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The reactions of $(Me_3Si)_3As$ with some group 13 trihalides have been explored. The reaction between $(Me_3Si)_3As$ and $GaCl_3$ results in the facile elimination of approximately two moles of Me_3SiCl at room temperature. Further elimination of Me_3SiCl occurs less readily and requires heating of the intermediate solid at temperatures up to 185°C in order to afford 93-94% of the total Me_3SiCl expected. Increasing the temperature does not result in the elimination of additional Me_3SiCl, rather a trace of unidentified yellow liquid is formed and gallium arsenide of 95-96% purity is isolated. The reaction between $(Me_3Si)_3As$ and $GaBr_3$ proceeds in a similar manner, but more by-products are observed and GaAs of 88% purity is obtained. The analogous reaction between $(Me_3Si)_3As$ and $InCl_3$ in refluxing benzene gives 87% of the theoretical amount of Me_3SiCl. Further heating of the resulting solid affords InAs of 98% purity. This is the first report of the use of dehalosilylation reactions to form GaAs and InAs.

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22a NAME OF RESPONSIBLE INDIVIDUAL: Richard L. Wells

22b TELEPHONE *(Include Area Code)*: (919)684-6404

22c OFFICE SYMBOL:

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The Use of Tris(trimethylsilyl)arsine to Prepare Gallium Arsenide and Indium Arsenide

by

R. L. Wells, C. G. Pitt, A. T. McPhail,
A. P. Purdy, S. Shafieezad, and R. B. Hallock

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Duke University
Department of Chemistry
Durham, NC 27706

October 3, 1988

[Communication]

The Use of Tris(trimethylsilyl)arsine to Prepare Gallium Arsenide and Indium Arsenide

Richard L. Wells,* Colin G. Pitt, Andrew T. McPhail, Andrew P. Purdy,
Soheila Shafieezad, and Robert B. Hallock

Department of Chemistry, Paul M. Gross Chemical Laboratory,
Duke University, Durham, NC 27706

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Sir:

One of the processes commonly used for the epitaxial growth of GaAs and other compound semiconductors is organometallic chemical vapor deposition (OMCVD).[1] For GaAs, it has been the general practice to utilize a trialkylgallium compound and AsH_3 in this process, as exemplified by equation 1. However, concerns regarding

$$Me_3Ga + AsH_3 \xrightarrow[\sim 700\ ^oC]{H_2} GaAs + 3MeH \qquad (1)$$

the use of AsH_3 have prompted a number of researchers to evaluate other sources of arsenic; thus, replacements for AsH_3 which have been studied include As, Me_3As, Et_3As, Et_2AsH, and t-$BuAsH_2$.[2] Alternatively, some adducts of gallium and arsenic compounds,[3-5] as well as a monomeric and a dimeric mono(arsino)gallane,[6,7] have been used as single source GaAs precursors.

Recent research in our laboratories has demonstrated that dehalosilyation reactions (e.g., equation 2) are a facile route to the

$$R_2AsSiMe_3 + GaX_3 \longrightarrow 1/3(R_2AsGaX_2)_3 + Me_3SiX \qquad (2)$$

$$R = Me_3SiCH_2;\ X = Cl \text{ or } Br$$

formation of the Ga-As covalent bond and, as a result, we have prepared and characterized a number of new Ga-As compounds.[8-11] We now report the first examples of the use of dehalosilylation reactions to prepare GaAs and InAs. Reactions between $(Me_3Si)_3As$ and MX_3 (M=Ga, X=Cl or Br; M=In, X=Cl) proceed at relatively low temperatures to eliminate Me_3SiX with the concurrent formation of GaAs and InAs, respectively (equation 3).

$$(Me_3Si)_3As + MX_3 \longrightarrow MAs + 3Me_3SiX \qquad (3)$$

(M=Ga, X=Cl or Br; M=In, X=Cl)

Tris(trimethylsilyl)arsine[12] (0.343g, 1.16 mmol) was added to a solution of $GaCl_3$ (0.205 g, 1.16 mmol) in 25 mL of ligroin (bp 90-110 °C) at room temperature.[13] Upon mixing, a white precipitate formed which quickly changed color to yellow then to orange. After stirring for 3 days at 75 °C, the volatiles were distilled off and shown to contain 2.89 mmol of Me_3SiCl.[14] The remaining brown solid was heated in the absence of solvent using a heating mantle while the reaction bulb was opened to a -196 °C trap on the vacuum line. As the temperature was increased to 85 °C, a small amount of colorless material began to collect in the trap. The bulb was further heated at 125 °C for 30 min, then the temperature was increased to 185 °C for 2 h. At this time it did not appear that any more material was collecting in the trap. The solid in the flask was dark brown to black. The colorless liquid was distilled from the trap and shown to contain 0.39 mmol of Me_3SiCl (total Me_3SiCl = 3.28 mmol, 94% theoretical). Further heating of the solid product to 380 °C for 90 min resulted in a trace of yellow liquid collecting in the trap beginning at 330 °C. The resulting black solid (0.136 g, 81% yield) was poured out of the bulb through the valve stem. It was shown to be GaAs of about 95% purity by partial elemental analysis[15] and comparison of its X-ray powder diffraction pattern with that for a bona fide sample of GaAs. In a separate experiment, $GaCl_3$ (0.411 g, 2.33 mmol) and $(Me_3Si)_3As$ (0.688 g, 2.33 mmol) were combined in pentane (30 mL). A precipitate formed as in the first experiment. The mixture was stirred overnight at room temperature and the precipitate appeared light brown. Removal of volatiles showed that 4.47 mmol of Me_3SiCl had formed. Toluene (30 mL) was distilled onto the brown solid and the slurry was stirred overnight at 90 °C, causing the formation of an additional 1.42 mmol of Me_3SiCl. The resulting solid was heated in the absence of solvent overnight at 140-160 °C, then for 3 h at 160-180 °C. An additional 0.60 mmol of Me_3SiCl was formed (total Me_3SiCl = 6.49 mmol, 93% theoretical). The bulb containing the solid was heated with a cool flame (propane, no oxygen; ~400-500 °C) for 2 h and a trace of yellow liquid collected in the trap. The resulting black solid (0.294 g, 87% yield) was shown to be GaAs of about 96% purity by complete elemental analysis[16] and comparison of its X-ray powder diffraction pattern with that for a bona fide sample of GaAs.

The reaction between $(Me_3Si)_3As$ and $GaBr_3$ did not proceed as readily as the corresponding reaction with $GaCl_3$. Stirring an equimolar mixture of $(Me_3Si)_3As$ and $GaBr_3$ (1.19 mmol) overnight in benzene at 47 °C resulted in the elimination of 1.39 mmol of Me_3SiBr; an additional 1.16 mmol of Me_3SiBr was eliminated after heating overnight at 75-85 °C. Further heating of the resultant reddish-brown solid in the absence of solvent to 410 °C did not result in the clean elimination of additional Me_3SiBr, rather the formation of an unidentified slightly volatile yellow liquid was observed. The nonvolatile black solid was shown to be GaAs of 88% purity by partial elemental analysis[17] and comparison of its X-ray powder diffraction pattern with that for a bona fide sample of GaAs. The ^1H NMR spectrum of the yellow liquid consists of broad peaks near 1 ppm.

The reaction of $(Me_3Si)_3As$ with $InCl_3$ proceeded in a manner similar to the analogous reactions with gallium halides. $InCl_3$ (0.314 g, 1.42 mmol) and $(Me_3Si)_3As$ (0.415 g, 1.41 mmol) were combined in 35 mL pentane. A salmon colored precipitate formed immediately upon mixing and rapidly changed color to dark brown. The mixture was stirred at room temperature for 3 days and 2.33 mmol of Me_3SiCl were evolved. Further heating in benzene at 70-75 °C for 4 days resulted in the formation of an additional 0.99 mmol of Me_3SiCl. Heating of the remaining brown solid in the solid state overnight at 150 °C caused the elimination of 0.32 mmol additional Me_3SiCl. Finally, the solid was heated for 15 min with a cool flame and a trace (0.05 mmol) of Me_3SiCl collected in the trap (total Me_3SiCl = 3.69 mmol, 87% yield). The resulting fluffy black solid (0.153 g, 57% yield) was shown to be InAs of 98% purity by complete elemental analysis[18] and comparison of its X-ray powder diffraction pattern with that for a bona fida sample of InAs.

This work demonstrates that dehalosilylation reactions provide a viable route to the formation of GaAs and InAs. These two compound semiconductors were isolated in 88-96% and 98% purity, respectively, from very crude experiments with no attempts to optimize the reaction conditions. The formation of GaAs and InAs with low incorporation of Si relative to C and to halogen in these experiments is of interest. This may be due to the decomposition of the Me_3Si group to form polysilanes at elevated temperatures. During the thermal decomposition of $(Me_3Si)_3Al$ polysilanes have been observed;[19] similar decomposition of the Me_3Si group may occur at high temperatures in our system. In contrast, the pyrolysis of $[(Me_3Si)_2AlNH_2]_2$ gave a solid solution of AlN and SiC.[20]

Tris(trimethylsilyl)arsine is a liquid with a relatively low vapor pressure (bp 50-52 °C at 10^{-3} mm)[12] and may prove useful as a safer alternative to AsH_3 gas in the vapor deposition of GaAs and other As containing alloys. Gallium trichloride has an appreciable vapor pressure at room temperature and has been applied to CVD growth of GaAs in other systems.[21] The extension of these prelimary results to vapor phase epitaxy is worth investigating as an alternative to typical OMCVD processes.

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References

1. Leys, M. R. *Chemtronics* **1987**, 2, 155.

2. See the following and references cited therein: Stringfellow, G. B. *J. Electron. Mater.* **1988**, 17, 327.

3. Zaouk, A.; LeBugle, A.; Constant, G. *J. Crystal Growth* **1979**, 46, 415.

4. Maury, F.; Constant, G.; Fontaine, P.; Biberian, J. P. *J. Crystal Growth* **1986**, 78, 185.

5. Maury, F.; El Hammadi, A.; Constant, G. *J. Crystal Growth* **1984**, 68, 88.

6. Byrne, E. K.; Theopold, K. H. *Science* **1988**, 241, 332.

7. Cowley, A. H.; Ekerdt, J. G.; Jones, R. A.; Kidd, K. B.; Miller, J. E. *Abstract of Papers*, Third Chemical Congress of North America, Toronto, Canada **1988**; INOR 210.

8. Pitt, C. G.; Purdy, A. P.; Higa, K. T.; Wells, R. L. *Organometallics* **1986**, 5, 1266.

9. Purdy, A. P.; Wells, R. L.; McPhail, A. T.; Pitt, C. G. *Organometallics* **1987**, 6, 2099.

10. Wells, R. L.; Shafieezad, S.; McPhail, A. T.; Pitt, C. G. *J. Chem Soc., Chem. Comm.* **1987**, 1823.

11. Wells, R. L.; Purdy, A. P.; McPhail, A. T.; Pitt, C. G. *J. Organomet. Chem.* (in press).

12. Becker, V. G.; Gutekunst, G.; Wessely, H. J. Z. *Anorg. Allg. Chem.* **1980**, 462, 113.

13. All manipulations were carried out on a vacuum line or in a nitrogen filled glove box. $(Me_3Si)_3As$ is an air sensitive liquid which has a very disagreeable odor and was handled with the assumption that it has some toxicity.

14. The quantities of Me_3SiCl or Me_3SiBr formed in the reactions were determined as HCl or HBr by vacuum distillation of all volatiles from the reaction mixture followed by hydrolysis and titration with standard NaOH solution.

15. Anal. Calcd (Found) for GaAs: C, 0.00 (1.35); H, 0.00 (0.98); Cl, 0.00 (2.36); Si, 0.00 (0.45).

16. Anal. Calcd (Found) for GaAs: C, 0.00 (1.68); H, 0.00 (0.30); As, 51.80 (50.08); Cl, 0.00 (2.51); Ga, 48.21 (45.96); Si, 0.00 (0.51); (Ga:As mol ratio=1.00:1.01).

17. Anal. Calcd (Found) for GaAs: C, 0.00 (3.58); H, 0.00 (0.19); Br, 0.00 (7.21); Si, 0.00 (<0.7).

18. Anal. Calcd (Found) for InAs: C, 0.00 (0.56); H, 0.00 (0.17); As, 39.49 (38.32); Cl, 0.00 (0.80); In, 60.51 (59.21); Si 0.00 (<0.1); (In:As mol ratio=1.00:0.99). The low yield of both InAs and Me_3SiCl obtained in this experiment may be due to the fact that a significant amount of material adhered to the walls of the reaction bulb and was not isolated.

19. Rosch, L. *Angew. Chem. Int. Ed. Engl.* **1977,** 16(7), 480.

20. Janik, J. F.; Duesler, E. N., Paine, R. T. *Inorg. Chem.* **1987,** 26, 4341.

21. Rubenstein, M.; Myers, E. *J. Electrochem. Soc.* **1966,** 113(4), 365.

(Abstract for use by Chemical Abstracts)

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Richard L. Wells,* Colin G. Pitt, Andrew T. McPhail, Andrew P. Purdy,
Soheila Shafieezad, and Robert B. Hallock

Department of Chemistry, Paul M. Gross Chemical Laboratory,
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