368. *Decomposition Reactions of the Aromatic Diazo-compounds. Part VII. Some Reactions of Diazonium Chlorides with Esters and Nitriles.*

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Solid diazonium chlorides have been decomposed under a number of esters and nitriles both with and without the addition of metals. In all cases the reactions $ArN_2Cl \longrightarrow ArH$ and $ArN_2Cl \longrightarrow ArCl$ occur, but the chief product is a complex black tar.

On decomposition in acetonitrile, diazonium chlorides also yield small quantities of the corresponding acetarylamides, $Ar{\cdot}NH{\cdot}CO{\cdot}CH_3$, and traces of the ketone $Ar{\cdot}CO{\cdot}CH_3$ may also be formed. These reactions seem to indicate that addition to the cyano-group can occur.

Acetaldehyde is invariably formed if diethyl ether is present in the reaction mixtures, but higher ethers appear to be inert solvents.

All these reactions are consistent with the view that a certain amount of decomposition of the diazonium chloride to neutral radicals can occur in these solvents.

Decompositions of Diazonium Chlorides in Esters.—The reactions between diazonium chlorides and esters, of which examples have been given in Parts II and IV (J., 1937, 2007; 1938, 843) have now been examined in greater detail, both benzenediazonium and *p*-chlorobenzenediazonium chloride being used with a number of aliphatic esters. By varying independently both the alkyl and the acyl group of the ester, it was found that the decomposition of diazonium chlorides proceeds less and less readily as one ascends a homologous series, and also that attack on the diazonium chloride by metals such as zinc or antimony becomes less evident. With methyl, ethyl, and *n*-propyl acetates, it has been shown that the reactions $ArN_2Cl \longrightarrow ArH$ and $ArN_2Cl \longrightarrow ArCl$ both occur to a total of about 5%, but the yield of hydrocarbon rapidly becomes less as one ascends the homologous series of acetates, and with amyl acetate as solvent the reaction is exactly similar to that occurring in an inert paraffin solvent.

The oxidation of an ester to an aldehyde by the action of a diazonium chloride has already been reported (*loc. cit.*), and it has been suggested (Part IV, *loc. cit.*) that the reactions $Cl\cdot + R\cdot CH_2\cdot O\cdot CO\cdot CH_3 \longrightarrow R\cdot CHCl\cdot O\cdot CO\cdot CH_3$ and $R\cdot CHCl\cdot O\cdot CO\cdot CH_3 + H_2O \longrightarrow R\cdot CHO + HCl + HO\cdot CO\cdot CH_3$ may occur, but this reaction mechanism has not been fully substantiated by the present experiments, since in most cases only a very small quantity of the aldehyde $R\cdot CHO$ can be obtained from the ester $R\cdot CH_2\cdot O\cdot CO\cdot CH_3$, and it has not been possible to isolate any α-chloro-esters. When methyl acetate was used, the formation of formaldehyde could not be proved; ethyl acetate certainly gave acetaldehyde, but *n*-propyl acetate and formate yielded only traces of propaldehyde.

In nearly every experiment, acetaldehyde was both detected and characterised: it must evidently result from a constant component of the reaction mixtures, and it is concluded that the acetaldehyde is formed from the diethyl ether used to precipitate and wash the solid diazonium chloride, since, when the chloride was subsequently thoroughly washed with the solvent used for the decomposition, acetaldehyde was not produced except from reactions in ethyl acetate. This production of acetaldehyde was also noticed in decompositions of diazonium chlorides in acetonitrile (see below).

The formation of acetaldehyde from diethyl ether by its interaction with the primary decomposition products of diazonium chlorides is in accordance with its formation upon the decomposition of both benzenediazoacetate (Grieve and Hey, J., 1934, 1805; Waters, J., 1937, 113) and also various *syn*-diazocyanides (following paper) in dry ether. It can be explained by postulating the dehydrogenation of ether by a free radical in accordance with the scheme

$$R\cdot + CH_3\cdot CH_2\cdot OEt \longrightarrow RH + CH_3\cdot \underset{|}{C}H\cdot OEt \longrightarrow CH_3\cdot CHO + \cdot Et$$

which has also been propounded by Evans and Braithwaite (*J. Amer. Chem. Soc.*, 1939, **61**, 898) to explain the production of aldehyde when Grignard reagents are electrolysed in dry ether. A similar mechanism of dehydrogenation by a free radical may be suggested for the decompositions of the esters themselves. However, it has been found that diazonium chlorides do not decompose under pure diethyl ether, and do not give aldehydes when decomposed by heating either in di-*n*-butyl ether or in diamyl ether. Moreover, butaldehyde could not be detected as a reaction product of decomposition of benzenediazonium chloride in a mixture of methyl acetate and di-*n*-butyl ether.

This decrease in the reactivity of aliphatic esters and ethers with diazonium chlorides as one ascends the homologous series is paralleled by the decrease in the reducing power of the higher aliphatic alcohols in their reactions with benzenediazonium sulphate (Hodgson and Kershaw, J., 1930, 2785), and also accords with Hantzsch's statement that diazonium chlorides do not oxidise either *n*- or *iso*-propyl alcohol (*Ber.*, 1903, **36**, 2061). It may be due to the general decrease in chemical reactivity that one would expect in the higher members of a homologous series. However, when the decomposition of a diazonium chloride is induced by heating in one of these higher-boiling solvents, it may become uncontrollably violent, and then results in the formation of only a small quantity of the corresponding aryl chloride in addition to a black tar. This somewhat explosive type of decomposition may well be that of the solid diazonium chloride, for the thermal decomposition of solid double salts of diazonium chlorides takes a similar course (Griess, *Annalen*, 1866, **137**, 52; Schwechten, *Ber.*, 1932, **65**, 1605), and the smoother lower-temperature reaction which is possible in acetone, ethyl acetate, or acetonitrile may be a reaction of dissolved substance which, as suggested in Part II, has the covalent structure $Ar{-}N{=}N{-}Cl$ and can give rise to neutral radicals. These considerations also apply to the violent decompositions which occur under dry hexane, carbon tetrachloride, and aromatic hydrocarbons.

Decompositions of Diazonium Chlorides in Nitriles.—A number of diazonium chlorides have been decomposed under acetonitrile kept neutral with chalk. Reaction sets in at about 40°, with nitrogen evolution, and some acetaldehyde is formed if the diazonium salt has not been freed from ether. The main reaction product is always a black tar, from which, however, small quantities of simpler products can usually be separated, indicating that the following chemical reactions can all occur :

$$\mathrm{Ar{\cdot}N_2Cl + CH_3{\cdot}C{\equiv}N} \begin{array}{ll} \nearrow \mathrm{ArH} & \ldots\ldots \quad (A) \\ \nearrow \mathrm{ArCl} & \ldots\ldots \quad (B) \\ \searrow \mathrm{Ar{\cdot}NH{\cdot}CO{\cdot}CH_3} & \ldots\ldots \quad (C) \\ \searrow \mathrm{Ar{\cdot}CO{\cdot}CH_3} & \ldots\ldots \quad (D) \end{array}$$

Of these, reactions (A) and (B) are to be expected when a diazonium chloride decomposes in any aliphatic solvent, but reactions (C) and (D) are distinctive of the acetonitrile. Reaction (C), which in the case of benzenediazonium chloride occurs to up to 10% of the whole, can be explained as an addition process involving free radicals :

(i) $\mathrm{Ar{\cdot}N{:}NCl \longrightarrow Ar{\cdot} + N_2 + {\cdot}Cl}$

(ii) $\mathrm{Ar{\cdot} + Cl{\cdot} + CH_3{\cdot}C{\equiv}N \longrightarrow CH_3{\cdot}CCl{:}NAr}$

(iii) $\mathrm{CH_3{\cdot}CCl{:}NAr + H_2O \longrightarrow CH_3{\cdot}CO{\cdot}NHAr + HCl}$

and cannot be due to any formation of acetic acid, since it occurs in neutral solutions.

Reaction (D) can similarly be explained by postulating the primary addition process

(iv) $\mathrm{CH_3{\cdot}C{\equiv}N + Ar{\cdot} \longrightarrow CH_3{\cdot}CAr{=}N{\cdot}}$

particularly as Schlenk and his colleagues have shown that metallic sodium will add on to certain compounds containing the C=N and the C≡N group to give products resembling the metal ketyls (*Ber.*, 1914, **47**, 482; *Annalen*, 1928, **463**, 1).

The formation of neutral radicals in these decompositions of diazonium chlorides under acetonitrile is substantiated by the fact that, when metals (*e.g.*, zinc or antimony) are added, the decomposition commences at room temperature. Both metals give their chlorides, but antimony does not seem to form an organo-metallic compound, and mercury is not attacked. In the presence of zinc the decomposition takes a different course, for reactions (B), (C) and (D) are suppressed, probably on account of the prompt union of the chlorine with the zinc.

Propionitrile is much less reactive than acetonitrile, and only reactions (A) and (B) have been proved to occur. No simple reaction products have been obtained from benzyl cyanide. Thus, in general, the reactivity of nitriles toward diazonium chlorides is less than that of the esters.

EXPERIMENTAL

Benzenediazonium chloride and *p*-chlorobenzenediazonium chloride were prepared in glacial acetic acid solution by Pray's method (*J. Physical Chem.*, 1926, **30**, 1477), and the other diazonium chlorides were prepared in alcohol, as described in Part IV (*loc. cit.*). The solids (about 20 g.) were precipitated and washed thoroughly with dry ether, and then transferred rapidly to flasks containing redistilled solvent (150 c.c.) and dry chalk (15 g.). Decomposition was induced by gentle warming under reflux, and any volatalising aldehydes were collected in water or in a solution of 2 : 4-dinitrophenylhydrazine. To complete the reaction, the mixtures were boiled under reflux and then cooled, filtered, and fractionated. The residual tars were distilled in steam and then extracted with organic solvents.

Decompositions in Esters.—*p*-Chlorobenzenediazonium chloride (from 20 g. of *p*-chloroaniline hydrochloride) gave the following aromatic products :

	PhCl, g.	p-$C_6H_4Cl_2$, g.		PhCl, g.	p-$C_6H_4Cl_2$, g.
In methyl acetate	2·8	0·1	In *n*-propyl acetate ...	0·5	1·2
In ethyl acetate	1·1	0·5	In amyl acetate	no simple reaction products.	

The particular yields of aromatic compounds from all other decompositions in esters were very similar in quantity. On distillation of the neutral ester solutions there was invariably obtained a fraction containing free hydrochloric and acetic acids.

With both benzenediazonium and *p*-chlorobenzenediazonium chloride, acetaldehyde (2 : 4-dinitrophenylhydrazone, m. p. and mixed m. p. 164°) was obtained from methyl, ethyl, and *n*-propyl acetates, methyl benzoate, and *n*-propyl formate, except when the diazonium salt had been washed thoroughly with pure ester in order to remove adhering ether. Under the latter conditions no aldehyde was obtained from methyl acetate, though sensitive spot tests for formaldehyde were carried out. Traces of aldehyde too minute to identify were obtained from both propyl formate and propionate, and from a decomposition of *p*-chlorobenzenediazonium chloride in propyl acetate a little propaldehyde was obtained (dinitrophenylhydrazone, m. p. and mixed m. p. 155°).

The decomposition of benzenediazonium chloride in amyl acetate, propyl propionate, and methyl benzoate did not commence until the mixture had been heated to nearly 100°, and then tended to become uncontrollable. The same was true of decompositions carried out in pure di-*n*-butyl or diamyl ether. No butaldehyde was obtained when a decomposition was carried out in a mixture of equal volumes of methyl acetate and dibutyl ether.

Benzenediazonium chloride, under methyl acetate, reacted vigorously with both antimony and zinc, giving metallic chlorides and, with the former, tri-*p*-chlorophenylstibine dichloride (m. p. and mixed m. p. 193°) was also obtained, but under amyl acetate there was no similar reaction with antimony. Under methyl benzoate, however, benzenediazonium chloride still reacted with zinc dust; and under ethyl acetate it reacted slowly with tellurium but gave no appreciable quantity of organic telluride.

Decompositions in Acetonitrile.—These were carried out in a similar manner, and with each diazonium chloride the formation of acetaldehyde was established except when the salt had been throughly washed free from ether by means of acetonitrile. The following reaction products have been isolated and characterised as described :

(i) Benzenediazonium chloride (from 22 g. of aniline hydrochloride) gave acetanilide (3 g.; m. p. and mixed m. p. 114°), benzene, diphenyl (0·1 g.; m. p. and mixed m. p. 70°), and a little oil, b. p. 180—200°, which was oxidised by alkaline permanganate to benzoic acid (m. p. and mixed m. p. 121°) and gave a trace of a 2 : 4-dinitrophenylhydrazone, m. p. 242°, not depressed by admixture with acetophenonedinitrophenylhydrazone. The residual tars, when refluxed with sodium hydroxide solution, yielded small quantities of ammonia, aniline, and an *iso*nitrile.

In the presence of zinc dust, this decomposition occurred at room temperature : zinc chloride was formed and diphenyl (0·3 g.) was the only solid isolated. Antimony powder also brought about reaction at room temperature, and antimony chloride was formed. Mercury, however, was without action. An explanation of the production of diphenyl has been given in Part VI (this vol., p. 864).

Rapid heating, even in the absence of metals, decreased the yield of acetanilide.

(ii) *o*-Toluenediazonium chloride (from 20 g. of *o*-toluidine) gave aceto-*o*-toluidide (0·5 g.; m. p. and mixed m. p. 110°) (Found : N, 9·4. Calc : N, 9·4%).

(iii) *p*-Toluenediazonium chloride (from 30 g. of base) gave aceto-*p*-toluidide (0·2 g.; m. p. and mixed m. p. 148°) and a little *p*-methylacetophenone, b. p. *ca.* 240°, identified as semicarbazone (0·1 g.; m. p. and mixed m. p. 204°) and by oxidation with sodium hypobromite to bromoform and 3-bromo-*p*-toluic acid, m. p. 204°. The residual tar, when boiled with sodium hydroxide, yielded both ammonia and *p*-toluidine.

(iv) *p*-Chlorobenzenediazonium chloride (from 21 g. of base hydrochloride) gave both chlorobenzene (0·6 g.) and *p*-dichlorobenzene (0·5 g.; m. p. and mixed m. p. 53°).

(v) 4-Chloro-*o*-toluenediazonium chloride (from 30 g. of base hydrochloride) gave 4-chloroaceto-*o*-toluidide (1·1 g.; m. p. and mixed m. p. 139°) (Found : N, 7·6. Calc. : N, 7·6%), and also 2 : 4-dichlorotoluene (*ca.* 3 g.) (3 : 5-dinitro-derivative, m. p. 104° alone or mixed with a specimen prepared by nitration of authentic 2 : 4-dichlorotoluene).

(vi) 5-Chloro-*o*-toluenediazonium chloride (from 20 g. of base hydrochloride) gave *m*-chlorotoluene (1·8 g.), identified as its trinitro-derivative, m. p. 149° alone or mixed with a specimen prepared from authentic *m*-chlorotoluene.

Benzenediazonium chloride when decomposed under propionitrile (same scale) gave no aldehyde. Both benzene and chlorobenzene were identified as reaction products, but no anilide could be isolated. No simple reaction products were isolated from a decomposition carried out under benzyl cyanide.

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