CLXXVIII.—*Action of Cuprous Hydride on Diazonium Salts. A Combined Sandmeyer–Gattermann Reaction.*

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The action of moist cuprous hydride (CuH) at 0° upon diazonium salts, in the presence of halogen acid and under other conditions, has been investigated. The greater part of the cuprous hydride apparently is decomposed, giving copper and cuprous halide in the reactions involving halogen acid, so that a Sandmeyer–Gattermann reaction occurs. The main organic product is the aryl halide, or a phenol from a diazonium sulphate in sulphuric acid, and diphenyl on addition of alcohol to the sulphuric acid solution. A small quantity of the diazonium salt is, however, reduced, the corresponding hydrocarbon being formed.

Cuprous hydride, prepared by the action of an excess of hypophosphorous acid, or of sodium hypophosphite and sulphuric acid, upon a solution of copper sulphate (50—75 g.), was gradually added to the ice-cold diazo-solution. On vigorous shaking, a brisk effervescence occurred and the colour of the cuprous hydride changed slowly to an orange or reddish tint (scarlet in the case of *o*-toluidine). These colours, which were probably due to the formation of double compounds, were destroyed by washing with alcohol, ether, or acetone.

After the reaction had proceeded in the cold for 2 hours, the product was steam-distilled, washed with sodium hydroxide solution to remove phenol, dried, and fractionally distilled, or, if solid, recrystallised.

Base diazotised (g.).	Acid used.	Main product (g.).	By-product (g.).
Aniline (22)	HCl	PhCl (8·8)	PhH (1·6)
,, (15)	HBr	PhBr (9·8)	,, (1·5)
o-Toluidine (10)	HCl	*o*-C_7H_7Cl (4·5)	C_7H_8 (1·5)
o- ,, (20)	HBr	*o*-C_7H_7Br (10·6)	,, (1·8)
m- ,, (10)	HCl	*m*-C_7H_7Cl (4·2)	,, (1·3)
p- ,, (15)	HCl	*p*-C_7H_7Cl (11·3)	,, (2·1)
p- ,, (20)	HBr	*p*-C_7H_7Br (11·6)	,, (2·2)
p- ,, (15)	$\begin{cases} H_2SO_4 \\ + KI \end{cases}$	*p*-C_7H_7I (13·5)	,, (1·6)
Anthranilic acid (11)	HCl	*o*-$C_6H_4Cl{\cdot}CO_2H$ (7·5)	None
p-Nitroaniline (10)	HCl	*p*-$C_6H_4Cl{\cdot}NO_2$ (7·6)	,,
p-Toluidine (15)	HCl *	*p*-C_7H_7Cl (2·5)	C_7H_8 (1·7)
p- ,, (20)	HCl †	*p*-C_7H_7Cl (8·5)	None
o- ,, (15)	H_2SO_4	—	C_7H_8 (1·2)
p- ,, (15)	H_2SO_4	—	,, (2·4)
Aniline (20)	H_2SO_4 ‡	Ph·Ph (2·4)	—

* Made faintly ammoniacal; † made neutral with NaOH; ‡ alcohol added before addition of CuH.

Crystalline cuprous chloride (Found: Cu, 63·6; Cl, 35·45%) and crystalline cuprous bromide (Found: Cu, 44·1%) were obtained in the reactions between cuprous hydride and diazonium chlorides and diazonium bromides, respectively, in presence of the corresponding halogen acid. They separated after filtration of the hot solutions left in the distilling flasks, and were purified from organic substances by repeated digestion with alcohol and ether.

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