CXX.—*Researches on Sulphuryl Chloride. Part II. A New Chlorinating Agent: Preparation of Polychloro-derivatives of Benzene.*

By Oswald Silberrad.

The new reagent consists essentially of a solution of sulphur monochloride in sulphuryl chloride, which, when brought into contact with aluminium chloride, gives rise to an aluminium sulphur chloride having the composition $Al_2S_2Cl_8$; this compound, in the presence of sulphuryl chloride, possesses the most remarkable chlorinating properties. In practice, it is not necessary to isolate the aluminium sulphur chloride; indeed, chlorination by its aid is most easily effected by allowing the solution of sulphur chloride in sulphuryl chloride to act on the compound to be chlorinated in the presence of aluminium chloride. In this manner, any degree of chlorination can be brought about. Thus chlorobenzene is readily converted into di-, tetra-, or hexa-chlorobenzene, according to the amount of sulphuryl chloride added, the operation being conveniently carried out on an ordinary water-bath. The activity of this reagent is the more remarkable when it is remembered that benzene may be boiled with pure sulphuryl chloride almost indefinitely without any appreciable quantity even of monochlorobenzene being produced (compare Dubois, *Z. Chem.* von Beilstein and Fritz Hübner, 1866, **2**, 705; Töhl and Eberhard, *Ber.*, 1893, **26**, 2941). The reactions involved appear to be rather complex; in the first place aluminium chloride dissolves in excess of sulphuryl chloride with evolution of chlorine and formation of the compound $AlCl_3{:}SO_2$, for which the name aluminium chlorosulphoxide is suggested (compare Adrianowsky, *Ber.*, 1879, **12**, 688; Ruff, *Ber.*, 1902, **35**, 4453). On adding sulphur to this solution, Ruff (*Ber.*, 1901, **34**, 1749) obtained sulphur mono-, di-, or tetra-chloride according to the temperature to which the reacting materials were allowed to rise. If, however, sulphur or sulphur monochloride be brought into contact with a fairly concentrated solution of the aluminium chlorosulphoxide, a thick, almost colourless crystalline magma possessing the composition Al_2Cl_6,S_2Cl_2 separates.* This

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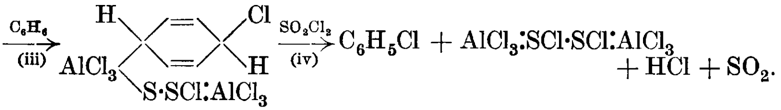
* It is interesting to note that, so far back as 1867, Baudrimot observed that "sheet aluminium reacts violently on gently warming with sulphur monochloride, a brown liquid distils over, and crystals, perhaps of a compound of aluminium chloride and sulphur chloride, are formed" (*Compt. rend.*, 1867, **64**, 368; *Jahresber.*, von Leibig and Kopp, 1867, 159). Until now, however, no one appears to have isolated this compound in a state of purity, or to have ascertained its composition. In this connexion, it should also be observed that under the conditions described above, no evidence was

compound is remarkably stable, and may be recrystallised from boiling thionyl chloride or sulphuryl chloride; in the latter case, however, considerable decomposition of the solvent occurs; but the chief peculiarity of this latter solution lies in its remarkable chlorinating properties. Thus, if a crystal of frozen benzene be added, chlorination occurs with almost explosive violence, and even such an inert substance as tetrachlorobenzene is readily converted into the hexachloro-derivative. It would appear that the remarkable activity of this reagent depends on the following series of reactions :

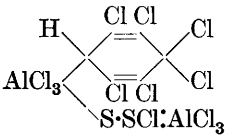
$$2AlCl_3 \xrightarrow[(i)]{2SO_2} 2AlCl_3{:}SO_2 \xrightarrow[(ii)]{S_2Cl_2} AlCl_3{:}SCl{\cdot}SCl{:}AlCl_3 + 2SO_2$$



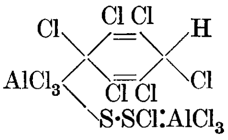
$$\xrightarrow[(iv)]{SO_2Cl_2} C_6H_5Cl + AlCl_3{:}SCl{\cdot}SCl{:}AlCl_3 + HCl + SO_2.$$

The reactions indicated by (iii) and (iv) appear to proceed continuously until either the sulphuryl chloride is expended or the hydrocarbon is completely chlorinated.

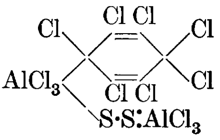
In studying these reactions, the formation of intense colours was observed in all cases so long as an unsubstituted group remained; the colour seems to disappear, however, as soon as substitution is complete. It would seem probable, therefore, that the deep moss-green compound to which pentachlorobenzene gives rise should be formulated as represented by I below, rather than by II, otherwise the compound represented by formula III should also be produced and possess chromophoric properties, which is contrary to experience :



(I.)



(II.)



(III.)

Such compounds, it will be observed, are strictly analogous to the substituted benzenoid chlorides described by Jungfleisch (*Z. Chem. von Beilstein and Fritz Hübner*, 1868, **4**, 468), Willgerodt (*J. pr. Chem.*, 1897, [ii], **55**, 416), Otto (*Annalen*, 1867, **141**, 101), Matthews (T., 1892, **61**, 104), and Barrals (*Bull. Soc. chim.*, 1895, [iii], **13**, 418), some of which, indeed, have been observed to form intensely

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obtained of the formation of the unstable compound possessing the approximate composition corresponding with the formula $AlCl_3,SCl_4$ described by Ruff and Plato (*Ber.*, 1901, **34**, 1755).

coloured derivatives with great ease (compare Barral, *ibid.*, 1897, [iii], **17**, 774). The action of this reagent on other hydrocarbons is being studied, and particularly with a view to obtain new chlorides of carbon.

EXPERIMENTAL.

Examination of Intermediate Compounds.

(1) *Aluminium Chlorosulphoxide*, $AlCl_3{:}SO_2$.—This compound is best prepared by adding recently sublimed and finely ground anhydrous aluminium chloride (15 grams) to sulphuryl chloride (30 c.c.) and agitating the mixture until solution is complete—this occupies about eight hours, during which time the temperature should be allowed to rise gradually from 0° to 30° and moisture be rigidly excluded. The product is then filtered through a warm, dry filter-paper in a completely enclosed funnel, whereby a ruddy brown, flocculent substance, which contains the iron originally present in the aluminium chloride, is removed.

The solution of this substance obtained in this manner fumes strongly in the air, coats everything with which it comes into contact with a white, scaly layer, and possesses an odour reminiscent of phosphorus pentachloride; it is decomposed by water with a hissing sound, and reacts vigorously with benzene or similar hydrocarbons, producing highly chlorinated derivatives.

A small quantity of the solution was run into a weighed bulb, freed from excess of sulphuryl chloride by warming at 30° in a vacuum until constant in weight, and analysed (Found: Al = 13·56; Cl = 53·73. $AlCl_3{:}SO_2$ requires Al = 13·71; Cl = 53·85 per cent.).

(2) *Aluminium Sulphur Chloride*, $Al_2S_2Cl_8$ or $AlCl_3{:}SCl{\cdot}SCl{:}AlCl_3$, separates as a solid mass when sulphur monochloride or finely ground sulphur is added to the above solution of aluminium chlorosulphoxide; it is, however, best prepared by adding 5 grams of sulphur monochloride, previously dissolved in 45 c.c. of thionyl chloride, to a solution of the aluminium chlorosulphoxide in sulphuryl chloride prepared as above described from 10 grams of aluminium chloride. On mixing these solutions at the ordinary temperature, a rise of about 7° ensues, the mixture becomes permeated with minute bubbles of sulphur dioxide, assumes a more viscid character, and on standing for a few minutes the desired compound crystallises out in tiny, colourless needles or leaflets.

The compound obtained in this way fumes strongly in the air, giving off the characteristic odour of sulphur monochloride; it is decomposed by water with a hissing sound, free sulphur being simultaneously precipitated. It is moderately soluble in warm thionyl chloride and sulphuryl chloride, from the former of which it crystallises out unchanged; its solution in sulphuryl chloride is less stable, as its presence induces the catalytic decomposition of this solvent, both sulphur dioxide and chlorine being evolved on heating.

In order to analyse this compound, a small quantity of the suspension of crystals prepared as above described was drawn into a weighed Gooch crucible through a tube fused into the side of the containing vessel, the bulk of the solvent drawn off by suction, and the last traces were washed out with carbon tetrachloride, the latter being finally removed by a current of dry air. The crucible, containing the pure dry crystalline compound, was then rapidly placed in a large weighing bottle and accurately weighed; the whole was then transferred to a wide-mouthed stoppered bottle partly filled with distilled water, and the weighing bottle so tilted as to cause the lid to roll off and the contents of the crucible to come into contact with the water. After the fumes produced had become completely absorbed, excess of pure nitric acid was added, and the solution filtered from asbestos (originally present in the Gooch crucible) and precipitated sulphur formed by the action of water on the compound. The solution was then made up to a known volume, and the chlorine estimated in the usual manner (Found: in three separate preparations, Cl = 69·2, 69·6, 70·1. Al_2Cl_6,S_2Cl_2 requires Cl = 70·6 per cent.).

Examination of the Chlorinating Properties of the New Reagent. Preparation of Polychlorobenzenes.

In order to avoid repetition, the method adopted in investigating the chlorinating properties of this reagent is here briefly set forth in general terms.

Preparation of the Chlorinating Agent.—In the first place, 25 kilos. of the required chlorinating reagent were made up by running the necessary quantity (250 grams) of sulphur monochloride into a large jar containing sulphuryl chloride; 68·2 grams of this mixture, which for the sake of brevity is subsequently referred to as the chlorinating agent, contains one gram-equivalent of active chlorine or half a gram-molecule of sulphuryl chloride.

General Procedure.—The compound to be chlorinated (generally 1 or 2 mols.) together with finely ground anhydrous aluminium chloride (5—10 grams) was placed in a flask submerged in a water-bath and provided with an efficient reflux condenser, the upper end of which was connected with a second condenser, the latter being loosely packed with asbestos; the two condensers were so arranged that the gases passed up the former and down the latter, the condensate from the second being returned through a trap to the reaction flask, whilst the gases evolved were conducted through a valve to a vessel containing 10 litres of water in order to absorb the sulphur dioxide and hydrochloric acid evolved during the reaction. By means of this arrangement, all risk is avoided of stopping up the reflux condenser with the solid, highly chlorinated compounds which are volatilised with the gases evolved, and any degree of chlorination can readily be effected. The chlorinating agent (5—10 per cent. excess) was then run down the reflux condenser by means of a suitable dropping funnel, the mixture being cooled or warmed according to the vigour of the reaction, which was completed by warming the bath for a short time, after which the product was washed with water and worked up in a manner dependent on its physical properties.

Where the number of chlorinations to be effected is not great, it will probably be found more convenient to use a single six-bulb reflux condenser and to drop the reagent down this, passing the gases evolved directly from the top of this condenser to the absorption vessel; in this case, the reagent carried off by the gases amounts to about 15 per cent., so that the quantity added should be adjusted accordingly.

o- *and* p-*Dichlorobenzenes.*—On adding the chlorinating agent (286 grams) to the mixture of chlorobenzene (225 grams) and aluminium chloride (5 grams), the product turns dark-vandyke brown and a vigorous reaction proceeds at the ordinary temperature; this was completed by raising the water-bath to boiling for a few minutes. After being washed with boiling water, 275 grams of an oil were obtained which yielded 190 grams of *p*-dichlorobenzene (m. p. 53°) and 60 grams of an oil which remained liquid at − 10°; this, on freeing from the remaining traces of *p*-dichlorobenzene by conversion into the sulphonic acid and hydrolysing the latter (compare Beilstein and Kurbaton, *Annalen*, 1876, **182**, 94; Friedel and Crafts, *Ann. Chim.*, 1887, [vi], **10**, 413), yielded 37 grams of pure *o*-dichlorobenzene boiling at 178°/758 mm. and having a setting point of − 18° (Found: Cl = 48·13 per cent.).

1 : 2 : 4-*Trichlorobenzene.*—*p*-Dichlorobenzene shows a great tendency to pass straight to the tetrachloro-compound. The best yield of trichlorobenzene is obtained by running the whole of the chlorinating agent (146 grams) at once into the mixture of dichlorobenzene (147 grams) and aluminium chloride (5 grams) contained in a suitable flask and surrounded with cold water. In these circumstances, the mixture gradually turns a deep vandyke-brown and a mild reaction sets in, until the whole of the dichlorobenzene has passed into solution; the water-bath is then filled with ice in order

to control the reaction, which is so vigorous that it is not advisable to operate with larger quantities at a time. After boiling with water, 190 grams of an oil are obtained; this, on fractionation, yields 105 grams of 1 : 2 : 4-trichlorobenzene boiling at 212—213° and setting at 16° (Found: Cl = 58·32 per cent.). From the other fractions, 5 grams of *p*-dichlorobenzene (m. p. 53°) were recovered and 16 grams of 1 : 2 : 4 : 5-tetrachlorobenzene (m. p. 141°).

1 : 2 : 4 : 5-*Tetrachlorobenzene.*—*p*-Dichlorobenzene (294 grams) and aluminium chloride (10 grams) were mixed, the surrounding water-bath was raised to 40°, and the chlorinating agent (582 grams) rapidly run in. The mass, which at first liquefies, rapidly sets to a solid block of almost pure tetrachlorobenzene, or rather the deep moss-green double compound of this substance with aluminium sulphur chloride. The reaction is completed by heating the water-bath to 80° for one hour. On heating the reaction mass with 200 c.c. of water and 200 c.c. of benzene, separating the benzene solution, and allowing it to cool, an almost solid mass of tetrachlorobenzene is obtained; this, on recrystallisation from benzene, yields 249 grams of the pure 1 : 2 : 4 : 5-compound (m. p. 141°) (Found: Cl = 65·74 per cent.). On distilling off the bulk of the solvent, adding an equal volume of absolute alcohol, and allowing to stand over-night, a crystalline deposit was obtained which on recrystallisation yielded a further 53 grams of 1 : 2 : 4 : 5-tetrachlorobenzene; this brings the yield up to 67 per cent. of theory.

Isolation of 1 : 2 : 3 : 5-*Tetrachlorobenzene.*—On fractionating the mother-liquor from three such batches as above (that is, from 882 grams of dichlorobenzene and 1746 grams of the chlorinating agent), 147 grams of a soft, crystalline mass boiling between 233° and 258°/759 mm. were obtained. This was ground up with 300 c.c. of cold absolute alcohol. The residue, 37 grams, consisted chiefly of 1 : 2 : 4 : 5-tetrachlorobenzene and melted, after several recrystallisations, at 140—141°. The alcoholic extract was then concentrated until an oil began to separate, just sufficient alcohol was added to redissolve this at 40°, and the solution was allowed to stand for several days. In this manner, 68 grams of a white, crystalline solid were obtained, which, after several recrystallisations from absolute alcohol, melted at 51° and proved to be the 1 : 2 : 3 : 5-isomeride (Found: Cl = 65·43 per cent.). The yield of the pure substance was 42 grams.

Pentachlorobenzene.—This compound cannot be obtained directly from dichlorobenzene, which, on treatment with the calculated quantity of the new reagent, yields a mixture of tetra- and hexachlorobenzene. Even tetrachlorobenzene shows a great tendency to pass directly to the hexachloro-derivative. A small yield of the pentachloro-compound can, however, be obtained by proceeding as follows, but the method cannot be recommended for the preparation of pentachlorobenzene.

1 : 2 : 4 : 5-Tetrachlorobenzene (108 grams, finely ground) should first be dissolved in thionyl chloride (1 litre) by the aid of gentle heat, and the solution kept just warm enough to prevent the tetrachloro-compound from crystallising out. To this solution the required chlorinating agent (73 grams) is then added, and, lastly, the anhydrous aluminium chloride (5 grams), which latter should be finely ground and added by degrees under vigorous agitation. The mixture should then be agitated for about eight hours at a temperature of about 40°, after which the reaction is completed by heating at 70—80° for three or four hours. In place of thionyl chloride, carbon tetrachloride may be used as a solvent.

On distilling off about 600 c.c. of the solvent and allowing the residue to cool, a considerable quantity of hexachlorobenzene crystallises out (m. p. 226° after recrystallisation from benzene). The filtrate is then freed from the remaining thionyl chloride by pouring into a large bulk (about 10 litres) of cold water, and the precipitated organic matter ground up with cold absolute alcohol; the residue, which constitutes the bulk of the product, consists chiefly of unchanged tetrachlorobenzene; it melted at 140—141° after recrystallisation. The alcoholic solution is then submitted to fractional precipitation by the addition of water, and the more soluble portions are recrystallised from alcohol; in this manner, a small quantity of a compound melting at 85—86° is ultimately obtained, which analysis proves to be pentachlorobenzene (Found : Cl = 70·22 per cent.).

Hexachlorobenzene.—A mixture of the chlorinating agent (314 grams), finely ground tetrachlorobenzene (216 grams), and aluminium chloride (10 grams) (in place of tetrachlorobenzene, the crude product obtained by treating 147 grams of dichlorobenzene with 291 grams of the chlorinating agent in the presence of 5 grams of aluminium chloride may be used) is warmed to gentle ebullition until the evolution of gas ceases; this occupies about eight hours. On boiling the product out with 800 c.c. of benzene and 100 c.c. of water, separating the benzene solution, and allowing it to cool, the hexachloro-compound crystallises out in beautiful, colourless needles which on recrystallisation melt at 226° (Found : Cl = 74·66 per cent.). The yield amounts to 200 grams of the pure substance, or 70 per cent. of the theoretical.

The author desires to express his thanks to Messrs. A. Boake, Roberts and Co. for supplying the sulphuryl chloride required for

this investigation, and also to Messrs. The United Alkali Co. for the thionyl chloride and dichlorobenzene used.

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[*Received, April* 20*th*, 1922.]