[Contribution from the College of Pharmacy, University of Michigan]

THE ACTION OF AROMATIC GRIGNARD REAGENTS ON ARSENIC TRIOXIDE

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This investigation is the first part of a study of certain arsenicals which we synthesized in the hope that they might be found to be of value as spirocheticides.

Tetra-arylarsyl oxides,[3] which were required for the preparation of other compounds, can be obtained quite readily by the interaction of aromatic Grignard reagents and arsenic trioxide; in addition to the oxides there are usually obtained varying amounts of triarylarsines. Hitherto there has been lack of agreement among various investigators regarding the optimum conditions for the formation of these compounds and the reaction mechanism by which they are produced.

Sachs and Kantorowicz[4] state that at a low temperature phenylmagnesium bromide and arsenic trioxide react to form tetraphenylarsyl oxide, while at a higher temperature triphenylarsine is produced. They claim, furthermore, that *p*-tolylmagnesium bromide and arsenic trioxide yield only tri-*p*-tolylarsine, regardless whether the reaction is carried out at a low or high temperature.

Recently, Matsumiya and Nakai[5] found that phenylmagnesium bromide and arsenic trioxide yield invariably a mixture of tetraphenylarsyl oxide and triphenylarsine, both at low and high temperatures; similar results were obtained with *p*-tolylmagnesium bromide, but in the case of α-naphthylmagnesium bromide only one product seemed to be formed, a compound stated to be either $(C_{10}H_7)_4As_2O \cdot H_2O$ or $(C_{10}H_7)_2As(OH)$. Experimental evidence which we obtained indicates that neither of these formulas is correct. If the compound possessed the first of the above formulas it should react with ethylmagnesium bromide with the liberation of two molecular equivalents of ethane; a compound of the second type should yield one equivalent of the gas. It was found that no gas was evolved when the

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[1] This paper represents the first part of a dissertation submitted to the Graduate School by Mr. Smith in partial fulfilment of the requirements for the degree of Doctor of Philosophy in the University of Michigan.

[2] The investigation was made with the assistance of the Parke, Davis and Company Fellowship and we wish to express our appreciation for the aid which has been given us.

[3] It seems to us that the use of the term "arsyl" [Steinkopf and Smie, *Ber.*, **59**, 1456 (1926)] permits one to apply a more rational system of nomenclature to the arsenic compounds which we have investigated than that commonly used. We have called AsH_3 and AsR_3, arsine and triarylarsine, respectively; $—AsH_2$ and $—AsR_2$, arsyl and diarylarsyl; $H_2As—O—AsH_2$ and $R_2As—O—AsR_2$, arsyl oxide and tetra-arylarsyl oxide; $H_2As—AsH_2$, diarsyl and $R_2As—AsR_2$, tetra-aryldiarsyl.

[4] Sachs and Kantorowicz, *Ber.*, **41**, 2767 (1908).

[5] Matsumiya and Nakai, *Mem. Coll. Sci., Kyoto Imp. Univ.*, **8**, 307 (1925).

naphthyl compound was treated with ethylmagnesium bromide. Furthermore, we found the molecular weight of the substance to be 680. The naphthyl compound, therefore, seems to possess the normal structure $(C_{10}H_7)_2As\text{-}O\text{-}As(C_{10}H_7)_2$.

We have studied the action of arsenic trioxide on phenyl-, *p*-tolyl-, *p*-anisyl-, α-naphthyl- and biphenylmagnesium halides. In the case of some of the tetra-arylarsyl oxides we have greatly increased the yields obtained by other investigators by the use of procedures which are fully described in the experimental part of this paper. Tetrabiphenylarsyl oxide has not been prepared hitherto. With the first three Grignard reagents mentioned above, mixtures of tetra-arylarsyl oxides and triarylarsines were obtained, regardless of the way in which the experimental conditions were varied, but with the last two arylmagnesium halides only tetra-arylarsyl oxides were found to be formed.

Concerning the manner in which the tetra-arylarsyl oxides and the triarylarsines are produced, Sachs and Kantorowicz suggested the following scheme but gave no experimental evidence in support of their view.

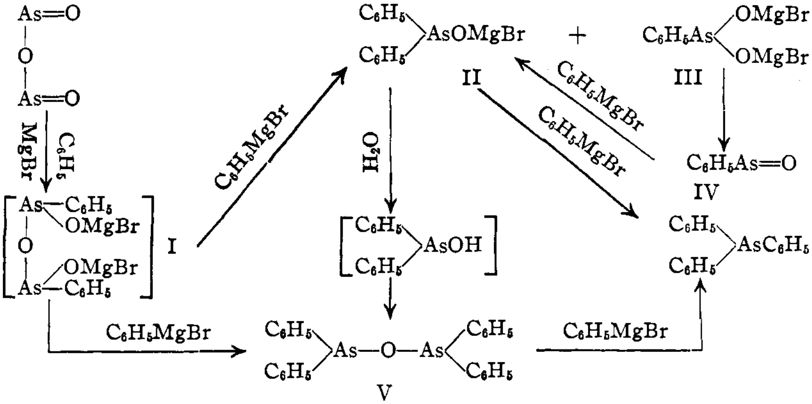
$$\begin{tikzcd}
As_2O_3 + 3RMgBr \arrow[r] \arrow[dr] & R_2As(OMgBr) \arrow[r] & R_2As{-}O{-}AsR_2 \\
& RAs(OMgBr)_2 \arrow[r, "RMgBr"] & AsR_3
\end{tikzcd}$$

$$R_2As(OMgBr) \xrightarrow{RMgBr} R_3As$$

Matsumiya and Nakai, as well as Gryszkiewicz-Trochimowski and Zambrzycki,[6] who studied the action of phenylmagnesium bromide on arsenic trioxide, considered it probable that the reaction proceeded in the following stages.

$$As_2O_3 \xrightarrow{4RMgBr} R_2As{-}O{-}AsR_2 \xrightarrow{2RMgBr} 2R_3As$$

A consideration of the various possible reactions which might take place when a Grignard reagent, phenylmagnesium bromide for example, reacts with arsenic trioxide leads to the following formulation.



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[6] Gryszkiewicz-Trochimowski and Zambrzycki, *Roczniki Chemij*, **6**, 798 (1926).

One of the first questions which arises in connection with the study of the mechanism of the reaction is this: Is tetraphenylarsyl oxide, V, formed directly from the inorganic oxide (possibly through intermediate formation of I) or is it produced from Compound II by the addition of water to the reaction mixture?

When phenylmagnesium bromide reacts with arsenic trioxide, in the presence of a mixture of ether and benzene, a heavy precipitate soon forms. After completion of the reaction and the removal of most of the ether, the precipitate was separated from the solvent and decomposed with water. Four-fifths of the total amount of tetraphenylarsyl oxide formed was obtained from the precipitate, while the remainder of the arsyl oxide and triphenylarsine was isolated from the benzene layer. If tetraphenylarsyl oxide had been formed directly from arsenic trioxide, and hence were present as such in the reaction mixture, it seems that *all* of the tetraphenylarsyl oxide should have been obtained from the benzene layer and none from the precipitate;[7] more than enough solvent was employed to hold in solution all of the tetraphenylarsyl oxide which could possibly have been formed from the amount of arsenic trioxide used.

It seems to us that the above phenomena may be accounted for if the assumption is made that $(C_6H_5)_2As\text{-}OMgBr$, a substance which might be expected to be only slightly soluble in benzene, is the precursor of tetraphenylarsyl oxide and that the latter compound is produced only after the addition of water to the precipitate mentioned above.

The same type of phenomenon was encountered in the case of α-naphthyl- and biphenylmagnesium bromide except that in the latter instance all of the tetra-aryl oxide was obtained from the precipitate after decomposition of the latter with water. No precipitates, however, were formed with the tolyl- and anisylmagnesium halides. We can only suggest that in these instances the compounds of the type $R_2As\text{-}OMgX$ may be more soluble.

Compound IV, which would probably be produced by spontaneous decomposition of III, could not be found among the reaction products from phenylmagnesium bromide and arsenic trioxide. We have shown that this substance reacts with phenylmagnesium bromide to form either a mixture of tetraphenylarsyl oxide and triphenylarsine or is converted quantitatively into triphenylarsine, depending on experimental conditions. It was found, also, that tetraphenylarsyl oxide, under proper conditions, reacts with phenylmagnesium bromide to form triphenylarsine in quantitative yield.

Finally, we prepared a number of diarylarsyl halides, some of which have not been described previously.

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[7] This consisted, in part, of inorganic magnesium salts.

Experimental Part

Aromatic Grignard Reagents and Arsenic Trioxide[8,9] Phenylmagnesium Bromide.—The reagent was prepared from 62.8 g. of bromobenzene (0.4 mole), 9.7 g. of magnesium (0.4 mole) and 200 cc. of ether in a liter, three-necked flask, fitted with a reflux condenser and then diluted with an equal volume of benzene. The flask was cooled in an ice-bath and a mechanical stirrer introduced. In this experiment, as well as in all of the following ones, moisture was prevented from entering the apparatus. Nineteen and eight-tenths g. (0.1 mole) of dry arsenic trioxide was added as rapidly as possible while the mixture was stirred vigorously. It was found that rapid addition of the arsenic trioxide to the thoroughly cooled reaction mixture reduced the amount of triphenylarsine to a minimum. After all of the oxide had been added, the ice-bath was removed. A colorless precipitate, probably $(C_6H_5)_2AsOMgBr$ and inorganic magnesium salts, soon formed with the evolution of considerable heat.

After the mixture had been stirred for four hours, the solvent was removed under diminished pressure, in a stream of dry nitrogen, until the reaction mixture was reduced to about one-third of its original volume. When the solid material had settled, the benzene layer was decanted and the former substance was decomposed with ice and a small amount of acetic acid. The organic material was extracted with benzene, the benzene solution was shaken with dilute aqueous sodium hydroxide and then dried with fused sodium sulfate. The solvent was removed on a steam-bath and the oily residue allowed to solidify. The material was washed thoroughly with petroleum ether (40–60°) and then with a mixture of ether and petroleum ether; m. p. 92.5–93.5°. This substance was pure tetraphenylarsyl oxide. The yield was 21 g.

The solvents with which the tetraphenylarsyl oxide had been washed were now added to the benzene layer mentioned above and the mixture was treated with ice and a small amount of acetic acid. After separation of the benzene layer, the latter was washed with dilute sodium hydroxide solution, dried and the solvent removed. The oily residue solidified to an amorphous mass. After the latter had been treated with petroleum ether several times, it melted at 91–92° and hence was tetraphenylarsyl oxide; yield, 5 g. The total yield of this oxide was 26 g., or 55% of the calculated amount. The petroleum ether with which the above material had been washed was concentrated to a very small volume and then diluted with 25 cc. of dry ether. Upon the addition of mercuric chloride dissolved in ether the mercuric chloride addition product of triphenylarsine was precipitated. The latter weighed 10.2 g. and corresponds to 5.4 g. of triphenylarsine.

The following experiment shows that triphenylarsine is precipitated practically quantitatively by mercuric chloride: 6.12 g. of pure triphenylarsine was dissolved in a small amount of absolute ether. Upon the addition of 5.42 g. of dry mercuric chloride, dissolved in 250 cc. of ether, a precipitate was obtained which weighed 11.30 g.; calcd. weight of addition product, 11.54 g. Triphenylarsine can be obtained from the addition product if the latter is suspended in alcohol and then treated with hydrogen sulfide.

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[8] Very little information is to be found in the literature regarding the action of aliphatic Grignard reagents on arsenic trioxide. Sachs and Kantorowicz, *Ber.*, **41**, 2769 (1908), state that *iso*-amylmagnesium bromide reacts with arsenic trioxide with the formation of an oil. Gryszkiewicz-Trochimowski and Zambrzycki, *Roczniki Chemij*, **6**, 749 (1926), studied the action of methyl-, ethyl-, propyl- and allylmagnesium halides on arsenic trioxide and were able to isolate only trialkylarsines in rather poor yields.

[9] Recently, Matsumiya and Nakai, *Mem. Coll. Sci., Kyoto Imp. Univ.*, **10**, 57 (1927), published their results on the action of arylmagnesium halides on arsenic trisulfide. They obtained triarylarsines and varying amounts of tetra-arylarsyl sulfides.

In one experiment an attempt was made to account for all of the material used. From 19.8 g. of arsenic trioxide and 62.8 g. of bromobenzene there were obtained 29 g. of tetraphenylarsyl oxide (equivalent to 12.1 g. of arsenic trioxide and 38.4 g. of bromobenzene), 10.2 g. of the mercuric chloride addition product of triphenylarsine (equivalent to 1.7 g. of arsenic trioxide and 8.3 g. of bromobenzene), 3.5 g. of biphenyl (equivalent to 7.1 g. of bromobenzene), 5.4 g. of unchanged arsenic trioxide and a small amount of phenol. The total amount of bromobenzene thus accounted for is 53.8 g., or 85.5% of that used; the amount of arsenic trioxide, 19.3 g., or 97% of that employed.

After conversion of the oxide into diphenylarsyl chloride, purification of the latter by distillation and hydrolysis of the chloride into the original oxide, the latter was recrystallized from alcohol; m. p. 95.5–96.5°. The highest melting point recorded previously was 92.5–93.5°.[10]

p-**Tolylmagnesium Bromide.**—After 68.4 g. of *p*-bromotoluene and 9.7 g. of magnesium in 200 cc. of ether had reacted completely, the solution was diluted with 200 cc. of dry benzene. The contents of the flask were then cooled, stirred vigorously and 19.8 g. of dry arsenic trioxide was added as quickly as possible. In this instance no precipitate formed. The mixture was stirred for four hours and then decomposed with ice and a small amount of acetic acid. The ether–benzene layer was separated, washed with dilute sodium hydroxide solution and then dried with fused sodium sulfate. The solvent was removed and the oily residue dissolved in absolute ether. The ether solution was treated with mercuric chloride dissolved in ether until a precipitate no longer formed. The precipitate, which was the mercuric chloride addition product of tritolylarsine, was removed by filtration. The filtrate was shaken with dilute hydrochloric acid to remove mercuric chloride, dried and the solvent removed. The solid residue was washed thoroughly with petroleum ether (40–60°). The yield of tetra-*p*-tolylarsyl oxide was 25.5 g., or 48% of the calculated amount. After recrystallization from alcohol the compound melted at 108.5–109.5°. The amount of tritolylarsine formed, calculated on the basis of the addition product, was 9 g.

Sachs and Kantorowicz[4] obtained only tritolylarsine but no arsyl oxide from *p*-tolylmagnesium bromide and arsenic trioxide. From the interaction of the two latter substances Matsumiya and Nakai[11] obtained a 10% yield of tetratolylarsyl oxide and recorded the melting point as 105–106°.

p-**Anisylmagnesium Iodide.**—The Grignard reagent was prepared from 93.6 g. of *p*-iodo-anisole,[12] 9.7 g. of magnesium and 250 cc. of ether. Two hundred and fifty cc. of dry benzene was then added; the subsequent procedure was the same as that described above for *p*-tolylmagnesium bromide.

There was obtained 33 g. of tetra-*p*-anisylarsyl oxide; m. p. 127–129°. This corresponds to a yield of 56%. In addition, 12 g. of trianisylarsine was formed.

Tetra-*p*-anisylarsyl oxide had been obtained previously by Michaelis and Weitz,[13] by the action of hydriodic acid on tri-*p*-anisylarsine and subsequent hydrolysis of the dianisylarsyl iodide. The substance obtained by them melted at 130°.

α-**Naphthylmagnesium Bromide.**—This reagent was prepared from 91 g. of pure α-bromonaphthalene[14] (0.44 mole), 9.7 g. of magnesium (0.40 mole) and 200 cc. of ether. An equal volume of benzene was then added to prevent the separation of solid naphthylmagnesium bromide from the solution. The mixture was stirred vigorously and 19.8 g. (0.10 mole) of arsenic trioxide was added. During the latter operation no external

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[10] McKenzie and Wood, *J. Chem. Soc.*, **117**, 412 (1920).

[11] Matsumiya and Nakai, *Mem. Coll. Sci., Kyoto Imp. Univ.*, **8**, 312 (1925).

[12] Blicke and Smith, THIS JOURNAL, **50**, 1229 (1928).

[13] Michaelis and Weitz, *Ber.*, **20**, 50 (1887).

[14] Blicke, THIS JOURNAL, **49**, 2846 (1927).

cooling was necessary. After some time a heavy precipitate formed. The mixture was stirred for four hours and then ice and a small quantity of acetic acid were added. The mixture was shaken vigorously and after a short time two distinct layers formed rather suddenly. The ether–benzene layer was then decanted immediately. Within a few minutes tetra-α-naphthylarsyl oxide began to separate, and was completely precipitated after a few hours. The organic oxide was filtered and air-dried. The material was recrystallized from tetralin, suspended in hot benzene to remove any tetralin and filtered; m. p. 250–253° with decomposition. The yields of crude tetranaphthylarsyl oxide averaged 52 g., which corresponds to 77% of the calculated amount. No trinaphthylarsine could be discovered among the reaction products. From α-bromonaphthalene and arsenic trioxide Matsumiya and Nakai[15] obtained a 32% yield of the arsyl oxide. They found the melting point of the substance to be 240–241°.

p-Bromobiphenylmagnesium Bromide.—The Grignard compound was prepared from 31 g. of *p*-bromobiphenyl,[16] 4.0 g. of magnesium and 200 cc. of ether in a 500-cc. round-bottomed flask which had been modified in the following manner. A glass tube 1 cm. wide and about 15 cm. long was sealed to the body of the flask a short distance from the neck of the latter. About 3 cm. beyond the point of attachment the glass side arm was bent at a right angle toward the bulb of the flask. During the preparation of the Grignard reagent the arm of the flask was closed with a cork. After the above mixture had been heated for about ten hours, the solution of the Grignard reagent was decanted through the side arm from unchanged magnesium and dibiphenyl into a liter 3-necked flask which had been fitted with a reflux condenser and a mechanical stirrer. Two hundred cc. of dry benzene and 100 cc. of ether were added to the mixture and the latter was cooled and stirred vigorously. Upon addition of the arsenic trioxide (6.6 g.) a vigorous reaction took place. A precipitate soon formed which coated the surface of the unchanged inorganic oxide. The reaction mixture was stirred for four hours and the precipitate was then allowed to settle. After twelve hours the liquid layer was decanted[17] and the solid material decomposed as usual. The organic matter was extracted with benzene; the benzene solution was dried and filtered. After removal of the solvent 10 g. of crude tetrabiphenylarsyl oxide was obtained; this yield corresponds to 39% of the calculated amount. The crude material melted about 132–138°. After conversion of the oxide into the chloride, recrystallization of the latter and hydrolysis into the tetra-arylarsyl oxide, the substance melted at 150–152°.

From the experiments described below it can be seen that in the interaction of phenylmagnesium bromide with phenylarsyl oxide, $(C_6H_5)As{=}O$ (or with $(C_6H_5)_2As\text{-}OMgBr$), a large excess of the arylmagnesium halide favors the formation of triphenylarsine to a very decided extent. In the first instance there was used twice the amount of phenylmagnesium bromide necessary for the formation of the arsine; in the second instance eight times the calculated amount of Grignard reagent.

Phenylmagnesium Bromide and Phenylarsine Oxide.—Presumably these two compounds react first in accordance with the following

$$C_6H_5MgBr + C_6H_5As{=}O \longrightarrow (C_6H_5)_2As{-}OMgBr$$

The diaryl compound then reacts with the Grignard reagent to form the tertiary arsine.

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[15] Matsumiya and Nakai, *Mem. Coll. Sci., Kyoto Imp. Univ.*, **8**, 313 (1925).

[16] Gomberg and Bachmann, "Organic Syntheses," John Wiley and Sons, Inc., New York, **1928**, Vol. VIII, p. 42.

[17] Upon evaporation of the solvent only biphenyl was obtained.

1. Phenylmagnesium bromide was formed from 5.7 g. of bromobenzene (0.037 mole), 0.9 g. of magnesium and 25 cc. of ether. After the addition of 2.7 g. of phenylarsine oxide (0.016 mole), dissolved in 25 cc. of benzene, the mixture was refluxed for three hours. There was obtained 3.0 g. of tetraphenylarsyl oxide and 0.5 g. of triphenylarsine.

2. The Grignard reagent was prepared from 31.4 g. of bromobenzene (0.2 mole), 4.8 g. of magnesium and 100 cc. of ether. Four and two-tenths g. of phenylarsine oxide (0.025 mole), dissolved in 100 cc. of benzene, was added and the mixture was refluxed for four hours. No tetraphenylarsyl oxide was formed. The yield of triphenylarsine was 7.4 g., or 97% of the calculated amount.

The following experiments show that triphenylarsine is produced by interaction of phenylmagnesium bromide with tetraphenylarsyl oxide. Inasmuch as the Grignard reagent and the arsyl oxide react readily even at 0° to form the arsine, it seems impossible to prevent the formation of the latter substance in the preparation of the tetra-arylarsyl oxide.

Phenylmagnesium Bromide and Tetraphenylarsyl Oxide.—The Grignard reagent was prepared from 7.3 g. of bromobenzene (0.05 mole), 0.8 g. of magnesium and 30 cc. of ether. The solution was cooled to 0° and 4.7 g. of tetraphenylarsyl oxide (0.01 mole) was added. After the mixture had remained at 0° for four hours, a heavy crystalline precipitate had formed. The ether layer was decanted from the crystalline deposit and decomposed with ice and ammonium chloride. The ether solution was dried with fused sodium sulfate and the triphenylarsine was precipitated by means of mercuric chloride. The mercuric chloride addition product was removed by filtration and the filtrate was shaken with dilute hydrochloric acid to remove excess mercuric chloride. The ether solution was dried again and the solvent removed. The pasty residue was washed with low-boiling petroleum ether to remove biphenyl. The product which remained was tetraphenylarsyl oxide. The crystalline deposit was decomposed with ice and ammonium chloride and after the addition of a small amount of ether to dissolve the material the solution was treated as described above. Tetraphenylarsyl oxide and triphenylarsine were obtained. The total yield of oxide was 2.6 g.; that of arsine was 2.1 g.

In a second experiment the reaction mixture was kept somewhat above 35°. Phenylmagnesium bromide was prepared from 31.4 g. of bromobenzene (0.2 mole), 4.8 g. of magnesium and 100 cc. of ether. Eleven and eight-tenths g. of tetraphenylarsyl oxide (0.04 mole), dissolved in 100 cc. of benzene, was added and the mixture was refluxed for four hours. The yield of triphenylarsine was 14.2 g.; the calculated amount is 15.3 g.

Finally, we found that arsenic trioxide and an excess of phenylmagnesium bromide react quantitatively to form triphenylarsine. Five g. of arsenic trioxide (0.025 mole) and the Grignard reagent (0.4 mole) obtained from 62.8 g. of bromobenzene, 9.7 g. of magnesium and 200 cc. of ether were refluxed for four hours. There was obtained 15.0 g. of triphenylarsine; the calculated amount of triphenylarsine is 15.2 g.

TABLE I

DIARYLARSYL HALIDES

	M. p., °C.	Formula	Analysis (Volhard) Calcd.	Found
1 Diphenylarsyl chloride	40–42[a]		....	......
2 Diphenylarsyl bromide	52–54[b]		....	......
3 Diphenylarsyl iodide	42–43[c]		....	......
4 Di-*p*-tolylarsyl chloride	44–45[d]		....	......
5 Di-*p*-tolylarsyl bromide	65–66	$C_{14}H_{14}AsBr$	Br, 23.73	23.65, 23.70

Table I (*Concluded*)

	M. p., °C.	Formula	Analysis (Volhard) Calcd.	Analysis (Volhard) Found
6 Di-*p*-tolylarsyl iodide	64–65	$C_{14}H_{14}AsI$	I, 33.07	33.10, 33.02
7 Di-*p*-anisylarsyl chloride	83–84[e]		....	....
8 Di-*p*-anisylarsyl bromide	60–62	$C_{14}H_{14}O_2AsBr$	Br, 21.68	21.20, 21.22
9 Di-*p*-anisylarsyl iodide	40–42[f]	$C_{14}H_{14}O_2AsI$	I, 30.52	30.60, 30.43
10 Di-*p*-naphthylarsyl chloride	167–168[g]		....	....
11 Di-*p*-naphthylarsyl bromide	172–173	$C_{20}H_{14}AsBr$	Br, 19.56	19.45, 19.41
12 Di-*p*-naphthylarsyl iodide	140–141	$C_{20}H_{14}AsI$	I, 27.85	27.65, 27.70
13 Dibiphenylarsyl chloride	145–147	$C_{24}H_{18}AsCl$	Cl, 8.52	8.48, 8.45
14 Dibiphenylarsyl bromide	147–149	$C_{24}H_{18}AsBr$	Br, 17.35	17.54, 17.23
15 Dibiphenylarsyl iodide	140–141	$C_{24}H_{18}AsI$	I, 25.00	24.73, 24.80

The chlorides were prepared from the tetra-arylarsyl oxides and hydrogen chloride; the bromides from the oxides and hot 48% hydrobromic acid; the iodides from the chlorides and sodium iodide in acetone.

Compounds 1, 2, 3, 4, 5, 6, 7, 8 and 9 were recrystallized from absolute alcohol; 10, 11, 12, 13 and 15 from benzene; 14 from a mixture of benzene and absolute alcohol.

[a] The m. p. recorded by Norris, *J. Ind. Eng. Chem.*, **11**, 824 (1919), is 34°.

[b] Michaelis and La Costa, *Ann.*, **201**, 230 (1880), described the compound as an oil; Pope and Turner, *J. Chem. Soc.*, **117**, 1452 (1920), give the m. p. as 55–56°; Steinkopf and Schwen, *Ber.*, **54**, 1459 (1921), record the m. p. as 54°.

[c] The m. p. given by Pope and Turner[b] is 45–46°; Steinkopf and Schwen[b] state the m. p. to be 40.5°.

[d] La Costa, *Ann.*, **208**, 18 (1881), recorded the m. p. as 31°; Michaelis, *Ann.*, **321**, 160 (1902), as 45°.

[e] Michaelis and Weitz, *Ber.*, **20**, 50 (1887), found the m. p. to be 79–80°.

[f] Michaelis and Weitz[e] obtained the substance as an oil.

[g] Matsumiya, *Mem. Coll. Sci., Kyoto Imp. Univ.*, **4**, 217 (1920).

Summary

A reaction mechanism has been suggested to account for the products which are formed from the interaction of aromatic Grignard reagents and arsenic trioxide.

Improved methods have been described for the preparation of tetraphenyl-, tetra-*p*-tolyl-, tetra-*p*-anisyl- and tetra-α-naphthylarsyl oxides. Tetra-*p*-biphenylarsyl oxide has been synthesized.

A number of diarylhalo-arsines have been prepared and described.

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