



TITLE:

On Organic Compounds of Antimony, Part I : Reaction between  $\alpha$ -Naphthylmagnesium Bromide and Inorganic Antimony Compounds : Tri- $\alpha$ -naphthylstibine and Some of its Derivatives

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Reaction between  $\alpha$ -Naphthylmagnesium Bromide  
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Tri- $\alpha$ -naphthylstibine and  
Some of its  
Derivatives.<sup>1</sup>

By

Kaoru Matsumiya.

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ABSTRACT.

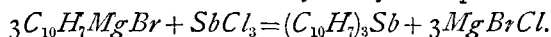
The reaction between  $\alpha$ -naphthylmagnesium bromide and various inorganic antimony compounds, such as antimony-trichloride, trioxide, oxychloride and trisulphide, were studied. The trichloride easily reacts and forms tri- $\alpha$ -naphthylstibine. An attempt was made to obtain di- $\alpha$ -naphthyl compounds by regulating the reaction, but it was unsuccessful. The trioxide and the oxychloride were entirely inactive. The crystalline modification of the trisulphide was practically inactive, but the amorphous modification entered into reaction and formed tri- $\alpha$ -naphthylstibine. Tri- $\alpha$ -naphthylstibine formed colourless crystals, M. p. 216–217°C. On treating a benzene or carbon bisulphide solution of the stibine with chlorine or bromine, the dichloride,  $(C_{10}H_7)_3SbCl_2$ , M. p. 256° C., and the dibromide,  $(C_{10}H_7)_3SbBr_2$ , M. p. 232° C., were obtained respectively. The dichloride or the dibromide was boiled with alcoholic potash and benzene for twenty hours, and the reaction product was recrystallised from carbon bisulphide-benzene. Colourless prisms were obtained with the composition  $(C_{10}H_7)_3SbO \cdot C_6H_6$ . On heating the crystals, the oxide,  $(C_{10}H_7)_3SbO$ , M. p. 219–220° C., was obtained as an amorphous powder.

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<sup>1</sup> This paper was read at the annual meeting of the Chemical Society of Japan on April 6th of this year.

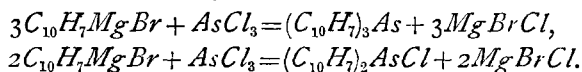
Among the organic compounds of antimony the naphthyl derivatives are still unknown, while the corresponding arsenic compounds have already been much studied. As it seems to me that the Grignard reaction, which was proved to be one of the most useful methods for the synthesis of organic arsenic compounds, has hitherto been but little used in the case of antimony, I have attempted to study the reaction between  $\alpha$ -naphthylmagnesium bromide and inorganic antimony compounds with the object of extending the range of the organic derivatives of antimony to the naphthyl region.

When antimony trichloride dissolved in ether was added to the ethereal solution of  $\alpha$ -naphthylmagnesium bromide, in the proportion of one mol. of the former to three mols. of the latter, a vigorous reaction took place, and tri- $\alpha$ -naphthylstibine was produced with a yield of 45 per cent of the theoretical. The reaction may be represented as follows :



It is stated by Pfeiffer,<sup>1</sup> and Morgan and Micklethwait,<sup>2</sup> that the yield of triphenylstibine is increased by adopting ether-benzene as the solvent of the Grignard reagent instead of ether. In the present case, however, no such influence could be observed.

As I have previously pointed out,<sup>3</sup> either tri- $\alpha$ -naphthylarsine or di- $\alpha$ -naphthylchloroarsine (di- $\alpha$ -naphthylarsenious chloride) is obtained at will by the Grignard reaction merely by controlling the mode of addition and the quantity of the reagents, thus



To see whether the reaction proceeds analogously with antimony trichloride, one mol. or less of  $\alpha$ -naphthylmagnesium bromide dissolved in ether was added to the ethereal solution of one mol. of antimony trichloride. At the beginning, the reaction was vigorous but it gradually subsided. After having been kept cool for several hours, it was decomposed with ice water and the solvent was distilled off and naphthalene was removed by hot alcohol. The solid residue was extracted with carbon bisulphide and recrystallised from benzene. From its melting point and the analytical results the product was shown to be tri- $\alpha$ -naphthylstibine. The experiment was repeated, care being taken especially against cooling and agitation; but the reaction product

1 Ber. D. Chem. Ges., **37**, 4621 (1904).

2 J. Chem. Soc., **99**, 2290 (1911).

3 These Memoirs, **4**, 217 (1920).

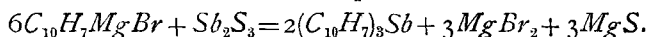
was always tri- $\alpha$ -naphthylstibine.

According to Sachs and Kantarowitz<sup>1</sup> arsenic trioxide reacts with phenyl-, tolyl- or benzyl-magnesium bromide, and we<sup>2</sup> have also found that arsenic trioxide reacts with  $\alpha$ -naphthylmagnesium bromide too. It was therefore deemed to be interesting to see how antimony trioxide reacts with the Grignard reagent. On boiling the trioxide with an ethereal solution  $\alpha$ -naphthylmagnesium bromide for several hours, however, no reaction was observed to take place.

Antimony oxychloride was next tried. Finely powdered antimony oxychloride was added to an ethereal solution of  $\alpha$ -naphthylmagnesium bromide, and the mixture was boiled for several hours. Neither  $\text{SbOCl}$  nor  $\text{Sb}_2\text{O}_3 \cdot 2\text{SbOCl}$  entered into the reaction.

Matsumiya and Nakai<sup>3</sup> have found that arsenic trisulphide easily reacts upon the Grignard reagent. To see whether an analogous reaction takes place with antimony trisulphide an experiment was conducted. Crystalline antimony trisulphide, finely powdered, was added to an ethereal solution of  $\alpha$ -naphthylmagnesium bromide, and after boiling on a water bath for several hours, the reaction product was decomposed with water. The ether and naphthalene were distilled off with steam. By extracting the remaining substance with carbon bisulphide, about 2 grm. of oily substance were obtained. The existence of antimony in it was proved, but no organic compound was isolated.

Next, amorphous antimony trisulphide was treated with an ethereal solution of  $\alpha$ -naphthylmagnesium bromide, when a reaction took place and a small quantity of fine crystals was isolated as the reaction product. It was confirmed to be tri- $\alpha$ -naphthylstibine from its properties and the analytical results. The reaction is represented as follows:—



This experiment shows that an inorganic antimony compound, insoluble in ether, may also enter into reaction with the Grignard reagent, and that the amorphous form of the sulphide is more reactive than the crystalline.

The derivatives of tri- $\alpha$ -naphthylarsine hitherto known, are the dihydroxide, hydroxybromide, tetrachloride, tetrabromide and impure dibromide. The first two were isolated as crystals and the others in the form of hard masses.

<sup>1</sup> Ber. D. Chem. Ges., **41**, 2767 (1908).

<sup>2</sup> Matsumiya and Nakai. The work will be published shortly.

<sup>3</sup> Ibid.

Now in trying to obtain the corresponding derivatives of antimony the dichloride and dibromide were isolated in crystal forms, though no hydroxyhalide and tetrahalide could be obtained.

Michaelis<sup>1</sup> has stated that tri- $\alpha$ -naphthylarsine hydroxybromide is obtainable by adding alcohol to the dichloride or dibromide, and that on treating the dibromide or hydroxybromide with alcoholic potash and then with water, he obtained the dihydroxide which when recrystallised from alcohol had the composition  $(C_{10}H_7)_3As(OH)_2 \cdot 2H_2O$ . In my experiment, when a benzene solution of tri- $\alpha$ -naphthylarsine was treated with chlorine and then with alcohol and water, the dihydroxide was obtained, which after recrystallising from alcohol and drying in vacuum over sulphuric acid, had the composition  $(C_{10}H_7)_3As(OH)_2$ . In tri- $\alpha$ -naphthylstibine dichloride or dibromide, however, the halogen atoms are not so easily replaceable. On boiling the dihalides with alcoholic potash and benzene for twenty hours the replacement took place. The reaction product crystallises from carbon bisulphide-benzene in colourless crystals with the composition  $(C_{10}H_7)_3SbO \cdot C_6H_6$ . On heating at  $90^\circ C$ ., it loses the benzene of crystallisation leaving tri- $\alpha$ -naphthylstibine oxide as a white amorphous powder.

From these facts, it is recognised that tri- $\alpha$ -naphthylstibine combines with halogen far more firmly than the corresponding arsine; the same relation is also conceivable between triphenylarsine and triphenylstibine.

#### EXPERIMENTAL PART.

##### 1. $\alpha$ -Naphthylmagnesium Bromide and Antimony Trichloride.

To the Grignard reagent prepared from 42 grm. of  $\alpha$ -bromonaphthalene, 5 grm. of magnesium and 100 c.c. of dry ether, 15 grm. of antimony trichloride dissolved in ether were gently added under constant agitation and cooling with cold water when an energetic reaction took place. It was boiled on a water bath for one hour, then cooled well and decomposed with water. After distilling off ether and naphthalene with steam, the remaining solid was dissolved in hot benzene, from which, on the addition of about an equal volume of alcohol, minute crystals gradually separated out. The yield was 15 grm. On recrystallising three times from benzene, it melted at  $216-217^\circ C$ . The analytical results were as follows:—

0.2343 grm. substance gave 0.6149 grm.  $CO_2$  and 0.0934 grm.  $H_2O$ .

<sup>1</sup> Lieb. Ann., 321, 242 (1902).

0.1823 gram. substance required 14.4 c.c. of N/20 iodine solution.

	Calc. for $(C_{10}H_7)_3Sb$	Found
C	71.57	71.57
H	4.21	4.46
Sb	24.22	24.05

Tai- $\alpha$ -naphthylstibine is crystalline in form, rather colourless, with a yellowish tint. It is slightly soluble in ether and alcohol, more easily soluble in benzene, carbon bisulphide and chloroform.

### 2. $\alpha$ -Naphthylmagnesium Bromide and Antimony Trioxide.

Five gram. of antimony trioxide were added little by little to the ethereal solution of  $\alpha$ -naphthylmagnesium bromide prepared with 21 gram. of  $\alpha$ -bromonaphthalene and 2.5 gram. of magnesium. The mixture was boiled on a water bath for five hours. After standing over night, it was decomposed with water and dilute acetic acid. After distilling off naphthalene (about 10.5 gram.) the residue was treated with carbon bisulphide. From the carbon bisulphide extract, 2 gram. of oily substance were obtained, in which no antimony was, however, detected, and the part insoluble in carbon bisulphide was no other than antimony trioxide.

### 3. $\alpha$ -Naphthylmagnesium Bromide and Antimony Trisulphide.

Six gram. of amorphous antimony trisulphide were gently added to the Grignard reagent prepared from 21 gram. of  $\alpha$ -bromonaphthalene, 2.5 gram. of magnesium and 50 c.c. of dry ether; a moderate reaction took place. The mixture was boiled for five hours and kept over night and then decomposed with water and dilute acetic acid. On distilling off the solvent, the residue was washed with alcohol and then extracted with carbon bisulphide. The solid mass obtained from the extract was dissolved in hot benzene and subsequently treated with about an equal volume of alcohol, when minute crystals gradually separated out. The yield was 0.9 gram. On recrystallising from benzene, the substance melted at 216—217°C. The results of analysis were found to be as follows:—

0.2703 gram. substance gave 0.7090 gram.  $CO_2$  and 0.1020 gram.  $H_2O$ .

0.1940 gram. substance required 15.4 c.c. of N/20 iodine solution.

	Calc. for $(C_{10}H_7)_3Sb$	Found
<i>C</i>	71.57	71.54
<i>H</i>	4.21	4.22
<i>Sb</i>	24.22	24.17

4. Tri- $\alpha$ -naphthylstibine dichloride.

On passing chlorine gas into the well cooled ether-benzene solution of 6 grm. of tri- $\alpha$ -naphthylstibine, a white crystalline precipitate was formed. The yield was 4.5 grm. On recrystallising from ether-benzene, it melted at 256°C. The analytical results were as follows:—

- 0.1222 grm. substance required 8.5 c.c. of N/20 iodine solution.
- 0.1677 grm. substance required 0.1003 grm. silver nitrate.

	Calc. for $(C_{10}H_7)_3SbCl_2$	Found
<i>Sb</i>	21.22	21.18
<i>Cl</i>	12.36	12.48

Tri- $\alpha$ -naphthylstibine dichloride forms colourless crystals which are slightly soluble in benzene and chloroform, sparingly soluble in carbon bisulphide and with difficulty soluble in ether, petroleum ether and alcohol.

5. Tri- $\alpha$ -naphthylstibine dibromide.

A carbon bisulphide solution of bromine was gradually added to tri- $\alpha$ -naphthylstibine dissolved in carbon bisulphide, until the colour of bromine became just permanent. In a short time, slightly yellow-coloured crystals separated out. The yield was almost theoretical. On recrystallising several times from carbon bisulphide, the substance melted at 232°C. The results of the estimation of antimony and bromine were as follows:—

- 0.0978 grm. substance required 5.8 c.c. of N/20 iodine solution.
- 0.1519 grm. substance required 0.0774 grm. silver nitrate.

	Calc. for $(C_{10}H_7)_3SbBr_2$	Found
<i>Sb</i>	18.38	18.06
<i>Br</i>	24.12	23.97

Tri- $\alpha$ -naphthylstibine dibromide forms slightly yellow-coloured crystals and is almost insoluble in alcohol and ether, slightly soluble in benzene and chloroform, more soluble in carbon bisulphide.

6. Tri- $\alpha$ -naphthylstibine oxide.

Finely powdered tri- $\alpha$ -naphthylstibine dichloride or dibromide was treated with alcoholic potash, benzene being added to aid the dissolution of the halide. The mixture was boiled on a water bath for twenty hours. After the solvent was distilled off, the remaining solid was treated with water and neutralised by passing carbon dioxide gas. The insoluble substance was collected, washed and dried. The brown coloured powder thus obtained was dissolved in carbon bisulphide, filtered and the solution was diluted with benzene, when glistening rectangular prisms gradually crystallised out. On recrystallising from carbon bisulphide-benzene, the substance melted at 219–220°C. It was noticed that the crystals become opaque when they were gently heated. On closer study, it was found that the crystals contained one molecule of benzene. The results of analysis were as follows:—

0.1213 grm. substance gave 0.3225 grm.  $CO_2$  and 0.0531 grm.  $H_2O$ .

0.2628 grm. substance required 18 c.c. of N/20 iodine solution.

	Calc. for $(C_{10}H_7)_3SbO \cdot C_6H_6$	Found
<i>C</i>	72.36	72.51
<i>H</i>	4.56	4.90
<i>Sb</i>	20.40	20.86

The crystals were heated at 90°C. until the constant weight was attained.

0.4010 grm. substance lost 0.0544 grm. on heating.

	Calc. for $(C_{10}H_7)_3SbO \cdot C_6H_6$	Found
$C_6H_6$	13.07	13.29

The remaining substance was a white amorphous powder and its analytical results were as follows:—

0.1367 grm. substance gave 0.3468 grm.  $CO_2$  and 0.0523 grm.  $H_2O$ .

0.1245 grm. substance required 9.6 c.c. of N/20 iodine solution.

	Calc. for $(C_{10}H_7)_3SbO$	Found
<i>C</i>	69.37	69.19
<i>H</i>	4.08	4.28
<i>Sb</i>	23.47	23.48

Tri- $\alpha$ -naphthylstibine oxide is slightly soluble in alcohol, moderately soluble in chloroform and carbon bisulphide, with difficulty soluble in ether, petroleum ether and benzene.



7. Tri- $\alpha$ -naphthylarsine dihydroxide.

When a benzene solution of tri- $\alpha$ -naphthylarsine was saturated with chlorine and the solvent distilled off, a resinous substance remained. On dissolving it in hot alcohol and adding hot water, a white curdy precipitate was formed. On recrystallising it from alcohol, colourless needles were obtained which melted at above 300°C. The substance was dried over sulphuric acid and analysed.

0.2059 gm. substance gave 0.5536 gm.  $CO_2$  and 0.0916 gm.  $H_2O$ .

0.1528 gm. substance required 12.5 c.c. of N/20 iodine solution.

	Calc. for $(C_{10}H_7)_3As(OH)_2$	Found
C	73.45	73.33
H	4.73	4.98
As	15.29	15.34

## Method of analysis.

For the estimation of antimony, Ewins' method<sup>1</sup> of arsenic determination in organic compounds was adopted. It consists essentially in the wet combustion of the organic compounds by means of concentrated sulphuric acid and potassium sulphate; the antimony present is converted into trioxide which is finally estimated volumetrically by means of iodine in the usual manner.

As it was found that halogen atoms directly combined with antimony were easily removed by boiling with silver nitrate and nitric acid, the sample was boiled with nitric acid in the presence of a definite quantity of silver nitrate, and the remaining quantity of silver nitrate was estimated by Volhard's method.

The preliminary analysis of several kinds of organic antimony compounds by these methods, always gave trustworthy results.

The author desires to acknowledge the valuable assistance rendered by Mr. W. Tachiiri in the experiments recorded here.

<sup>1</sup> J. Chem. Soc., 109, 1356 (1916).