

424. *Decomposition Reactions of the Aromatic Diazo-compounds.
Part II. Some Reactions of Benzenediazonium Chloride.*

By WILLIAM A. WATERS.

The decomposition of solid benzenediazonium chloride under acetone, hexane, carbon tetrachloride, ethyl iodide, and ethyl acetate has been studied. Hydrogen chloride and chlorobenzene were the usual products, though with ethyl iodide some iodo-benzene also was formed. The reaction under acetone kept neutral by chalk yielded benzene and chloroacetone.

Under acetone in presence of chalk benzenediazonium chloride attacked mercury, antimony, bismuth, lead, tin, nickel, iron, copper, and silver, giving the metallic chlorides. With mercury, phenylmercuric chloride also was produced, and with antimony triphenylstibine dichloride. The latter reaction affords a new method of synthesis of aromatic antimonials.

The theoretical aspects of the decomposition of benzenediazonium chloride are considered in detail and, in absence of water, it is suggested that the diazonium salt,

$(\text{PhN}_2)^+\text{Cl}^-$, first undergoes molecular rearrangement to diazobenzene chloride, $\text{Ph}\cdot\text{N}:\text{NCl}$, which then decomposes, either by the spontaneous elimination of nitrogen with the production of the free neutral phenyl radical and atomic chlorine, $\text{Ph}\cdot$ and $\text{Cl}\cdot$, or, less probably, by a bimolecular decomposition upon collision with another reagent.

The theoretical consideration of the alternative processes necessitates a discussion of the possible modes of reaction of all substances now regarded as containing "positive" or "electrophilic" halogen atoms, for example, dichloramine-T. It is not unfeasible that all such halogen compounds may react by undergoing a non-ionic fission of a covalent link, in consequence of which transient halogen atoms may be produced. Support for this new suggestion is drawn from the experimental fact that dichloramine-T, when dissolved in dry acetone, benzene, or carbon tetrachloride, was found to react with mercury.

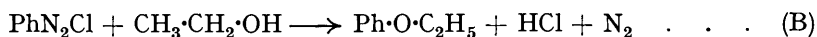
HITHERTO the mechanism of decomposition of diazonium salts has been considered chiefly in relation to reactions occurring in aqueous solution, from which no conclusive deductions can be made, for the decomposition might be either that of the diazonium kation or of a wholly covalent molecule. When, however, the decomposition of benzenediazonium chloride is studied in absence of water, other features of the process become apparent, and significant theoretical deductions may be drawn from the experimental evidence.

Dry benzenediazonium chloride is explosive, but, although it is practically insoluble in solvents other than water, its decomposition under organic liquids can be regulated if one operates on a small scale, taking due precautions. The decomposition regularly seems to involve an interaction with the organic liquid—though whether this occurs prior or subsequent to the fission of the nitrogen is a moot point—and, from the nature of the mixtures of products which have been isolated by using liquids such as ethyl alcohol, acetone, and ethyl iodide (and others), it is evident that benzenediazonium chloride does not always behave in the way that would be anticipated of an ionic substance such as any other substituted ammonium halide.

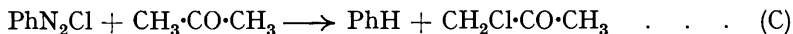
It is well known that an alcohol can be oxidised during the decomposition of a diazonium salt,



though, in general, an aryl ether is produced simultaneously :



The oxidation of the alcohol (A), which is not a reaction one would anticipate of an ionised halide, has been ascribed to the initial formation of an alkyl hypochlorite (*e.g.*, $\text{C}_2\text{H}_5\cdot\text{OCl}$) (compare Hantzsch, *Ber.*, 1930, **63**, 1786), and this may well be the case, since with acetone a very similar reaction occurs,



which leads to the production of chloroacetone. By a concurrent reaction, however, a considerable quantity of hydrogen chloride is produced. Hydrogen chloride is also evolved in decompositions under ethyl acetate, hexane, and carbon tetrachloride. In the latter case, however, the sample of benzenediazonium chloride used may have contained a little moisture and the trace of water can have been the source of some of the hydrogen which combined with the chlorine.

Whenever hydrogen chloride was evolved during the reaction, chlorobenzene was found amongst the products, and, as in the decomposition of benzenediazonium chloride in concentrated hydrochloric acid (Hantzsch, *Ber.*, 1900, **33**, 2525), it may possibly have been formed by an interaction between undecomposed benzenediazonium chloride and molecular hydrogen chloride.

Under carbon tetrachloride the decomposition of benzenediazonium chloride gives a large yield (40%) of chlorobenzene. This may, to a great extent, be a product of a direct reaction between the diazonium salt and the carbon tetrachloride, for when another organic

halide, ethyl iodide, was used, both chlorobenzene and iodobenzene were found as products.

Benzenediazonium chloride under acetone, in presence of chalk, attacks silver, mercury, lead, antimony, bismuth, tin, copper, iron, and nickel, yielding metallic chlorides. Phenylmercuric chloride is produced in the reaction with mercury, and triphenylstibine dichloride in that with antimony. Both these reactions afford new methods of synthesis of aryl organo-metallic compounds.

The Mechanism of the Decomposition Process.—A decomposition process involving interaction with the organic liquid is in accord with the later theories of Hantzsch (*Ber.*, 1930, **63**, 1786), who pictured the reaction (A) between benzenediazonium chloride and ethyl alcohol as the decomposition of an addition product, $\text{Cl}\cdot\text{NAr}\cdot\text{NH}\cdot\text{OEt}$, containing a covalent link between nitrogen and chlorine. He pointed out that chloride anions, such as would be present in the salt $(\text{PhN}_2)^+\text{Cl}^-$, never react with alcohols to yield alkyl hypochlorites, though compounds with covalent N-Cl links can do so. The same consideration applies to the reaction (C) between benzenediazonium chloride and acetone, for substituted ammonium chlorides are not chlorinating agents (compare Waters, *Nature*, 1937, **140**, 466) and do not interact with acetone, whereas compounds containing the N-Cl covalent link will chlorinate it (compare Behal and Detœuf, *Compt. rend.*, 1911, **153**, 1229). The reactions of benzenediazonium chloride with metals also do not accord with decompositions of diazonium salts, but do accord with possible decompositions of covalent chlorides.

However, though the inference that the reaction between benzenediazonium chloride and alcohol or acetone involves decomposition of a covalent chloride can be deduced in the manner set forth above, one need not suppose, with Hantzsch, that the diazonium chloride must form *addition* compounds which then decompose, for the diazonium salt itself might undergo a molecular rearrangement to give wholly covalent diazobenzene chloride :

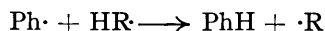


Pray (*J. Physical Chem.*, 1926, **30**, 1477) has argued that it is not an addition compound between a diazonium salt and an alcohol which decomposes, for he found that the rate of decomposition of benzenediazonium chloride in various alcohols was independent of the nature of the alcohol, which would not be the case if the decomposing complex (see above) contained an alkyl group the identity of which could be varied at will. In the reaction with acetone one would scarcely have reason to suppose that a hydrazine derivative such as $\text{NPhCl}\cdot\text{NH}\cdot\text{CH}_2\cdot\text{CO}\cdot\text{CH}_3$ would be produced, or that such a compound would tend to decompose with elimination of nitrogen and formation of chloroacetone.

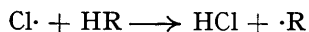
It is much simpler, therefore, to suppose that benzenediazonium chloride undergoes molecular rearrangement on warming to give an unstable diazobenzene chloride, of which the steric structure cannot as yet be specified, which decomposes either spontaneously or upon collision with another molecule. This theory is in accord with the fact that, in absence of metals, benzenediazonium chloride does not decompose under organic solvents below 50° . It can be heated under dry boiling diethyl ether without change, but under a number of other solvents it softens at $50\text{--}60^\circ$ and a vigorous decomposition then sets in immediately.

In Part I (this vol., p. 113) evidence was brought forward to support the hypothesis that diazobenzene acetate, $\text{Ph}\cdot\text{N}:\text{N}\cdot\text{O}\cdot\text{CO}\cdot\text{CH}_3$, decomposes spontaneously into the free neutral radicals $\text{Ph}\cdot$ and $\cdot\text{O}\cdot\text{CO}\cdot\text{CH}_3$,* which then interact with vicinal solvent molecules. The spontaneous decomposition of covalent diazobenzene chloride into nitrogen and the free neutral phenyl radical and atomic chlorine can, with equal justification, be advanced to account for one stage in the decomposition reactions of benzenediazonium chloride mentioned above, since it will explain :

(i) The formation of benzene with alcohol and with acetone as :

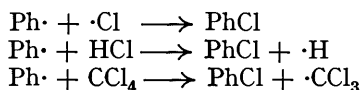


(ii) The formation of hydrogen chloride in all reactions :



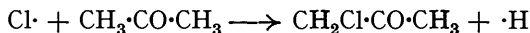
* A fine dot is used in this series of papers to denote an unshared electron.

(iii) The formation of chlorobenzene by any of the reactions :



(iv) The formation of iodobenzene from ethyl iodide.

(v) The chlorination of acetone : Neutral atomic chlorine is an electron-seeking (" elec-



trophilic" or " kationoid ") reagent, since it is deficient of its complete octet of electrons. It is therefore a chlorinating agent just as much as molecular chlorine, which may, in certain cases, act by fission to chlorine atoms.

(vi) The reaction of benzenediazonium chloride with silver, lead, mercury, antimony, bismuth, copper, iron, tin and nickel. None of these metals will react easily with either alkyl or acyl halides, but all are attacked by atomic or molecular chlorine, to which they will supply electrons. Many of them also are attacked by free alkyl radicals.

(vii) The formation of phenylmercuric chloride with metallic mercury and of triphenylstibine dichloride with metallic antimony. These again are reactions which require reagents of strong electron-seeking character, for the phenyl group in each case is bound to the metallic atom in the product by a covalent link. Alkyl or aryl halides do not react with either mercury or antimony alone; the free alkyl radicals, however, react instantaneously.

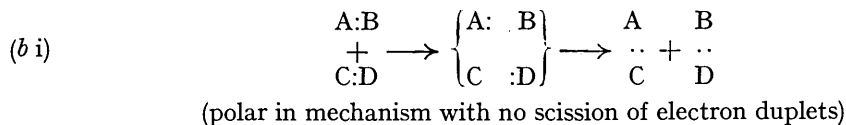
A very strong case can therefore be put forward to justify the theory of the non-ionic fission of nitrogen from aromatic diazo-compounds in the presence of non-hydroxylic solvents on the basis of the new experimental evidence detailed above. As additional evidence it may be mentioned that Möhlau and Berger (*Ber.*, 1893, **26**, 1994) found that benzenediazonium chloride gave diphenyl, phenyl-naphthalene, and phenylpyridine (not phenylpyridinium chloride) on reaction with benzene, naphthalene, and pyridine respectively. It thus reacts with these substances just as do diazobenzene acetate and diazobenzene hydroxide (Grieve and Hey, *J.*, 1934, 1797).

In a private communication, however, Professor R. Robinson has very kindly pointed out that the reactions discussed above could all be considered as typical interactions between covalent diazobenzene chloride and another reagent. Diazobenzene chloride, like any other *N*-chloroamine (*e.g.*, dichloramine-T), should contain a " positive " or " kationoid " halogen atom. It should therefore be capable of chlorinating acetone and of reacting with metals. The formation of the organo-metallic compounds is a little difficult to understand upon this theory, for it is not easy to conceive why an " anionoid " phenyl (or Ph·N:N) group should react with mercury or antimony in addition to the " kationoid " chlorine group. From inspection of the reaction as a whole, however, it is evident that these metals act by supplying two extra electrons to each molecule of the decomposing diazo-compound, and this may occur during, and not subsequent to, the disruption of the diazo-structure.

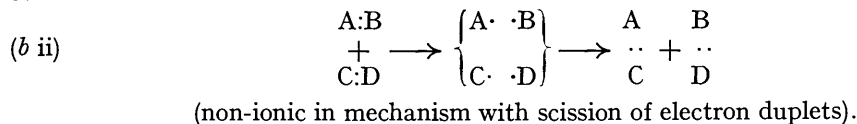
The Properties and Reactivity of " Positive " Halogen Compounds.—Since mercury is one of the inert metals, it was of interest to see whether other *N*-halogen compounds would react with it. Solutions of dichloramine-T in dry acetone, benzene, and carbon tetrachloride were refluxed with mercury; as soon as the solutions were warmed, reaction set in, giving a white insoluble mixture of mercurous chloride with the mercuric salt of toluene-*p*-sulphonamide. This reaction certainly provides conclusive evidence of the great electron-seeking character of *N*-chlorine compounds, showing that their halogen reactivity is comparable with that of free halogen atoms.

Only by making quantitative kinetic measurements of the rate of the decomposition processes can one decide between the alternative hypotheses of (*a*), a free radical decomposition, followed by an interaction of both the radicals produced as a covalent bond breaks with vicinal molecules, and (*b*), a bimolecular decomposition upon activated collision with another reactant, since, for any bimolecular decomposition process, (*b*), one can as yet give no more than a vague pictorial representation of the nature of the collision complex. At all events one cannot provide any *experimental* evidence to demonstrate how bonds are broken

in a bimolecular process, for the nature of the ultimate products gives no information as to whether or not there is a scission of electron duplets. Thus a bimolecular reaction, $A:B + C:D \longrightarrow A:C + B:D$ may equally well be



or



The initiation energetics of the two reaction processes will, however, be different, for the actual transition state will be that requiring the lesser energy increment. Now, since chlorine is an electronegative element, much more energy will be needed to form a transient Cl^+ kation, containing but six electrons in its outer shell, than a transient neutral atom containing seven electrons, and hence, even in a bimolecular reaction of a compound containing an electron-seeking halogen atom, the process (b ii) may be more probable than the process (b i). If one examines critically the reactions of compounds containing electrophilic (*i.e.*, "kationoid") halogen atoms, one finds that no decisive evidence can be brought forward to refute an assertion that all these compounds may interact so that the electron duplet which binds the halogen is broken momentarily with production of a pair of neutral radicals each of which has a tendency to rectify this electron deficit by acquiring, or sharing, an extra electron from another reagent. In brief, all compounds containing electrophilic halogen atoms are oxidising agents which, like bromine or iodine molecules, tend to acquire two more electrons.

The possibility that reactions of compounds containing electrophilic halogen atoms are all reactions involving non-ionic bond fission opens up too wide a field of investigation to be discussed adequately in this paper, but attention may be directed to some significant work of Kharasch, Alsop, and Mayo (*J. Organic Chem.*, 1937, 2, 76) and of Kharasch, Sternfeld, and Mayo (*J. Amer. Chem. Soc.*, 1937, 59, 1655), who have shown that two compounds which have long been regarded as typical substances containing electrophilic or "positive" halogens, *viz.*, carbon tetraiodide and α -bromoacetoacetic ester, are stable except in the presence of oxygen or peroxides, which are substances now considered to catalyse the formation of free halogen atoms.

In conclusion, the author wishes to point out that the reactions of benzenediazonium chloride are not unique amongst those of diazo-compounds, but are paralleled exactly by those of substances such as diazobenzene acetate (Part I) and diazobenzene hydroxide (Part III; following paper), which do not contain any covalent nitrogen-to-halogen linkages. Moreover a large number of experimental facts, drawn from numerous branches of organic chemistry, indicate that free neutral radicals can exist momentarily in solutions and that they have exactly the properties which have been ascribed to the neutral phenyl radical and to atomic chlorine in this paper (compare Hey and Waters, *Chem. Reviews*, 1937, 21, 169).

EXPERIMENTAL.

Benzenediazonium chloride was prepared by the method of Hantzsch and Jochem (*Ber.*, 1901, 34, 3337) as improved by Pray (*loc. cit.*). For use, the hygroscopic white solid was washed with dry ether, then with the solvent to be employed, and rapidly transferred, whilst still damp with this solvent, to the reaction flask. No attempt was made either to dry or to preserve it. The flask was provided with a reflux condenser and a calcium chloride guard-tube in every reaction.

Reaction with Acetone.—(a) 10 G. of benzenediazonium chloride were covered with 50 c.c. of A.R. acetone. Hardly any reaction occurred at room temperature, but at 50° there was a regular evolution of both nitrogen and hydrogen chloride and the mixture became purplish-

brown. When reaction had slackened, the mixture was refluxed for 1 hour and the acetone was then distilled off on the water-bath. 20 C.c. of pure hexane were added to the distillate to extract any aromatic contents, and the acetone was dissolved with aqueous sodium bisulphite. The residual hexane solution, which was shown to contain an aromatic compound by the iodic acid reaction of Masson and Race (this vol., p. 1718), was nitrated. From the nitration product was separated a small quantity of a yellowish oil, which reacted with aniline in dilute alcohol to give 2 : 4-dinitrodiphenylamine, m. p. 157°. (Isolation of 2 : 4-dinitrodiphenylamine, as described above, was regularly used as a diagnostic test for the presence of small quantities of chlorobenzene : larger quantities could be characterised by the separation of solid nitration products.) The residue from distillation of the acetone was distilled in steam and gave a small quantity of a yellow oil, insoluble in alkali, which on fractionation yielded a little chlorobenzene together with traces of products of higher boiling point.

(b) *Reaction in neutral solution.* To obviate side reactions due to the presence of hydrogen chloride the decomposition was repeated, with 20 g. of benzenediazonium chloride, 20 g. of dry precipitated chalk, and 100 c.c. of acetone. Reaction set in at 45° and was easily regulated. After refluxing for 1 hour, the mixture was cooled and the solid residue after filtration was extracted with dry ether. The extract was fractionated in an all-glass apparatus. The fraction, b. p. 40—100°, was washed repeatedly with aqueous sodium bisulphite and refractionated; it then gave 2.2 g. of benzene, b. p. 80—82°, which was converted into *m*-dinitrobenzene, m. p. and mixed m. p. 90—91°. Above 100° chloroacetone distilled, b. p. 118—119° (yield, after refractionation, 6.1 g.), identified by hydrolysis, colour reaction with alkali, and by conversion into its 2 : 4-dinitrophenylhydrazone, m. p. 124° (compare Bülow and Siedel, *Annalen*, 1924, 439, 48), and into its semicarbazone, m. p. 147—148° (decomp.) after crystallisation from benzene [Found (micro-analysis by Dr. G. Weiler) : C, 32.5; H, 5.4; N, 27.8; Cl, 23.7. Calc. : C, 32.1; H, 5.4; N, 28.1; Cl, 23.7%]. This is in accord with Hoogeveen and Jansen (*Rec. trav. chim.*, 1932, 51, 262), who describe the semicarbazone as decomposing at "about 150°," but not in accord with Michael (*J. pr. Chem.*, 1899, 60, 286; compare Heilbron's "Dictionary"), who, however, allowed this easily hydrolysed substance to stand for several hours with water.

No chlorobenzene could be found under these conditions and no other definite product could be isolated from the tarry residue.

Reaction under Hexane.—8 G. of benzenediazonium chloride, after being washed with dry hexane, were covered with 60 c.c. of pure hexane. It remained unaltered for a day at room temperature, but at 50° the solid became sticky and both nitrogen and hydrogen chloride were evolved with such rapidity that the reaction had to be controlled by rapid cooling. The hexane was distilled off and found, by the iodic acid reaction, to contain chlorobenzene (identified as 2 : 4-dinitrodiphenylamine). The purplish residue was distilled in steam; from the distillate, ether extracted 3.0 g. of chlorobenzene, b. p. 130—134°, and about 1 g. of a substance, b. p. 180—220°, which could be nitrated (product, m. p. 179—186°) but not identified.

Reaction with Carbon Tetrachloride.—Benzenediazonium chloride (from 22 g. of aniline hydrochloride) was carefully washed with dry ether, then several times with carbon tetrachloride which had been dried with sodium, and quickly transferred to a flask containing 200 g. of dry carbon tetrachloride. No reaction occurred below 60°, the white powder floating in the clear liquid, but at this temperature decomposition set in and the solid softened with some frothing. Cooling in ice and water was necessary to control the reaction. A large quantity of hydrogen chloride was liberated and the mixture became dark purple as if an azine dye had been produced. When reaction had ceased, the carbon tetrachloride was distilled off on the water-bath, and the residue steam-distilled. The distillates gave 8 g. of chlorobenzene, b. p. 132°, which was identified by nitration. Phenol also was formed, but the quantity isolated (less than 1 g.) seemed scarcely an amount equivalent to the quantity of hydrogen chloride which had been liberated.

Reaction with Ethyl Iodide (compare Oddo, *Gazzetta*, 1890, 20, 631).—6 G. of benzenediazonium chloride were mixed with 30 c.c. of ethyl iodide, and reaction induced by warming to 60°; nitrogen and a hydrogen halide were then evolved. After 1 hour's refluxing the excess of ethyl iodide was distilled off, and the residue distilled in steam. The distillate was washed with alkali and fractionated, giving (i) 1.5 g. of chlorobenzene, b. p. ca. 130°, identified by nitration to *p*-chloronitrobenzene, m. p. and mixed m. p. 83°, and (ii) 1.2 g. of iodobenzene, b. p. 184—187°, identified by conversion into *p*-iodonitrobenzene, m. p. and mixed m. p. 174°.

Reaction with Ethyl Acetate.—8 G. of benzenediazonium chloride were washed with dry ethyl acetate and then placed in 60 g. of this solvent. Reaction started at 50—60° and was completed by refluxing for 1 hour. Both nitrogen and hydrogen chloride were evolved. The

ethyl acetate was then distilled off on the water-bath, and the residue distilled in steam. By treatment with pure hexane, followed by hydrolysis with alkali in excess, the ethyl acetate fraction was shown to contain a little chlorobenzene (identified as 2 : 4-dinitrodiphenylamine) and from the steam-distillate were separated 1.0 g. of chlorobenzene, identified by nitration to 2 : 4-dinitrochlorobenzene, m. p. and mixed m. p. 53° , and 1.4 g. of phenol. There was no evidence of the formation of an ester of high boiling point.

To another mixture of equal bulk were added 10 g. of dry precipitated chalk, and the reaction was carried out as above. The ethyl acetate fraction gave a positive reaction with Schiff's reagent and again contained a little chlorobenzene. Benzene was not found. The steam-distillate yielded 3.0 g. of chlorobenzene, identified by conversion into *p*-chloronitrobenzene.

Reaction between Benzenediazonium Chloride and Mercury.—5 G. of benzenediazonium chloride, 10 g. of calcium carbonate, and 20 g. of mercury were mixed in 40 c.c. of acetone. Reaction set in *in the cold* with evolution of heat. The mixture was well shaken and cooled in water. After completion of the reaction by $\frac{1}{2}$ hour's refluxing, the acetone was distilled off, and the residue treated with dilute acetic acid, which yielded a solution containing both calcium and chloride ions. The insoluble remainder was extracted (Soxhlet) with benzene, and from the benzene extract 3.1 g. of phenylmercuric chloride, m. p. 254° , were separated. The residue insoluble in benzene was a mixture of mercury and mercurous chloride which blackened instantly on treatment with ammonia.

Reaction between Benzenediazonium Chloride and Antimony.—(a) 5 G. of benzenediazonium chloride, 10 g. of calcium carbonate, and 20 g. of powdered antimony were mixed in 40 c.c. of acetone; reaction commenced instantly and had to be controlled by cooling the mixture in water. After $\frac{1}{2}$ hour's refluxing on the water-bath, the acetone was evaporated. The residue on treatment with water evolved some carbon dioxide, probably on account of hydrolysis of antimony chloride, which would produce acid to interact with the calcium carbonate. The solution contained only calcium and chloride ions, but after the residue had been warmed with sodium hydrogen tartrate solution an extract containing a considerable quantity of an antimony salt was obtained. The remainder from this treatment was washed with warm dilute hydrochloric acid in excess and then treated with warm sodium hydroxide solution. The alkaline extract gave on acidification a gelatinous white precipitate, insoluble in hydrochloric acid but soluble in aqueous ammonia, which contained both carbon and antimony (positive Marsh test; carbon dioxide formed on heating with copper oxide), and was presumed to be a phenyl-stibonic or -stibinic acid. It gave an insoluble barium salt.

(b) Benzenediazonium chloride (from 22 g. of aniline hydrochloride) was shaken with a mixture of 30 g. of powdered antimony and 10 g. of calcium carbonate in 100 c.c. of acetone. At once a vigorous reaction set in, which continued when the mixture was cooled in ice and water. After completion of the reaction by 2 hours' refluxing, the product was cooled, the liquid filtered, and the solid washed with more acetone. By evaporation of the acetone solutions a solid was obtained from which, by crystallisation from alcohol containing some hydrochloric acid, 3.1 g. of triphenylstibine dichloride, m. p. and mixed m. p. 143° were separated (Found : Sb, 28.7. Calc. : Sb, 28.6%). The residues from this crystallisation seemed to contain phenylstibonic acids, probably formed by hydrolysis of arylstibonyl chlorides.

Reaction between Benzenediazonium Chloride and Other Metals.—5 G. portions of benzenediazonium chloride were added to separate mixtures of 10 g. of calcium carbonate, 40 c.c. of acetone, and 20 g. portions of powdered lead, bismuth, and tin. Portions of 2 g. of benzenediazonium chloride and 2 g. of calcium carbonate in 20 c.c. of acetone were treated with 10 g. portions each of iron and nickel filings, and also with 5 g. of copper bronze powder and with 3 g. of thin silver foil.

In each case reaction started in the cold and the mixture had to be cooled in water. After refluxing for $\frac{1}{2}$ hour, the acetone was evaporated from each reaction mixture, and the residues were examined as follows.

From the reaction mixture with lead a little lead chloride was extracted by means of hot water, and a considerable quantity of a lead salt by extraction with cold dilute acetic acid.

From the mixture with bismuth a solution containing bismuth ions in quantity was obtained by extraction with warm 2*N*-hydrochloric acid. From that with tin a solution containing stannous ions in quantity was obtained by extraction with cold dilute acetic acid. This reagent had scarcely any action upon the tin powder alone.

Aqueous extraction of the reaction mixture with nickel gave a pale green solution containing nickel ions, and the formation of a green nickel salt was most evident. Similarly a green salt was produced from the reaction with iron, and an aqueous extract contained ferrous ions.

By ammoniacal extraction the reaction mixtures with copper and with silver were proved to contain cuprous and silver chloride respectively.

Reactions of Dichloramine-T with Mercury.—(a) 20 G. of mercury were shaken with a solution of 5 g. of dichloramine-T in 25 c.c. of acetone, and the mixture warmed. Reaction soon occurred and a bulky white precipitate formed.

Similar reactions were carried out, 20 g. portions of mercury being used with a solution of 5 g. of dichloramine-T in 60 g. of sodium-dried benzene and with a solution of 5 g. of dichloramine-T in 100 g. of dry carbon tetrachloride. In each case reaction rapidly occurred on warming, with the formation of an insoluble white precipitate. This precipitate was extracted with the solvent employed. The residue was then extracted with hot water and gave a solution containing mercuric ions. Dilute hydrochloric acid also removed a solid, which crystallised from the solution on cooling and proved to be *p*-toluenesulphonamide. In each case there remained a bulky white residue, which blackened instantly on treatment with aqueous ammonia and was therefore presumed to be mercurous chloride.

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