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13. ABSTRACT *(Maximum 200 words)*

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This report summarizes the results obtained in the second year of the grant. During this time, experiments were conducted which demonstrated that phenyl groups on heavier main group atoms undergo migration with great facility. This mobility has been utilized to prepare novel materials with a broad range of semiconducting and optoelectronic properties. Gallium arsenide and gallium phosphide have been prepared at modest temperatures (~400 °C) from easily prepared single source precursors. Work conducted in this time period led to the discovery that ternary compounds composed of tin, sulfur and selenium can be prepared in high yields at ~400 °C as phase pure materials in nonstoichiometric ratios from readily available compounds. Conventional procedures call for temperatures >1000 °C. Also discovered was that pyrolysis of perbenzylated compounds is very efficient for producing binary and ternary compounds of the main group. They have numerous advantages over the alkylated analogues among which are lower toxicity, faster decomposition times and lower contamination of target products.

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Principal Investigator: Philip Boudjouk F49620-92-J-0431

ANNUAL TECHNICAL REPORT for August 15, 1993 - August 14, 1994

I. List of Objectives

The objectives in this project arose from an accidental discovery during the work we began under another Air Force project (AFOSR Grant No 91-0197) in which we observed that heating of certain organotin sulfides and selenides produced high yields of tin sulfide and tin selenide in high purity, i.e., with carbon contamination of less than 1%. Under this grant we had the following original objectives:

1-Determine the breadth and scope of the applicability of the relatively nontoxic **perphenylated** group 14-16 chalcogenides as single source precursors to phase pure binary and ternary materials such as SnS, SnSe and SnS_xSe_{1-x}, as well as the germanium, lead and tellurium analogues.

2-Investigate the possibility that group 13-15 analogues such as GaAs could be prepared by the low temperature pyrolysis of perphenylated precursors.

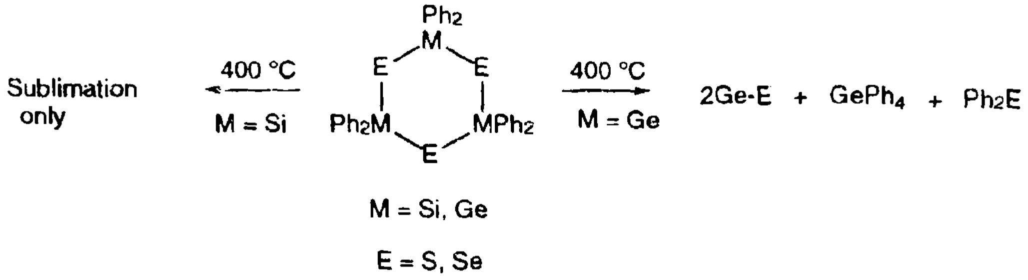
3-Attempt to determine the mechanism of the production of these materials.

To these we have added a new objective: to investigate the feasibility of benzyl derivatives as single source precursors for potential semi conducting and optoelectectronic materials.

II. Status of Research Effort

Cyclic Group 14-16 Chalcogenides

We have extended our investigation of cyclic systems to include silicon and germanium as the main group metal. We have found that the silicon derivatives sublime rather than undergo the rearrangement of phenyl groups observed in the organotin compounds (see Technical Report for 8/15/92 - 8/14/93). Germanium compounds exhibit good promise for the synthesis of germanium sulfide and germanium selenide but we have not yet optimized the procedures.



We now know it is going to be more profitable to pursue these binaries from linear precursors. Our work has progressed to the point that we feel that further work on **perphenylated ring**

systems is not justified and that linear systems offer considerably more potential for preparing binary and ternary compounds of the main group elements.

Linear Group 14-16 Chalcogenides

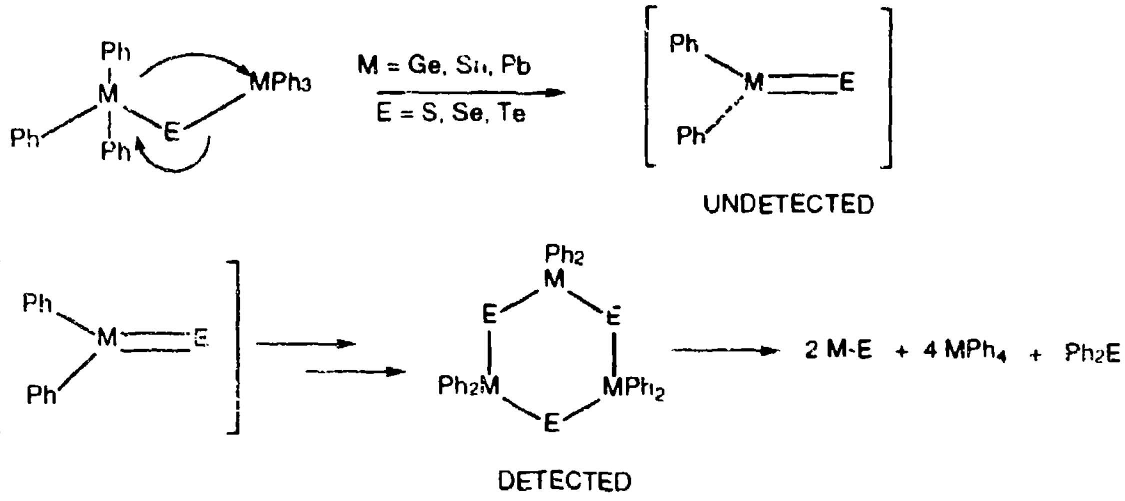
As described in the report for the period 8/15/92 - 8/14/93, we discovered that linear organotin chalcogen compounds of the general formula, $(Ph_3Sn)_2E$, E = S, Se, Te, are very efficient sources of SnS, SnSe and SnTe respectively. We have since extended the series to include germanium and lead resulting in a simple, efficient and generally useful methodology for preparing phase pure binaries composed of group 14 - 16 elements. The general equation below applies remarkably well:

$$Ph_3M\text{-}Cl + Na_2E \xrightarrow[-\,NaCl]{} Ph_3M\text{-}E\text{-}MPh_3$$

$$Ph_3M\text{-}E\text{-}MPh_3 \xrightarrow{400\ ^\circ C} 2\ M\text{-}E + 4\ Ph_4Sn + Ph_2X$$

Typically our yields are within a few percent of the theoretical maximum. The notable exceptions are the cases where the metal is lead. The organolead precursors tend to decompose to give some elemental lead in the product mixture.

We have done some mechanistic work on these systems and, except for the cases where M = Pb, we observe intermediates of the general formula $(Ph_2M\text{-}E)_3$. We believe the dominant mechanism involves production of the highly reactive intermediates which possess multiple bonds between the metal and the chalcogen. These intermediates are heavy atom analogues to ketones. We have proposed the following mechanism (Boudjouk, P.; Seidler, D.; Bahr, S. R.; McCarthy, G. J. *Chem. Mater*, in press, copy included as part of this report):



Linear Group 13-15 Compounds as Single Source Precursors

The successes with the combinations of elements from groups 14 - 16 naturally raised the question as to whether or not our approach would work with elements from groups 13 and 15. The question that is central to this approach is whether or not phenyl groups would be as prone to migration in compounds with atoms from groups 13 and 15 as in the compounds with atoms from groups 14 and 16. Our estimation was that phenyl groups would migrate well because atoms from group 13 are Lewis acids and atoms from group 15 are Lewis bases and both of these types of species promote phenyl migration. The results bear this out. We prepared Ph_2M-EPh_2 compounds in > 70% yields where M = Ga and In and E = As and P as described below:

$$Ph_3M + Ph_2E\text{-}H \rightarrow Ph_2M\text{-}EPh_2 + Ph\text{-}H$$
$$M = Ga, In; E = As, P$$

Pyrolysis led to the desired group 13 - 15 binaries. Thus, we developed a new and convenient route to gallium arsenide and gallium phosphide, both useful materials. Yields are >90%

$$3\,Ph_2M\text{-}EPh_2 \rightarrow M\text{-}E + 2\,Ph_3M + 2\,Ph_3E$$
$$M = Ga; \quad E = As, P$$

for GaAs and GaP. We are now investigating the indium derivatives.

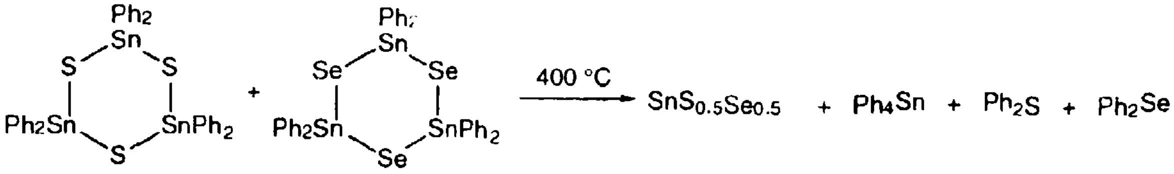
In summary, we now can produce **very pure and highly crystalline gallium arsenide** in multigram quantities in a matter of minutes from a readily available and safe precursor.

Nonstoichiometric Compounds

Preparing nonstoichiometric compounds to specifications is of general interest. It is of particular importance for the design of materials with targeted electrical and optoelectronic properties. We have developed a convenient new method for the synthesis of nonstoichiometric compounds of group 14 - 16 in which **three** elements are involved. The standard method of preparing ternary compounds of any composition is to mix the elements (high purity) and heat the sample in pressured sealed tubes to temperatures in excess of 1000 °C for one or more days. The sample is then cooled and ground to a fine powder and reheated. This process is repeated several times to ensure homogeneity. The danger of explosion is frequently mentioned by workers in the field.

Our procedure, in contrast, involves modest temperatures (<500 °C), simple apparatus (a tube furnace) at atmospheric pressure and easily prepared starting materials (perphenylated organotin sulfides and selenides). This procedure need be done only once, requiring 10 - 50 minutes. There is no potential for explosion since it is conducted at atmospheric pressure in a flow system, i.e., an inert gas is passed over the sample throughout the reaction.

In our last report we described how we prepared a pure, homogeneous sample of $SnS_{0.5}Se_{0.5}$ simply by heating a 1:1 mixture of the ring systems $(Ph_2SnS)_3$ and $(Ph_2SnSe)_3$:



In the past year we extended our study to demonstrate that this approach is quite general, i.e., we prepared the full range of solid solutions of the formula, SnS_xSe_{1-x} simply by mixing the two ring systems in the appropriate ratio and heating to 400 °C. We prepared **ten different solid solutions** of tin sulfide with the formula SnS_xSe_{1-x} in which x is varied incrementally from 0.1 through 0.9. Remarkably, the ratio of S and Se in the reagent mixture is preserved in the product! Thus, a 4:1 mixture of $(Ph_2SnS)_3$ and $(Ph_2SnSe)_3$ results in $SnS_{0.8}Se_{0.2}$.

As with the synthesis of the simple binary compounds, the other products are volatile and the ternary tin chalcogenide contains <1% carbon. The potential for this methodlogy is far reaching and we will explore this work more fully in the third and final year of this project.

Benzyl Derivatives of Group 14 - 16 Chalcogenides

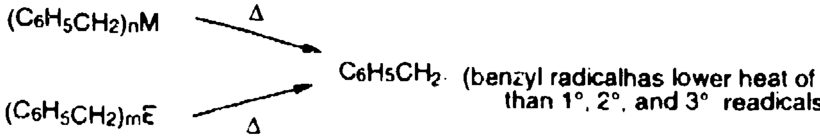
A frequently used approach in Organometallic Chemical Vapor Deposition (OMCVD) for preparing binary compounds of the main group elements and of main group - transition metal combinations has been to use small organic fragments on the central atoms and use high temperatures (typically >700 °C) to cause dissociation of the fragments:

$$R_3M\text{-}ER \longrightarrow M\text{-}E + R\cdot$$

R = organic radicals, e.g., $CH_3\cdot$, $C_2H_5\cdot$, and tert-$C_4H_9\cdot$

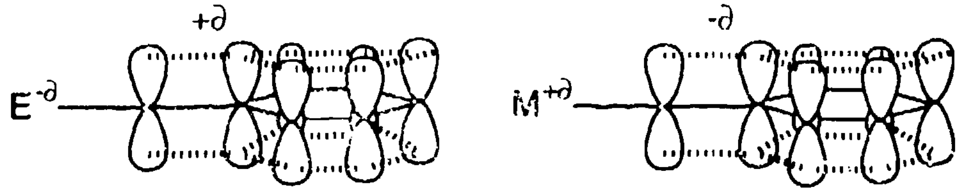
This methodology is suffers from several disadvantages: alkyl derivatives of main group and transition metal compound are toxic and volatile; the high temperatures required usually lead to multipathway reactions, resulting in contamination of the target materials; the equipment and techniques required for these syntheses are sophisticated and, normally, the limitation to the gas phase confines one to small quantities that can be produced in any one experiment.

The essential consideration in this approach is the heat of formation of the organic radical. We have studied the heats of formation of organic radicals and surmised that, base on its greater stability, the benzyl radical should be an excellent candidate for dissociation from metal and nonmetal atoms.



(benzyl radicalhas lower heat of formation than 1°, 2°, and 3° readicals)

Use of the benzyl group as a leaving group also offered another important advantage: its electronic structure is such that it can stabilize positive or negative partial charges during the cleavage process. Thus, the effect of the electronegativity of the main group atom or metal could be minimized. This would be expected to lower the activation barrier and increase the reaction rate. Of course, this translates into lower temperatures required for pyrolysis.



partial charges, + or -, stabilized by resonance during bond breakage

Our initial experiments were successful beyond our expectations: **perbenzylated organometallics** are excellent single source precursors for binary materials cotaining main group elements.

$$(C_6H_5CH_2)_3M\text{-}ECH_2C_6H_5 \xrightarrow{400\ °C} M\text{-}E + 2\ C_6H_5CH_2\text{-}CH_2C_6H_5$$

$$M = Ge, Sn;\ E = S, Se$$

Typical yields of binary compounds are 90-95% with less than 2% carbon contamination. This contrasts sharply with substrates in which alkyl groups are the leaving groups. Yields as low as 20% are quite common and carbon contamination is usually more than 10%. Preliminary studies to prepare ternary compounds by simply heating a mixture of perbenzylated substrates showed that nonstoichiometric compounds can be readily prepared by this method:

$$\begin{array}{l} (C_6H_5CH_2)_3Sn\text{-}S\text{-}CH_2C_6H_5 \\ \quad + \\ (C_6H_5CH_2)_3Sn\text{-}Se\text{-}CH_2C_6H_5 \end{array} \xrightarrow{400\ °C} Sn\text{-}S_x\text{-}Se_{1\text{-}x} + C_6H_5CH_2\text{-}CH_2C_6H_5$$

We are now exploring the applicability of this approach to other main group elements and to transition metal systems as well. The ease with which benzyl groups can be attached to other atoms greatly enhances the range of perbenzylated compounds we can prepare. This of course, opens the way to a broad range of intermetallics and metalloidal compounds that can be prepared "to meet specifications".

There is no question that we have vastly improved the chemist's ability to prepare novel binary and ternary materials composed of main group elements in bulk and in high purity. We expect that this methodolgy will replace much of the current approaches to the preparation of these materials.

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IV. List of Professional Personnel (funded by F49620-929-J-0431)

Senior Personnel	Philip Boudjouk, Principal Investigator
Postdoctoral Associate	Youlin Pan
Graduate Assistants	Dean Seidler Duane Simonson
Undergraduate Assistant	Chris Meyer

V. Interactions (based on F49620-929-J-0431)

A. Presentations at meetings, conferences and seminars

1. Papers (presenter underlined)

None

2. Posters (presenter underlined)

AMERICAN CHEMICAL SOCIETY POSTERS
Division of Inorganic Chemistry, 206th ACS National Meeting (Chicago) 8/22/93 - 8/27/93

1) GROUP 13/15 COMPOUNDS WITH PHENYL SUBSTITUENTS.
Abstract No. **Inor 93.** ; Youlin Pan and Philip Boudjouk

2) A MECHANISTIC INVESTIGATION OF THE SYNTHESIS OF GROUP 14-16 SEMICONDUCTOR MATERIALS FROM ORGANOMETALLIC PRECURSORS.
Abstract No. **Inor 166.** ; Dean J. Seidler and Philip Boudjouk

3. Seminars

1) "Simple and Efficient Routes to Semiconductor Materials from Organometallic Reagents", Chungnam National University, Daejon, Korea October 21, 1993.

2) "Simple and Efficient Routes to Semiconductor Materials from Organometallic Reagents", Konju National University, Konju, Korea, October 27, 1993.

4. Invited Lectures

None

5. Invited Plenary Lectures

None

B. Consultative and Advisory Functions

None

C. New discoveries, inventions or patent disclosures

None

D. Additional information

None