The action of antimony trichloride upon diazotised diamines / by W.H. Gray.

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Gray, William Herbert.
Wellcome Chemical Research Laboratories.

Publication/Creation

London : Wellcome Chemical Research Laboratories, [1926.]

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No. 208

THE ACTION OF ANTIMONY TRICHLORIDE UPON DIAZOTISED DIAMINES

m2022

BY

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(From the Transactions of the Chemical Society, 1926)

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Reprinted from the Journal of the Chemical Society, 1926.

CCCCXXIX.—*The Action of Antimony Trichloride upon Diazotised Diamines.*

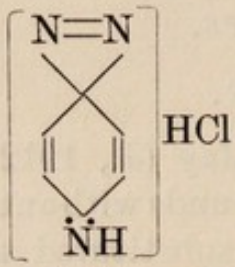
By William Herbert Gray.

Certain diazonium chlorides were found by May (J., 1912, **101**, 1037) to form insoluble crystalline additive compounds with antimony trichloride. Compounds containing amino- or substituted amino-groups were not investigated. Some of these have now been prepared and found to show two features of interest. They have special properties due to intramolecular condensation between the amino- and the diazo-group; secondly, the whole of the antimony can be removed from them, leaving the organic portion undecomposed. Their small solubility, together with this latter fact, has provided a means of isolating substances such as p-*acetylaminobenzenediazonium chloride* and the *hydrochloride* of the hypothetical *p*-diazoiminobenzene, hitherto undescribed.

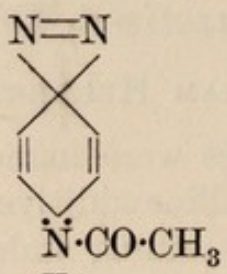
The only salt of *p*-aminodiazobenzene that has been analysed seems to be a chromate, first obtained indirectly by Meldola and Williams (P., 1899, **15**, 196) from *p*-nitrobenzeneazophenol. To this was assigned the formula $NH_2 \cdot C_6H_4 \cdot N_2 \cdot HCrO_4$ (Meldola and Eynon, J., 1905, **87**, 3), although it separated from solution in excess of acetic or sulphuric acid, the presence of a free amino-group under such unlikely conditions being passed over without comment. The same peculiarity is now met with in an antimony trichloride compound and the diazo-compound obtained from it as above. Diazotised acetyl-*p*-phenylenediamine yields with antimony trichloride an almost colourless, crystalline precipitate (see p. 3177) consisting mainly of *di*-(p-*acetylaminobenzenediazonium chloride*)–*antimony trichloride*, $(CH_3 \cdot CO \cdot NH \cdot C_6H_4 \cdot N_2Cl)_2,SbCl_3$ (I). This is immediately transformed by boiling dilute hydrochloric acid into a bright yellow substance, with an empirical formula corresponding to $NH_2 \cdot C_6H_4 \cdot N_2Cl,SbCl_3$ (II), which crystallises from the excess of acid. Water decomposes this into insoluble basic antimony chlorides and a strongly acid solution, from which is obtained by evaporation a yellow substance with an empirical formula corresponding to $NH_2 \cdot C_6H_4 \cdot N_2Cl$ (III), instead of the expected hydrochloride, $HCl,NH_2 \cdot C_6H_4 \cdot N_2Cl$.

Formula (III) is inadequate: since acidic substituents are absent, it does not explain this lack of salt formation; further, it does not account for the yellow colour. The latter suggests a quinonoid arrangement (IV) such as is given to acyl-*p*-diazoimides (V) by Morgan and his collaborators (compare Morgan and Cleage, J., 1918, **113**, 588; Morgan and Upton, J., 1917, **111**, 195), but it remains

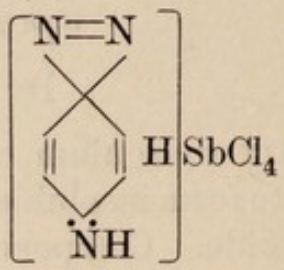
to reconcile this with the pronounced stability of the substance. In the first place the formation in presence of hydrochloric acid is



(IV.)



(V.)



(VI.)

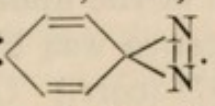
in marked contrast to the immediate reversion to diazonium salt which is effected by this reagent in the cases studied by Morgan. There is, in fact, a certain amount of evidence that in hydrochloric acid solution very little, if any, diazonium salt is present, for solutions in acetic or hydrochloric acid at 100° slowly evolve nitrogen at approximately the same rate, whereas from the following considerations formation of a diazonium salt in the latter should be indicated by a more rapid evolution of nitrogen. Replacement of hydrochloric acid by acetic acid in the case of benzenediazonium chloride is without influence on the decomposition (Cain, *Ber.*, 1905, **38**, 2511), but a diazotised acetic acid solution of acetyl-*p*-phenylenediamine decomposes on heating much more rapidly than a diazotised hydrochloric acid solution (Cain and Nicoll, J., 1902, **81**, 1436). No explanation of this was suggested by Cain; in the light of the present work, it is reasonable to infer that his acetic acid solution contained diazonium salt, and the other, diazoimine salt.

It must be concluded, then, that in the absence of the acyl groups or acidic nuclear substituents which occur in Morgan's compounds, the combined basic influence of the quinonoid imino-group and the group $>C<^{N}_{N}$ suffices to permit the formation of a stable diazoimine salt with one molecule of acid. An example of this phenomenon from a different class of compounds has been described by Morgan and Reilly (J., 1914, **105**, 436): 4-Amino-3 : 5-dimethylpyrazole, a diacidic base yielding a dihydrochloride, furnishes after diazotisation only a monohydrochloride. The authors attribute this to the strengthening of one salt-forming centre at the expense of the other —an explanation which appears to cover the case of *p*-diazoiminobenzene also. Willstätter and Mayer (*Ber.*, 1904, **37**, 1494) have shown that the quinonoid imino-group itself is weakly basic; p-*diazoiminobenzene hydrochloride* (IV), on the other hand, is neutral to litmus. Introduction of an acetyl group into this leads to the formation, not of a yellow acetyl compound, that is, the hydrochloride of Morgan's base (V), but of a colourless substance identical with the one obtained by the removal of antimony from (I), namely,

p-*acetylaminobenzenediazonium chloride*, $CH_3{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}N_2Cl$ (VII).

The stability of (IV) and of p-*diazoiminobenzene hydrochloride–antimony trichloride* (VI) to another change, the loss of diazo-nitrogen, also supports the quinonoid formula. Both remain unchanged for an indefinite period in the solid state (in the dark) and the latter can be repeatedly crystallised from boiling hydrochloric acid. *Di*-(m-*acetylaminobenzenediazonium chloride*)-*antimony trichloride*, $(CH_3{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}N_2Cl)_2,SbCl_3$ (VIII), from diazotised acetyl-*m*-phenylenediamine, on the other hand, in which no quinonoid configuration is to be looked for, decomposes spontaneously in a few days to a tar, and immediately on warming with acid; that this is the normal behaviour is seen from benzenediazonium chloride–antimony trichloride, prepared for comparison, which was found to be equally unstable.

Schmidt and Hofmann (*Ber.*, 1926, **59**, 555) attribute the yellow colour of the diazotised aminophenylstibine dichlorides obtained by them to a bridge of residual affinity, $Cl_2Sb{\cdot}C_6H_4{\cdot}N_2Cl$. It is clear that such a formulation is inapplicable to the compounds now under discussion, since the yellow colour persists after removal of the antimony.

Attempts to obtain the free base, *p*-diazoiminobenzene, from (IV) were unsuccessful. Addition of a trace of alkali caused immediate evolution of nitrogen and formation of dark-coloured products; treatment in suspension in non-aqueous media with silver oxide led to similar results, and addition of an aqueous suspension of ferric hydroxide was without effect. The corresponding antimony compound (VI) behaved similarly when treated with alkali, and no substance with the properties of a stibinic acid was obtained from the tarry reaction mixture. The acetylated antimony compound (I), on the other hand, yielded sodium *p*-acetylaminophenylstibinate, thus falling into line with May's compounds (compare D.R.-P. 261825). The considerable stability of the hydrochloride (IV) thus accompanies great instability of the base. Morgan and Micklethwait (J., 1908, **93**, 606) have shown that the stability of diazoimines of the type $C_6H_{5-n}(NO_2)_n{\cdot}N{:}C_6H_4N_2$ diminishes with n. The least stable member of their series ($n = 0$) was the compound prepared by Ikuta (*Annalen*, 1888, **243**, 282) by the action of sodium hydroxide upon diazotised *p*-aminodiphenylamine, and considered by Hantzsch (*Ber.*, 1902, **35**, 895) to be phenyl-*p*-phenylenediazoimine, $C_6H_5{\cdot}N{:}$  . Ikuta's compound, however, only gradually decomposed in solution; *p*-diazoiminobenzene, in which acidic

substituents have been entirely removed, is therefore still less stable.

The acetylation of (IV) with acetic anhydride, already mentioned, takes place only in bright sunlight. If concentrated sulphuric acid is added, this is not necessary, but the acetylated product is a sulphur-containing diazonium *compound*, $C_{10}H_{13}O_5N_3S$. This is neutral, but is not a sulphate. Sulphuric acid is, however, slowly set free on boiling with dilute hydrochloric acid. The sulphur is immediately removed by various reagents (p. 3180) with formation of derivatives of *p*-acetylaminodiazobenzene.

Experimental.

*The Action of Antimony Trichloride on Diazotised Acetyl-*p*-phenylenediamine.*—Acetyl-*p*-phenylenediamine (22·5 g.) was dissolved in a previously warmed mixture of 40% hydrochloric acid (36 c.c.) and water (465 c.c.), and the solution, after decoloration, was rapidly cooled to 12—14° and diazotised during 1 hour with sodium nitrite (10·5 g.) in water (150 c.c.). When diazotisation was carried out below 5°, a considerably poorer yield of antimony compound was obtained. Ice-cold 40% hydrochloric acid in excess (166 c.c.) was then added, followed by a filtered solution of antimony trioxide (19·7 g.) in 40% hydrochloric acid (49 c.c.), with vigorous stirring. A pale brown, crystalline precipitate separated, and was dried on a porous tile in the air until free from hydrochloric acid (yield, 38 g.). By adding the antimony trichloride in several portions, fractions differing in colour could be obtained; the last was very light-coloured, but although homogeneous in appearance, its antimony content and melting point, together with the action of methyl alcohol upon it (see below), showed that it was a mixture of the two compounds (I) and (VI), the former greatly predominating. No separation could be effected by straightforward fractional crystallisation; they were separated as described below. A certain amount of hydrolysis and diazoimine formation evidently occurs during the diazotisation. Sodium hydroxide in slight excess caused a characteristic decomposition with frothing and formation of sodium *p*-acetylaminophenylstibinate.

Di-(p-*acetylaminobenzenediazonium Chloride*)*–Antimony Trichloride* (I).—The pale-coloured fraction (see above) was extracted several times with cold methyl alcohol, which removed bright yellow material, raised the melting point, and lowered the antimony content from 22% to 20%. By a single recrystallisation of the undissolved portion from boiling methyl alcohol, the substance was obtained quite pure in colourless, square plates, m. p. 147° (corr.) (Found: Sb, 19·5; Cl, 28·8. $C_{16}H_{16}O_2N_6Cl_5Sb$ requires Sb, 19·5; Cl, 28·4%).

p-*Acetylaminobenzenediazonium Chloride* (VII).—This was prepared from the foregoing compound by the action of water, or more advantageously from the crude antimony chloride precipitate. In the latter case, the yellow (hydrolysed) impurity could be retained in solution if sufficient alcohol were used in the precipitation. After grinding the crude substance (10 g.) with water (50 c.c.) and filtering, the pale yellow filtrate was treated with alcohol (200 c.c.), kept for a short time to precipitate a small amount of finely-divided solid, and filtered through charcoal. It was then treated with a further 200 c.c. of alcohol and 1370 c.c. of ether; thereafter the compound separated in white, lustrous leaflets, m. p. 131° (corr.), readily soluble in water to a colourless neutral solution, becoming yellow on boiling, with liberation of acetic acid. It is soluble in alcohol, and insoluble in chloroform or cold acetone, the latter giving a deeply coloured solution when warmed. On drying over sulphuric acid at the ordinary temperature the substance retained $\frac{3}{4}$ mol. of water of crystallisation, most of which was lost at 40° in a vacuum over phosphorus pentoxide (Found: N, 20·6; Cl, 17·6; atomic ratio N : Cl = 2·96 : 1. $C_8H_8ON_3Cl$ requires N, 21·3; Cl, 17·95%).

p-*Diazoiminobenzene Hydrochloride–Antimony Trichloride.*—The above crude antimony trichloride precipitate (20 g.) was finely ground and suspended in 10% hydrochloric acid (200 c.c.), heated rapidly to boiling, and boiled for 5 minutes; long, yellow needles then separated from the boiling solution. Yield, 12·4 g.; m. p. 179° (corr.) with sudden decomposition. Use of stronger hydrochloric acid gave a poorer yield. Occasionally the same substance separated in thin, bright yellow plates. It is sparingly soluble in ethyl alcohol or acetic acid, more readily soluble in methyl alcohol or formic acid, from which it crystallises unchanged, readily soluble in aqueous tartaric acid solution, and dissolves with frothing and darkening in sodium hydroxide solution (Found: C, 19·05; H, 1·9; N, 10·9; Cl, 37·1; Sb, 31·8. $C_6H_6N_3Cl_4Sb$ requires C, 18·8; H, 1·6; N, 10·95; Cl, 36·95; Sb, 31·7%).

p-*Diazoiminobenzene Hydrochloride* (IV).—The foregoing antimony compound (16·4 g.) was ground with successive small portions of water (170 c.c. in all) until the water was no longer coloured, and the water-bright extract evaporated at low pressure, the bath being at 60—70°. An orange-coloured paste of small, rectangular plates remained, which was dissolved in warm alcohol (50 c.c.). On cooling, large, yellow, rectangular plates (4·7 g.) separated, m. p. 119° (corr.), still retaining 1 mol. of water even on further recrystallisation from alcohol or precipitation by ether. This water is lost on drying at 60° in a vacuum over phosphorus pentoxide, after which the substance explodes sharply at 155° (corr.). It is extremely soluble

in water to a bright yellow, neutral solution, fairly readily soluble in acetic acid, rather sparingly soluble in alcohol, and insoluble in acetone. Strong daylight decomposes the solid, which becomes black and insoluble in water, but it is stable in the dark. A solution in 10% hydrochloric acid gives an immediate precipitate of large, yellow needles (VI) with antimony trichloride. The aqueous solution remains unchanged at the ordinary temperature for a long period (Found : N, 24·3; Cl, 20·5; atomic ratio N : Cl = 3·0 : 1; atomic ratio after drying, N : Cl = 3·0 : 1. $C_6H_6N_3Cl,H_2O$ requires N, 24·2; Cl, 20·4%). It couples slowly and to a slight extent with R-salt (compare the hydrolysed solution of diazotised acetyl-*p*-phenylenediamine, D.R.-P. 205037, which doubtless contains this substance), but immediately to a chocolate-coloured solid with alkaline β-naphthol. The action of alkali alone led to immediate effervescence and the formation of a black solid, which was not further investigated.

Picrate. By mixing aqueous solutions of the foregoing salt and picric acid, glistening plates were obtained, exploding at 160° (corr.), burning rapidly but quietly on a heated spatula, and remaining unaltered by crystallisation from alcohol. It is sparingly soluble in boiling alcohol or acetone (Found : N, 23·9. $C_{12}H_8O_7N_6$ requires N, 24·1%). The same picrate was obtained from a solution of the antimony compound (VI) in tartaric acid.

Chromate. On the addition of chromic acid to an aqueous solution of the hydrochloride, rectangular plates separated, exploding violently at 160° (corr.), insoluble in alcohol, soluble with darkening in glacial acetic acid. It could be recrystallised from water (Found : Cr, 22·3. $C_6H_7O_4N_3Cr$ requires Cr, 21·9%). The chromate described by Meldola and Eynon (p. 3174) exploded feebly at 144—148° and contained Cr, 21%. The above is doubtless the same substance in a purer state.

Acetylation of p-*diazoiminobenzene hydrochloride.* (a) *With acetic anhydride.* No action took place in the cold, in the dark or in diffused light, when *p*-diazoiminobenzene hydrochloride was suspended in acetic anhydride for several weeks, either alone or in presence of pyridine; warming caused decomposition and darkening. When an acetic acid solution was kept with excess of acetic anhydride in the cold, the molecule of water of crystallisation (p. 3178) was removed, but no acetylation took place. If, however, the suspension in acetic anhydride (28 c.c.) was kept in bright sunlight, the solid (5·6 g.) gradually dissolved, a pale brown, clear solution being obtained in about 8 hours. After treatment with charcoal, this was cooled in ice, treated with ice-cold alcohol (28 c.c.), and immediately with 450 c.c. of ether. A small amount of dark oil

was first precipitated, and removed as quickly as possible by repeatedly decanting the solution into fresh flasks. When no more oil separated, the solution was set aside to cool. Colourless needles separated, not depressing the melting point of (VII) (Found : Cl, 17·9. $C_8H_8ON_3Cl$ requires Cl, 17·95%).

(b) *With acetic anhydride and sulphuric acid.* *p*-Diazoiminobenzene hydrochloride (1 g.) was suspended in acetic anhydride (16 c.c.), and concentrated sulphuric acid (0·33 c.c. = 1·1 mols.) added drop by drop. The temperature was allowed to rise slightly. After 15 minutes, the clear, pale red solution was poured into dry ether (65 c.c.) and the crystalline precipitate was thoroughly washed with ether (yield, 1·4 g.) and recrystallised from alcohol–acetic anhydride, from which it separated in lustrous, colourless needles (see p. 3177), m. p. 140° (corr.; decomp.) (Found : C, 41·7; H, 4·8; N, 14·7; S, 11·2. $C_{10}H_{13}O_5N_3S$ requires C, 41·8; H, 4·6; N, 14·6; S, 11·1%). A solution in cold 10% hydrochloric acid gave a white, sulphur-free, crystalline precipitate with antimony trichloride, immediately changed on warming to *p*-diazoiminobenzene hydrochloride–antimony trichloride. It also gave a bright red, sulphur-free azo-compound with β-naphthol. The same sulphur compound was obtained more conveniently from the crude antimony chloride compound of diazotised acetyl-*p*-phenylenediamine in a similar way; 2 mols. of sulphuric acid were here necessary for complete solution, and the ether precipitate was free from antimony.

The following two substances were obtained from it.

p-*Acetylaminobenzenediazonium Chromate.*—The sulphur compound (1·4 g.) was dissolved in water (28 c.c.) and treated with 80% chromic acid solution (0·6 c.c.). Dark yellow prisms (0·9 g.) separated which melted at 136° (corr.) with mild explosion. The substance was free from sulphur (Found : Cr, 18·4. $C_8H_9O_5N_3Cr$ requires Cr, 18·6%).

p-*Acetylaminobenzenediazonium Picrate.*—Solutions of the sulphur compound and picric acid in alcohol were mixed and treated with a little ether. Rosettes of needles quickly separated, m. p., with slight explosion, 146·5° (corr.). The substance was free from sulphur (Found : N, 21·3. $C_{14}H_{10}O_8N_6$ requires N, 21·6%).

Di-(m-*acetylaminobenzenediazonium Chloride*)*-Antimony Trichloride.*—Acetyl-*m*-phenylenediamine hydrochloride, prepared by the method of Wallach and Schulze (*Ber.*, 1882, **15**, 3020), was readily obtained pure by two recrystallisations from water; m. p. 259° (corr.). 3·7 G. of this were dissolved in a mixture of water (47 c.c.) and 40% hydrochloric acid (3 c.c.) and diazotised at 0° during 1 hour with sodium nitrite (1·4 g.). An ice-cold mixture of water (50 c.c.) and 40% hydrochloric acid (28 c.c.) was then added, followed by a

filtered solution of antimony trioxide (3 g.) in 40% hydrochloric acid (7·4 c.c.). The antimony compound separated in yellow platelets, m. p. 94° (corr.) with slight explosion. When treated with water, this gave an amorphous, white precipitate, the suspension giving an immediate deep red colour with R-salt and darkening with frothing on the addition of alkali. Unlike the *p*-acetyl compound, it cannot be crystallised from dilute hydrochloric acid, being at once decomposed on heating, nor dried at 60°, which changes it to a tar. On heating the aqueous suspension, aniline was detected in the steam. For analysis, it was dried on a tile in a desiccator for 2 hours (Found : Sb, 19·5. $C_{16}H_{16}O_2N_6Cl_5Sb$ requires Sb, 19·5%). After several days in the dark at room temperature, it decomposes to a dark, frothing tar.

m-*Acetylaminobenzenediazonium Chromate.*—The foregoing compound (1·25 g.) was ground with several small portions of ice-cold water, and the clarified extract precipitated with cold aqueous chromic acid. Clusters of yellow plates (0·5 g.) separated. After drying in the desiccator, these exploded violently when pressed by a spatula, or even on the addition of cold ammonia solution. In a comparative test, a small quantity of this compound detonated when heated on a spatula and the corresponding *p*-compound (see above) burned rapidly but quietly (Found : Cr, 19·5. $C_8H_9O_5N_3Cr$ requires Cr, 18·6%).

Analytical.—The estimation of antimony in organic compounds by oxidation with permanganate followed by iodometric titration (Fargher and Gray, *J. Pharm. Expt. Ther.*, 1921, **18**, 356; compare Gray, J., 1923, **123**, 641) has now been improved and shortened by the use of oxalic acid to remove the manganese oxides and urea to remove nitrous acid. 0·2 G. of the substance, mixed with powdered potassium permanganate (3 g.), is treated with 50% sulphuric acid (15 c.c.) and then gradually with concentrated sulphuric acid (15 c.c.). The mixture is diluted with water (15 c.c.), boiled gently for 5 minutes, and decolorised with saturated oxalic acid solution. It is then diluted to 120 c.c., urea (1 g.) and potassium iodide (2·5 g.) are added, and the liberated iodine is determined by thiosulphate after 15 minutes' standing. Towards the end, the liquid should again be diluted considerably with water; the yellow colour, not due to iodine, which otherwise persists past the end-point, is thus destroyed.

Chlorine. After a number of methods had been tried for the determination of chlorine in presence of antimony in these compounds, the following was found to be the only practicable one. The substance (0·2 g.) is mixed with a little water and potassium permanganate (1 g.) in a small flask containing a tube of concentrated sulphuric acid. The

flask is then connected to absorption bulbs containing potassium iodide solution, the tube of sulphuric acid emptied by tilting, and the flask heated until all the chlorine has been evolved. A small correction, found from a control experiment on a substance of known chlorine content, is applied.

The author wishes to thank Dr. T. A. Henry for the kind interest he has taken in the work, and also Mr. A. Lovecy for help in the preparation and analysis of the products described.

THE WELLCOME CHEMICAL RESEARCH LABORATORIES,
LONDON. [*Received, October 1st*, 1926.]

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BUNGAY, SUFFOLK.