraction (5 g.), b. p. 160—200°/6 mm., which crystallised. Recrystallisation from aqueous methanol gave colourless crystals of 4 : 4′-diaminodiphenylmethane, m. p. 94° (Found : C, 78·5; H, 6·9; N, 13·9. Calc. for $C_{13}H_{14}N_2$ : C, 78·8; H, 7·05; N, 14·15%). Reaction with acetic anhydride gave the diacetyl derivative, m. p. 219° (Found : C, 72·5; H, 6·7; N, 9·4. Calc. for $C_{17}H_{18}O_2N_2$ : C, 72·35; H, 6·4; N, 9·9%).

*Reaction of Substituted Anilines with Carbon Monoxide.*—In all experiments the amine (40 g.) and hydrochloric acid (0·2 c.c., 35%) were heated to 250° in an 80-c.c. vessel, and carbon monoxide was compressed in to 3000 atm. The reaction was continued with stirring for 23 hours without further addition of carbon monoxide.

*Methylaniline.* The pressure fell to 2700 atm. The product, a dark liquid, was distilled under reduced pressure, giving *N*-methylformanilide (20 g.), b. p. 95°/4 mm., m. p. 10°, mixed m. p. with authentic specimen 10° (Found : C, 71·2; H, 6·7; N, 9·7. Calc. for $C_8H_9ON$ : C, 71·1; H, 6·7; N, 9·7%).

*Mesidine.* The pressure fell to 2620 atm., but the residual gas contained no carbon dioxide. The product, a crystalline solid, was recrystallised from aqueous methanol to give formomesidide (37 g.), m. p. 179°, undepressed on admixture with an authentic specimen (Found : C, 73·5; H, 7·7; N, 8·6. Calc. for $C_{10}H_{13}ON$ : C, 73·6; H, 8·0; N, 8·6%).

vic-m-*Xylidine.* The pressure fell to 2600 atm. and the residual gas contained carbon dioxide. The product, a crystalline solid, recrystallised from 90% formic acid to give colourless crystals of 4 : 4′-*diformamido*-3 : 3′ : 5 : 5′-*tetramethyldiphenylmethane* (37 g.), m. p. 335—337° (Found : N, 9·0. $C_{19}H_{22}O_2N_2$ requires N, 9·0%). Distillation with soda-lime gave 4 : 4′-diamino-3 : 3′ : 5 : 5′-tetramethyldiphenylmethane, which after crystallisation from methanol had m. p. 124° (Found : C, 80·55; H, 8·6; N, 11·4. Calc. for $C_{17}H_{22}N_2$ : C, 80·3; H, 8·65; N, 11·0%). On boiling with 90% formic acid a diformyl derivative identical with that described above was formed. Reaction of the base with acetic anhydride gave the diacetyl derivative, m. p. 305° (Found : C, 74·2; H, 7·7; N, 8·5. Calc. for $C_{21}H_{26}O_2N_2$ : C, 74·55; H, 7·7; N, 8·3%). Friedländer and Brand (*Monatsh.*, 1898, **19**, 640) give m. p. 126° for the diamine and m. p. above 280° for the diacetyl derivative.

as-m-*Xylidine.* The pressure fell to 1800 atm. and the residual gas contained 12% of carbon dioxide. Unchanged xylidine was removed by steam-distillation, and the residue which was insoluble in N-hydrochloric acid was dissolved in ether. After standing for some days, the crystals which separated were collected and recrystallised from light petroleum (b. p. 100—120°). This gave formo-*as*-*m*-xylidide (18 g.), m. p. 114°, undepressed on admixture with an authentic specimen. The mother-liquors were evaporated, and the dark residue was heated in a sealed tube with concentrated hydrochloric acid (20 c.c.) for 12 hours. The reaction product was cooled, diluted with water, made strongly alkaline with sodium hydroxide, and extracted with ether. The extract was dried (NaOH), the ether removed by distillation, and the residue distilled under reduced pressure. This gave a solid, b. p. 170—200°/1·5 mm., which was crystallised from ethanol to give colourless crystals of 6 : 6′-*diamino*-2 : 2′ : 4 : 4′-*tetramethyldiphenylmethane*, m. p. 122—123° (Found: C, 80·2; H, 8·6; N, 10·9. $C_{17}H_{22}N_2$ requires C, 80·3; H, 8·65; N, 11·0%). Reaction with acetic anhydride gave the *diacetyl* derivative, m. p. 252—253° (Found: C, 74·5; H, 7·6; N, 8·4. $C_{21}H_{26}O_2N_2$ requires C, 74·55; H, 7·7; N, 8·3%).

o-*Toluidine*. The pressure fell to 2500 atm. and the residual gas contained carbon dioxide. The product was steam-distilled to remove traces of unchanged toluidine. The non-volatile residue was a pitch-like solid, completely soluble in 0·1N- but largely insoluble in 3N-hydrochloric acid (Found: C, 80·0; H, 7·8; N, 12·2; $NH_2$, 13·8%).

p-*Toluidine*. The pressure fell to 2230 atm. and the residual gas contained carbon dioxide. The product, a brown powder, was completely soluble in 0·1N- but largely insoluble in 3N-hydrochloric acid.

*Ethyl anthranilate*. The residual gas contained carbon dioxide. The product, a dark brown solid, was completely soluble in 0·1N- but largely insoluble in 3N-hydrochloric acid.

p-*Bromoaniline*. The residual gas contained carbon dioxide. The product was a dark solid, undistillable and completely soluble in 0·1N-hydrochloric acid (Found: C, 51·5; H, 3·9; N, 8·6; Br, 31·2%).

m-*Phenylenediamine*. The pressure fell to 2300 atm. and the residual gas contained carbon dioxide. The product, a dark brown powder, was completely soluble in 0·1N- but largely insoluble in 3N-hydrochloric acid (Found: N, 20·4; $NH_2$, 12·4%).

*Benzidine*. The product (65 g.) was a purple-black solid, infusible and insoluble in organic solvents but swollen in benzene. It was insoluble in all concentrations of hydrochloric acid, but it absorbed sulphuric and hydrochloric acids from 0·01N-solutions (Found: C, 76·2; H, 6·25; N, 13·95%; acetyl value 350 mg. KOH/g.).

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