

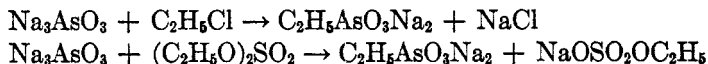
ALKYLATION REACTIONS OF TETRAETHYLLEAD. A NEW SYNTHESIS OF ETHYLDICHLOROARSINE AND RELATED COMPOUNDS¹

M. S. KHARASCH, ELWOOD V. JENSEN, AND SIDNEY WEINHOUSE

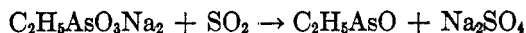
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The methods described in the literature for the preparation of ethyldichloroarsine and the analogous compounds of phosphorus and antimony are rather involved. For example, the preparation of ethyldichloroarsine (1) involves the following three steps.

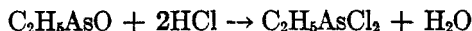
1. Treatment of sodium arsenite with ethyl chloride or ethyl sulfate to form disodium ethylarsonate.



2. The reduction of disodium ethylarsonate with sulfur dioxide to form ethylarsenious oxide.



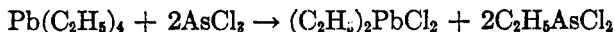
3. The treatment of ethylarsenious oxide with hydrogen chloride to form ethyldichloroarsine.



The method developed in this laboratory for the preparation of ethyldichloroarsine and the analogous compounds of phosphorus and antimony consists in treating arsenic trichloride with tetraethyllead. The over-all reaction is



The reaction appears to proceed in two stages. The first stage



proceeds spontaneously at room temperature. At temperatures below 50°, however, even an excess of arsenic trichloride will not detach a third ethyl radical from the diethyllead dichloride. The second stage



proceeds slowly at 80° and rapidly at temperatures above 90°.

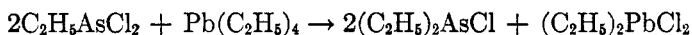
The reaction may be carried out either in the presence or absence of solvents. When low-boiling solvents are used only the first stage occurs. When the reaction is carried out at temperatures above 80°, either without a solvent or with

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a high-boiling solvent (*e.g.*, nitrobenzene) both stages proceed simultaneously. The ethyl chloride is readily recovered by chilling the evolved gases.

The synthesis was found to be most convenient when no solvent was used; tetraethyllead was slowly dropped into the calculated amount of arsenic trichloride with stirring at 100°. The product was then distilled directly from the solid lead chloride produced. Under these conditions, the yield of ethyldichloroarsine was from 95 to 97% of the calculated amount.

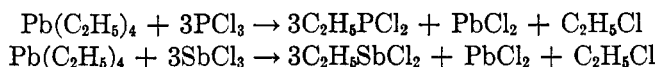
At higher temperatures (120°) ethyldichloroarsine reacts further with excess tetraethyllead to form diethylchloroarsine



Diethylchloroarsine is much less stable than ethyldichloroarsine; on contact with air it instantly begins to form a white solid.

Ethylarsenious oxide was prepared from ethyldichloroarsine. The high-boiling point of ethylarsenious oxide (158°/10 mm.) as compared with that of ethyldichloroarsine (74°/50 mm.) led us to examine the molecular weight of the oxide. The molecular weight (in benzene) of ethylarsenious oxide is 376. The compound is, therefore, a trimer $(\text{C}_2\text{H}_5\text{AsO})_3$, and not a monomolecular compound as it is represented by all investigators and in all texts on the chemistry of organic arsenicals.

When phosphorus trichloride and antimony trichloride were treated with tetraethyllead in a manner similar to that described for arsenic trichloride, wholly analogous reactions occurred.



The yields of ethyldichlorophosphine obtained were excellent, varying from 89 to 96%. In the only reaction carried out with antimony trichloride the yield of ethyldichlorostibine was 71%.

EXPERIMENTAL

Materials used. The tetraethyllead used in these experiments was the commercial product obtained from the Ethyl Gas Corporation. Two types of arsenic trichloride were used, a technical-grade material obtained from the Hooker Chemical Company and a reagent-grade material obtained from the J. T. Baker Chemical Company. The yields and product purity were identical with both grades of arsenic trichloride.

The phosphorus trichloride was reagent-grade material obtained from the General Chemical Company.

The antimony trichloride was a C.P. grade obtained from Eimer and Amend.

Preparation of ethyldichloroarsine. The reaction should be carried out in an efficient hood, preferably one equipped with windows which can be closed. In handling either the reactants or the products, rubber gloves and a gas mask should be worn.

A five-liter three-necked flask was fitted with a 250-ml. dropping-funnel, an efficient mechanical stirrer, and a one-meter bulb condenser leading to a 500-ml. trap cooled with Dry Ice and acetone. In the flask was placed 2730 g. (15 moles) of arsenic trichloride; the air in the flask was then swept out with a current of nitrogen. The flask was heated to 100° and, after the arsenic trichloride had reached that temperature, a few cubic centimeters of

tetraethyllead was added from the dropping-funnel to the stirred arsenic trichloride. The start of the reaction (which occurred in a few minutes) was indicated by clouding of the liquid and separation of a white precipitate. A total of 1620 g. (5 moles) of tetraethyllead was then added through the dropping-funnel at such a rate that the reaction mixture kept gently boiling. During this addition of the tetraethyllead, and for one hour after the addition, the mixture was vigorously agitated. The oil-bath temperature was maintained at 100–110°. About seven hours was required for the addition of tetraethyllead.

After the product had cooled to room temperature (usually by standing overnight), the condenser, dropping-funnel and stirrer were removed, the side necks were closed with ground-glass stoppers, and the center neck was fitted with a Claisen still-head. The product was distilled directly from the reaction mixture at 75 mm. During the distillation, the oil-bath was maintained at 120°; the product distilled at 82–83°. About 80% of the product distilled in four to five hours. The distillation of the remainder was very slow, because of the large amount of lead chloride in the flask. The distillation process may be hastened by gradually reducing the pressure further. It required about 10 hours to distill 2500 g. of ethyldichloroarsine. The yield in this experiment was 95% of the calculated amount. In other experiments yields as high as 97% were obtained.

The density of the crude, water-white product varied in four runs from 1.6735 to 1.6799 as compared with 1.6570 for very pure material distilled through a column. Hence, the distillate obtained as described above was 95 to 97% pure. The impurity is arsenic trichloride (d 2.163), the boiling point of which is 20° below that of ethyldichloroarsine. Fractionation through a column readily separated the two substances. The percentages thus obtained check well with the composition calculated from the density of the crude material.

The material collected in the cold-trap (ca. 225 g.) boiled at 12°; it was ethyl chloride.

Anal. Calc'd for C_2H_5Cl : Mol. wt., 64.5. Found: Mol. wt., 65.1.

The solid residue remaining in the reaction flask was nearly pure lead chloride.

Anal. Calc'd for $PbCl_2$: Cl, 25.5. Found: Cl, 25.8.

Other experiments related to the preparation of ethyldichloroarsine. An account of some other experiments conducted with arsenic trichloride and tetraethyllead is given because of the light which these experiments throw on the course and mechanism of the reaction. The low-temperature preparation of ethyldichloroarsine described below is not recommended as a preparative method.

Tetraethyllead (54 g., 0.167 mole) was added to a well-stirred solution of 91.5 g. (0.5 mole) of arsenic trichloride in 235 cc. of carbon tetrachloride. The reaction began at the end of 1.5 hours. The mixture was stirred continuously for about 12 hours at room temperature. The solid reaction product was then collected and the filtrate concentrated to remove the solvent. The residue was distilled through a two-foot Fenske column. Unchanged arsenic trichloride (11 g., b.p. 61.5–63° at 75 mm.) and ethyldichloroarsine (40 g., b.p. 82–83° at 75 mm.) were obtained. This yield of ethyldichloroarsine is 69%, if the first stage reaction is used as a basis of calculation; it is 46%, if the over-all reaction is used. Similar results were obtained when benzene or ligroin were used as solvents and the reaction carried out at room temperature.

In another experiment the proportion of arsenic trichloride to tetraethyllead was four moles to one. The solvent was benzene, and the reaction was carried out at room temperature. The recovered arsenic trichloride amounted to 1.3 mole equivalents; the ethyldichloroarsine obtained was equivalent to 2 moles of arsenic trichloride. These results show that at room temperature, a large excess of arsenic trichloride removed only two ethyl groups from the tetraethyllead.

When an equimolecular mixture of diethyllead dichloride and arsenic trichloride was heated to 125°, there was a vigorous reaction and a gas, presumably ethyl chloride, was evolved. The reaction mixture was distilled at 75 mm. The product obtained was ethyldichloroarsine (yield 75%); it boiled at 148–152° when distilled at atmospheric pressure.

Preparation of ethylarsenious oxide. Ethylarsenious oxide was prepared from ethyldichloroarsine by the method of Steinkopf and Mieg (2). An 80% yield of colorless liquid

was obtained (b.p. 158°/10 mm.). The molecular weight of this substance was found to be 376 by the cryoscopic method in benzene [calc'd for $(C_2H_5AsO)_2$, 360].

Preparation of diethylchloroarsine. Ethyldichloroarsine, 52.5 g. (0.3 mole) was heated to 120°, and 48.5 g. (0.15 mole) of tetraethyllead was slowly added. The separation of a white precipitate indicated that a reaction had occurred. After the mixture had been kept at 120° for two hours, the product was distilled directly from the reaction flask. The 39.3 g. of diethylchloroarsine obtained, boiled at 74–78°/74 mm.; d_{20}^{20} 1.215.

Anal. Calc'd for $C_4H_{10}AsCl$: Cl, 21.1. Found: Cl, 18.0.

The product is, therefore, diethylchloroarsine contaminated with a small amount of triethylarsine. It is quite unstable; on contact with air it immediately forms a white solid.

The white residue from the reaction was washed with benzene; it weighed 49 g. Assuming this substance to be diethyllead dichloride, the theoretical yield is 50.5 g.

Anal. Calc'd for $C_4H_{10}Cl_2Pb$: Cl, 21.2. Found: Cl, 21.9.

Preparation of ethyldichlorophosphine. Phosphorus trichloride (137 g., 1 mole) was placed in a 500-ml. three-necked flask fitted with a dropping-funnel with a side-arm through which gas could be introduced, a mechanical stirrer, and a reflux condenser. While a slow stream of nitrogen was passed into the flask, tetraethyllead (100 g., 0.3 mole) was added to the stirred reaction mixture. The reaction was slow; no precipitation of lead chloride occurred until the mixture had been refluxed for two hours. The reaction mixture was heated in an oil-bath kept at 110° until refluxing ceased (about 30 hours). The volatile material was then distilled directly from the reaction vessel. A colorless, evil-smelling distillate was collected (b.p. 113–116°/760 mm.). The yield was never lower than 117 g., 89% of the theoretical. In one experiment a yield of 96% was obtained.

Ethyldichlorophosphine, on exposure to air, rapidly forms a yellow solid. The reaction with air can be minimized by dissolving it in a suitable solvent (*e.g.*, benzene).

Preparation of ethyldichlorostibine. In the apparatus described for the preparation of ethyldichlorophosphine, 68.4 g. (0.3 mole) of dried and pulverized antimony trichloride was suspended in 160 cc. of benzene. Tetraethyllead (32.3 g., 0.1 mole) was then added slowly. The mixture was heated under reflux for 8 hours and then allowed to stand overnight. After the benzene had been removed by distillation, the residue was distilled under reduced pressure. The product which boiled between 113° and 120° at 25 mm. was redistilled. A total of 48.6 g. (71%) of a colorless liquid was obtained (b.p. 62–83° at 1 mm.; d 2.182). No fraction with a sharp boiling point could be obtained.

Anal. Calc'd for $C_2H_5Cl_2Sb$: Cl, 31.9. Found: Cl, 31.4.

SUMMARY

The method of preparing ethyldichloroarsine, ethyldichlorophosphine, ethyldichlorostibine, and diethylchloroarsine from tetraethyllead and arsenic trichloride, phosphorus trichloride, antimony trichloride, and ethyldichloroarsine is described.

CHICAGO 37, ILL.

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