118. *The Decomposition of Zinc Chloride Double Salts of Diazonium Compounds by Alcohols and Phenol.*

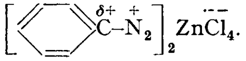
By Herbert H. Hodgson and Clifford K. Foster.

Methyl and ethyl alcohols decompose the zinc chloride double salts of diazonium compounds normally, hydrogen or an alkoxy-group replacing the diazo-group according to the nature of the substituents in the aromatic nucleus. Phenol, however, gives rise to three simultaneous reactions whereby (*a*) chloro-compounds, (*b*) hydroxydiphenyls, and (*c*) diphenyl ethers are produced; reaction (*a*) predominates throughout and its mechanism appears analogous to that given by Hodgson, Birtwell, and Walker, (J., **1941**, 770) for the Sandmeyer reaction.

THE decomposition of the zinc chloride double salts of diazonium compounds by methyl and ethyl alcohols proceeds normally, replacement of the diazo-group by hydrogen or alkoxyl depending on the nature of the substituents in the aromatic nucleus; electrophilic (kationoid) substituents favour hydrogen replacement and nucleophilic (anionoid) groups favour alkoxyl replacement (cf. Saunders, "The Aromatic Diazo-Compounds," 1936, p. 144 et seq.). In the presence of zinc dust the influence of the substituents is overcome, and only the hydrogen reaction occurs. Hodgson and Marsden (J., 1940, 207), decomposing the stable compounds of diazonium salts and naphthalene-2 : 5-disulphonic acid by zinc dust, found that the hydrogen reaction proceeded in solvents which contain no hydrogen. Hence the hydrogen must have come from the sulphonic acid group. In the present case the hydrogen can only come from the alcohol, and the zinc appears to activate the alcohol in some way, thereby making the reaction violent in certain cases.

By the decomposition of diazonium salts by phenol Hirsch (*Ber.*, 1890, **23**, 3075) and Norris, Macintire, and Corse (*Amer. Chem. J.*, 1903, **29**, 120) obtained hydroxydiphenyl derivatives, and Hofmeister (*Annalen*, 1871, **159**, 191) observed the formation of diphenyl ether from benzenediazonium sulphate and dry phenol.

Zinc chloride double salts of diazonium chlorides have now been decomposed by molten phenol and in the cases where a nitro-group is not present in the aromatic nucleus of the diazonium chloride, three simultaneous reactions occur : (*a*) chiefly replacement of the diazo-group by chlorine, (*b*) formation of a hydroxydiphenyl, (*c*) formation of a diphenyl ether (Table II).

The three different mechanisms involved may be illustrated from the complex involving benzenediazonium chloride,  The kationoid carbon δ+ to which the diazo-group is attached reacts (*a*) with anionoid chlorine in the complex, whereby electron release to the carbon occurs with separation of neutral chlorine, evolution of nitrogen, and subsequent linkage of the aryl radical with neutral chlorine to form chlorobenzene, a mechanism analogous to that of the Sandmeyer reaction (Hodgson, Birtwell, and Walker, J., 1940, 770); (*b*) with the anionoid *p*-carbon atom of the phenol to form, by similar release of electron, etc., the 4-hydroxydiphenyl; (*c*) with the anionoid oxygen of the hydroxyl group of the phenol, whereby the diphenyl ether is produced.

The zinc chloride double salts of *o*-, *m*-, and *p*-nitrobenzenediazonium chlorides all coupled with the phenol to form *o*-, *m*-, and *p*-nitrobenzeneazophenol. This enhanced coupling power is due to the well-known stabilising effect of the nitro- on the diazo-group.

EXPERIMENTAL.

The double compounds of diazonium chlorides and zinc chloride were prepared by adding solid zinc chloride (20% excess of the theoretical amount) to the well-cooled solution of the diazonium chloride and washing the precipitate with a little ether before drying it in a desiccator. The best results were obtained when the volume of solution was kept to a minimum during diazotisation.

Decomposition of the Double Salts.—(a) *By methyl or ethyl alcohol.* The double compound (in amount equivalent to 15 g. of the diazonium chloride) was refluxed with alcohol (100 c.c.) until decomposition was complete as indicated by the absence of colour in a spot test with alkaline β-naphthol; *ca.* 75% of the alcohol was then distilled through a fractionating column, the residue steam-distilled, and the distillate extracted with ether or chloroform. The products from α- and β-naphthalenediazonium chlorides were twice fractionally distilled in steam, a good separation being effected.

(b) *By methyl or ethyl alcohol in presence of zinc dust.* The course of the reaction depended on the method of mixing the reactants; *e.g.*, when a mixture of the zinc chloride double compound of *o*-nitrobenzenediazonium chloride and zinc dust was treated with alcohol, a reaction of explosive violence occurred, fumes having the odour of nitrobenzene being evolved and a considerable amount of carbonaceous matter produced. When, however, the zinc dust was stirred or shaken with the alcohol (50 c.c.) and the double compound (equivalent to 10 g. of diazonium chloride) added slowly, rapid but not violent decomposition ensued, with evolution of much heat. Subsequent operations were carried out as in (a). The results of (a) and (b) for ten decompositions are Table I.

TABLE I.

Products of Decomposition of Zinc Chloride Double Salts of Diazonium Chlorides by Methyl or Ethyl Alcohol.

Diazotised amine in the double salt.	Product.	% (MeOH).	% (EtOH).	% (Zn dust and MeOH.	EtOH).
α-Naphthylamine	Naphthalene	43	45	66	68
	α-Naphthyl alkyl ether	36	34	None	
β-Naphthylamine	Naphthalene	41·5	49	63	61
	β-Naphthyl alkyl ether	35	31	None	
p-Toluidine	Toluene	Trace	Trace	59	65
	Tolyl alkyl ether	77	75	None	
o-Toluidine	Toluene	Trace	Trace	70	68
	o-Tolyl alkyl ether	70	73	None	
p-Chloroaniline	Chlorobenzene	Trace	67	64	60
	p-Chlorophenyl alkyl ether	65	Trace	None	
o-Chloroaniline	Chlorobenzene	71	69	67	66
o-Nitroaniline	Nitrobenzene	72	67	63	65
m-Nitroaniline	Nitrobenzene	64	65	60	63
p-Nitroaniline	Nitrobenzene	61	66	68	63
p-Anisidine	Anisole	No decomposition		70	67

(c) *By molten phenol.* The double salt (equivalent to 20 g. of diazonium chloride) was slowly added to molten phenol (40 g.) at 60°, the mixture being gradually heated after each addition until the evolution of gas ceased. Nitrogen and hydrogen chloride were evolved and the temperature was so regulated as to keep the reaction under control. In some cases, *e.g.*, β-naphthalenediazonium chloride, reaction occurred rapidly at 60°, in others only at *ca.* 130°. The mixture was then cooled to 60°, poured into an equal volume of water, and fractionally steam-distilled until all the phenol had been removed. Any solid fractions were washed with water to remove phenol; any liquid matter was extracted with a suitable solvent, and the extract shaken with aqueous sodium hydroxide and washed with water prior to removal of solvent. The non-volatile products usually included a substituted 4-hydroxydiphenyl and sometimes a diphenyl ether. The hydroxy-compound was isolated by either hot water or aqueous sodium hydroxide, followed by acidification at 0°, and converted into its acetyl derivative, which was hydrolysed with caustic soda solution. The filtrate was acidified, and the product crystallised from dilute alcohol and identified. The results for six decompositions are in Table II.

TABLE II.

Products of Decomposition by Molten Phenol of Zinc Chloride Double Salts of Diazonium Chlorides.

Diazotised amine in the double salt.	% Chloro-compound.	% Hydroxydiphenyl.	% Diphenyl ether.
p-Aminophenol	*ca.* 40	*ca.* 41	*ca.* 11
p-Anisidine	48	36	13
p-Chloroaniline	41	31	15
Aniline	40	26	20
α-Naphthylamine	46	29	20
β-Naphthylamine	44	35	18

When the zinc chloride double salts of *o*-, *m*-, and *p*-nitrobenzenediazonium chlorides were treated with phenol as above below 90°, there was no evolution of gas and only traces of steam-volatile matter were obtained. The residue, usually a mixture of tar and crystals, was first crystallised from alcohol and then from toluene, *o*-, *m*- and *p*-nitrobenzeneazophenols being obtained in almost quantitative yield.

In the reaction between phenol and the double salt of *p*-nitrobenzenediazonium chloride at 130—140°, nitrogen was evolved and the main product was a non-steam-volatile tar.

4-*Chloro*-4′-*acetoxydiphenyl* crystallised from aqueous alcohol in colourless plates, m. p. 72° (Found : Cl, 14·0. $C_{14}H_{11}O_2Cl$ requires Cl, 14·2%).

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TECHNICAL COLLEGE, HUDDERSFIELD. [*Received, May 22nd* 1942.]