212. *The Decomposition of* p-*Hydroxybenzenediazonium Salts by Alcohols.*

By Herbert H. Hodgson and Clifford K. Foster.

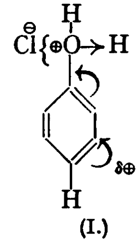
Cameron's observation (*Amer. Chem. J.*, 1898, **20**, 229) that *p*-hydroxybenzenediazonium chloride gives phenol when decomposed with methyl or ethyl alcohol has been confirmed. It has been shown, however, that *pp*′-azophenol also is formed, in greater amount than phenol in this reaction but in smaller amount when zinc oxide is present. Sodium methoxide produces a similar decomposition. The stable double compound of zinc chloride and *p*-hydroxybenzenediazonium chloride gives almost identical results. The corresponding compound of *p*-methoxybenzenediazonium chloride resists decomposition in the same circumstances. When bromine is present during the first-named decomposition, 2 : 4 : 6-tribromophenol and bromoanil are the only products isolable.

During a study of the influence of substituent groups on the decomposition of diazonium salts by methyl and ethyl alcohols, Cameron (*Amer. Chem. J.*, 1898, **20**, 229) found that *o*- and *p*-hydroxybenzenediazonium chlorides both gave phenol as the main product, *i.e.*, the diazo-group was replaced by hydrogen. This anomalous effect of phenolic hydroxyl, particularly with respect to methyl alcohol, is contrary to all other experience of its reactivity, since it here promotes the formation of the same product as would a nitro-group, and no longer behaves like other *op*-directing groups, which favour replacement of the diazo- by the alkoxy-group.

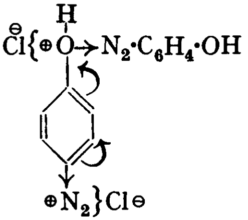
Cameron's results, so far as they went, have been confirmed. The amount of phenol obtained from *p*-hydroxybenzenediazonium chloride is, however, less than 40%, and the considerable amount of tar remaining after removal of the phenol by stream-distillation is mainly *pp*′-azophenol. This tar, after treatment with excess of alkali and methyl sulphate, gives a trace of *p*-dimethoxybenzene on steam-distillation.

It appears, therefore, that the primary decomposition product of *p*-hydroxybenzenediazonium salts by alcohols is phenol, and that the formation of *pp*′-azophenol is due to its coupling with undecomposed diazonium salt. The velocity of coupling must be much slower than the rate of formation of phenol, since *ca.* 40% of phenol remains after decomposition is complete. To test this conclusion, the decomposition was carried out in presence of bromine: the sole products isolated were 2 : 4 : 6-tribromophenol (87·3%) and bromoanil (6·3%), it thereby being shown that the rapid bromination of phenol had prevented coupling. The bromoanil was doubtless formed by further bromination and oxidation of the tribromophenol.

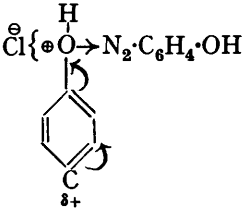
When the hydrochloric acid formed during the reaction is destroyed by the addition of zinc oxide, the yield of phenol is raised to 60%, which is in accord with previous experience (cf. Saunders, " The Aromatic Diazocompounds and their Technical Applications," 1936, p. 153). A probable explanation is that the removal of the hydrochloric acid accelerates the decomposition of the diazonium salt and phenol is produced much more rapidly than before, whereas its rate of coupling with unchanged diazonium salt is probably unaltered. Paradoxically, a similar result is obtained when excess of hydrogen chloride is introduced into the system: this is obviously due to inhibition of coupling either by repression of ionisation of the phenolic hydroxyl or more probably by partial oxonium salt formation at this group, whereby the oxygen acquires a positive charge and coupling is prevented (I).



(I.)



(II.)



(III.)

Oxonium salt formation at the phenolic hydroxyl is probably the reason why this group behaves like a nitro-group in the decomposition now discussed. Since phenol is formed in the decomposition whether the alcoholic medium is acid, neutral, or alkaline, and whatever be the nature of the alcohol, there must be a cause for its formation independent of these reagents. Further, for replacement of the diazo-group by hydrogen to occur, the attached aromatic carbon atom must have an electrically positive bias (δ+) similar to that given by the nitro-group when a nitro-diazonium salt is decomposed by alcohol. Since the free phenolic hydroxyl would give an electrically negative bias (δ—), it cannot be free but must be part of an oxonium salt, and the electrons of the *o*- and *p*-carbons atoms in the attached nucleus are attracted towards it, leaving the carbon atom with an incipient positive charge. Such a possibility of oxonium salt formation is envisaged in Karrer's theory of coupling (*Ber.*, 1915, **48**, 1938), and in the case now considered the salt formation may be depicted as in (II). Evolution of nitrogen from the free diazonium group of this complex would transiently leave the attached carbon with a positive bias (δ+) (III), which apparently has to be sufficient in intensity to cause oxidation of the alcohol, the carbon atom acquiring hydrogen therefrom.

As it was found much more convenient to work with the stable double compound of zinc chloride and *p*-hydroxybenzenediazonium chloride than with the unstable chloride, decompositions were carried out with this double compound and alcohols (methyl, ethyl, and *tert.*-butyl). The results were practically identical with those given by Cameron's procedure.

The intensity of the above positive bias is apparently considerably decreased in the case of the stable double compound of zinc chloride and *p*-methoxybenzenediazonium chloride, since this fails to react with methyl alcohol alone, although, when zinc dust is added, anisole is formed.

EXPERIMENTAL.

The Double Compound of p-*Hydroxybenzenediazonium Chloride and Zinc Chloride.*—A paste of *p*-aminophenol hydrochloride (29·1 g.; 0·2 g.-mol.), hydrochloric acid (30 c.c., *d* 1·16), and water (15 c.c.) was stirred and treated dropwise below 5° with sodium nitrite (14 g.; 0·2 g.-mol.) in the minimum quantity of water until diazotisation had taken place. The dark violet solution was filtered and treated at 0° with zinc chloride (15 g.; 0·2 g.-mol. + 10% excess), and the mixture kept for 45 minutes with occasional stirring. The greyish crystals of the double compound were filtered off, washed with alcohol–ether (1 : 1) and with ether, and dried at 50°. A further crop obtained by salting-out the filtrate was contaminated with *ca.* 5% of sodium chloride. The double salt was stable when dry (Found : Cl, 31·8. Calc. for $2OH{\cdot}C_6H_4{\cdot}N_2Cl,ZnCl_2$: Cl, 31·6%).

Decomposition of the Double Compound with Methyl and Ethyl Alcohols.—The double compound (14·4 g., equivalent to 10·0 g. of *p*-hydroxybenzenediazonium chloride) was refluxed for 12 hours with methyl alcohol (80 c.c.); the deep red solution was then diluted with an equal volume of water and steam-distilled until a test portion of the distillate gave no precipitate with bromine water. The steam-distillate was made up to a known volume with water, and the phenol therein estimated both volumetrically by the bromide–bromate method and gravimetrically by precipitation as tribromophenol. The tar which separated in the steam-flask on cooling was filtered off, and a further crop obtained by evaporation of the filtrate to small bulk. The experiment was repeated with ethyl in place of methyl alcohol.

Decomposition of the Double Compound with Methyl Alcohol in Presence of Zinc Oxide.—Hydrochloric acid was produced during the above decomposition. In another experiment, its effect on the reaction was nullified by mixing zinc oxide (3 g.) with the double compound. When the products of decomposition were poured into water, a brown precipitate was obtained. The filtrate from this was distilled in steam : no tar remained in the steam-flask, but on evaporation of the orange liquid to small bulk some tar was produced. The experiment was repeated with ethyl alcohol, and similar results obtained.

Conversion of the Tar and the Brown Solid into pp'-*Azophenol Diacetate.*—A solution of the tar (1 g.) in 20% aqueous sodium hydroxide (30 c.c.) was diluted with water to 250 c.c. and neutralised at 0° (ice in liquid) with 10% hydrochloric acid. The brown precipitate was filtered off, washed with water to remove sodium chloride, dried at room temperature, and refluxed for 2 hours with acetic anhydride (20 c.c.); it dissolved completely. The solution was poured into water (250 c.c.) or filtered hot and allowed to crystallise. The yields of *pp'*-azophenol diacetate in various experiments exceeded 90%, calculated on the tar taken. The brown solid from the zinc oxide–alcohol decomposition was converted directly into *pp'*-azophenol diacetate by refluxing with acetic anhydride. The diacetate crystallised from glacial acetic acid in fine yellow needles, m. p. 198° (Lauer, Klug, and Harrison, *J. Amer. Chem. Soc.*, 1939, **61**, 2775, give m. p. 198°; cf. Willstätter and Benz, *Ber.*, 1907, **40**, 1578), which were insoluble in cold aqueous sodium hydroxide (Found : N, 9·3. Calc. for $C_{16}H_{14}O_4N_2$: N, 9·4%).

Conversion of the Tar into Tetrabromo-pp'-*azophenol.*—A solution of the purified tar (2 g.) and sodium acetate (3 g.) in glacial acetic acid (130 c.c.) was stirred and treated dropwise with a solution of bromine (3 g.) in glacial acetic acid (50 c.c.) during 30 minutes. The dark-coloured precipitate was filtered off and crystallised four times from glacial acetic acid; it then melted at 274°, confirming the result of Lauer, Klug, and Harrison (*loc. cit.*) (Found: Br, 60·2. Calc. for $C_{12}H_6O_2N_2Br_4$: Br, 60·4%). Tetrabromo-*pp'*-azophenol diacetate, prepared from the above product, crystallised from glacial acetic acid in yellow plates, m. p. 262° (Lauer, Klug, and Harrison give m. p. 263—264°).

Decomposition Results :

Decomposition reagent.	% Phenol.	% Tar.	% Brown solid.	% Total products accounted for.
Methyl alcohol	38·4	57·2	—	95·6
Methyl alcohol + zinc oxide	63·2	21·4	13·9	98·5
Ethyl alcohol	38·0	58·6	—	96·6
Ethyl alcohol + zinc oxide	60·2	16·4	17·6	94·2

Decomposition of the Double Compound with Sodium Methoxide.—Sodium (3·5 g.) was dissolved in methyl alcohol, and the double compound (14·4 g.) added in small portions to the cold solution; a vigorous reaction occurred with evolution of nitrogen and rise of temperature. The product was diluted with water and treated at 0° with excess of 2N-hydrochloric acid to dissolve zinc hydroxide and to precipitate *pp'*-azophenol (4·8 g., which on acetylation afforded *pp'*-azophenol diacetate in yellow needles, m. p. 198°). The filtrate was steam-distilled to remove the phenol; the distillate afforded 4·7 g. of 2 : 4 : 6-tribromophenol, corresponding to a yield of 21·8% of phenol. Total products, 92·2%.

Decomposition of the Double Compound with tert.-*Butyl Alcohol, alone, and in Presence of Zinc Dust.*—*tert.*-Butyl alcohol (30 c.c.) at 30° was mixed with the double compound (7·2 g.) and refluxed for 12 hours. Decomposition occurred very slowly, and long before completion the mixture was poured into an equal volume of water and steam-distilled. The distillate contained phenol, and the non-volatile matter consisted mainly of *pp'*-azophenol. The decomposition was repeated with the addition of zinc dust (2·1 g.); it appeared to be complete in 90 minutes and gave phenol (35·7%) and *pp'*-azophenol (58·5%).

In another experiment the evolved gas was passed through an aqueous methyl-alcoholic solution of *p*-nitrophenylhydrazine and then collected over water; it was sweet-smelling, burned with a luminous flame, and decolorised both bromine water and alkaline permanganate. The same gas was obtained in a blank experiment with *tert.*-butyl alcohol, and appeared to be *iso*butylene. No hydrazone was formed.

Decomposition of the Double Compound by Methyl Alcohol in Presence of Bromine.—The double compound (7·2 g.) was added in portions of *ca.* 1 g., with shaking, to a solution of bromine (6·5 c.c.) in methyl alcohol (100 c.c.); the mixture became warm and nitrogen was evolved. The reaction was completed by heating under reflux for 2 hours, bromoanil separating from the clear solution. On cooling, more bromoanil separated (total weight, 0·87 g.) (m. p. and mixed m. p. with an authentic specimen, 300°). The filtrate was poured into water; the precipitated 2 : 4 : 6-tribromophenol weighed 9·2 g. No other products were found. The amount of the double compound accounted for was 93·6%.

The authors thank Imperial Chemical Industries, Ltd. (Dyestuffs Group), for gifts of chemicals.

TECHNICAL COLLEGE, HUDDERSFIELD.

[*Received, December* 12*th*, 1939.
Revised, May 29*th*, 1940.]