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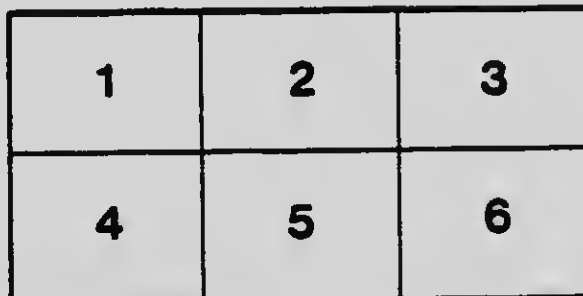
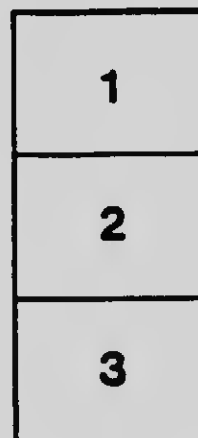
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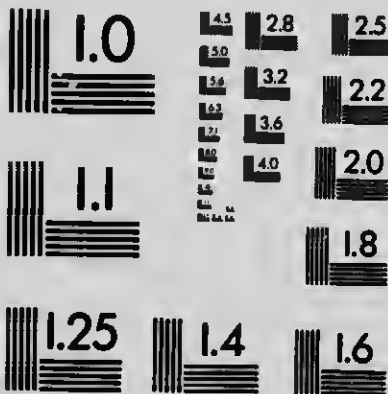
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PART 1—SOME ESTERS OF ARSENIOS ACID
PART 2—SOME ESTERS OF ANTIMONY TRIOXIDE

(2) Thesis

Submitted for the degree of Doctor of Philosophy in the
University of Toronto

by

(1)

JOHN FRANCIS MACKAY
III

To the
SENATE OF THE UNIVERSITY OF TORONTO.

We, the examiners appointed by the Board of Postgraduate Studies for the consideration of the theses submitted by Mr. J. F. MacKey for the degree of Ph. D., are of the opinion that they are a distinct contribution to Chemical knowledge and beg to recommend that they be accepted for the degree of Doctor of Philosophy in this University.

W. R. LANG
T. L. WALKER
W. H. ELLIS
F. B. ALLAN
W. LASH MILLER
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May 6, 1909.

I hereby certify that the theses above mentioned have been accepted by the Senate of the University of Toronto for degree of Doctor of Philosophy in accordance with the terms of the statute in that behalf.

JAMES BREBNER,

Registrar

The University of Toronto,

June 9, 1909.

PART 1—SOME ESTERS OF ARSENIOS ACID
PART 2—SOME ESTERS OF ANTIMONY TRIOXIDE

Thesis

Submitted for the degree of Doctor of Philosophy in the
University of Toronto

JOHN FRANCIS MACKAY

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PART I—SOME ESTERS OF ARSENIOS ACID

By WILLIAM ROBERT LANG, JOHN FRANCIS MACKAY, and
ROSS AITKEN GORTNER.

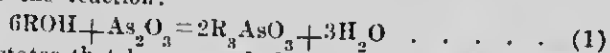
J.M. Crafts (*Bull. Soc. chim.*, 1870, [11], 14, 99), in referring to the existence of compounds of arsenic with alcohol radicals, pointed out that no esters of arsenious or of arsenic acid had been prepared up to the year 1870, and described a method by which he obtained ethyl, methyl, and amyl arsenates; this consisted in heating the corresponding iodides in sealed tubes at 100° with normal silver arsenate. The esters were purified by washing with ether and distilling under diminished pressure. They are liquids of high boiling point, above 200°, and suffer partial decomposition if distilled under atmospheric pressure; in the case of the amyl arsenate so much so that he found it impossible to obtain it pure even when distilled in a vacuum. The addition of water to them causes immediate and complete decomposition into arsenic acid and the alcohol. Crafts determined their composition by weighing the precipitated arsenic acid as the magnesium salt and the carbon and hydrogen by combustion, and gave them the formula R^3AsO_4 . For the arsenites of the alkyl radical he used three methods, a sealed tube being employed: (1) the interaction of arsenious oxide and ethyl silicate at 200°, (2) the interaction of ethyl iodide and silver arsenite at 150°; and (3) the interaction of arsenic bromide and sodium ethoxide, which last method he considered the best, although in it a secondary reaction between the ester formed and the sodium ethoxide causes a condition of equilibrium to be set up, and no more ester is formed.

It is to be noted that even if disodium hydrogen arsenite is employed the resulting arsenite is always the trialkyl salt. Crafts states that arsenious oxide and alcohol do not react when heated in a sealed tube, nor does arsenious oxide either with ether alone or with the addition of ethyl acetate, even when in contact for twenty hours.

These esters prepared by Crafts are specified by Auger (*Compt. rend.*, 1902, 134, 238) as the only ones known, and he refers in a later paper (*Compt. rend.*, 1906, 143, 907) to Crafts' inability to obtain any ester by heating the alcohols and oxides of arsenic in a sealed tube. Auger has his conviction that an ester is produced on the fact that arsenious oxide is volatile in alcohol vapour, although not in water vapour, and concludes that this cannot be accounted for unless there is an ester formed. Also he succeeded in preparing an ester from glycerol and arsenic oxide,

and from ethyl, methyl, isopropyl, isobutyl, and isoamyl alcohols and arsenious oxide. He heated the alcohols with crystalline arsenious oxide for some hours, evidently in a sealed tube, as the temperatures quoted are far above the boiling points of the alcohols, and gives 6.5 per cent. as extreme limit of esterification in the case of methyl alcohol, and 1.2 per cent. in that of ethyl alcohol. Calculating from his figures, the yield of ester for the higher alcohols appears to be 2.62 per cent., 0.25 per cent., 1.00 per cent., and 0.63 per cent. for propyl, isopropyl, isobutyl, and isoamyl alcohols respectively.

So far as can be gathered from the paper, Auger takes no account of the extreme solubility, as we have found, of arsenious oxide in the ester. These small yields and the difficulty found by Crafts in obtaining any results from the action of the acid on the alcohol are evidently due to the reversal of the reaction:



Auger states that he removed the water as it was formed by fractional distillation (in the case of isobutyl and isoamyl esters), or by passing the mixture of alcohol and water vapour over calcium carbide placed in an adapter, thus removing the water and allowing the alcohol to drop back into the flask in which the reaction takes place. An excellent yield, how much is not stated, of propyl, *n*-butyl and isobutyl arsenites was thus obtained. Phenol, in the same way, yielded an ester hitherto only prepared by the action of sodium phenoxide on arsenic trichloride.

The nature of the reaction expressed by equation (1) and the properties of the ester clearly show that only by removing the water as it is formed can one expect to get a large yield. Our work has been done in two ways, namely, by heating the mixture in a vessel to which is attached a modified Soxhlet tube and condenser, the Soxhlet containing anhydrous copper sulphate, and by adding this dehydrating agent directly to the mixture. A comparison of the yields obtained is given in the sequel. By these two methods yields of from 14.8 per cent. (cold) to 58.6 per cent. (hot) have been obtained with aliphatic alcohols, and with the phenols as high as 90 per cent. Experiments have also been made, with very encouraging results, on benzyl alcohol and on esters of hydroxy-acids. We hope to show that the use of such a dehydrating agent as copper sulphate in a Soxhlet tube will allow of the preparation of a series of esters from the oxides and possibly sulphides of arsenic, antimony, tin, and perhaps bismuth with compounds containing hydroxyl, where the boiling points of such esters are higher than that of water, as, indeed, is the case with all of these; also with anhydrous copper sulphate in contact with the substances themselves. In many preparations, too, of esters generally and allied products, the formation of water in the reaction produces an equilibrium resulting in a very low yield. It is expected that by removing this water, as is done in the instances described in the present paper, the yields will be greatly increased in many commercial processes.

*We have passed the vapour of methyl alcohol over arsenious oxide heated in a sealed tube, and the ether obtained differs entirely from methyl arsenite.

EXPERIMENTAL.

Heating with Inverted Condenser Only.—Weighed quantities of propyl, isobutyl, and isoamyl alcohols were mixed with excess of arsenious oxide and heated with a direct flame for forty-five minutes in a flask to which a reflux condenser was attached. The clear liquid obtained was poured off from the excess of arsenious oxide and fractionated under diminished pressure. The esters so purified were analysed and the yield compared with that calculated from equation (1).

Our method of ascertaining the composition of the esters differs from that used by Anger.* The ester was decomposed with water, forming arsenious oxide and liberating the alcohol. The arsenious oxide was dissolved in sodium carbonate and titrated with N/10 iodine (a preliminary test having shown that the alcohol did not react with iodine). By this means the quantity of arsenic in the ester was determined.

isoAmyl Arsenite.—1.4 Grams were decomposed with 10 c.c. of water, sufficient sodium carbonate added to dissolve the arsenious oxide, and the whole diluted to 100 c.c.; 25 c.c. of this required 17 c.c. of standard iodine for oxidation, corresponding with 22.4 per cent. of arsenic. In 50 grams of the ester, the alcohol was determined and found to weigh 39 grams, or 78 per cent. *isoButyl* and propyl arsenites were also analysed in a similar way:

Ester	Per cent. As found.	Per cent. As calculated as $(RO)_3As$.
Methyl	44.5	44.6
Ethyl	—	—
Propyl	29.6	29.7
isoButyl	25.7	25.5
Amyl	22.2	22.3
isoAmyl	22.4	22.3

Expressing these as salts of arsenious acid, the formulae become $(C_5H_{11})_3AsO_3$, $(C_4H_9)_3$, and $(C_3H_7)_3AsO_3$.

Propyl arsenite is a yellow, mobile liquid boiling at 216° and decomposing very readily on addition of water.

isoButyl arsenite is a deep yellow, mobile liquid of specific gravity 1.069; it decomposes rapidly in presence of water into isobutyl alcohol and arsenious oxide; under 760 mm. pressure it decomposes at 242°, and boils at 157° under 30 mm. pressure.

isoAmyl arsenite is a yellow liquid of specific gravity 1.050; it boils at 185° under 30 mm. pressure, and under atmospheric pressure it decomposes at 284°; in the presence of water, it decomposes into isoamyl alcohol and arsenious oxide.

*Anger determined the amount of arsenic in the cooled liquid obtained (a mixture of the ester and alcohol) by means of iodine. The difference between this and the amount of arsenious oxide that would dissolve in the same quantity of alcohol in the cold was taken as representing the amount of ester formed (*Compt. rend.*, 1906, 143, 908). No account was taken of the solubility of arsenious oxide in the esters themselves.

Heating with Soxhlet Attachment and Anhydrous Copper Sulphate.—

To eliminate the water as it is formed and so increase the yield of ester, the conditions of the experiments were modified. One hundred and sixty grams of isoamyl alcohol were added to 70 grams of arsenious oxide in a 300 c.c. flask. An ordinary Soxhlet tube was connected with the flask, and a condenser, fitted with a calcium chloride tube, was attached to the Soxhlet, which contained a large filter paper filled with anhydrous copper sulphate. The liquid in the flask was heated to boiling, and the water formed was absorbed by the anhydrous copper sulphate, which turned blue as soon as the first drops of condensed liquid fell on it. Heating was stopped after forty-five minutes, when small rings of a compound of high boiling point began to form on the sides of the flask; after cooling, the clear product was filtered and fractionated under diminished pressure. 110.25 grams of ester were obtained, being a yield of 58.6 per cent. as compared with 13.22 per cent. obtained without the use of a dehydrating agent.

In similar experiments with isobutyl and propyl alcohols, yields of 56.25 per cent. and 56.75 per cent. respectively were obtained, as compared with 11.09 and 8.79 per cent. when no dehydrating agent was employed.

Use of Dehydrating Agent in the Cold.—The esterification of these three alcohols by arsenious oxide can be carried out even in the cold if a dehydrating agent is used; 120 grams of the alcohol were shaken in a stoppered bottle at room temperature with 60 grams of arsenious oxide and 70 grams of anhydrous copper sulphate for three days. The following yields were obtained: isoamyl arsenite, 17.2 per cent.; isobutyl arsenite, 15.8 per cent.; propyl arsenite, 14.8 per cent.

The following table indicates the comparative yields (per cent.) by different methods:

Ester	Auger (in sealed tube)	With anhydrous copper sulphate:		
		Reflux condenser.	in Soxhlet.	in the cold
Methyl	6.5	—	33.8*	—
Ethyl	1.2	—	4.5*	—
Propyl	2.62	8.79	56.75	14.8
isoButyl	0.25	11.09	56.25	15.8
Trimethylcarbinol	—	—	54.27	—
Amyl	1.00	—	54.00	—
isoAmyl	0.63	13.22	58.62	17.2

*The Soxhlet was not used, but the anhydrous copper sulphate was placed with the alcohol and arsenious oxide in a flask fitted with a reflux condenser.

A probable explanation of the low yield in the case of the ethyl arsenite lies in the fact that ethyl alcohol itself has a strong affinity for water which for small quantities of water present, cannot be overcome by the anhydrous sulphate. This is really shown by adding a drop of water to 5 c.c. of ethyl alcohol in which a little anhydrous copper sulphate has been placed. The copper sulphate is apparently not affected, whilst in the case of the higher alcohols a blue color appears almost instantly, showing the hydration of the copper sulphate. Methyl alcohol does not respond to this test as readily as do the higher alcohols, but it responds to this test as readily as do the

higher alcohols, but it responds more readily than does ethyl alcohol. The yield in each case, using the copper sulphate, probably bears a direct relation to the respective affinities of the alcohol and of the copper sulphate for the water of the reaction. If a substance could be used which had a greater dehydrating power and at the same time was insoluble in alcohol, a higher yield would doubtless be obtained. Calcium carbide (Auger, *Compt. rend.*, 1906, 143, 908) is not such a material; we have compared the yields obtained by replacing the anhydrous copper sulphate in the Soxhlet with fresh calcium carbide, using various alcohols, and the highest yield was in the case of *isoamyl* alcohol where 40.2 per cent. of ester was obtained after two hours' heating.

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Esters obtained with Phenol and its Homologues.—For the esterification of these with arsenious oxide a side-necked flask was used the neck of which was bent upwards and attached to the Soxhlet, leaving the mouth of the flask free to receive a thermometer.

Phenyl Arsenite.—Weighed quantities of phenol (140 grams) and arsenious oxide (80 grams) were heated together, and in all cases it was observed that the reaction began at 100°, the mixture boiling violently at that temperature. The thermometer gradually rose to 133°, when a thick cloud formed in the flask. The temperature remained constant at that point for a few minutes and then gradually rose to a maximum, where it was kept for about five minutes: the heating was then stopped and the contents of the flask allowed to cool. The mixture of phenol, ester, and arsenious oxide, the latter of which is very soluble in the ester, was shaken with benzene, causing the precipitation of the arsenious oxide dissolved in the ester. The mixture was then filtered and the benzene solution of the ester fractional under diminished pressure. The benzene distilled at 20°, the phenol at 69°, and the ester at 305°. The ester, purified by redistillation, weighed 105 grams, representing a yield of 60 per cent. *Phenyl arsenite* is a deep yellow, viscous liquid with a specific gravity of 1.59; it freezes at 31°, and boils 305° under a pressure of 30 mm. It dissolves readily in methyl alcohol, benzene, ethyl acetate, or chloroform, and decomposes on addition of water, but not so readily as the fatty arsenites. It was found on analysis to correspond with the formula $(C_6H_5O)_3As$, or $(C_6H_5)_3AsO_3$.

o-, m-, and p Toly Arsenites.—One hundred grams of each of the cresols were heated with arsenious oxide for thirty minutes in the apparatus previously described, the arsenious oxide being separated by benzene. The liquid was then fractionated, and the esters, after having been purified and analyzed as in the case of the phenyl arsenite, were found to correspond with the formulae $(C_6H_4Me)_3As$, or $(C_6H_4Me)_3AsO_3$.

Naphthyl Arsenite.—One hundred grams of naphthol were heated with 30 grams of arsenious oxide for thirty minutes and the arsenious oxide in the ester separated by means of benzene. As yet, however, the pure ester has not been isolated.

Benzyl Arsenite.—One hundred grams of benzyl alcohol were heated with 35 grams of arsenious oxide for thirty minutes. The maximum temperature was 240°. The clear liquid was decanted and 75 c.c. of benzene added, the arsenious oxide collected, and the filtrate fractionated under 30

mm. pressure. The *benzyl arsenite* distilled at 285° , suffering partial decomposition. Although in the case of the fatty alcohols a drying agent in the Soxhlet was essential to absorb the water formed and to allow only the alcohols themselves to drop into the mixture, no such device 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 this apparatus, there being never sufficient volume of liquid produced to cause the syphon attachment to come into play.

To ascertain if it was possible to obtain these esters without the removal of the water formed during the reaction, the same quantities of phenol, benzyl alcohol, *o*-, *m*-, and *p*-cresol respectively, as were used in the previous experiments, were heated with arsenious oxide in a flask fitted with a reflux condenser only, but in no case was any arsenite formed in quantities sufficient to enable it to be isolated.

Method of Analysis for Esters of Phenol and its Homologues.—To determine the composition of the esters, it was found necessary to distil them several times in order to remove all traces of arsenious oxide which is readily soluble in them, in some cases to the extent of 30 per cent. About 3 grams of the ester were decomposed by 5 c.c. of water and 10 c.c. of potassium hydroxide (containing 700 grams of potassium hydroxide per litre), and the whole diluted to 500 c.c. Two samples of 10 c.c. each were taken for analysis; to one sample 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° . The mixture was then cooled, acidified with sulphuric acid, and diluted to 500 c.c. with water. The excess of iodine in 100 c.c. of this was titrated against standard thio-sulphate, using starch as indicator. The quantity of thio-sulphate necessary, multiplied by five, represents the quantity of iodine used. This quantity, subtracted from the original amount of iodine added, gave the amount necessary to change both the phenol to tri-iodophenol and the arsenious oxide to arsenic oxide. To determine the quantity of arsenious oxide present in the ester, an excess of standard potassium dichromate was added to the second sample and this excess was determined with standard ferrous sulphate. The ratio between the dichromate and iodine being known, the number of c.c. of iodine equivalent to the amount of dichromate used was found and subtracted from the total iodine obtained in the previous determination, the difference being the amount combined with the phenol. From these data the relative quantities of arsenious oxide and phenol, formed by decomposing the ester, were obtained, and the composition of the ester thus determined.

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

(a) To 0.8826 gram of phenol, 5 c.c. of potassium hydroxide (700 grms per litre) were added and the whole diluted to 250 c.c. . . (1)

Ten c.c. of this solution were found to be equivalent to 25.75 c.c. of standard iodine.

(b) To 0.5 gram of arsenious oxide, 5 c.c. of the same potassium hydroxide were added and diluted to 250 c.c. (2)

Ten c.c. of this solution were found to be equivalent to 6.5 c.c. of

standard iodine.

(c) To 10 c.c. of solution (1), 10 c.c. of solution (2) were added and found to require 32.30 c.c. of standard iodine.

Thus 10 c.c. of solution (1) required 27.75 c.c. of iodine, and 10 c.c. of solution (2) required 6.50 c.c. of iodine; in all 32.25 c.c. as compared with 32.30 c.c. when mixed, a difference which is well within the limits of experimental error.

In order to see if arsenious oxide can be determined accurately in the presence of phenol by means of dichromate, experiments similar to those made with iodine were carried out with it. Ten c.c. of solution (2) required 6.07 c.c. of dichromate, a mixture of 10 c.c. of (2) with 10 c.c. of (1) required 6.09 c.c. of dichromate, or an error of less than 0.3 per cent.

Properties of the Arsenites prepared from Phenol and its Homologues.

	Phenyl arsenite.	Benzyl arsenite.	<i>o</i> -Tolyl arsenite.	<i>m</i> -Tolyl arsenite.	<i>p</i> -Tolyl arsenite.
Yield (per cent)					
(a) with Soxhlet	60	100	96	94	95
(b) without Soxhlet	nil	nil	nil	nil	nil
Specific gravity	1.59	1.43	—	1.45	1.46
Refractive index*	—	1.572	—	—	—
Boiling point † under 30 mm.	305°	255°	—	346°	—
Freezing point	-31°	-36°	—	—	—
Colour.	yellow	blue	dark brown	dark brown	brown

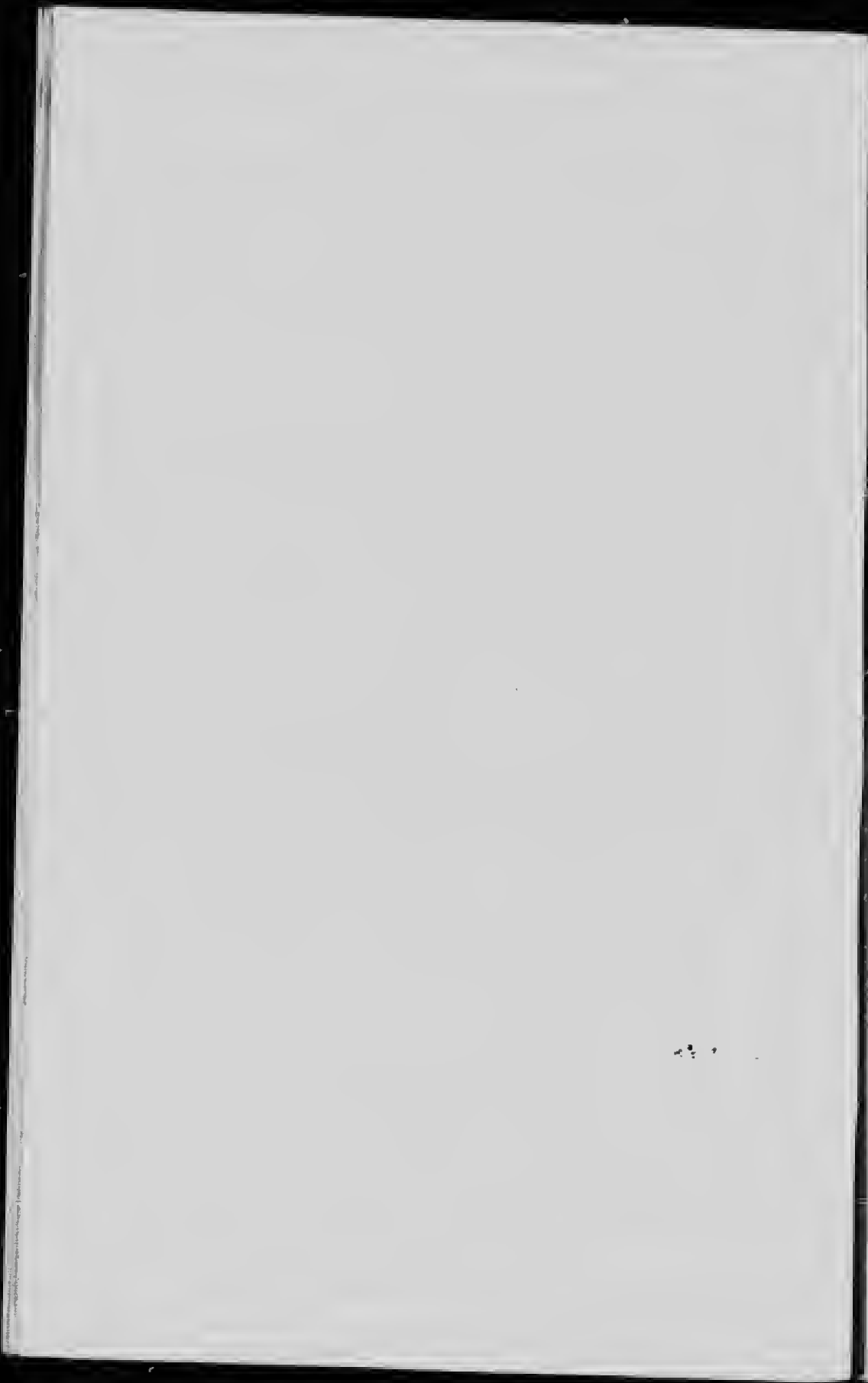
* The blanks indicate that the refractive index is greater than 1.62098, the limit of the prism used.

† Where the boiling point is not given it is above 360°.

All these esters are soluble in methyl and ethyl alcohols, ether, benzene, ethyl acetate, or chloroform, and are decomposed at once by water.

This method of esterification is being carried out with arsenious oxide and the dihydric and trihydric phenols, but the quantitative results are not ready. A successful attempt has also been made to form similar esters with hydroxy-acids, methyl salicylate being heated with arsenious oxide. The products of the reaction, namely, water and an oil, were driven up into the Soxhlet where the latter decomposed, liberating arsenious oxide. The oil boils at about the same temperature as the methyl salicylate and has an almost unburnable odour. When the dehydrating agent is used in the Soxhlet it is expected the new ester will readily be separated.

Experiments have also been tried with arsenious sulphide in place of the oxide and a small yield of an ester obtained, presumably of the composition R_3AsS_3 , but the upper portions of the flask and the condenser became coated with the orange-colored arsenious sulphide, showing that decomposition had occurred. The work is being continued.

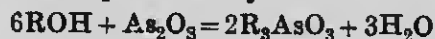


PART II

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 R_3AsO_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° ; (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° , 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	8.09 per cent.
Ethyl	"	"	"	3.00* "
Propyl	"	"	"	13.3 "
<i>isoButyl</i>	trace	"	trace	15.11 "
Amyl	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 antimony tetroxide by treatment with fuming nitric acid and ignited:

1.0057 gave 0.4024 Sb_2O_4 . Sb=31.57.

$\text{C}_{15}\text{H}_{33}\text{O}_3\text{Sb}$ requires 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 R_3SbO_3 .
Methyl	56.68	56.41
Ethyl	—	57.41
Propyl	40.29	40.40
isoButyl	35.37	35.10
Amyl	31.44	31.48
isoAmyl	31.34	31.48

Expressing these as salts of antimonous acid, we arrive at the general formula R_3SbO_3 for them.

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

Methyl antimonite is a colourless liquid, b. p. 65° , sp. gr. 1.025.

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

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° .

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° 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° , 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 ... grams of each of the cresols were heated with about 30 grams of antimony trioxide, using ... 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 $(C_6H_4 \cdot CH_3)_3O \cdot Sb$. *o*-Tolyl antimonite crystallises in dark brown masses, and melts at 16° ; its specific gravity is 1.480, and it boils at 352° . *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° , 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° . 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 the 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.

(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.	<i>o</i> -Tolyl.	<i>m</i> -Tolyl.	<i>p</i> -Tolyl.
Percentage yield	40.0	48.2	48.3	40.8
B. p./30 mm.....	250°	352°	300°	345°
Sp. gr.	1.021	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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