

On Organic Compounds of Arsenic. Part III. Reaction between Arsenic Trichloride and α -Naphthyl Compounds of Mercury.

By

Kaoru Matsumiya.

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ABSTRACT.

The action of arsenic trichloride and antimony trichloride upon α -naphthyl compounds of mercury were studied. Arsenic trichloride and α -naphthylmercuric chloride at 160° gave α -naphthylchloroarsine and mercuric chloride. On heating mercury di- α -naphthyl, arsenic trichloride and benzene in a sealed tube at 145° for several hours, mercuric chloride, α -naphthylmercuric chloride, di- α -naphthylchloroarsine and tri- α -naphthylarsine were produced. Antimony trichloride and α -naphthylmercuric chloride remained unchanged even when heated with xylene in a sealed tube at 145° for 8 hours. On heating mercury di- α -naphthyl and antimony trichloride with xylene at 145° for 8 hours, α -naphthyl mercuric chloride and antimony trichloride were obtained together with an organic compound of antimony whose composition has not yet been decided.

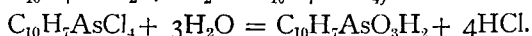
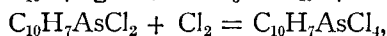
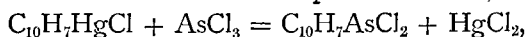
The α -naphthyl compounds of mercury used in the reaction were prepared by the Grignard reaction, as for example α -naphthylmercuric chloride from α -naphthylmagnesium bromide and mercuric chloride, and mercury di- α -naphthyl from α -naphthylmercuric chloride and α -naphthylmagnesium bromide.

In the course of the study on the reaction between the organic compounds of magnesium and inorganic arsenic or antimony compounds, the author found that tertiary arsine or stibine are generally obtained as the resulting products, the secondary arsine derivatives being only produced in some special cases.¹ Perhaps the activity of the organic magnesium compound is so great that it is almost difficult to stop the action of the Grignard reagent in such a stage that two chlorine atoms of arsenic or antimony trichloride still remain unaffected. It was expected

¹ Matsumiya, These Memoirs, **4**, 217 (1920); **8**, 11 (1925); Matsumiya and Nakai, These Memoirs **8**, 307 (1925).

that primary and secondary compounds would be obtained if we use organo-metallic compounds of less activity, such as organic mercury compounds, and with this expectation the work was undertaken.

On boiling α -naphthylmercuric chloride with excess of arsenic trichloride in a reflux apparatus at 160° for one hour, mercuric chloride and α -naphthyldichloroarsine were produced, the latter of which was isolated in the form of α -naphthylarsinic acid by treating it with chlorine and water as usual. The reaction is represented thus ;

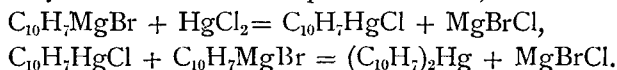


Mercury di- α -naphthyl and arsenic trichloride were mixed in molecular proportion, and the mixture was heated with a small quantity of benzene in a sealed tube at 145° for several hours. As the reaction products mercuric chloride, α -naphthylmercuric chloride, di- α -naphthylchloroarsine and tri- α -naphthylarsine were obtained, the last two substances having been isolated as di- α -naphthylarsinic acid and tri- α -naphthylarsine dihydroxide.

Antimony trichloride was found not to act upon α -naphthylmercuric chloride even when heated with xylene in a sealed tube at 145° for 8 hours. Mercury di- α -naphthyl and antimony trichloride, however, were brought into reaction under similar treatment, and α -naphthylmercuric chloride was produced together with a certain organic compound of antimony, the analysis of which did not give concordant results. Thus a distinct difference existing between the actions, which are brought about by organic halides of magnesium and mercury, will be clear. Acting with arsenic trichloride, α -naphthylmagnesium bromide usually yields tri- α -naphthylarsine, and sometimes di- α -naphthylchloroarsine, but never the corresponding primary compound. If α -naphthylmercuric chloride is used instead of the magnesium compound, α -naphthyldichloroarsine is generally formed. While antimony trichloride and α -naphthylmagnesium bromide react together to form tri- α naphthyl stibine, α -naphthylmercuric chloride and antimony trichloride do not react to each other even at a high temperature and under pressure.

The reaction between arsenic trichloride and mercury di- α -naphthyl seems to be produced so as to replace the naphthyl radicals of the latter with halogen, as mercuric chloride may be found among the reaction products. By the action of antimony trichloride upon mercury di- α -naphthyl, however, no mercuric chloride was produced, though α -naphthylmercuric chloride was detected among the reaction products.

Mercury di- α -naphthyl has hitherto been prepared by the sodium method,¹ and α -naphthylmercuric chloride was derived from it.² The author believes that the method given below will be found more simple and satisfactory. The reaction is represented thus;



By introducing finely powdered mercuric chloride to the ethereal solution of α -naphthylmagnesium bromide and boiling the mixture for several hours, α -naphthylmercuric chloride is first prepared. The yield amounts to 63 % of the theory. α -Naphthylmercuric chloride is then treated with the ethereal solution of α -naphthylmagnesium bromide when an energetic reaction sets in. The reaction mixture is now boiled for several hours and the mercury di- α -naphthyl thus produced is purified by washing it with aniline, which readily dissolves α -naphthylmercuric chloride. The yield is about 69 %.

EXPERIMENTAL PART.

1. α -Naphthylmagnesium Bromide and Mercuric Chloride.

To the Grignard reagent prepared from 42 grms. of α -bromonaphthalene, 5 grms. of magnesium and 100 c.c. of dry ether, 71 grms. of powdered mercuric chloride was added little by little. After boiling on a water bath for several hours, the mixture was treated with water, and the ether was distilled off. The remaining solid was well washed first with dilute hydrochloric acid to remove the mercuric chloride and then with alcohol to remove the naphthalene. On recrystallising it from hot carbon bisulphide, 46 grms. of a white crystalline powder were obtained. When recrystallised from hot benzene it melted at 188-189°. The analytical results were as follows:-

0.1644 gram. substance gave 0.1056 gram. HgS.

	Calc for $\text{C}_{10}\text{H}_7\text{HgCl}$	Found
Hg	55.22	55.38

The α -naphthylmercuric chloride thus prepared is with difficulty soluble in petroleum ether and cold alcohol, moderately soluble in ether, benzene and carbon bisulphide, more easily soluble in aniline and most readily so in pyridine. When boiled with conc. hydrochloric acid, it decomposes entirely into naphthalene and mercuric chloride.

¹ Otto and Möries, Lieb. Ann., **147**, 167 (1868); Otto, Lieb. Ann., **154**, 188 (1870); Michaelis, Ber. D. Chem. Ges., **27**, 249 (1894).

² Steinkopf, Lieb. Ann., **413**, 330 (1917).

2. *α -Naphthylmagnesium Bromide and α -Naphthylmercuric Chloride.*

Thirty-six grms. of α -naphthylmercuric chloride were cautiously added to the Grignard reagent prepared from 42 grms. of α -bromonaphthalene, 5 grms. of magnesium and 100 c. c. of ether, and the mixture was boiled for several hours. It was then decomposed with water and acidified with dilute acetic acid. On distilling off the ether, the residue was dried and washed with aniline to remove the unchanged α -naphthylmercuric chloride and the naphthalene, and recrystallised from carbon bisulphide. The yield was 31 gm. Its melting point was found to be 234° which just coincides with that of mercury di- α -naphthyl. It was confirmed to be mercury di- α -naphthyl by the analysis which gave the following values :-

0.4834 gm. substance gave 0.2459 gm. HgS.		
Calc. for $(C_{10}H_7)_2Hg$	Found	
Hg	44.12	43.85

Mercury di- α -naphthyl is with difficulty soluble in aniline, easily soluble in pyridine, hot carbon bisulphide and chloroform. It is decomposed by boiling with conc. hydrochloric acid.

3. *α -Naphthylmercuric Chloride and Arsenic Trichloride.*

Twelve grms. of α -naphthylmercuric chloride were added to 60 grms. of arsenic trichloride in which the former completely dissolved. The solution was heated in a reflux apparatus at 160° for one hour. Then the unaltered arsenic trichloride was distilled off, and the remaining solid was treated with benzene, when a crystalline substance which proved to be mercuric chloride remained undissolved. The benzene solution was repeatedly shaken with dilute hydrochloric acid, until the aqueous solution ceased to react on the hydrogen sulphide. It was then saturated with chlorine and extracted with dilute caustic soda solution repeatedly. On acidifying the alkaline solution, white precipitates were formed, which were dissolved in hot alcohol, decolourised with animal charcoal and crystallised. The yield was 4.5 grms. It melted at 197° . The analysis of the substance gave the following value for arsenic.

0.1913 gm. substance required 30.4 c.c. of N/20 iodine solution		
Calc. for $C_{10}H_7AsO_3H_2$	Found	
As	29.74	29.79

4. *Mercury Di- α -naphthyl and Arsenic Trichloride.*

Nine grms. of mercury di- α -naphthyl, 3.6 grms. of arsenic trichloride

and 20 c.c. of dry benzene were heated together in a sealed tube at 145° for 6 hours. When cooled the contents of the tube were well crystallised. They were washed with ether, and then dissolved in aniline and filtered. On adding an ample quantity of alcohol to the aniline solution, colourless crystals were precipitated, which were again recrystallised from carbon bisulphide. Its melting point and other properties showed it to be α -naphthylmercuric chloride.

The ethereal mother liquor was repeatedly shaken with dilute hydrochloric acid until the acid solution became quite free from mercury. From the total aqueous hydrochloric solution 1.6 grms. of mercuric sulphide were produced. On gently evaporating the ethereal solution, crystals gradually separated out. The portion less soluble in ether showed the melting point of tri- α -naphthylarsine and the more soluble part was found to have the properties of di- α -naphthylchloroarsine. The complete separation of them, however being rather difficult, they were transformed into quinquevalent arsenic compounds. The mixed crystals were dissolved in ether-benzene, saturated with chlorine, decomposed with water and then extracted with a caustic soda solution successively. On acidifying the alkaline solution white crystals were precipitated which on recrystallising from ether-benzene melted at 228°. The other properties also well agreed with those of di- α -naphthylarsinic acid. Arsenic was estimated for confirmation.

0.1621 grm. substance required 17.9 c.c. of N/20 iodine solution.

	Calc. for $(C_{10}H_7)_2AsO_2H$	Found
As	20.79	20.70

The solid insoluble in alkali was dissolved in hot alcohol, decolourised with animal charcoal and precipitated by adding water. When recrystallised from alcohol, it melted above 300°. After drying in vacuo over sulphuric acid it gave the following value for arsenic.

0.1731 grm. substance required 14.2 c.c. of N/20 iodine solution.

	Calc. for $(C_{10}H_7)_3As(OH)_2$	Found
As	15.29	15.38

5. α -Naphthylmercuric Chloride and Antimony Trichloride.

3.6 Grms. of α -naphthylmercuric chloride, 2.3 grms. of antimony trichloride and 10 c.c. of xylene were heated in a sealed tube at 145° for 8 hours. The tube was opened and the contents consisting of colourless crystals and yellow liquid were treated with petroleum ether.

About 3 grms. of a crystalline substance were left undissolved. On recrystallising it from carbon bisulphide, α -naphthylmercuric chloride melting at 188-189° was obtained. The petroleum ether solution when moistened and evaporated gave 1.5 grms. of antimony oxychloride.

6. *Mercury Di- α -naphthyl and Antimony Trichloride.*

Six grms. of mercury di- α -naphthyl, 3 grms. of antimony trichloride and 20 c.c. of xylene were heated in a sealed tube at 145° for 8 hours. When cooled, the contents of the tube solidified to a crystalline mass. It was washed with ether, dissolved in aniline and precipitated by alcohol and then recrystallised from carbon bisulphide. 4.1 Grms. of α -naphthylmercuric chloride melting at 188-189° were obtained. The result of the analysis was as follows :-

0.2289 gm. substance gave 0.1461 gm. HgS.

	Calc. for $C_{10}H_7HgCl$	Found
Hg	55.22	55.03

By treating the ether-xylene solution with water white precipitates of antimony oxychloride were formed. The ether-xylene solution separated from the antimony oxychloride was shaken with dilute hydrochloric acid, but, contrary to expectation no mercuric chloride was extracted from it. Beside antimony oxychloride, a small quantity of an oil and a crystalline substance were obtained from the ether-xylene solution, but no definite organic antimony compound could be detected.

The ether-xylene solution was also treated as follows:- It was shaken with a sufficient quantity of a saturated sodium bicarbonate solution so as to make the aqueous layer distinctly alkaline. White precipitates thus formed were collected, washed, dried and finally washed with carbon bisulphide. The white powder which remained undissolved in carbon bisulphide was antimony trioxide. From the carbon bisulphide solution an organic compound of antimony still in an impure state was obtained, but owing to the lack of material further examination could not be performed.