Highly efficient synthesis of trimethylarsine

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A convenient, highly efficient, and environmentally safe procedure for the preparation of trimethylarsine was proposed. A quantitative yield of this compound in the reaction of As_2O_3 with $AlMe_3$ was attained for the first time by using mechanochemical activation of the process.

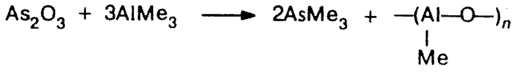
Key words: trimethylarsine, trimethylaluminum, synthesis, ecological safety.

In recent years, volatile arsenic compounds — arsine (AsH_3) and its organic derivatives like AsR_3, $RAsH_2$, and R_2AsH (R = Me, Pr^i, Bu^t, *etc.*) — have become the objects of systematic studies aimed at the development of new methods for the preparation of gallium arsenide involving the epitaxial technology. The great practical significance of these studies is due to the fact that gallium arsenide (AsGa) is among the most efficient semiconducting materials used in microelectronics.[1]

Methods for the synthesis of organoarsenic derivatives including trimethylarsine have been surveyed in monographs and papers.[2—9] According to these publications, the yield of $AsMe_3$ did not exceed 70 %. Reaction wastes contained much arsenic; hence, the reported methods were not environmentally safe.

The main purpose of the present study was to intensify the process of the synthesis of $AsMe_3$ based on the reaction of As_2O_3 with $AlMe_3$,[10] to increase the yield of the target product, and to make this process environmentally safe. It should be noted that the preparation of $AsMe_3$ by this method as reported in the literature[11] involved conducting the reaction in hydrocarbon solvents in the presence of a large excess of $AlMe_3$, which was then bound in a complex with KF, and distillation of $AsMe_3$, whose yield was 60 %.

Our attempts to carry out this reaction in a hydrocarbon solvent in a common flask equipped with a stirrer failed. The exothermic reaction ended very rapidly with the formation of a "lump." Evidently, the methylalumoxanes formed immediately "casehardened" the As_2O_3 surface, the mass exchange ceased, and the reaction stopped. This drawback was eliminated when the reaction was carried out in a ball mill.[12] In addition, the replacement of hydrocarbon solvents by ethers such as di-*n*-butyl ether, di-*n*-pentyl ether, and diglyme made it possible to partially dissolve the methylalumoxanes, especially their low-molecular-weight forms. The reaction occurs selectively to give $AsMe_3$ and methylalumoxanes only when the molar ratio of the reactants is 1:3.



$$As_2O_3 + 3AlMe_3 \longrightarrow 2AsMe_3 + -(\underset{\displaystyle Me}{\underset{|}{Al}}-O-)_n$$

This ratio of the reactants should be strictly obeyed, since with excess $AlMe_3$, formation of its 1 : 1 complex with $AsMe_3$ is possible; in addition, in the presence of ethers, the corresponding etherates of $AlMe_3$ can be obtained. If the reaction is carried out with excess As_2O_3, cacodyl oxide $(Me_2As)_2O$ is formed as a side product.

Experimental

All the experiments including purification of the solvents were carried out in an atmosphere of dry argon in a well ventilated exhaust hood. During the experiments, for the sake of safety, the setup was screened off with an additional protecting screen made of organic glass. Di-*n*-butyl ether and diglyme were held over KOH for a week, then distilled from $LiAlH_4$ or $NaAlH_4$ at 10 Torr, and stored under argon. Before use, commercial As_2O_3 was maintained at 100 °C *in vacuo* (1 Torr) for 2 h and stored under argon. $AlMe_3$ was obtained by a known procedure,[13] distilled from a flask with a dephlegmator at 130 °C and stored in sealed tubes.

Trimethylarsine. The reaction was conducted in a 250-mL cylindrical glass (or stainless-steel) vessel with 2—3 mm thick walls. The vessel was one-quarter filled with steel balls 2—4 mm in diameter and equipped with a metallic stirrer with a hermetic gasket. The setup was also equipped with joints for a dropping funnel and for a reflux condenser, with an inlet for the supply of solids, and with an orifice for a thermometer placed in a metallic tube. The reflux condenser was connected through a system of vacuum tubes to a trap cooled with solid CO_2 in acetone (−80 °C) and to an additional trap cooled with liquid nitrogen (−196 °C). Then the setup was connected through a three-way valve to a water-jet pump and to an inert gas supply system. The setup was filled with the inert gas and charged with As_2O_3 (19.7 g, 0.1 mol); then di-*n*-butyl ether (30—35 mL) was added, and the stirrer was switched on for 5—10 min. After that, one-fourth of the solution of $AlMe_3$ in di-*n*-butyl ether was added to the vessel in one portion. This solution was prepared beforehand from $AlMe_3$ (21.6 g, 0.3 mol) and 100 mL of di-*n*-butyl ether.

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The reaction mixture was heated to 80 °C; at this temperature, the exothermic reaction began, and the temperature rapidly raised to 110—120 °C. This temperature was maintained by gradual addition of the solution of $AlMe_3$ over a period of 10—15 min. Then the reaction mixture was additionally heated for 10—15 min at 120—130 °C, cooled to 80 °C, and $AsMe_3$ was gradually distilled off by slow evacuation of the system. The distillation was terminated at 50 °C and 16 Torr under conditions of reflux of di-*n*-butyl ether when the reflux condenser was flooded. The setup was filled with the inert gas. $AsMe_3$ frozen in the liquid-nitrogen trap (1.5—2 g) was recondensed into the trap with $AsMe_3$ maintained at −80 °C. Then the whole amount of $AsMe_3$ was distilled using a vacuum system in a Stock-type apparatus and finally distilled under argon with a rod-and-disk type dephlegmator (120 mm), b.p. 52 °C. 23.6 g of $AsMe_3$ was obtained, yield 98.5 %.

The waste reaction mixture, *viz*., the suspension and the solution of methylalumoxanes in di-*n*-butyl ether, was quenched with 10 % HCl; di-*n*-butyl ether was separated from the aqueous solution, through which a flow of hydrogen sulfide was passed. No precipitation of As_2S_3 was observed, which indicated that arsenic was completely extracted from As_2O_3.

The high rate of the formation of $AsMe_3$ by the procedure suggested makes it possible to prepare up to 100 g of $AsMe_3$ over a period of 5—6 h.

The reaction in diglyme was carried out in a similar way at a temperature of up to 140 °C.

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ESR spectroscopic study on the addition of $PhCONH\dot{C}HCO_2Me$ radicals to alkenes and spin traps

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Using ESR spectroscopy, the rate constants for the addition of $PhCONH\dot{C}HCO_2Me$ radicals to alkenes $CH_2{=}CXY$ (X = Me, Y = Ph; X = H, Y = Ph; X = Me, Y = CO_2Me; X = H, Y = CO_2Me; X = H, Y = CN) and nitrosodurene were determined at 22 °C. It is shown that a linear dependence exists between the donor-acceptor properties of the substituents at the vinyl group and the rate constants for the addition.

Key words: spin trap method, rate constants for addition, alkenes.

Addition of acyclic carbon-centered radicals to compounds with multiple bonds is successfully used to form carbon—carbon and carbon—element bonds regio- and stereoselectively.[1—7] The rate of the radical addition to mono- and disubstituted alkenes essentially depends on the polar properties of substituents,[8] which manifests

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