

THE REACTIONS OF AMYLENE WITH ARSENIC TRICHLORIDE
AND THE NATURE OF THE PRODUCTS FORMED

by

LLOYD LANDER WOODS

A. B. Friends University, Wichita, 1930

A THESIS

submitted in partial fulfillment of the
requirements for the degree of

MASTER OF SCIENCE

KANSAS STATE COLLEGE
OF AGRICULTURE AND APPLIED SCIENCE

1934

Docu-
ment
LD
2668
T4
1734
u61
C.2

TABLE OF CONTENTS

	Page
INTRODUCTION	2
HISTORICAL	4
EXPERIMENTAL	8
The Reaction Between Arsenic Trichloride and Amylene	8
Separation of the Reaction Mixture and Analysis of the Different Fractions	10
SUMMARY	18
ACKNOWLEDGMENT	18
APPENDIX	19
Determination of Arsenic	19
Determination of Chlorine	20
LITERATURE CITED	22

INTRODUCTION

During the past thirty years there has been much interest in medicinals and insecticides that contain arsenic.

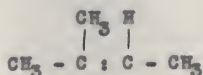
The investigations which are recorded in this thesis were undertaken for the purpose of studying: (a) the reactions of arsenic trichloride with olefines, and (b) the chemical nature of the products formed.

It was thought that if the reaction between arsenic trichloride and a rather high molecular weight olefine could be effected, a product might be obtained, which, either before or upon hydrolysis, would have some insecticidal or medicinal value.

Reactions of arsenic trichloride with acetylene and acetylene derivatives have been successfully carried out (1) and the literature also records the simple addition of arsenic trichloride to low molecular weight olefines such as ethylene (2). However, the literature does not record any case in which arsenic trichloride has been successfully added to or condensed with fairly high molecular weight olefines.

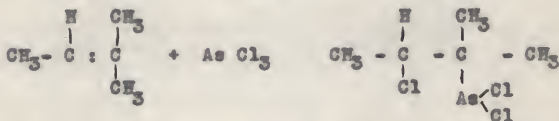
The cracking distillation of petroleum gives rise to olefinic by-products which are on the market, and one of these, amylene, was chosen for this work. Commercial

amylene is mainly a mixture of the pentene isomers and we have considered it to be chiefly trimethylethylene.



Since acetylene and acetylene derivatives are more highly unsaturated and are much more endothermic in nature than olefines, we should expect them to be, therefore, more reactive with arsenic trichloride. To effect a reaction between amylene and the arsenic trichloride, possibly different procedures, different reaction conditions, and different catalysts would need to be used.

If arsenic trichloride could be made to add in the most simple way to amylene (considered as the trimethyl ethylene isomer) it should give rise to β -chloro tertiary amyl dichloro arsine, according to the following equation:



A search through the literature shows that this compound has not been prepared although alkyl arsine dichlorides and dialkyl arsine chlorides have (3). Since the quantitative determination of arsenic and chlorine are

comparatively simple procedures, it should be rather easy to check up on the chemical nature of the products of the reaction between arsenic trichloride and the olefines, and to check up on the chemical nature of any derivative formed from the products of the reaction.

HISTORICAL

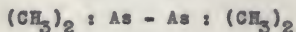
Although the most important development in the study of compounds containing arsenic have been within the past 30 years, some of the earlier investigations are of interest and importance.

Cadet (5) was the first to prepare an arsenic-containing organic compound. He distilled a mixture of potassium acetate and arsenic trioxide and obtained a mixture of two liquids which was later called, "Cadet's fuming arsenical liquid." Although this reaction could be easily carried out and gives a very interesting reaction product, the exact composition of this mixture was not known until a long time later.

No constructive investigation was done on the molecular composition of the compound contained in "Cadet's fuming arsenical liquid" until Bunsen (6) began his researches. After six years of investigation Bunsen decided that this liquid mixture, which he called "Alkarsin", was

a polymeric alcohol with the oxygen replaced with an equal number of arsenic atoms, and corresponding to the formula $(\text{CH}_3)_2 \text{As}$.

Berzelius (7) became interested in this work on the identity of the compounds composing "Cadet's fuming arsenical liquid" after the appearance of Bunsen's first article. His investigations led him to believe, "Alkarsin" was the oxide of "Cacodyl" to which he assigned the following constitutional formula:



However, the final proof of this formula was reached through the researches of Cahours and Riche (8).

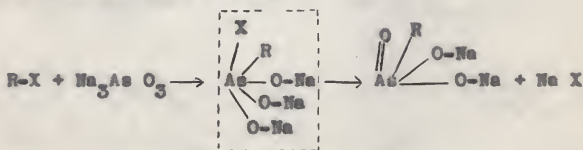
Other investigations along the same line were carried out by Frankland (9) who had just discovered that zinc reacted with alkyl halides to form zinc alkyls. He considered the union of arsenic in "Cacodyl" to be analogous to that of zinc in zinc organo compounds.

In 1903 Ehrlich (10) began his brilliant researches on arsenic compounds with the study of the therapeutic use of atoxyl and its related compounds. He started a series of experiments to produce an arsenical which would be effective in destroying trypanosomes in the body of syphilitic sufferers, and cure the disease of sleeping sickness. He

finally synthesized a drug which he called 606, through the help of his brilliant student Bertheium (11). Salvarson or 606, fulfilled all of Ehrlich's hopes in that it quickly ridded the blood stream of trypanosomes in a short while and also destroyed spirillae and spirochetes. However, the drug was still a little toxic to the host so Ehrlich continued his work until he had isolated neoarsphenamine (924) which had the same efficiency as 606 but was not so toxic to the host.

Some of the more important methods for the preparation of arsenic containing organic compounds which were used by the early investigators are as follows:

Meyer (12) prepared arsonic acids by heating alkyl iodides with sodium arsenite.

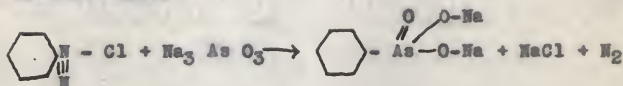


Quick and Adams (13) improved Meyer's method and removed several of the objectionable features by using alkyl bromides or chlorides instead of iodides.

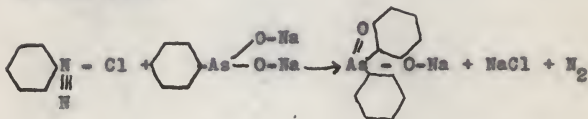
Bart (14) used a method for the preparation of organic compounds containing arsenic which has made possible a

great many aryl arsenic acids. These arsenic containing acids are formed by bringing aryl diazonium halides and sodium arsenite together in the presence of copper salts. Even better results may be obtained by using various metallic catalysts in place of the copper salts. The reaction is always carried out in an alkaline medium when metallic catalysts are used.

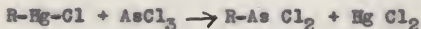
Arsonic acids:



Arsinic acids:

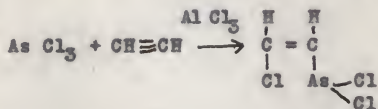


Roeder and Blasi (15) used a very good general method for preparing arsenicals. In their procedure arsenic trichloride was treated with mercury halides of the formula R-Hg-Cl . They found that R- might be an aryl, an alkyl, or even a heterocyclic group.



Green and Price (1) added arsenic trichloride to acetylene by passing dry acetylene into a cooled mixture

of arsenic trichloride containing aluminium chloride. There was formed a mixture of β -chloro vinyl dichloro arsine, β -chloro di vinyl chloro arsine, and β -chloro tri vinyl arsines.



EXPERIMENTAL

The Reaction Between Arsenic Trichloride and Amylene

To effect a reaction between arsenic trichloride and amylenes, several procedures were used.

The amylenes (1 mole) and the arsenic trichloride (1 mole) were mixed together and heated under an efficient reflux condenser for 16 hours. The method did not seem to effect a marked reaction as most of the amylenes and arsenic trichloride could be recovered unchanged. Similar results were obtained when 2 moles of amylenes and 1 mole of arsenic trichloride were used.

The addition of anhydrous aluminium chloride to the above mixtures seemed to increase the interaction, for upon distillation a small amount of a blue colored compound

was found after the unchanged amylene and arsenic trichloride had been distilled out. The yields of this material were too small for identification.

The results obtained by refluxing arsenic trichloride, amylene, and aluminium chloride together suggested that a much greater reaction could be effected if they were heated together under pressure.

Accordingly, amylene (1 mole) was mixed with arsenic trichloride (1 mole) and resublimed aluminium chloride (1 gram) added. Care was taken to exclude traces of moisture. The mixture was then placed in a Carius tube and sealed with an oxygen flame while the lower end of the tube containing the reaction mixture was held in a bath of ice water.

The tube was then placed in an iron pipe two inches in diameter and immersed in an oil bath. The oil bath was heated to 130° - 150° for 25 hours. The bath was allowed to cool over night. When the tube was removed and opened, there was no evidence of internal pressure or liberation of hydrochloric acid vapors.

Separation of the Reaction Mixture and Analysis of the Different Fractions

The reaction mixture was filtered into a dry 200 cc. distilling flask to remove the aluminium chloride. The flask was attached to a Liebig condenser and the mixture distilled by heating the flask in an oil bath. This was to avoid super-heating and to maintain a fairly uniform temperature.

The temperature of the oil bath was raised to 158° and the distillate collected in fractions at 44° - 49° , 58° - 62° , and 129° - 134° . These fractions were further separated by fractional distillation and their arsenic content determined by analysis. When the temperature of the oil bath reached 158° , no more volatile products were obtained, but a heavy liquid residue remained. This residue had a very nauseating garlic-like odor and was blue black in color. This non-volatile fraction was further purified by filtration.

The arsenic content of the fractions and the residue were determined to be as follows:

Found	B.P.	Arsenic (per cent)
Fraction 1	44°-47°	Only traces
Fraction 2	58°-62°	9.62
Fraction 3	129°-134°	39.9
Fraction 4	(Non-volatile)	30.7

These results indicate that fraction 1 was very nearly pure amylene; fraction 2 was mostly amylene but did contain considerable arsenic trichloride as an impurity; and fraction 3 was very nearly pure arsenic trichloride since the arsenic content corresponds closely to the theoretical of 40.8 per cent. The physical nature and the arsenic content of the fraction not volatile from the flask in the oil bath at 158° shows that it was not pure arsenic trichloride and probably did not contain much arsenic trichloride since the latter boils at a temperature of 122°. Since the arsenic content of this substance agrees very closely with that of β -chloro tertiary amyl dichloro arsine. Its chemical nature was further investigated and methods for improving its yield attempted. The chlorine content of fraction 4, the non-volatile fraction, was determined and found to be 47.1 per cent. The following method for the

purification of the residual material was then used.

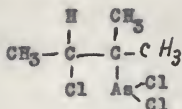
The fractional distillation of the volatile material was carried out in the previously described way. When the temperature of the distilling material reached 134° the condenser was removed and the residual material was heated under a reduced pressure of 1 mm. The temperature of the oil bath was not allowed to exceed 158° in order to protect the sample from decomposition. When heated in this way under reduced pressure, only a very small amount of volatile material was obtained.

The residue, which was a blue black colored oil liquid, was filtered and analyzed for chlorine and arsenic.

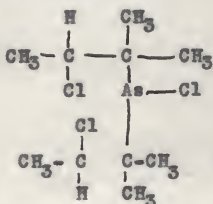
Found	: :	Arsenic (per cent)	: :	Chlorine (per cent)
1		25.3		25.5
2		24.14		25.5
3		23.9		25.2
4		24.1		25.2
5		23.94		25.2
6		24.1		25.2

The results of the arsenic and chlorine determination upon the residue obtained from the distillation of the non-

volatile fraction under reduced pressure are uniform. They do not, however, correspond to the arsenic or chlorine content which should be found in arsenic trichloride or the β -chloro tertiary amyl dichloro arsine.



The arsenic content of this fraction does correspond very closely with that which we should expect if the addition were between 1 mole arsenic trichloride and 2 moles of amylene to give a di β -chloro tertiary amyl chloro arsine having the following formula:



However, the chlorine content doesn't agree for a compound of this structure.

Theory	: Arsenic : (per cent)	: Chlorine : (per cent)
Arsenic trichloride	40.8	59.2
Mono alkyl product	29.83	42.33
Di alkyl product	23.32	33.1

There seemed to be considerable decomposition of fraction 4 when it was heated under reduced pressure, as has been explained. Accordingly, the fractional distillation of the entire reaction mixture between amylene and arsenic trichloride was carried out as previously described, but in an atmosphere of carbon dioxide. The reaction mixture was separated by fractional distillation in an atmosphere of carbon dioxide into fractions of the following temperature ranges: $< 40^{\circ}$, 52° - 53° , 88° - 96° , 102° - 108° . The temperatures at which the volatile material boiled were consistently lower than obtained in ordinary distillation, due possibly to the effect of the atmosphere of carbon dioxide.

The residue obtained by distillation in an atmosphere of carbon dioxide, still had a blue-black color and was more mobile and seemed to contain less decomposition material. It was freed from traces of small, solid particles

by filtering with suction through a Gooch crucible.

Arsenic and chlorine determination on the purified residue gave the following results:

Found	: :	Arsenic (per cent)	: :	Chlorine (per cent)
1		30.69		42.7
2		30.1		41.5
3		39.99		40.56
4		30.45		40.12
5		29.8		
6		30.55		
7		29.68		

These figures agree closely with the chlorine and arsenic content of β -chloro tertiary amyl dichloro arsine.

Theory	: :	Arsenic (per cent)	: :	Chlorine (per cent)
β -chloro tertiary amyl dichloro arsine		29.83		42.33

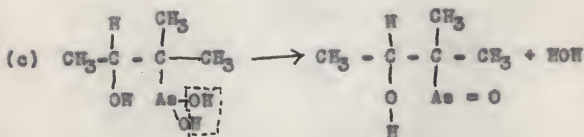
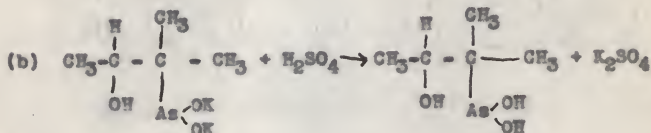
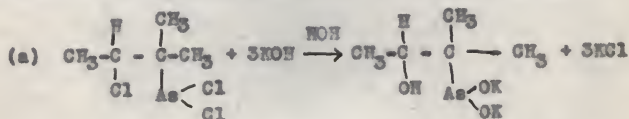
This substance, which was considered to be β -chloro tertiary amyl dichloro arsine, was found to have a specific gravity of 1.66 and was found to be readily soluble in the inert organic solvents such as ligroin, benzene, and ether. It reacts slowly with moist air, giving vapors of hydrochloric acid, and is hydrolyzed by dilute sulphuric acid. Dilute and concentrated hydrochloric acid give a yellow colored substance lighter than water. The β -chloro tertiary amyl dichloro arsine is also hydrolyzed by dilute alkalis, and by boiling it with concentrated potassium hydroxide, a brown colored homogeneous solution is obtained.

The steam distillation of this solution gave a very small amount of colorless oily globules, which upon cooling, crystallized out in indefinite shape. The aqueous part of the distillate was filtered and gave no indication of containing any dissolved material as nothing could be salted out with potassium carbonate.

When the residual liquid was cooled, a small amount of a flocculent material floated upon the surface of a brown colored solution. When this residual liquid was extracted with ether, nothing dissolved and the aqueous solution still retained its brown color. When the residue was acidified with sulfuric acid, no oily compound was obtained. However, when it was extracted with ether, there was an appreciable

loss of color.

The reactions of β -chloro tertiary amyl dichloro arsine with aqueous potassium hydroxide and the acidification of the reaction mixture with sulphuric acid could probably be represented with the following equations:



The products of these reactions have not been studied.

The β -chloro tertiary amyl dichloro arsine unites with aniline to form a double salt which is very insoluble in inert solvents, and decomposes upon being exposed to the effects of air or moisture.

SUMMARY

1. The reaction of amylene and arsenic tri chloride was effected by heating them together under pressure in the presence of aluminium chloride.

2. The isolation of the reaction product was best accomplished by fractional distillation in an atmosphere of carbon dioxide.

3. β -chloro tertiary amyl dichloro arsine was obtained as a non-volatile blue-black colored liquid.

4. The physical properties of β -chloro tertiary amyl dichloro arsine are given and some of its reactions are described.

ACKNOWLEDGMENT

This work was made possible through the effort and guidance of Dr. C. W. Colver to whom I wish to extend my sincere appreciation.

LITERATURE CITED

- (1) Green, S. J. and Price, T. S.
Chloro Vinyl Chloro Arsines. J. Amer. Chem. Soc.
119:448. 1921.
- (2) Nekrassow, W. W. and Nekrassow, A. S.
-Chloro Substituted Arsenic Compounds. Ber.
61b; 1816-21. 1928.
- (3) Dehn William and Wilcox, Burton
Secondary Arsines. Amer. Chem. J. 35: 52-54.
1906.
- (5) Cadet de Gassicourt, L. C.
Organic Arsenical Compounds. New York. Chemical
Catalogue Company, 17 p. 1923.
- (6) Bunsen, R.
Organic Arsenical Compounds. New York. Chemical
Catalogue Company, 17-18 p. 1923.
- (7) Berzelius, J. J.
Organic Arsenical Compounds. New York. Chemical
Catalogue Company, 18 p. 1923.
- (8) Cahours, A. and Riche, A.
Recherches Sur de Nouveaux Radicaux Organiques
Referant de L'Arsenic. Compt. Rend. 39: 541-48.
1854.
- (9) Frankland, E.
Organic Arsenical Compounds. New York. Chemical
Catalogue Company, 18 p. 1923.
- (10) Ehrlich, P.
Uber den Jetztigen Stand der Chemotherapie. Ber.
42: 17-47. 1909.
- (11) Bertheim, A.
Organic Arsenical Compounds. New York. Chemical
Catalogue Company, 22 p. 1923.
- (12) Meyer, G.
Ueber Einige Anomale Reaktionen. Ber. 16: 1439.
1883.

- (13) Quick, A. J. and Adams, Rodger
Aliphatic Arsinic Acids and Aliphatic-Aromatic
Arsenious Acids. J. Amer. Chem. Soc. 44:
805-16. 1922.
- (14) Bart, Heinrich
Preparation Organic Arsenic Compounds. J. Chem.
Soc. London (abstracts), 1913A., 1, 415.
1914A., 1, 216.
- (15) Roeder, G. and Blasl, H.
Neue Arsenierung Organischer Verbindungen.
Ber. 47: 2748-52. 1914.
- (16) Robertson, G. R.
Estimation of Arsenic in Organic Compounds.
J. Amer. Chem. Soc. 43: 182. 1921.

APPENDIX

Determination of Arsenic

Two-tenths gram of the substance is weighed into a 150 cc. Erlenmeyer flask and 5.5 cc. of concentrated sulfuric acid and 1 cc. of fuming nitric acid are added. The mixture is set upon a hot plate which is heated to such a temperature that a similar flask filled with water boils, but not excessively. The actual temperature of the mixture is approximately 250° . After one hour the flask is removed and cooled somewhat and 10 to 15 drops more fuming nitric acid are added. The flask is then replaced on the hot plate for five minutes to complete the oxidation.

One gram of ammonia sulphate is added cautiously to expell all traces of nitrogen. The mixture is shaken well and set aside to cool. Cold water is then added until the volume is 60 to 70 cc. and one gram of potassium iodide is added with a few pieces of porous plate.

The liquid is then boiled down on the hot plate to 40 cc. A solution of 0.01 N sodium thiosulphate is added drop by drop until the tint of the iodine is just discharged. The solution is quickly made up to 100-120 cc. with cold water and then transferred to a 500 cc. Erlenmeyer

flask containing 50 cc. 4 N sodium carbonate. The solution is then made neutral by adding an excess of a saturated solution of sodium hydrogen carbonate. Starch solution is then added and the arsenic is titrated against a standard iodine solution. An iodine solution of such strength that 1 cc. is equal to .002 grams of arsenic is convenient.

Determination of Chlorine

(A) Two-tenths gram of the substance is placed in an Erlenmeyer flask and 20 cc. alcoholic silver nitrate is added. The mixture is then gently heated (just boiling) for five minutes. The mixture is then allowed to set in the dark for one hour. Twenty-five cc. of distilled water is added and just enough nitric acid to make the solution distinctly acid.

The precipitate is then filtered off in a Gooch crucible and washed repeatedly with slightly acidified water, then with alcohol, and dried at 110° and weighed.

(B) Five-tenths gram of the substance is placed in a 200 cc. round bottom flask and 25 cc. alcoholic potassium hydroxide added. The mixture is refluxed for one hour, acidified with dilute nitric acid, cooled to 20° , and made up to 250 cc. with distilled water. Aliquotes of 25 cc. each were taken and aqueous silver nitrate is added.

The precipitated silver chloride is filtered off in a Gooch crucible and washed repeatedly with slightly acidified water, then with alcohol, and dried at 110° and weighed.

