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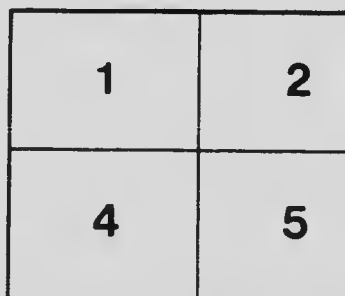
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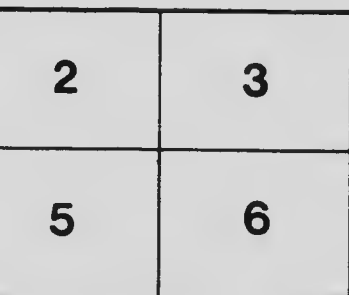
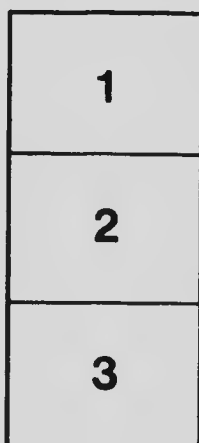
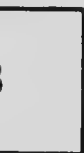
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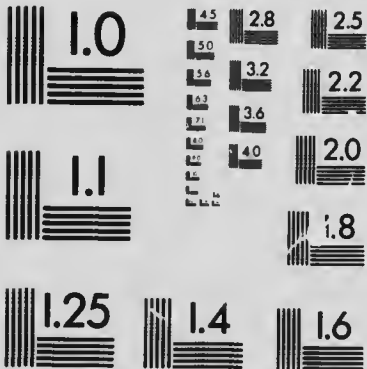
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FRANCIS MACKEY

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SOME ESTERS OF ANTIMONY TRIOXIDE.

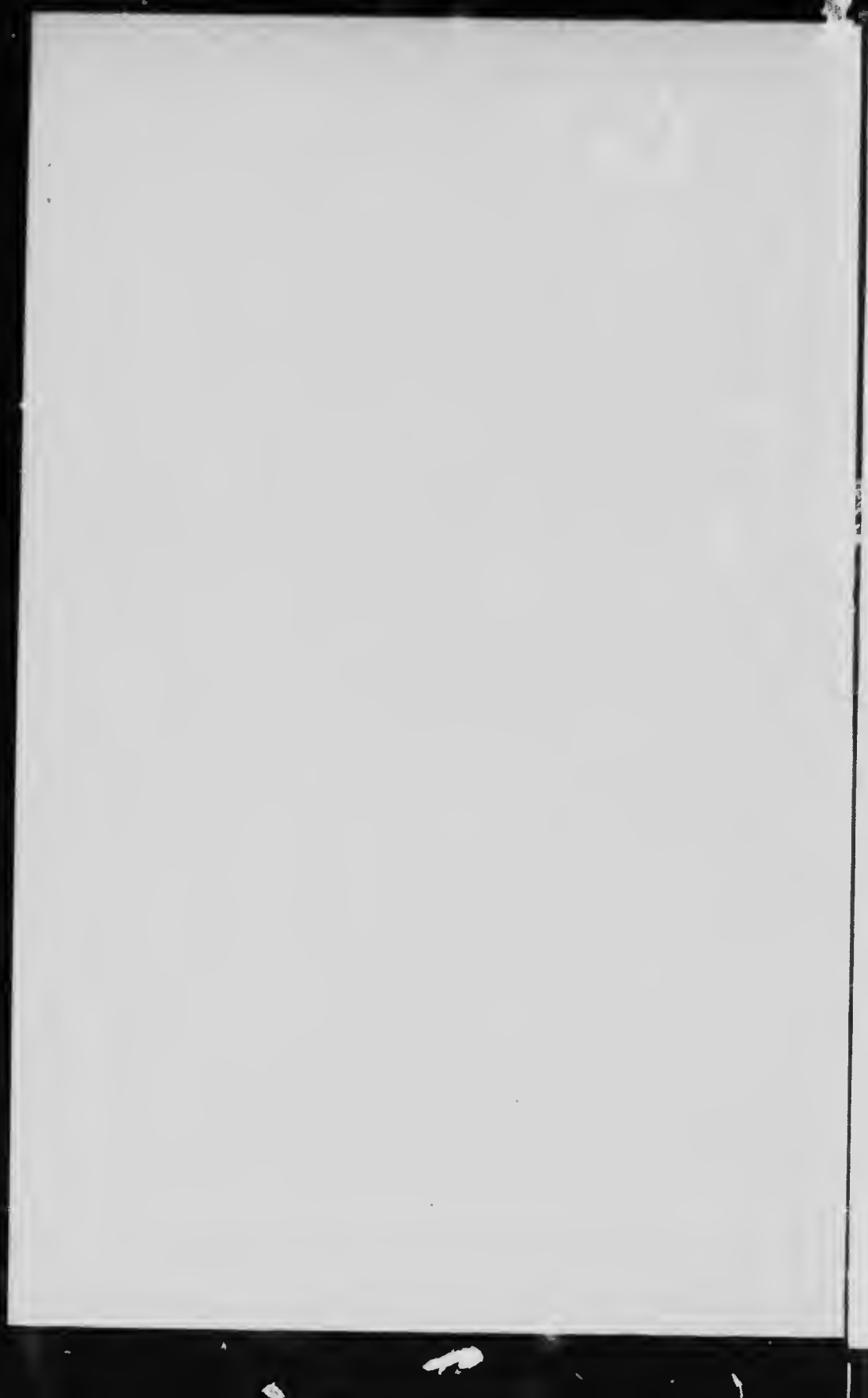
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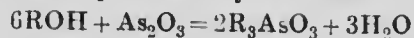




## LXXVII.—*Some Esters of Antimony Trioxide.*

By JOHN FRANCIS MACKEY.

IN a previous paper, Lang, MacKey, and Gortner (Trans., 1908, 93, 1364) described a method for the esterification of arsenious oxide with the fatty alcohols and with phenol and its homologues by removing the water produced by the reaction:



as quickly as it was formed by means of anhydrous copper sulphate placed in a Soxhlet tube attached to a flask containing weighed quantities of the reacting substances. By this means a large number of esters, which other methods had failed to produce, were prepared in quantity, and found to correspond with the general formula  $\text{R}_3\text{AsO}_3$ . In the present work, attempts were made to form the corresponding esters of antimony by five different methods, namely: (1) heating a mixture of the alcohol and antimony trioxide in a flask to which a reflux condenser was

attached; (2) heating a mixture of the alcohol and antimony trioxide in a sealed tube at  $150^{\circ}$ ; (3) shaking a mixture of the alcohol and antimony trioxide with anhydrous copper sulphate in the cold; (4) heating a mixture of the alcohol and antimony trioxide in a flask with a Soxhlet tube, filled with anhydrous copper sulphate, attached; (5) heating a mixture of the alcohol, antimony trioxide, and calcium turnings in a flask with reflux condenser. A comparison of the yields obtained is given in the sequel. By means of these methods, and more particularly the last two, esters were formed with methyl, ethyl, propyl, *isobutyl*, *amyl*, and *isoamyl* alcohols; also with phenol, *o*, *m*-, and *p*-cresols. The esters were found to correspond with the general formula  $R_3SbO_3$ . In all cases the yields obtained with antimony trioxide were very much lower than the corresponding arsenites previously described.

#### EXPERIMENTAL.

(i) *Heating with reflux condenser only.*—Weighed quantities of methyl, ethyl, propyl, *isobutyl*, *amyl*, and *isoamyl* alcohols were mixed with an excess of antimony trioxide, and heated for different periods of time in a flask to which a reflux condenser was attached. After five hours' heating not a trace of ester could be detected in any of the reacting mixtures; but, after fifteen hours' heating, evidence was obtained that, in the case of *isobutyl* and *isoamyl* alcohols, esters were formed, but not in quantities sufficient to permit of their being isolated. That an ester was formed was shown by pouring the clear liquid into water-free benzene,\* in which antimony trioxide is very sparingly soluble, and filtering. By this means any antimony trioxide merely dissolved in the alcohol was separated, and, if antimony were found in the above filtrate, it must have been present in the form of an ester. The filtrate gave a distinct precipitate of antimony sulphide when acidified, treated with hydrogen sulphide, and warmed; thus, whilst there is no doubt that both *isobutyl* and *isoamyl* antimonites are formed under these conditions, the yields are so small that it is impossible to isolate them by fractional distillation.

(ii) *Heating in sealed tubes.*—Quantities of the various alcohols were mixed with antimony trioxide and heated for six hours in sealed tubes at  $150^{\circ}$ , but in no case could the presence of any ester be detected.

(iii) *Using a dehydrating agent in the cold.*—Weighed quan-

\* Great difficulty was found in obtaining benzene absolutely free from water. The samples of benzene at hand were found to contain enough water to decompose partly the esters formed. It was necessary to heat the benzene with calcium turnings for about forty-eight hours.

ties of the various alcohols were mixed with antimony trioxide and a considerable amount of anhydrous copper sulphate. The mixture was then placed in a shaking machine for three days at room temperature. In the case of *isobutyl* and *isoamyl* alcohols, esters were formed, but not in quantities sufficient to enable them to be isolated.

(iv) *Heating with Soxhlet attachment and anhydrous copper sulphate.*—Thirty grams of antimony trioxide were added to 160 grams of *isoamyl* alcohol in a 250 c.c. flask. An ordinary Soxhlet tube was connected with the flask, and a condenser, fitted with a calcium chloride tube, attached to the Soxhlet, which contained a large filter paper filled with anhydrous copper sulphate; the mixture in the flask was heated to boiling, and the water formed by the reaction was absorbed by the copper sulphate, which turned blue as soon as the first drops of condensed liquid fell on it. Heating was continued for about fifteen hours; after cooling, the clear product was poured off from the antimony trioxide and fractionated under diminished pressure. About 10.8 grams of the ester were formed, representing a yield of 13.62 per cent.

By this method esters were formed with methyl, ethyl, propyl, *isobutyl*, *amyl*, and *isoamyl* alcohols, as shown in the following table:

Table of yields by various methods.

Ester	Reflux condenser.	In sealed tubes.	Anhydrous copper sulphate.	
			In the cold.	In Soxhlet.
Methyl .....	nil	nil	nil	8.99 per cent.
Ethyl .....	"	"	"	3.00* "
Propyl .....	"	"	"	13.3 "
<i>isobutyl</i> .....	trace	"	trace	15.11 "
<i>Amyl</i> .....	nil	"	nil	13.16 "
<i>isoAmyl</i> .....	trace	"	trace	13.62 "

\* It will be noticed that the same extremely low yield of ester with ethyl alcohol occurred in the preparation of the esters of arsenious acid, described in a former paper, where a possible explanation was advanced.

These esters were purified and analysed, the following methods of analysis being employed.

*Method of analysis for esters of the aliphatic alcohols (using isoamyl antimonite as an example).*—Two methods were employed for the determination of the antimony. In the first method, iodine was used to oxidise the trioxide to the pentoxide, but was not found to give accurate results, so that the following procedure was adopted.

1.0057 Grams of the ester were decomposed by 5 c.c. of concentrated hydrochloric acid, 50 c.c. of tartaric acid solution were

added, and the antimony was precipitated from this solution by means of hydrogen sulphide; the antimony sulphide thus formed was converted into antimouy tetroxide by treatment with fuming nitric acid and ignited:

1.0057 gave 0.4024  $\text{Sb}_2\text{O}_4$ .  $\text{Sb} = 31.57$ .

$\text{C}_{15}\text{H}_{33}\text{O}_3\text{Sb}$  requires  $\text{Sb} = 31.48$  per cent.

This method of analysis gave the following results:

Ester.	Percentage of Sb found.	Percentage of Sb calculated from the formula $\text{R}_3\text{SbO}_3$ .
Methyl.....	56.68	56.41
Ethyl.....	—	47.41
Propyl.....	40.29	40.46
isoButyl.....	35.37	35.40
Amyl.....	31.44	31.48
isoAmyl.....	31.34	31.48

Expressing these as salts of antimonous acid, we arrive at the general formula  $\text{R}_3\text{SbO}_3$  for them.

*Properties of the Esters of the Aliphatic Alcohols with Antimony Trioxide.*

*Methyl antimonite* is a colourless liquid, b. p.  $65^\circ$ , sp. gr. 1.025.

*Ethyl antimonite* is a colourless liquid, b. p.  $115\text{--}120^\circ$ .

*Propyl antimonite* is a yellow liquid, sp. gr. 1.042, b. p.  $143^\circ/30$  mm.; at atmospheric pressure it decomposes into propyl alcohol and antimony trioxide at  $200^\circ$ .

*isoButyl antimonite* is a yellow, mobile liquid, sp. gr. 1.058, b. p.  $144^\circ/30$  mm.; it decomposes into *isobutyl* alcohol and antimony trioxide at  $250^\circ$  under atmospheric pressure.

*Amyl antimonite* is a yellow liquid, sp. gr. 1.079, b. p.  $170^\circ/30$  mm.

*isoAmyl antimonite* is a yellow, mobile liquid, sp. gr. 1.081, b. p.  $163^\circ/30$  mm.; at  $250^\circ$ , under atmospheric pressure, it decomposes into antimony trioxide and *isoamyl* alcohol.

All these esters are readily soluble in absolute alcohol, ether, chloroform, or benzene, but decompose immediately on addition of water into antimony trioxide and the alcohol from which they were prepared.

The fifth method was not employed for the aliphatic alcohols.

*Esters obtained with Phenol and its Homologues.*

For the esterification of these substances with antimony trioxide, two methods were used, namely, heating the mixture of phenol and antimony trioxide in a flask to which a Soxhlet apparatus

containing anhydrous copper sulphate was attached, and heating the mixture of phenol and antimony trioxide with calcium turnings in a flask under a reflux condenser. By these means esters were obtained with phenol, *o*-, *m*-, and *p*-cresols. In the case of phenol and *m*-cresol, unsuccessful attempts to obtain the esters were made by heating these materials with antimony trioxide with a reflux condenser only.

*Phenyl antimonite*.—One hundred and twenty-five grams of phenol and 25 grams of antimony trioxide were heated in a flask fitted with a Soxhlet apparatus containing anhydrous copper sulphate. Clouds of steam began to form at 100°, indicating that the reaction began at that temperature; the thermometer rose very quickly to the boiling point of phenol, and remained very close to that temperature (varying from 170° to 180°) for about seven hours, when the temperature gradually rose, and, after fifteen hours' heating, reached a maximum of 290°. This maximum is the highest temperature to which the ester can be heated without decomposition. The mixture of phenol, ester, and antimony trioxide was then shaken with water-free benzene, causing the precipitation of the antimony trioxide dissolved in the ester and in the phenol, and, after filtering, fractionated under diminished pressure. The benzene distilled at 30°, phenol at 70°, and the ester at 250°.\* The ester was purified by dissolving in benzene, filtering from any antimony trioxide, and separating by passing a current of hot, dry air over the benzene solution placed in a vacuum desiccator. The crystals thus obtained had no very definite melting point owing to the presence of some phenol. To remove the latter, the crystals were heated to 200° for twenty minutes, dissolved in benzene, filtered, and crystallised as before. The crystals thus obtained were light brown in colour, and melted at 13°. At 18°, *phenyl antimonite* has a specific gravity of 1.621, and boils at 250°/30 mm. It dissolves readily in absolute alcohol, ether, chloroform, or benzene, and decomposes on addition of water into phenol and antimony trioxide. On analysis, it was found to correspond with the formula  $(C_6H_5)_3SbO_3$  or  $(C_6H_5O)_3Sb$ . This ester was also prepared by heating a mixture of phenol, antimony trioxide, and calcium turnings in a flask fitted with a reflux condenser. By this method, a yield of 62 per cent. was obtained after two hours' heating. By the former method the yield is not more than 40 per cent. after fifteen hours' heating.

*o*-, *m*-, and *p*-Tolyl Antimonites.—One hundred and fifty grams of each of the cresols were heated with about 30 grams of antimony trioxide, using the methods described above. The excess of

\* Even at 250° the ester suffers partial decomposition.

antimony trioxide was separated by means of benzene, filtered, and the esters fractionated. After purification they were analysed, and found to correspond with the formula  $(C_6H_4 \cdot CH_3)_3SbO_3$  or  $(C_6H_4 \cdot CH_3 \cdot O)_3Sb$ . *o*-Tolyl antimonite crystals in dark brown masses, and melts at  $16^\circ$ ; its specific gravity is 1.480, and it boils at  $352^\circ$ . *m*-Tolyl antimonite is a yellow liquid, with a specific gravity of 1.475, and boils at  $300^\circ/30$  mm. *p*-Tolyl antimonite is a dark brown, crystalline solid, melts at  $14^\circ$ , has a specific gravity of 1.495, and boils at  $345^\circ/30$  mm.

Whilst in the case of the aliphatic alcohols a drying agent in the Soxhlet apparatus was essential to absorb the water formed and allow the alcohols only to drop back into the mixture, no drying agent was necessary with the phenols, as practically no phenol or ester ever found its way further than the side-tube of the Soxhlet.

The water formed remained in the Soxhlet, there being never sufficient volume of water produced to cause the syphon attachment to come into play. The use of metallic calcium, it will be noticed, gave a better yield of ester than the Soxhlet method.

*Method of Analysis of Phenyl and Tolyl Esters.*—To 1.5960 grams of phenyl antimonite, 5 c.c. of potassium hydroxide (containing 7 grams per 10 c.c.) were added, and then an excess of tartaric acid. The excess of tartaric acid was neutralised by sodium carbonate, and 25 c.c. of sodium hydrogen carbonate added. The whole was diluted to 500 c.c., and two samples of 20 c.c. each were taken for analysis. To each, 20 c.c. standard iodine was added in excess (shown by the formation of a precipitate of tri-iodophenol and the appearance of a clear yellow solution), the temperature being kept at  $65^\circ$ . The mixture was then cooled, acidified with dilute sulphuric acid, and diluted with water to 500 c.c. The tri-iodophenol was filtered off, and the excess of iodine in 100 c.c. of the filtrate was titrated against standard thiosulphate, using starch as indicator. The quantity of thiosulphate necessary, multiplied by five, represents the quantity of iodine that was in excess. This quantity, subtracted from the original amount of the iodine added, gave the amount necessary to change both the phenol to tri-iodophenol and the antimony trioxide to antimony pentoxide.

Owing to the presence of tartaric acid in the above, it was impossible to estimate at all accurately the antimony trioxide by means of dichromate. The method previously described under *isoamyl antimonite*, namely, weighing antimony as antimony tetroxide, was used. The percentage of antimony, as determined in this way, was found to be 30.10. The strength of the iodine

being known, the number of c.c. of iodine equivalent to 30.10 per cent. of antimony was subtracted from the iodine obtained in the previous determination, the difference being the amount combined with phenol.

To test the accuracy of this method, estimations were made with weighed quantities of (a) phenol, (b) antimony trioxide, (c) a mixture of these.

(a) To 0.8826 gram of phenol, 5 c.c. of a solution of potassium hydroxide (7 grams per 10 c.c.) were added, and the whole diluted with water to 250 c.c. ... (1)  
10 c.c. of this solution were equivalent to 28.90 c.c. of iodine.

(b) To 0.5000 gram of antimony trioxide were added 25 c.c. of a saturated solution of tartaric acid; sufficient sodium carbonate to neutralise the excess of the tartaric acid and 50 c.c. of sodium hydrogen carbonate were then added, and the whole diluted with water to 500 c.c. ... (2)  
100 c.c. of this solution were equal to 13.70 c.c. of iodine.

(c) To 10 c.c. of (1) were added 100 c.c. of (2), and together required 42.45 c.c. of iodine.

Thus 100 c.c. of (2) required 13.70 c.c. of iodine, and 100 c.c. of (1) required 28.90 c.c. of iodine; in all, 42.60 c.c., as compared with 42.45 c.c. when mixed, a difference of less than one-third of 1 per cent., which is well within the limits of experimental error.

#### Properties of the Esters of Phenol and its Homologues.

	Phenyl.	o-Tolyl.	m-Tolyl.	p-Tolyl.
Percentage yield .....	40.0	48.2	48.3	40.8
B. p./30 mm.....	250°	352°	300°	345°
Sp. gr. ....	1.621	1.480	1.475	1.495
M. p. ....	13°	16°	—	14°

The preparation of other esters from the oxides of arsenic and antimony and compounds containing alcoholic hydroxyl is being proceeded with in this laboratory. Attempts are also being made to overcome the difficulties experienced in obtaining the esters of sulphoarsenious acid in sufficient quantities to allow of their compositions being determined.

I wish to express my thanks to Professor W. R. Lang for suggesting this research, and for the interest he has taken in the work.

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