163. *The Influence of* p-*Substituents on the Decomposition of Zinc Chloride Double Salts of Diazonium Chlorides by Acetic Anhydride.*

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Five double salts of *p*-substituted diazonium chlorides and zinc chloride were decomposed by acetic anhydride with simultaneous replacement of the diazo-group mainly by acetoxyl or chlorine, the former predominating. The comparative influence of the *p*-substituents towards acetoxyl replacement is in the decreasing order of the negative (−*I*) effects, *viz.*, Cl>OMe>Me. The special case of the hydroxyl group is discussed.

Five typical double salts of diazonium chlorides and zinc chloride have been decomposed by acetic anhydride, which gives rise mainly to two simultaneous reactions : (1) External replacement of the diazo-group by the acetoxy-group, due to nucleophilic attack by the pronounced anionoid acetic anhydride-oxygen at the kationoid carbon atom to which the diazo-group is attached (cf. also Hodgson and Foster, this vol., p. 30). (2) Replacement of the diazo-group by attack of the less anionoid chlorine of the zinc chloride complex under the anhydrous conditions of the reaction medium at the same carbon atom (cf. Hodgson, Birtwell, and Walker, J., 1941, 770).

In the cases of the double salts with diazotised β-naphthylamine and *p*-aminophenol, β-naphthyl acetate and *p*-diacetylquinol were readily isolated in yields of 48% and 70% respectively; but for purposes of quantitative comparison the corresponding acetoxy-compounds afforded by *p*-toluidine, *p*-chloroaniline, and *p*-anisidine were first subjected to alkaline hydrolysis, after which the *p*-cresol, *p*-chlorophenol, and *p*-hydroxyanisole respectively formed were readily isolated and estimated. In all five cases reaction (1) was appreciably greater than (2), and the combined yields of acetoxy- and chloro-products were of the order of 80%. When the yields of phenols above are calculated as amounts of acetoxy-compound formed per g.-mol. of zinc chloride double salt taken, the decreasing order is : *p*-hydroxy (21·3) > *p*-chloro (16·3) > *p*-methoxy (13·0) > *p*-methyl (11·6), and except for the first member this sequence is the order of the decreasing negative (−*I*) inductive effects of the *p*-substituents, *i.e.*, in the order of decreasing positivity of the carbon atom to which the diazo-group is attached, as would be expected. Since the product isolated from the reaction between the zinc chloride double salt of *p*-hydroxybenzenediazonium chloride and acetic anhydride is diacetylquinol, it is a reasonable assumption that, under the favourable conditions present for acetylation, the double salt becomes acetylated prior to decomposition at 110°, and that it is the acetoxy-group which is exerting the observed powerful (−*I*) inductive effect on the carbon atom. Alternatively, the phenolic group, if not acetylated, has nevertheless exercised such an electron-attracting effect that the oxygen must be in a partial oxonium (positive) condition due to two-point attack of the polarised acetic anhydride on the polarised phenolic group (cf. the analogous decomposition of *p*-hydroxybenzenediazonium salts by alcohols; Hodgson and Foster, J., 1940, 1150). In the case of the double salt decompositions by phenol (Hodgson and Foster, this vol., p. 581), where chlorine substitution is the predominant reaction, the special effect of the phenolic group found above is absent.

Experimental.

The various double salts decomposed, $(ArN_2)_2ZnCl_4$, are referred to below by the initial amine employed.

β-Naphthylamine.—The double compound (13·6 g.) (equivalent to 10 g. of naphthalene-*β*-diazonium chloride) was added portionwise to acetic anhydride (50 c.c.) at 60°; the heat of reaction raised the temperature to 90°, nitrogen was evolved briskly, and the temperature was maintained at 90—95° by the rate of addition. When reaction was completed, the mixture was diluted with glacial acetic acid (50 c.c.), poured into water, and fractionally steam-distilled; 2-chloronaphthalene [2·0 g. (23·5% yield), m. p. 56°] passed over first, and was followed much more slowly by 2-naphthyl acetate [3·4 g. (35% yield), m. p. after recrystallisation from aqueous ethyl alcohol, 70°]; *β*-naphthol (1 g., 13·3% yield) was also collected and was doubtless formed by hydrolysis of the acetate during the prolonged steam-distillation; 0·7 g. of non-volatile tar remained in the steam flask.

p-*Toluidine.*—The double compound (14·4 g.) was added gradually to acetic anhydride (50 c.c.) at 90°, at which temperature reaction occurred, and after its completion, the mixture was diluted with glacial acetic acid (50 c.c.), stirred into cold aqueous sodium hydroxide until alkaline, boiled for 20 minutes, and steam-distilled; *p*-chlorotoluene then passed over (2·7 g., 33·4% yield). When the flask liquor was just acidified with sulphuric acid and steam-distilled, *p*-cresol (2·7 g., 38·6% yield), formed by the above hydrolysis of the initially formed *p*-tolyl acetate, passed over.

p-*Chloroaniline.*—The double compound (14·0 g.) was brought into reaction as above. On steam distillation of the alkaline hydrolysis mixture, *p*-dichlorobenzene (2·6 g., 31% yield) first passed over, and then much more slowly, traces of an unidentified, pale yellow substance which was not *pp*′-dichlorodiphenyl. On steam-distillation of the acidified flask liquor and treatment of the distillate with bromine water, 4-chloro-2 : 6-dibromophenol (8 g., corresponding to a 49% yield of *p*-chlorophenol in the original reaction) was obtained.

p-*Anisidine.*—With decomposition details as for *p*-toluidine, 14 g. of the double salt being used, evolution of nitrogen did not occur until a temperature of 125—130° was attained. On steam-distillation of the alkaline hydrolysis liquor, *p*-chloroanisole (2·4 g., 29% yield) passed over. The flask liquor was then treated with excess of methyl sulphate, quinol dimethyl ether being obtained (3·2 g., corresponding to a 39% yield of *p*-hydroxyanisole).

p-*Aminophenol.*—With 14·4 g. of double salt and decomposition as above by acetic anhydride (75 c.c.), a temperature of *ca.* 110° was required before evolution of nitrogen commenced. At the end of the reaction, glacial acetic acid (75 c.c.) was added, and the cooled solution poured into ice-water (500 c.c.); diacetylquinol was obtained (8·7 g., 70% yield), m. p. after recrystallisation from aqueous ethyl alcohol and mixed m. p. with an authentic specimen, 123°. The filtrate was made alkaline with sodium hydroxide, and the mixture refluxed for 20 minutes, made acid, and steam-distilled; *p*-chlorophenol passed over and was estimated as 4-chloro-2 : 6-dibromophenol (3·8 g., corresponding to a yield of 18·8% of *p*-chlorophenol).

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