

165. *Decomposition Reactions of the Aromatic Diazo-compounds.*
Part IV. A New Synthesis of Aromatic Antimony Compounds.

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The reactions described in Part II (J., 1937, 2007) have been applied to substituted benzenediazonium chlorides. Mixtures containing triarylstibine dichlorides, Ar_3SbCl_2 , triarylstibines, Ar_3Sb , and diarylstibinous chlorides, Ar_2SbCl , are formed when solid diazonium chlorides react with metallic antimony under acetone or ethyl acetate, kept neutral with chalk. Under other solvents, such as water, ethyl alcohol, *cyclohexane*, benzene, carbon tetrachloride, carbon disulphide, diethyl ether, and dioxan, the reaction does not occur, and it is inferred that diazonium chlorides react with antimony only after tautomeric change has occurred to the wholly covalent form $\text{Ar}\cdot\text{N}:\text{NCl}$.

The similarity between this reaction and those of Nesmejanov and his colleagues (*Ber.*, 1929, **62**, 1010; 1935, **68**, 1877) has been demonstrated; *e.g.*, both the antimony and the zinc double diazonium chlorides can be used for the preparation of aromatic antimonials by this new reaction, which gives the organometallic compounds in very good yields. Diazonium chlorides seem to be able to chlorinate ethyl acetate as well as acetone.

It was reported in Part II (J., 1937, 2007) that phenylmercuric chloride and triphenylstibine dichloride were formed in appreciable quantities when benzenediazonium chloride was allowed to react, under acetone kept neutral with chalk, with mercury and antimony respectively. Both these syntheses of organometallic compounds have now been investigated more fully, with use of substituted benzenediazonium chlorides, and appear to be general reactions.

Particular attention has been paid to the reaction of diazonium chlorides with metallic antimony, and the earlier surmise (J., 1937, 2013) of the complexity of the reaction has been confirmed. Aromatic antimony compounds of three types, (a) triarylstibine dichlorides, Ar_3SbCl_2 , (b) triarylstibines, Ar_3Sb , and (c) diarylstibinous chlorides, Ar_2SbCl , have been isolated as primary products in addition to antimony trichloride. Solid diazonium chlorides do not decompose spontaneously under acetone at room temperature, but immediately powdered antimony is added reaction sets in and much heat is evolved. The aromatic antimony compounds are obtained in the best yields when the mixture is kept neutral with chalk and cooled externally, for then the slower general reaction between a diazonium chloride and acetone, $\text{Ar}\cdot\text{N}_2\text{Cl} + \text{CH}_3\cdot\text{CO}\cdot\text{CH}_3 = \text{N}_2 + \text{ArH} + \text{CH}_2\text{Cl}\cdot\text{CO}\cdot\text{CH}_3$ (A), which requires a higher temperature for initiation, is almost entirely excluded.

Under ethyl acetate also diazonium chlorides react fairly rapidly with metallic antimony, with formation, in good yield, of a similar mixture of aromatic antimony compounds. Under a number of other solvents, however, no reaction occurs until the mixture is heated to the self-decomposition temperature of the diazonium chloride; a small amount of antimony trichloride but no aromatic antimony compounds then seem to be formed. Solvents useless for the synthesis of aromatic antimony compounds by this new reaction are water and ethyl alcohol, which dissolve and dissociate diazonium chlorides, and also *cyclohexane*, benzene, carbon tetrachloride, carbon disulphide, diethyl ether, and dioxan, in all of which diazonium chlorides are insoluble.

From the complete absence of any action in water or alcohol it is evident that diazonium kations do not react with antimony, or with other metals with the possible exceptions of copper (in Gattermann's reaction) and mercury (in the reaction of McClure and Lowy, *J. Amer. Chem. Soc.*, 1931, **53**, 319). It has already been pointed out that the occurrence of reaction between diazonium chlorides and metals such as antimony, bismuth, lead, silver and tin (amongst others), in the presence of acetone, is most simply explained by supposing that diazonium chlorides, $(\text{ArN}_2)^+\text{Cl}^-$, can undergo tautomeric change to the wholly covalent, unstable diazo-form, $\text{Ar}\cdot\text{N}=\text{NCl}$, which then loses nitrogen with production of transient free neutral radicals. The new experimental fact that aromatic antimony compounds of different structural types are produced simultaneously in this reaction is in full accord with this theory, for neutral aryl radicals and chlorine atoms would be expected to combine

independently of each other with any available substance containing an uncompleted electronic shell.

The occurrence of this reaction of diazonium chlorides under acetone and ethyl acetate, but not under the other organic solvents enumerated above, is remarkable. The authors suggest tentatively that the necessary condition for occurrence of any reaction between a diazonium salt and a metal is the presence of a solvent which is able somehow to promote the tautomeric change mentioned above. Metals themselves too must be catalysts for this change or for the subsequent decomposition of the covalent diazo-chloride, since, in the absence of a metal, no reaction occurs in the cold with acetone or ethyl acetate. The hypothesis that copper is an effective catalyst for the tautomeric change of a diazonium halide molecule to an unstable diazo-halide would explain its function in the well-known reactions of Gattermann.

Acetone and ethyl acetate may perhaps be effective catalysts for the tautomeric change of the diazonium chlorides in virtue of their highly polar character. It happens that nearly all the other solvents examined as yet have been non-polar liquids, although they have widely differing chemical characters. Alternatively, acetone and ethyl acetate may promote the tautomeric change of diazonium salt molecules by dissolving slightly the isomeric non-ionic form, for obviously the chance of a reaction occurring between two solid powders (*e.g.*, benzenediazonium chloride and antimony under *cyclohexane*, which dissolves neither) is much less than that of reaction between one solid and a solute with which it can get into intimate contact.

An examination of the decomposition of diazonium chlorides under ethyl acetate has shown that there is a similarity between this solvent and acetone, for both seem to be chlorinated by diazonium chlorides. When a mixture of a diazonium chloride and ethyl acetate is not kept neutral by addition of chalk, hydrogen chloride is formed on warming and an aryl chloride is produced; *e.g.*, benzenediazonium chloride yields some chlorobenzene (Part II) and *p*-chlorobenzenediazonium chloride yields some *p*-dichlorobenzene. When, however, the decomposition is carried out in the presence of an excess of chalk, a considerable quantity of acetaldehyde is formed. This may well result from chlorination of the ethyl acetate with production of the easily hydrolysed substance α -chloroethyl acetate, the reaction $\text{Cl}\cdot + \text{CH}_3\cdot\text{CH}_2\cdot\text{O}\cdot\text{CO}\cdot\text{CH}_3 \longrightarrow \text{CH}_3\cdot\text{CHCl}\cdot\text{O}\cdot\text{CO}\cdot\text{CH}_3$ (B) being exactly analogous to the chlorination of acetone (A).

Although the decomposition of simple aryl diazonium salts under acetone and ethyl acetate in the presence of metals has not been utilised previously for the preparation of their organometallic compounds, several reactions of very similar type have been described by Nesmejanov and his colleagues (*Ber.*, 1929, **62**, 1010, 1018; 1935, **68**, 1877; *J. Gen. Chem. Russ.*, 1936, **6**, 144, 167; *Sci. Rep. Moscow State Univ.*, 1934, No. 3, 291; see *Brit. Chem. Abstr.*, 1936, **A**, 837, 1004; 1937, **A**, ii, 282), who have worked with double salts of diazonium chlorides and the chlorides of the heavy metals mercury, tin, and lead. On decomposition with metals such as copper and tin (amongst others) these double salts, which can be prepared from aqueous solutions, yield arylmercuric chlorides or mercurydiaryls, diaryltin dichlorides, Ar_2SnCl_2 , and triaryl-lead chlorides, Ar_3PbCl , respectively. Further, Dunker, Starkey, and Jenkins (*J. Amer. Chem. Soc.*, 1936, **58**, 2309) have reported that mixtures of diazonium borofluorides with mercuric chloride can be reduced under acetone with stannous chloride and yield arylmercuric chlorides in good yield. Nesmejanov (see *Brit. Chem. Abstr.*, 1937, **A**, ii, 282) seems to favour the view that the metal forming the organometallic compound is derived from the double chloride and need not be present as the free metallic element, although this may sometimes be formed during the reaction by a displacement process. However, if one adopts the hypothesis that neutral radicals are produced as the diazo-compound decomposes, one would expect these aryl radicals to attack, in the first instance, the free metal and not a stable metallic kation. Of course the organometallic compounds thereby produced might subsequently react with the metallic chloride to yield a more stable organometallic compound (compare Challenger and Ridgway, *J.*, 1922, **121**, 107).

The latter hypothesis receives strong support from the present work with metallic antimony, for the double salt decomposition method of Nesmejanov is also a satisfactory

procedure for the production of aromatic antimony compounds. Both the double antimony salts of the type $\text{ArN}_2\text{Cl}_2\text{SbCl}_3$ described by May (J., 1912, **101**, 1037) and also the better known double zinc diazonium chlorides can be decomposed under acetone with antimony and yield a mixture of organic antimony compounds exactly similar to that obtained with the simple diazonium chlorides, which are so much more difficult to prepare in the solid state. The best yields of aromatic antimony compounds have been obtained by using the double zinc diazonium chloride precipitated from an aqueous solution of an aromatic amine after its diazotisation with sodium nitrite in the usual way.

The products were best isolated from the acetone or ethyl acetate solutions by evaporating the solvent and extracting the residue with light petroleum or benzene. The triaryl-stibine dichlorides and the diarylstibinous chlorides were identified, after isolation, by quantitative hydrolysis with alcoholic potash and estimation of the liberated chloride ions. Both the triaryl-stibines and the diarylstibinous chlorides were established as being compounds of trivalent antimony by addition of chlorine in carbon tetrachloride solution. Further, the aromatic amines used—*p*-chloroaniline, *p*-bromoaniline, 4-chloro-*o*-toluidine, 5-chloro-*o*-toluidine, and 4-chloro-*o*-anisidine—although primarily chosen on the advice of Mr. K. H. Saunders for their ease of formation of pure diazonium chlorides, all contained halogen atoms as nuclear substituents, and estimation of the total halogen content of their organometallic products gave valuable confirmatory evidence of structure. From aniline, *p*-chloroaniline, and *p*-bromoaniline, the chief products were the triaryl-stibine dichlorides, but from the other bases, which contained *o*-substituents, only traces of quinquivalent antimony compounds were formed, the chief products being the triaryl-stibines accompanied by a smaller quantity of the diarylstibinous chlorides. This difference in the nature of the products may perhaps be due to steric hindrance, and, in accordance with this view, it was noticed that the substituted triaryl-stibines which were obtained did not react rapidly with halogens.

EXPERIMENTAL.

The substituted diazonium chlorides were prepared by diazotising, with amyl nitrite, a suspension of the dry hydrochloride of the requisite base in absolute alcoholic hydrogen chloride at 0–10° and treating the resulting clear solution with anhydrous ether (compare Knoevenagel, *Ber.*, 1890, **23**, 2995). With the exception of the salt obtained from 4-chloro-*o*-toluidine, the diazonium chlorides were strongly hygroscopic. They were thoroughly washed with the solvent to be employed and then used immediately.

Reactions of Substituted Diazonium Chlorides with Acetone.—(i) *Decomposition in absence of chalk.* 20 G. of *p*-chlorobenzenediazonium chloride were covered with 100 c.c. of acetone. No reaction occurred in the cold, but at 50° nitrogen and hydrogen chloride were evolved. On fractionation the resulting mixture yielded 1 g. of pure chlorobenzene and 3 g. of chloroacetone (semicarbazone, m. p. 147·5°).

(ii) *Decomposition in presence of chalk.* The same quantities were used together with 20 g. of precipitated chalk. The product gave 1·5 g. of chlorobenzene and 6 g. of chloroacetone. *p*-Dichlorobenzene was not detected in either experiment.

p-Bromobenzenediazonium chloride (from 26 g. of the amine hydrochloride), decomposed in acetone containing chalk, gave 10·5 g. of chloroacetone and 7·9 g. of bromobenzene (identified by conversion into *p*-bromonitrobenzene, m. p. and mixed m. p. 126°).

(iii) *Decomposition in presence of lead, silver, and bismuth.* To separate portions of 5 g. of *p*-chlorobenzenediazonium chloride under 100 g. of acetone containing 5 g. of chalk were added (a) 20 g. of lead filings, (b) 5 g. of silver powder, and (c) 10 g. of precipitated bismuth. In each case reaction set in in the cold, and was completed by refluxing for $\frac{1}{2}$ hour. After cooling, each solution was filtered. The residue from (a) was extracted with hot water, but no lead chloride was removed. However, a solution containing lead ions in quantity was obtained by warming the insoluble residue with dilute acetic acid and filtering.

The residue from (b) was extracted with warm dilute aqueous ammonia; the filtered extract gave, on acidification with nitric acid, 1·3 g. of silver chloride.

The residue from (c) was extracted with warm dilute acetic acid, but did not yield a solution containing bismuth ions. The acetone solution, however, when evaporated, left a tarry residue which, on extraction with dilute hydrochloric acid, gave a solution containing bismuth ions in quantity.

(iv) *Reaction with mercury.* 15 G. of *p*-chlorobenzenediazonium chloride were shaken under

100 c.c. of acetone with 30 g. of mercury and 20 g. of chalk and the reaction was completed by warming for $\frac{1}{2}$ hour. After cooling, the solid was removed by filtration and found to contain both mercurous and mercuric salts. The filtrate on evaporation yielded 1.5 g. of *p*-chlorophenylmercuric chloride, m. p. 241° (Found: Hg, 57.7; total Cl, 20.4. Calc.: Hg, 57.6; total Cl, 20.4%). Hanke (*J. Amer. Chem. Soc.*, 1923, **45**, 1321) gives m. p. 225° , and Nesmejanov (*Ber.*, 1929, **62**, 1010) m. p. 240° .

From *p*-bromobenzenediazonium chloride, 0.8 g. of *p*-bromophenylmercuric chloride, m. p. 248° , was obtained by a similar method.

Reactions of Diazonium Chlorides with Ethyl Acetate.—(i) *Decomposition in presence of chalk.* 20 G. of *p*-chlorobenzenediazonium chloride were added to 200 c.c. of purified ethyl acetate and 20 g. of chalk. Reaction set in at 60° and the mixture became red. After refluxing for $\frac{1}{2}$ hour, the mixture was cooled, and the filtered liquid fractionated. The ethyl acetate fraction, b. p. $75-80^\circ$, contained acetaldehyde in sufficient quantity for the preparation of its 2:4-dinitrophenylhydrazone, m. p. and mixed m. p. 161° . A small quantity of yellowish oil, distilling between 100° and 160° , contained hydrolysable chlorine and had an acidic reaction. No chlorobenzene, however, was detected. The remainder was distilled under reduced pressure and yielded 0.4 g. of pure *p*-dichlorobenzene, m. p. and mixed m. p. 53.5° .

(ii) *Decomposition in presence of lead, silver, and bismuth.* To separate portions of *p*-chlorobenzenediazonium chloride in ethyl acetate containing chalk were added powdered lead, silver, and bismuth. In each case reaction set in in the cold and was completed by refluxing, some acetaldehyde being evolved. The solutions were then cooled and filtered. The residue from the reaction with lead was extracted with hot water; the extract yielded lead chloride. The filtrate from this reaction, when distilled, gave a fraction, b. p. $100-125^\circ$, containing acetaldehyde and hydrogen chloride.

The residue from the reaction with silver was extracted with warm dilute aqueous ammonia; the extract on acidification gave silver chloride. The filtrate from this reaction, on fractionation, gave a portion, b. p. $100-145^\circ$, acid to litmus, containing acetaldehyde, hydrogen chloride and acetic acid. The filtrate from the reaction with bismuth deposited bismuth oxychloride on evaporation.

The Influence of Solvents on the Reaction of Benzenediazonium Chloride with Metallic Antimony.—(i) *Acetone.* A simpler method for isolating the reaction product, Ph_3SbCl_2 , than that described in Part II was to evaporate the acetone solution to dryness and extract the residue with light petroleum (b. p. $60-80^\circ$). This established that the triphenylstibine dichloride was a primary reaction product. No other aromatic antimony compounds were isolated.

(ii) *Water.* 0.2 G.-mol. of aniline was diazotised in 300 c.c. of 3*N*-hydrochloric acid at 0° and 20 g. of antimony powder were then added to the vigorously stirred liquid. The antimony did not react and, after warming, only phenol was obtained.

(iii) 6 G. of benzenediazonium chloride, 5 g. of sieved antimony powder, and 5 g. of chalk were mixed under 50 g. of absolute ethyl alcohol. There was no reaction in the cold, but, on warming, acetaldehyde was evolved. After cooling, the liquid was filtered; it did not contain any aromatic antimony compound.

The above experiment was repeated with cyclohexane, benzene, carbon tetrachloride, carbon disulphide, diethyl ether, and dioxan. In no case did any reaction occur in the cold. After decomposition by heat (except in the case of the ether mixture, which could be refluxed without change) a tarry mass resulted, from which traces of inorganic antimony compounds but no aromatic antimony compounds could be isolated. When carbon disulphide was used, a little diphenyl disulphide was formed (compare Parts I and III).

Preparations of Organic Antimony Compounds from Substituted Benzenediazonium Chlorides.—

(i) 20 G. of *p*-chloroaniline hydrochloride were converted into the solid diazonium chloride, which was then mixed with 20 g. of chalk and 200 c.c. of acetone. On addition of 30 g. of antimony powder a vigorous reaction ensued and the acetone boiled. After reaction had subsided, the mixture was refluxed for $\frac{1}{2}$ hour, filtered hot, and the residue extracted with more warm acetone. The filtrate was evaporated to dryness, and the residue extracted with light petroleum (b. p. $60-80^\circ$). On cooling, colourless needles of *tri-p-chlorophenylstibine dichloride* (1.4 g.) separated, m. p. 193° (Found: Sb, 23.0; hydrolysable Cl, 13.4. $\text{C}_{18}\text{H}_{12}\text{Cl}_2\text{Sb}$ requires Sb, 23.1; hydrolysable Cl, 13.4%).

When ethyl acetate was used as the solvent, the reaction was not so vigorous, but the same product was isolated in an identical yield.

(ii) The diazonium salt from *p*-bromoaniline hydrochloride (26 g.) reacted similarly in each solvent. In ethyl acetate, *tri-p-bromophenylstibine dichloride* (4.1 g.), m. p. 200° , was obtained;

in acetone the yield was 3.0 g. (Found: Sb, 18.5; hydrolysable Cl, 10.3. $C_{18}H_{12}Cl_2Br_3Sb$ requires Sb, 18.3; hydrolysable Cl, 10.7%).

(iii) The solid diazonium chloride from 4-chloro-*o*-toluidine hydrochloride (20 g.) was allowed to react, in the cold, with antimony powder in acetone containing chalk. After refluxing, the solid residue was thoroughly extracted with acetone; when the combined extracts were evaporated, *tri*-(4-chloro-*o*-tolyl)stibine (6.1 g.) separated, which crystallised from benzene in long matted needles, m. p. 226° (Found: Sb, 24.4; total Cl, 21.5; hydrolysable Cl, 0. $C_{21}H_{18}Cl_3Sb$ requires Sb, 24.4; total Cl, 21.4%).

When ethyl acetate was used as the solvent, *tri*-(4-chloro-*o*-tolyl)stibine (5.6 g.) was obtained and also a small quantity of the more soluble di-(4-chloro-*o*-tolyl)stibinous chloride (see below).

(iv) The diazonium chloride from 5-chloro-*o*-toluidine reacted similarly to its isomer. The products were crystallised first from ethyl acetate containing alcohol and finally from light petroleum. *Tri*-(5-chloro-*o*-tolyl)stibine, which formed fine needles, m. p. 176°, was obtained both with acetone and with ethyl acetate (Found: Sb, 24.45; total Cl, 21.5; hydrolysable Cl, 0. $C_{21}H_{18}Cl_3Sb$ requires Sb, 24.4; total Cl, 21.4%). From the ethyl acetate reaction there was isolated also a small quantity of *tri*-(5-chloro-*o*-tolyl)stibine dichloride. This was also prepared by treating the corresponding stibine with chlorine in carbon tetrachloride solution. It crystallised from light petroleum in prisms, m. p. 238° (Found: Sb, 21.5. $C_{21}H_{18}Cl_5Sb$ requires Sb, 21.4%).

(v) Similar reactions were carried out, acetone and ethyl acetate being used, with the diazonium salt from 4-chloro-*o*-anisidine hydrochloride. After removal of the solvents, the products were washed with dilute hydrochloric acid and with methyl alcohol to remove antimony chloride and tar, and then crystallised successively from ethyl acetate, alcohol, and light petroleum. From the reaction in acetone there was obtained *di*-(5-chloro-2-methoxyphenyl)stibinous chloride, m. p. 144° (Found: Sb, 27.3; hydrolysable Cl, 8.1. $C_{14}H_{12}O_3Cl_3Sb$ requires Sb, 27.0; hydrolysable Cl, 8.05%). It reacted slowly with solutions of chlorine and bromine in carbon tetrachloride.

From the reaction in ethyl acetate there were obtained *tri*-(5-chloro-2-methoxyphenyl)stibine, m. p. 188° (Found: Sb, 22.2; hydrolysable Cl, 0. $C_{21}H_{18}O_3Cl_3Sb$ requires Sb, 22.2%), and also a little *tri*-(5-chloro-2-methoxyphenyl)stibine dichloride, m. p. 281° (decomp.) (Found: Sb, 19.7. $C_{21}H_{18}O_3Cl_5Sb$ requires Sb, 19.7%). The latter compound was also obtained by treating the corresponding stibine with chlorine in carbon tetrachloride solution.

Use of the Antimony Chloride Double Salt.—From 20 g. of aniline, May's double salt of benzenediazonium chloride and antimony chloride was prepared from aqueous solution, washed with acetone, and added to 30 g. of antimony powder and 20 g. of chalk in 200 c.c. of acetone cooled in ice. After the vigorous reaction had subsided, the mixture was refluxed for $\frac{1}{2}$ hour, and the filtered liquid evaporated. The residue was crystallised from alcohol containing some hydrochloric acid and yielded 3.5 g. of triphenylstibine dichloride, m. p. 143°.

Use of Zinc Chloride Double Salts.—(i) 20 G. of aniline were diazotised in aqueous solution (100 c.c.) and the crystalline double zinc diazonium chloride was precipitated by the addition of a concentrated solution of zinc chloride. This was washed with acetone and added to antimony and chalk under acetone. After the reaction had subsided, the mixture was refluxed for $\frac{1}{4}$ hour and cooled; after filtration, the residue was washed with more acetone. The acetone solution was evaporated, and the residue redissolved in alcohol containing some hydrochloric acid; on cooling, triphenylstibine dichloride (8.5 g.) separated.

(ii) 40 G. of 4-chloro-*o*-toluidine hydrochloride were diazotised in 100 c.c. of 3*N*-hydrochloric acid and the filtered diazonium salt solution was added to a concentrated solution of zinc chloride. The precipitated double salt was collected, washed with acetone, and added to 40 g. of antimony powder and 30 g. of chalk in 250 c.c. of acetone. Reaction was completed by refluxing for $\frac{1}{2}$ hour. After cooling, the liquid was filtered, and the residue washed with cold acetone. The acetone solution was evaporated to dryness, leaving a residue, which was extracted first with light petroleum and then with benzene. From the petroleum solution 7 g. of *di*-(4-chloro-*o*-tolyl)stibinous chloride, m. p. 131°, were obtained (Found: Sb, 29.8; hydrolysable Cl, 8.9. $C_{14}H_{12}Cl_3Sb$ requires Sb, 29.8; hydrolysable Cl, 8.7%). This slowly decolorised bromine in carbon tetrachloride solution; with chlorine in carbon tetrachloride solution it yielded *di*-(4-chloro-*o*-tolyl)stibinic trichloride, m. p. 162° (Found: Sb, 25.5. $C_{14}H_{12}Cl_5Sb$ requires Sb, 25.4%). From the benzene extract was isolated 0.2 g. of *tri*-(4-chloro-*o*-tolyl)stibine dichloride, m. p. 264° (Found: Sb, 21.1. $C_{21}H_{18}Cl_5Sb$ requires Sb, 21.4%). This was also obtained by treating the corresponding stibine with chlorine in warm carbon tetrachloride solution. It crystallised from carbon tetrachloride, but was sparingly soluble in petrol.

The residue containing the excess of antimony and the chalk was also extracted (Soxhlet) with acetone. 12 G. of tri-(4-chloro-*o*-tolyl)stibine, m. p. 226° (see above), were obtained.

A zinc chloride double salt could not be obtained from diazotised 5-chloro-*o*-toluidine.

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