

LXIII.—*The Interaction between Alkyl Grignard Reagents and Antimony Trichloride.*

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ON treating magnesium ethyl bromide in ethereal solution with excess of antimony trichloride, Auger and Billy (*Compt. rend.*, 1904, **139**, 599) obtained a mixture which they supposed to contain ethyl-dichloro- and -dibromo-stibine. Using equivalent weights of magnesium, methyl iodide, and antimony trichloride, Hibbert (*Ber.*, 1906, **39**, 160) prepared trimethylstibine (which he isolated as dibromide representing a yield of 60—70%), together with high-boiling by-products, which were not further examined. Subsequently, Hibbert's method was employed both by Hantzsch and Hibbert (*Ber.*, 1907, **40**, 1512), and by Morgan and Yarsley (*J.*, 1925, **127**, 184), who devised a special form of apparatus in which the trimethylstibine was purified by distillation of its dibromide with zinc in an inert atmosphere. Morgan and Yarsley also used triethyl- and tri-*n*-butyl-stibine in attempts to prepare bistralkylstibinedichloroplatinums, but they do not describe the properties of the butylstibine. The reactions of the substituted chloro- and iodo-stibines with alkyl Grignard reagents have been investigated by Grüttner and Wiernik (*Ber.*, 1915, **48**, 1484, 1759), by Grüttner and

Krause (*Ber.*, 1916, **49**, 437), and by Ingold, Shaw, and Wilson (*J.*, 1928, 1283).

The purpose of the present work was twofold, *viz.*, (1) to investigate the character and yields of products other than tertiary stibines, and (2) to characterise the tertiary stibines and investigate their general properties.

In all cases hydrocarbon, formed by the synthetic action of the magnesium on the alkyl bromide, was isolated by exhaustively treating the first runnings, obtained in the isolation of the stibine, with concentrated sulphuric acid.

No evidence of any considerable formation of alkylhalogenostibine, such as that supposed by Auger and Billy (*loc. cit.*), was obtained. Moreover, no higher-boiling product than the stibine (compare Hibbert, *loc. cit.*) was produced in appreciable amount, except the stibine oxide, which, in spite of careful exclusion of air, was always formed to a slight extent.

Interaction between alkyl Grignard reagents and antimony trichloride is always accompanied by separation of finely divided antimony. Direct experiment has proved that on mixing alkylstibines with antimony trichloride there is immediate reduction to antimony.

The total yield of stibine in a preparation, determined iodometrically (see Experimental), was generally 60—70% of the theoretical, in agreement with that found by Hibbert in the case of trimethylstibine, but for triethylstibine the yield was 80—85%.

In view of the ease of oxidation of the trialkylstibines, special precautions were taken to exclude air, both during reactions and in the subsequent separation and manipulation of the products.

Trimethylstibine (Landolt, *Annalen*, 1851, **78**, 91) and triethylstibine (Löwig and Schweizer, *ibid.*, 1850, **75**, 315, 327) have long been known, but, excepting the preparation of tri-*n*-butylstibine by Morgan and Yarsley (*loc. cit.*), no preparations of higher trialkylstibines have been recorded since 1856, when Berlé (*Annalen*, 1856, **97**, 316) prepared a triamylstibine.

The higher trialkylstibines are clear liquids of peculiar odour. Their density falls regularly as the series is ascended, whilst their boiling points rise. When distilled under reduced pressure, the lower members pass over undecomposed, but tri-*n*-hexylstibine is partly decomposed. When cooled to the temperature of liquid air, they crystallise. They are only slightly miscible with water, but at the ordinary temperature they mix in all proportions with alcohol, ether, benzene, and carbon disulphide.

Trialkylstibines combine vigorously with oxygen, which causes an immediate clouding of the originally clear liquid, considerable

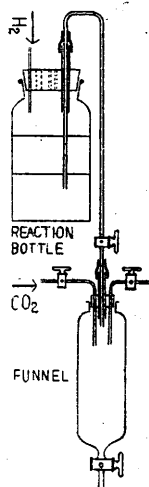
heat being evolved. The avidity for oxygen, however, falls off with increased molecular weight. Stibines readily ignite when warmed in the air, burning with the greyish-green flame characteristic of antimony and evolving clouds of antimonous oxide. When allowed to fall on filter paper, they cause charring and, if in quantity, ignition. Chlorine, bromine, and iodine readily combine with the stibines, dihalides being formed quantitatively. In contradistinction to the phosphines, trialkylstibines combine only lethargically with methyl and other alkyl iodides, and with carbon disulphide they yield no coloured compounds. They reduce mercuric salts in cold aqueous solution, and, on warming, auric and silver salts also, to the metal.

Antimony was determined in the stibines by heating the compound with sodium carbonate in a stream of oxygen in a combustion tube. The contents of the tube were dissolved in 10% hydrochloric acid and antimony trisulphide was precipitated from the boiling solution by the passage of hydrogen sulphide for $\frac{1}{2}$ hour. An equal volume of hot water was then added to the liquid, and the stream of hydrogen sulphide was continued for 5 minutes. The precipitate was collected on a Gooch crucible, washed, and dried for 2 hours at 130° and for 2 hours at $280-300^{\circ}$ in carbon dioxide.

EXPERIMENTAL.

The apparatus consisted of a wide-necked bottle, of 1 litre capacity, fitted with a rubber stopper carrying a mercury-sealed stirrer, a dropping funnel, a reflux condenser, an inlet tube for hydrogen, and a siphon whereby liquid layers could be withdrawn and separated in absence of air. The exterior limb of the siphon was fitted with a tap and it slid smoothly through a glass jacket fixed in the stopper of a separating funnel (see fig.). Air-tightness was secured by stretching rubber tubing over both the jacket and the limb of the siphon. The other limb of the siphon passed into the reaction bottle by a similar device, which permitted adjustment of the siphon to any desired level. The separating funnel was provided with two tubes with taps to serve either as inlet and outlet, respectively, for carbon dioxide, or for the application of suction.

The Grignard solution was prepared by dropping the freshly prepared alkyl halide, dissolved in 150 c.c. of ether, on 12.1 g. of magnesium turnings immersed in 150 c.c. of ether to which a granule of iodine had been added. Throughout the preparation of this



solution and its interaction with antimony trichloride, pure dry hydrogen was passed over the liquid. The liquid was then cooled to 0° and 38.1 g. of freshly redistilled antimony trichloride in 100 c.c. of ether were added drop by drop. After the addition was complete the mixture was warmed for $\frac{1}{2}$ hour, again cooled to 0°, and then treated with ammonium chloride solution. The separating funnel was now filled with pure dry carbon dioxide, and the ethereal layer was transferred from the reaction bottle into the funnel. In this way an unclouded solution was obtained.

In the estimation of the total yield of stibine a standard solution of iodine in ether, or of bromine in carbon tetrachloride, was run into the funnel through the inlet tube until the colour persisted, indicating quantitative conversion into the dihalide.

In cases where the stibine was isolated, the ethereal solution was dried with anhydrous sodium sulphate, the ether distilled off in an atmosphere of carbon dioxide, and the residue fractionally distilled under reduced pressure. A 2° fraction containing the stibine was collected in a pycnometer-receiver with a tubular neck and ground-glass stopper. The stibine was thus obtained as a clear liquid.

Triethylstibine was prepared by the addition of the equivalent of antimony trichloride in ether to the Grignard solution prepared from 55 g. of ethyl bromide. The total yield of stibine in the ethereal solution was 80—85%.

Tri-n-propylstibine, obtained by the addition of antimony trichloride to magnesium *n*-propyl bromide prepared from 62 g. of the alkyl bromide, has b. p. 100°/25 mm., 113°/39 mm.; d_4^{25} : 1.241 (Found: C, 43.2; H, 8.5; Sb, 48.1. $C_9H_{21}Sb$ requires C, 43.1; H, 8.4; Sb, 48.5%). The total yield of stibine was 60—70%, and the yield of purified material 11 g. The stibine possesses a penetrating, alliaceous odour.

The residue after removal of ether in the case of the interaction between antimony trichloride and magnesium *isopropyl* bromide, on being heated under reduced pressure, continuously emitted gaseous decomposition products. This result is comparable with that obtained in the interaction between various phosphorus chlorides and the Grignard reagent of *isopropyl* bromide (Davies, Pearse, and Jones, J., 1929, 1268).

From the products of the interaction between magnesium *n*-butyl bromide (from 69 g. of *n*-butyl bromide) and its equivalent of antimony trichloride, a first fraction containing *n*-octane was obtained. From this, 5 g. of the purified hydrocarbon, b. p. 125°/760 mm., were isolated. The distillation was continued under reduced pressure, whereupon there were obtained 11 g. of *tri-n-butylstibine*,

b. p. 131°/12 mm.; d_4^{25} 1.191 (Found: C, 48.8; H, 9.9; Sb, 40.5. $C_{12}H_{27}Sb$ requires C, 49.2; H, 9.3; Sb, 41.5%).

Triisobutylstibine, b. p. 135°/31 mm., d_4^{25} 1.323 (Found: Sb, 41.8. $C_{12}H_{27}Sb$ requires Sb, 41.5%), was prepared (yield, 11 g.) by the interaction between the antimony halide and magnesium *isobutyl* bromide made from 69 g. of the alkyl bromide. The first runnings furnished 6 g. of $\beta\epsilon$ -dimethylhexane, b. p. 109°/760 mm. The butylstibines possess a mixed alliaceous-butylic odour. The *isobutylstibine* is distinctly yellow.

The preparation of *tri-n-amylstibine* was effected by adding antimony trichloride to the Grignard reagent obtained from 76 g. of *n*-amyl bromide; yield, 15 g., b. p. 168°/16 mm., d_4^{25} 1.136 (Found: C, 53.8; H, 9.3; Sb, 37.2. $C_{15}H_{33}Sb$ requires C, 53.7; H, 9.9; Sb, 36.3%). In the preparation of this stibine there were obtained 8 g. of *n*-decane, b. p. 88°/50 mm. (Krafft, *Ber.*, 1882, 15, 1695, gives b. p. 90°/50 mm.).

Tri-dl- β -methylbutylstibine, obtained from the Grignard reagent made from 76 g. of *dl*- β -methylbutyl bromide (yield, 10 g. of purified product), has b. p. 150°/14 mm.; d_4^{25} 1.242 (Found: Sb, 36.5. $C_{15}H_{33}Sb$ requires Sb, 36.3%). The synthetic action of the magnesium gave 6 g. of $\gamma\zeta$ -dimethyloctane, b. p. 159°/760 mm.

The interaction between equivalents of antimony trichloride and magnesium *isoamyl* bromide yielded 10 g. of *triisoamylstibine* (*tri- γ -methylbutylstibine*), b. p. 149°/14 mm.; d_4^{25} 1.227 (Found: Sb, 36.2. $C_{15}H_{33}Sb$ requires Sb, 36.3%). There were obtained 10 g. of $\beta\eta$ -dimethyloctane, b. p. 159°/760 mm. When distilled in a stream of carbon dioxide under *atmospheric pressure*, the stibine passed over with considerable decomposition at about 260°. All the amyl stibines have a preponderatingly amylic smell. *n*-Amylstibine is colourless, but β - and γ -methylbutylstibines are both yellowish.

Tri-n-hexylstibine, prepared (yield 10 g.) from the Grignard reagent made from 83 g. of *n*-hexyl bromide, boils at 190°/10 mm. with partial decomposition and liberation of antimony. The distillate had d_4^{25} ca. 1.15. For the purpose of analysis the separated antimony was allowed to settle out of the liquid (Found: Sb, 31.2. $C_{18}H_{39}Sb$ requires Sb, 32.3%). The smell resembles that of *n*-hexyl alcohol. In this preparation 12 g. of *n*-dodecane, b. p. 95°/12 mm. (Krafft, *loc. cit.*, gives b. p. 98°/15 mm.), were obtained.

Investigation of derivatives of the trialkylstibines is being pursued.