This report summarizes the significant results obtained during the three period of this grant. Support for this project resulted in several major new developments in the synthesis of materials with a broad range of semiconducting and optoelectronic properties. Binary and ternary materials of Groups 14-16, 13-15, and 12-16 can now be prepared in bulk or as thin films from readily prepared single source precursors at moderate temperatures (190 - 450 °C) as opposed to the more typical preparations at 800 - 1000 °C. The precursors developed under this grant feature phenyl, benzyl and allyl groups and have numerous advantages over the conventional alkylated analogues among which are lower toxicity, faster decomposition times and lower contamination of target products.
I. List of Objectives

II. Status of Research Effort

   Cyclic Group 14-16 Chalcogenides
   Linear Group 14-16 Chalcogenides
   Linear Group 13-15 Compounds as Single Source Precursors
   Nonstoichiometric Compounds
   Benzyl Derivatives of Group 14-16 Chalcogenides
   Thin Films of Binary Compounds and of Metals
   Metal Bis(benzylthiolates). Metal Sulfides at Low Temperatures

III. List of Publications

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

V. Interactions 92-95

   A. Presentations at meetings, conferences and seminars
      1. Papers (presenter underlined)
      2. Posters (presenter underlined)
      3. Seminars
      4. Invited Lectures
      5. Invited Plenary Lectures

   B. Consultative and Advisory Functions

   C. New discoveries, inventions or patent disclosures

   D. Additional information
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\textsubscript{x}Se\textsubscript{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 new objectives:

4. Investigate the feasibility of benzyl derivatives as single source precursors for potential semi conducting and optoelectronic materials.

5. Investigate the feasibility of benzyl derivatives as single source precursors for potential semi conducting and optoelectronic materials.

II. Status of Research Effort

Cyclic Group 14-16 Chalcogenides

We have extended our investigation of cyclic systems from tin 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). The germanium analogs are efficient sources of germanium sulfide and germanium selenide.

\[
\begin{align*}
&\text{Sublimation only} \\
&\begin{array}{c}
\text{400 °C} \\
M = \text{Si, Ge}
\end{array} \\
&\begin{array}{c}
\text{Ph}_2\text{M} \\
\text{MPh}_2
\end{array} \\
&\begin{array}{c}
\text{400 °C} \\
M = \text{Ge}
\end{array} \\
&2\text{Ge-E} + \text{GePh}_4 + \text{Ph}_2\text{E}
\end{align*}
\]
We now know it is going to be more profitable to pursue these binaries from linear precursors. During the second year of the project the work progressed to the point where we felt 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, \((\text{Ph}_3\text{Sn})_2\text{E}, \text{E} = \text{S, Se, Te}\), are very efficient sources of \(\text{SnS, SnSe and SnTe}\) 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:

\[
\begin{align*}
\text{Ph}_3\text{M-Cl} & + \text{Na}_2\text{E} \rightarrow \text{Ph}_3\text{M-E-MPh}_3 \\
\text{Ph}_3\text{M-E-MPh}_3 & \rightarrow 2\text{M-E} + 4\text{Ph}_4\text{Sn} + \text{Ph}_2\text{X}
\end{align*}
\]

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 \(\text{M} = \text{Pb}\), we observe intermediates of the general formula \((\text{Ph}_2\text{M-E})_3\). 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.*, **1994**, 6, 2108):
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 Ph₂M-EPh₂ compounds in > 70% yields where M = Ga and In and E = As and P as described below:

\[
\text{Ph}_3M + \text{Ph}_2E\cdot\text{H} \rightarrow \text{Ph}_2M\cdot\text{EPh}_2 + \text{Ph\cdotH}
\]

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%

\[
3 \text{Ph}_2M\cdot\text{EPh}_2 \rightarrow \text{M}\cdot\text{E} + 2 \text{Ph}_3M + 2 \text{Ph}_3E
\]

M = Ga; 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 SnS0.5Se0.5 simply by heating a 1:1 mixture of the ring systems (Ph2SnS)3 and (Ph2SnSe)3:  

\[
\begin{align*}
\text{Ph}_2\text{Sn} & \quad \text{Sn} \quad \text{S}^4 \quad \text{S}^4 \quad \text{Se}^4 \quad \text{Se}^4 \\
\text{Ph}_2\text{Sn} & \quad \text{Sn} \quad \text{Sn} \quad \text{Ph}_2 \quad \text{Ph}_2
\end{align*}
\]

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 (Ph2SnS)_3 and (Ph2SnSe)_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 methodology is far reaching and in the third year of the project we extended the approach to include the synthesis of solid solutions of the formula Pb_{n}Sn_{1-n}S and Pb_{n}Sn_{1-n}Se.

**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:
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 bond dissociation energy of the organic radical. We have studied the bond dissociation energies of organic radicals and surmised that, base on its greater stability, the benzyl and the allyl radicals should be excellent candidates for dissociation from metal and nonmetal atoms.

\[
\begin{align*}
\text{(C}_6\text{H}_5\text{CH}_2)_{\text{n}}\text{M} & \xrightarrow{\Delta} \text{C}_6\text{H}_5\text{CH}_2 \cdot \quad (\text{benzyl radical has lower heat of formation than 1°, 2°, and 3° radicals}) \\
\text{(C}_6\text{H}_5\text{CH}_2)_{\text{n}}\text{E} & \xrightarrow{\Delta} \text{C}_6\text{H}_5\text{CH}_2 \cdot \quad (\text{benzyl radical has lower heat of formation than 1°, 2°, and 3° radicals})
\end{align*}
\]

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.

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

\[
\begin{align*}
\text{(C}_6\text{H}_5\text{CH}_2)_{\text{3}}\text{M-ECH}_2\text{C}_6\text{H}_5 & \xrightarrow{400 \, ^\circ\text{C}} \text{M-E} + 2 \text{C}_6\text{H}_5\text{CH}_2\text{-CH}_2\text{C}_6\text{H}_5 \\
\text{M} = \text{Ge, Sn}; \quad \text{E} = \text{S, Se}
\end{align*}
\]

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 in which yields as low as 20% are quite common and carbon contamination is usually more than 10%. 
Preliminary studies in the second year of the grant in which a few ternary compounds were prepared by simply heating a mixture of perbenzylated substrates showed that nonstoichiometric compounds were a reasonable target:

$$\begin{align*}
(C_6H_5CH_2)_3Sn-S-CH_2C_6H_5 \\
+ 400 \degree C \rightarrow Sn-S_x-Se_{1-x} + C_6H_5CH_2-CH_2C_6H_5 \\
(C_6H_5CH_2)_3Sn-Se-CH_2C_6H_5
\end{align*}$$

In the final year of the project, we prepared the complete series of $SnS_xSe_{1-x}$ compounds in which $x$ was varied stepwise in increments of 0.1 from 0.1 - 0.9. It is important to note that no tin, sulfur or selenium is found in the byproduct. All of those atoms are in the target material.

We also demonstrated 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".

The flexibility of this approach can be seen in two very simple but very different examples:

1) Tin selenide or tin diselenide can be prepared by simply choosing the correct precursor.

$$\begin{align*}
(Bn_2SnSe)_3 & \rightarrow SnSe + 3 Bn-Bn \\
Bn & = Ph_2CH_2
\end{align*}$$

The 1:1 ratio of Sn to Se is preserved in the product

$$\begin{align*}
Bn_2Sn(SeBn)_2 & \rightarrow SnSe_2 + 2 Bn-Bn \\
\end{align*}$$

The 1:2 ratio of Sn to Se is preserved in the product

2) The synthesis of indium sulfide from a mixture of perbenzylated compounds:

$$2InBn_3 + 3Bn_2S \rightarrow In_2S_3 + 6 Bn-Bn$$

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 (and, in some cases, transition metals) in bulk and in high purity. We expect that this methodology will revolutionize the synthesis of these kinds of compounds.

**Thin Films of Binary Compounds and of Metals**

The perbenzylated materials that we discussed above have surprisingly high vapor pressures making them good candidates for thin film deposition. We found that the easily prepared
perbenzylated tin sulfur compound, \((\text{Ph}_2\text{CH}_2)_3\text{Sn}-\text{SCH}_2\text{Ph}\), produces high quality thin films of tin sulfide at temperatures below 400 °C. All of the tin and sulfur are incorporated in the thin film. The byproduct is bibenzyl, following the same pattern established in the cyclic and linear systems above. It was also found that the very easily prepared compounds, dibenzylindihydride and tetrabenzyltin, produce very high quality thin films of equiaxed tin.

\[(\text{Ph}_2\text{CH}_2)_4\text{Sn} \quad \text{or} \quad (\text{Ph}_2\text{CH}_2)_2\text{SnH}_2 \quad \rightarrow \quad \text{Sn (equiaxed thin film)} + \quad \text{Ph}_2\text{CH}_2\text{-CH}_2\text{Ph}\]

**Metal Bis(benzylthiolates). Metal Sulfides at Low Temperatures**

Efforts in our research laboratories have demonstrated that metal sulfides in which the metal may or may not be a main group element can be easily prepared by low temperature (~150 °C) pyrolysis of the appropriate metal bis(benzylthiolates). A series of metal sulfides in >95% yields have been prepared by the equation below:

\[\text{C}_6\text{H}_5\text{CH}_2\text{-S-M-S-CH}_2\text{C}_6\text{H}_5 \quad \rightarrow \quad \text{MS} + \quad \text{C}_6\text{H}_5\text{CH}_2\text{-S-CH}_2\text{C}_6\text{H}_5\]
\[\text{M} = \text{Zn}, \text{Cd}, \text{Ni}, \text{Pb}\]

The approach also works for selenides. The opportunity is now at hand to make mixed metal sulfides and selenides as well as quarternary materials conveniently. Our plan is to investigate this possibility to prepare systems such as \(\text{Cd}_n\text{Zn}_{1-n}\text{Te}\) which are used in the fabrication of medium and longwavelength IR sensors and beta and gamma ray nuclear detectors.

**III. List of Publications**
(overlaps with support from AFOSR 91-0197)


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

**Senior Personnel**
Philip Boudjouk, Principal Investigator

**Postdoctoral Associates**
Jang-Hwan Hong
Youlin Pan

**Graduate Assistants**
Dean Seidler
Duane Simonson
Gregory Schmitz
David Garlie

**Undergraduate Assistants**
Chris Meyer, Bill Korinek

**V. Interactions 92-95**
(overlaps with AFOSR 91-0197)

**A. Presentations at meetings, conferences and seminars**

1. **Papers (presenter underlined)**


"THE PYROLYSIS OF BENZYL-SUBSTITUTED TIN CHALCOGENIDES. SINGLE SOURCE PRECURSORS FOR TIN SELENIDE AND SN (SₓSE₁₋ₓ) SOLID SOLUTIONS" Dean Seidler, Philip Boudjouk, Gregory J. McCarthy and Dean Grier, The 28th Great Lakes Regional Meeting of the American Chemical Society, La Crosse WI, June 5 - 8, 1995.


2. **Posters (presenter underlined)**

*Inor 92.* HYDROMETALLATED POLYMERS AS PRECURSORS TO (M₁₃¹₅)ₓ(SiC)ᵧ.
Timothy A. Splinter and Philip Boudjouk, Division of Inorganic Chemistry, 206th ACS National Meeting 8/22/93 - 8/27/93

*Inor 93.* GROUP 13/15 COMPOUNDS WITH PHENYL SUBSTITUENTS.
Youlin Pan and Philip Boudjouk, Division of Inorganic Chemistry, 206th ACS National Meeting 8/22/93 - 8/27/93
**Inor 94.** EFFECTS OF PULSING SONIFICATION ON THE SYNTHESIS OF POLYSILANES. Kimihiro Matsukawa and Philip Boudjouk, Division of Inorganic Chemistry, 206th ACS National Meeting 8/22/93 - 8/27/93

**Inor 95.** SYNTHESIS AND CHARACTERIZATION OF 2,3,4,5-TETRAETHYL-1-GERMACYCLOPENTADIENIDE GERMOLE DIANIONS. Jang-Hwan Hong and Philip Boudjouk, Division of Inorganic Chemistry, 206th ACS National Meeting 8/22/93 - 8/27/93

**Inor 96.** RING OPENING REACTIONS OF BULKY SILIRANES. SYNTHESIS OF HIGHLY HINDERED SILYL ETHERS AND SILYL AMINES. Ioana Stoenescu, Rajkumar Kumarathasan and Philip Boudjouk, Division of Inorganic Chemistry, 206th ACS National Meeting 8/22/93 - 8/27/93

**Inor 166.** A MECHANISTIC INVESTIGATION OF THE SYNTHESIS OF GROUP 14-16 SEMICONDUCTOR MATERIALS FROM ORGANOMETALLIC PRECURSORS. Dean J. Seidler and Philip Boudjouk, Division of Inorganic Chemistry, 206th ACS National Meeting 8/22/93 - 8/27/93

**Inor 382.** MECHANISTIC AND REACTIVITY STUDY OF THE COPPER-TMEDA HYDROSILYLATION CATALYST. Steven D. Kloos and Philip Boudjouk, Division of Inorganic Chemistry, 206th ACS National Meeting 8/22/93 - 8/27/93

**Inor 383.** HYDROSILYLATION OF ALKynes CATALYZED BY PLATINUM ON CARBON. Brian J. Hauck, Byung-Hee Han and Philip Boudjouk, Division of Inorganic Chemistry, 206th ACS National Meeting 8/22/93 - 8/27/93

**P-18:** "SYNTHESIS AND CHARACTERIZATION OF SILYL-SUBSTITUTED SILOLE ANIONS (INCLUDING A SILICON ANALOG TO THE FULVALENE DIANION)" J.-H. Hong and P. Boudjouk, XXVII National Organosilicon Symposium (Troy, NY) March 18, 19 1994

**P-23:** "EFFECTS OF PULSING SONICATION ON POLYSILANE SYNTHESIS", D. Garle, K. Matsukawa and P. Boudjouk, XXVII National Organosilicon Symposium (Troy, NY) March 18, 19 1994

SYNTHESIS AND CHARACTERIZATION OF TRIS (GERMOLE) DIANION, THE FIRST SANDWICH COMPLEX OF [(2,3,4,5-TETRAETHYLGERMOLE)3]2[2Li+], Jang-Hwan Hong, Seok-Bong Choi, and P. Boudjouk, The 28th Great Lakes Regional Meeting of the American Chemical Society, La Crosse WI, June 5 - 8, 1995

THE REACTION OF HYDRILOSILOLES WITH SODIUM BIS (TRIMETHYLSILYL) AMIDE, Youlin Pan, Jang-Hwan Hong, Philip Boudjouk, The 28th Great Lakes Regional Meeting of the American Chemical Society, La Crosse WI, June 5 - 8, 1995.


Abstract No: INOR 514 "UNUSUAL REACTION OF 1,4-DILITHIO-1,2,3,4-TETRAPHENYL-1,3-BUTADIENES WITH SOME MONO AND DISILANES" Y. Pan and P. Boudjouk, 210th National ACS mtg in Chicago, August 20-24, 1995.
"SIMPLE AND EFFICIENT ROUTES TO SEMICONDUCTOR MATERIALS FROM ORGANOMETALLIC REAGENTS", Chungnam National University, October 21, 1993.

"NEW CATALYTIC PROCESSES FOR THE SYNTHESIS OF ORGANOSILANES", Korean Advanced Institute for Science and Technology, October 26, 1993. (Daejon)

"SIMPLE AND EFFICIENT ROUTES TO SEMICONDUCTOR MATERIALS FROM ORGANOMETALLIC REAGENTS", Konju National University, October 27, 1993.

"NEW CATALYTIC PROCESSES FOR THE SYNTHESIS OF ORGANOSILANES", Korean Institute of Science and Technology, October 29, 1993. (Seoul)

"ULTRASONIC ACCELERATION OF HETEROGENEOUS REACTIONS", Instituto Mexicano del Petroleo, Mexico City, Mexico, October 20, 1994

"FUNDAMENTALS OF SONOCHEMISTRY", Instituto Mexicano del Petroleo, Mexico City, Mexico, October 20, 1994

"NEW STABLE AROMATIC COMPOUNDS OF SILICON", Kyonggi University, Suwon, Korea, November 15, 1994.


"OXIDATIVE CLEAVAGE OF UNSATURATED FATTY ACIDS” Union Camp Corporation, Princeton, NJ. January, 1995

4. Invited Lectures

"HYPOVALENT REACTIVE INTERMEDIATES CONTAINING SILICON", Philip Boudjouk; National Meeting of the Korean Chemical Society held at Wonkwang University - October 22-23, 1993

"SOME NEW CHEMISTRY OF SILOLE ANIONS AND DIANIONS" Philip Boudjouk; International Symposium, "The Frontiers of Organosilicon Chemistry" held in Sendai, Japan November 1-4, 1994

"SYNTHESIS OF HIGHLY HINDERED SILYLENES. CONVENIENT REAGENTS FOR STRAINED SILACYCLES", MINI SYMPOSIUM "NEW GERATIONS IN ORGANOSILICON CHEMISTRY", hosted by the Korean Institute of Science and Technology, in Seoul, Korea, November 9 and 10, 1994.

"AROMATIC SILICON. SYNTHESIS AND CHARACTERIZATION OF SILACYCLOPENTADIENIDE ANIONS AND DIANIONS." Philip Boudjouk and Jang-Hwan Hong. The 28th Great Lakes Regional Meeting of the American Chemical Society, La Crosse WI, June 5 - 8, 1995

5. Invited Plenary Lectures

B. Consultative and Advisory Functions

Dow Corning Corporation-Catalytic Processes in Silicon Chemistry
Union Camp Corporation-Heterogeneous Catalysts for the Oxidation of Unsaturated Fatty Acids
Instituto Mexicano del Petroleo-Ultrasonic Activation of Catalysts for Petroleum Feedstocks

C. New discoveries, inventions or patent disclosures

The process whereby benzyl groups are used as leaving groups in the synthesis of binary and ternary compounds with semiconducting and optoelectronic properties is under review as a potential patentable process.

D. Additional information

None