CCCLXV.—*The Action of Halogens on Ethyldi-iodostibine. Antimony Bromodi-iodide.*

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As is well known, antimony pentaiodide is either non-existent or exceedingly unstable. It was therefore thought probable that an analogous compound, containing one iodine atom replaced by an alkyl group, would readily decompose. Such decomposition might take two courses : either (*a*) iodine and ethyldi-iodostibine might be produced, in which case these reactants would not be expected to combine readily; or (*b*) ethyl iodide and antimony tri-iodide might be formed, according to the equation $SbEtI_4 = EtI + SbI_3$. Owing to the instability of the alkyl–antimony bond, it was expected that the latter course, involving elimination of the alkyl group, would be preferred.

When ethyldi-iodostibine (Auger and Billy, *Compt. rend.*, 1904, **139**, 599) was treated with iodine, a deep red, quaternary compound was formed. This was too unstable for isolation, but on decomposition, antimony tri-iodide was the only isolable product, elimination of the alkyl group therefore having occurred according to scheme (*b*).

The interaction of ethyldi-iodostibine and bromine produced a transitory quaternary compound, which decomposed to give *antimony bromodi-iodide* : this is the first mixed halide of tervalent antimony to be described.

Numerous attempts to prepare antimony chlorodi-iodide in the same manner were unsuccessful, and no conclusive evidence of the intermediate formation of a quaternary compound was obtained.

Incidentally, the previously unrecorded observation that ethyldi-iodostibine is photosensitive has been made. Antimony tri-iodide results, but no other indication as to the course of the reaction has been obtained.

EXPERIMENTAL.

Action of Iodine on Ethyldi-iodostibine.—A solution of 1·2 g. of the stibine in chloroform (10 c.c.) was added dropwise to 0·75 g. of iodine dissolved in the minimum quantity of chloroform. The deep red colour produced was largely discharged when the mixture was refluxed for a few minutes and allowed to cool. Red needles (1·2 g.) of antimony tri-iodide separated which, alone or mixed with an authentic specimen (m. p. 170·5°), melted at 168—170·5°.

Action of Bromine.—A solution of 12·0 g. of ethyldi-iodostibine in the minimum quantity of chloroform (*ca.* 15 c.c.) was cooled in a freezing mixture, and bromine (1·6 c.c., dissolved in 5 c.c. of chloroform) was added drop by drop. A vigorous reaction took place on each addition, and a red oil (presumably the quaternary compound), which showed no tendency to crystallise, separated. When the liquid was refluxed for a few minutes, much of the colour was discharged. After being cooled to 0°, the chloroform was decanted from a mixture of *antimony bromodi-iodide* and iodine. This mixture was washed with small quantities of xylene until it was free from iodine. The residue, recrystallised from chloroform or light petroleum (b. p. 80—100°), gave long yellow needles (2·9 g.) moderately stable in air. Repeated crystallisation did not alter the melting point, 88° (Found : Sb, 26·8. $SbBrI_2$ requires Sb, 26·6%).

On hydrolysis with sodium hydroxide, sodium iodide and bromide were formed.

Action of Chlorine.—Preliminary quantitative experiments showed that (*a*) chlorine was only slowly absorbed by solutions of ethyldi-iodostibine, unless the temperature was above *ca.* 25° : at lower temperatures, as at higher ones, a red colour was observed, but this was apparently due to the formation of antimony tri-iodide; (*b*) if the quantity of chlorine employed was equal to or greater than the theoretical weight, iodine was liberated in large amount; (*c*) under all conditions, hydrogen halide was evolved, although comparatively little was formed until the theoretical weight of chlorine had reacted; (*d*) under all conditions, antimony tri-iodide was produced.

Based on this experience, the following (typical) experiment was conducted. Into a solution of 10·0 g. of ethyldi-iodostibine in warm chloroform (10—15 c.c.), chlorine (530 c.c. in all; calc., 600 c.c.) was passed at the maximum rate (in this case, 35 c.c. per minute) at which complete absorption resulted for the temperature employed (25—30°). Antimony tri-iodide began to be precipitated at once. Finally the liquid was boiled, filtered, and allowed to cool. It deposited red antimony tri-iodide and the metastable yellow modification, but no other substance was detected. Fractional crystallisation of the residue from xylene gave no indication of the presence of a substance with the expected properties.

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