

On Organic Compounds of Arsenic. I

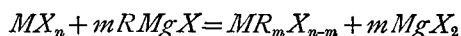
Reaction between the Grignard Reagent and Arsenious Chloride

By

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The action of the halides of metals and metalloids on the Grignard reagent has been widely utilized as the general reaction for the synthesis of the organo-metallic, and -metalloid, compounds. This reaction was discovered by P. Pfeiffer¹, and in the same year, V. Auger and M. Billy², W. I. Pope and S. J. Peachey³ published the results of their researches on the same subject. Pfeiffer and Pope further continued their investigations in the same direction⁴, and Pfeiffer⁵ finally proposed the following general equation for the reaction.



Taking great interest in this reaction, the author studied it in connection with the preparation of the organic derivatives of arsenic. In almost all cases recorded in this field, the halogen atoms combined with arsenic were completely replaced by alkyl or aryl radicals, corresponding to the case when $m=n$ in the above equation. The

¹ P. Pfeiffer and K. Schnurmann, Ber. D. Chem. Ges., **37**, 319, (1904); P. Pfeiffer and P. Truskier, Ber. D. Chem. Ges., **37**, 1125, (1904); P. Pfeiffer, I. Heller and H. Pietsch, Ber. D. Chem. Ges., **37**, 4620, (1904).

² V. Auger and M. Billy, C. R., **139**, 597, (1904).

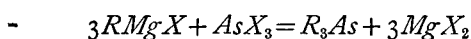
³ W. I. Pope and S. J. Peachey, Proc. Chem. Soc., **19**, 290, (1904).

⁴ P. Pfeiffer and R. Prade, Ber. D. Chem. Ges., **44**, 1273, (1911); S. Möller and P. Pfeiffer, J. Chem. Soc., **112**, 1, 122, (1917); W. J. Pope and S. J. Peachey, Proc. Chem. Soc., **23**, 86, (1907); J. Chem. Soc., **95**, 571, (1909).

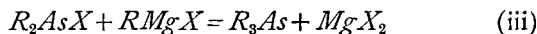
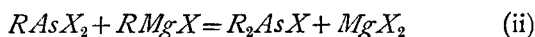
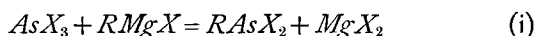
⁵ P. Pfeiffer and K. Schnurmann, loc. cit.

author, therefore, attempted to restrain the reaction so as to replace any desired number of the halogen atoms attached to arsenic by organic radicals. For this purpose several experiments have been carried out, and in the present paper the author has to communicate the results of his researches on the aryl compounds of arsenic.

According to Pfeiffer's method, arsenious halide was added to the Grignard reagent in the proportion of one molecule of aryl magnesium halide for each halogen atom of arsenious halide. The main product of the reaction was always tertiary arsine compound; primary and secondary compounds were obtained only as by-products. The reaction is represented thus,



The reaction between arsenious halide and the Grignard reagent, however, may be presumed to take place in the following three stages.



If this be the case, the proportion of the two compounds in action may be expected to have some effect on the reactions. In order to ascertain this point experimentally, the Grignard reagent prepared from α -bromonaphthalene and magnesium, was treated with arsenious chloride in a molecular proportion. Contrary to expectation, tri- α -naphthylarsine was obtained with a good yield. Phenylmagnesium bromide was also found to react with arsenious chloride in an exactly analogous way and produced triphenylarsine as the main product.

The experiments, above stated were conducted, as usual, by adding an ethereal solution of arsenious chloride to the Grignard reagent, so that the action accompanying each addition of the former evidently took place always in presence of an excess of the latter.

Now it is necessary to study the effect produced when an excess of an ethereal solution of arsenious chloride acted on aryl magnesium bromide. For this purpose, the Grignard reagent was allowed to drop upon an ethereal solution of arsenious chloride, the proportion having been taken as in equation I. In this connection, the work of Auger and Billy¹ should be mentioned who studied the action of methyl-

¹ V. Auger and M. Billy, loc. cit.

magnesium bromide on phosphorous chloride, ethylmagnesium bromide on arsenious chloride and on antimonious chloride in this way, and obtained three kinds of methylphosphine and ethylarsine compounds, and a monoethylstibine compound.

The reaction thus brought about was vigorous and a quantity of precipitate, which was found to belong to the type R_2AsX , was produced. Although the expected primary arsine compound was not obtained, the effect of the different mode of application of the Grignard reagent was thus confirmed. The author proposes this way of working as the best synthetical method for secondary aryl arsine compounds. In the experiments, the following results were obtained:—

With the phenyl compound, in the usual process, the chief product was triphenylarsine, while in the author's process it was diphenylarsenious chloride. With the naphthyl compound, tri- α -naphthylarsine was mainly produced in the usual process while in the author's process the chief product was di- α -naphthylarsenious chloride in a yield of about 60 percent of the calculated amount.

Tri- α -naphthylarsine was prepared with Grignard reagent in a yield of about 70 percent of the calculated amount, while it was obtained by sodium method in a yield of 20 percent.

EXPERIMENTAL PART

1. *Action of Arsenious Chloride upon Phenylmagnesium Bromide*

32.5 grm. of bromobenzene were treated with 5 grm. of magnesium and a piece of iodine in dry ether. To the ethereal solution of phenylmagnesium bromide thus obtained, 37.5 grm. of arsenious chloride dissolved in dry ether were cautiously added and a white precipitate was produced. Then it was boiled for about one hour so as to complete the reaction. After it was well cooled, the ethereal solution was treated with water which completely composed the precipitate. A small quantity of a white substance which remained insoluble in ether and water, was proved, by its chemical reaction to be arsenious oxide. The ethereal solution was filtered and evaporated. A colourless crystal and a small quantity of yellowish-coloured oil were obtained. To isolate the tertiary arsine completely, the whole substance was dissolved in ether again and treated with an ethereal

solution of mercuric chloride¹, until the white precipitate ceased to be produced. Then the double salt was dissolved in boiling absolute alcohol and then alcoholic potash was added in an excess, whereby mercuric oxide instantly formed as a reddish brown precipitate. The precipitate was filtered off and the filtrate was saturated with carbon dioxide, filtered again and the solution concentrated and set aside. Colorless crystals were formed which, on recrystallising from alcohol, melted at 59–60°. The yield was 10.5 gm. The arsenic was estimated by Ewins' method².

0.1901 gm. substance required 24.9 c. c. of N/20 iodine solution.

	Calc. for $(C_6H_5)_3As$	Found
As	24.45	24.56

2. Action of Phenylmagnesium Bromide upon Arsenious Chloride

The ethereal solution of phenylmagnesium bromide, prepared from 32.5 gm. of bromobenzene and 5 gm. of magnesium, was added to 37.5 gm. of arsenious chloride in dry ether. A brisk reaction took place on each addition, causing a white precipitate. After boiling for an hour, it was cooled well and then treated with water. The precipitate was decomposed so energetically that the solution strongly boiled. When the reaction subsided, the whole solution became quite clear, only a small quantity of arsenious oxide remaining at the bottom. On evaporating off the ether, only a yellow coloured oil was obtained. The whole substance was dissolved in ether again and treated with an ethereal solution of mercuric chloride to remove the triphenylarsine. A small quantity of a white precipitate formed was filtered off and the ethereal solution was repeatedly shaken with water containing hydrochloric acid so as to remove the mercuric chloride. The washing was repeated until the aqueous layer no longer became coloured by the hydrogen sulphide. The ethereal solution was dried with calcium chloride and then distilled. The distillate between 300–350° was a yellow oil, which, from its properties, was proved to be diphenylarsenious chloride. The yield was 12 gm.

¹ A. Michaelis, *Ann.*, **321**, 141, (1902).

² A. J. Ewins, *J. Chem. Soc.*, **109**, 1355, (1916).

As a portion having a constant boiling-point was hardly obtainable, the whole substance was transformed to diphenylarsinic acid by the usual method. That is, the oil was dissolved in ether and the ethereal solution was saturated with chlorine, when a slightly yellow-coloured precipitate was formed. The whole substance was decomposed with water and the aqueous solution was evaporated to dryness. The remaining solid was recrystallised from ether. Colourless needles thus produced melted at $173\text{--}174^\circ$. Its analysis gave the following value for arsenic.

0.2079 grm. substance required 31.7 c.c. of N/20 iodine solution.

	Calc. for $(C_6H_5)_2AsO.OH$	Found
As	28.63	28.59

3. Preparation of Tri-*a*-naphthylarsine

62.5 grm. of *a*-bromonaphthalene, 7.2 grm. of magnesium and a piece of iodine were added to an ample quantity of dry ether and boiled on a water bath under a reflux condenser until the magnesium was completely dissolved. 18.2 grm. of arsenious chloride dissolved in dry ether, were little by little poured upon the ethereal solution of *a*-naphthylmagnesium bromide. An energetic reaction took place and a white precipitate was formed which was at first redissolved by shaking but subsequently became permanent. After distilling off the ether, the residue was treated with water and the insoluble matter was collected and dried. This product was extracted with hot benzene, concentrated somewhat and treated with alcohol, when a slightly yellow-coloured crystalline deposit was obtained. On recrystallising from a mixture of benzene and alcohol, colourless crystals melting at 248° were finally obtained. The yield was 33 grm. The analytical results were as follows:

0.1305 grm. of the sample gave 0.3759 grm. CO_2 and 0.0567 grm. H_2O

0.1060 grm. substance required 9 c.c. of N/20 iodine solution.

	Calc. for $(C_{10}H_7)_3As$	Found
C	78.95	78.56
H	4.61	4.83
As	16.44	15.85

4. *Action of Arsenious Chloride upon α -Naphthylmagnesium Bromide*

36.4 gm. of arsenious chloride in dry ether were added to an ethereal solution of α -naphthylmagnesium bromide, prepared with 41.4 gm. of α -bromonaphthalene and 5 gm. of magnesium in dry ether. After boiling for an hour, the ether was distilled off and the residue treated as in the former case. Colourless crystals were obtained which melted at 248°. The yield was 20 gm. The substance was analysed and the value of arsenic was found as follows:

0.0722 gm. substance required 6.2 c.c. of N/20 iodine solution.

	Calc. for $(C_{10}H_7)_3As$	Found
As	16.44	16.10

5. *Action of α -Naphthylmagnesium Bromide upon Arsenious Chloride*

A solution of α -naphthylmagnesium bromide, prepared with 41.4 gm. of α -bromonaphthalene and 5 gm. of magnesium in dry ether, was added drop by drop to 36.4 gm. of arsenious chloride dissolved in dry ether, with constant cooling and shaking. Each drop caused a hissing sound and produced a precipitate. To complete the reaction, the mixture was boiled for an hour, cooled well and water was added cautiously. A brisk reaction took place and the precipitate was almost dissolved. The ethereal solution was washed with water and filtered. On distilling off the ether, a yellow mass was obtained, which was dissolved in hot alcohol-benzene and decolourised with animal charcoal. Fine crystals thus obtained were slightly yellow-coloured and melted at 116–117°. The yield was 21 gm. It was recrystallised three times from alcohol-benzene and analysed. The results were as follows:

0.1208 gm. of the substance gave 0.2921 gm. CO_2 and 0.0448 gm. H_2O .

0.0740 gm. substance required 7.8 c.c. of N/20 iodine solution. Chlorine was estimated by Dean and Wilcox's method¹.

¹ W. M. Dean and B. B. Wilcox, Amer. Chem. J., 1, 7, (1906).

0.1469 grm. substance required 0.0659 grm. silver nitrate.

	Calc. for $(C_{10}H_7)_2AsCl$	Found
C	65.84	65.95
H	3.84	4.12
As	20.58	19.76
Cl	9.74	9.39

Di- α -naphthylarsenious chloride is slightly soluble in alcohol, sparingly soluble in hot alcohol and ether, easily soluble in benzene, carbon bisulphide and carbon tetrachloride, more readily so in hot benzene and chloroform.
