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NEW APPROACHES TO THE SYNTHESIS OF NOVEL ORGANOSILANES  
(U) NORTH DAKOTA STATE UNIV FARGO DEPT OF CHEMISTRY  
P BOUDJOUK OCT 83 AFOSR-TR-84-0439 AFOSR-80-0239

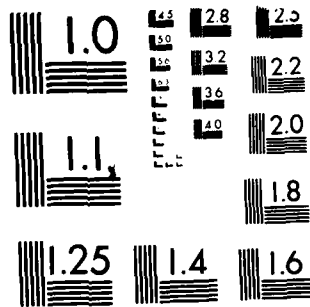
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"New Approaches to the Synthesis of Novel Organosilanes"

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Three major efforts in organosilicon chemistry were initiated during the tenure of this grant: 1) synthetic organosilicon electro-chemistry; 2) synthetic applications of Lewis Acid catalyzed redistribution reaction; and, 3) synthetic applications of ultrasonic waves. All three projects were successful to varying degrees. In electrochemistry, the first electrochemical characterizations of functionalized organosilanes was carried out and will be submitted for publication during 1984. Additionally, the first syntheses of a variety of disilanes from chlorosilanes under controlled potential conditions was effected. The redistribution reaction was successfully applied to prepare cyclic and caged silanes. A wide variety of cyclics were synthesized in good yield. Ultrasonic irradiation of heterogeneous reactions was found to greatly accelerate reaction rates giving a narrow distribution of products in high yields. Improved yields under milder conditions for many reactions were observed. Projected for the future are intense efforts to find catalysts or new electrodes that will drop the required voltage for reducing organofunctional silanes and to broaden our work in sonochemistry. New efforts in sonochemistry will include widening the scope of reactions investigated and making inroads into the mechanism of the phenomenon responsible for the rate accelerations.

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TABLE OF CONTENTS

OBJECTIVES AND ACCOMPLISHMENTS.....1

ELECTROORGANOSILICON CHEMISTRY.....1  
 Characterization.....1  
 Electrosynthesis.....2

LEWIS ACID CATALYZED REDISTRIBUTION REACTIONS.....4

SONOCHEMISTRY.....5

SUMMARY.....9

REFERENCES.....10

PAPERS PUBLISHED WITH SUPPORT OF AFOSR 80-0239.....11

PERSONNEL SUPPORTED BY AFOSR 80-0239.....12



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## OBJECTIVES AND ACCOMPLISHMENTS

The original objectives of this program were

- a) to investigate the applicability of electrosynthetic methods to the synthesis of novel organosilanes and reactive intermediates containing silicon and
- b) to develop further the use of Lewis Acids to synthesize a wide variety of simple and complex organosilanes.

During the course of these efforts a third area of research, the acceleration of chemical reactions using ultrasonic waves, was undertaken.

## ELECTROORGANOSILICON CHEMISTRY

### Characterization

A program was initiated to investigate preparative electrochemical methods as a useful new route to the synthesis of interesting disilanes. This technique, widely used in synthetic organic chemistry[1], had not been applied to silanes. Our immediate project goal was to develop this technique as a complement to the present methods of Si-Si bond formation which are very limited. Preparative electrochemistry could be a powerful tool for the synthetic organosilicon chemist because with it one can execute reactions under mild conditions that usually require high temperatures and/or static conditions that overexpose delicate molecules to vigorous reagents.

The possibility of flow electrolysis at controlled electrical potential is particularly exciting because sensitive molecules can be generated at the electrode surface and removed before further electrolysis occurs. This opens the way to preparing compounds that are more reactive towards electrolysis than the starting silanes.

The first phase of our research plan called for the electrochemical characterization of a wide variety of functionalized silanes. We set out to determine the reduction potentials of organosilicon compounds that encompassed a broad spectrum of "electrochemically inert" groups such as alkyl, aryl, vinyl and hydro moieties as well as a full range of functional groupings like chloro, bromo, iodo, alkoxy, aryloxy, siloxy, acetate, and tosylate. Our plan also included the study of difunctional silanes as well.

The chemistry of functionalized silanes is marked by the ease with which nucleophilic substitution occurs, even with mild nucleophiles such as water. Additionally, reactive silicon species generated during the course of chemical reactions have a remarkably high affinity for oxygen, not only free oxygen but oxygen already bonded to other atoms in stable molecules.

The inherent reactivity of functionalized organosilanes make them difficult subjects of study by electrochemical techniques. However, using rigorously controlled conditions that kept our apparatus free of oxygen and moisture, we were able to obtain fundamental data on a broad spectrum of silicon compounds using cyclic voltammetry, differential pulse polarography and coulometry. This data is tabulated in the Appendix under Electrochemical Data on Functionalized Silanes.

We can summarize our findings here:

1-all reductions were at very high potentials and were irreversible;

2-the reduction waves for all trialkylsilylfunctionals coincide with the onset of the reduction wave for the solvent;

3-aryl substitution on silicon has the effect of lowering the reduction potential of the functionalized silane sufficiently that it can be distinguished from the reduction of solvent;

4-only the tosylate functional group appears to affect the reduction potential in a significant way; and

5-difunctional silanes are not greatly different, electrochemically, from monofunctional silanes.

Of these results, 4 and 5 were the most surprising to us in view of the chemical reactivity of those classes of compounds. These observations support the view that the reduction potential is not related to the ease of removal of a functional group during a chemical reaction, or its polarity, but is, instead, directly related to its bond energy

### Electrosynthesis

Electrochemical coupling of C-X (X=halogen) groups to form C-C bonds is a well established and synthetically useful practice that has been applied to the preparation of stable compounds and reactive intermediates not readily accessible by conventional methods[2].



Experimentally, preparative electrochemical reactions are often easier to run and work-up than the traditional funnel and flask syntheses. In our laboratory we have purchased, built (and borrowed) the necessary pieces to construct several types of preparative electrochemical units. We have, in operation, several classical "batch" cells of the "H" configuration as well as the simple multiple probe cavity type.

In addition, we have two flow units: 1) a capillary cell system that permits the electrolyte solution to pass over the surface of the electrode as a thin film and 2) a "flow through" electrode composed of RVC (reticulated vitreous carbon), a highly conductive sponge of carbonized material. Both of these flow systems maximize conduction and maintain high current efficiency.

Our preliminary efforts in this area have been very successful in that we have been able to show that electroreduction of chlorosilanes leads to high yields of disilanes with high current efficiencies. Some of our results are summarized in the table below:

#### REDUCTIVE COUPLING OF SOME CHLOROSILANES

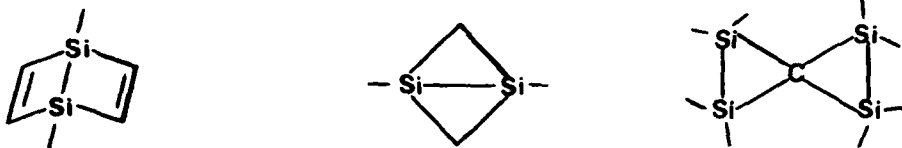
<u>Organosilane</u>	<u>Product</u>	<u>% yield*</u>	<u>% current efficiency†</u>
Me <sub>2</sub> HSiCl	Me <sub>2</sub> HSiSiHMe <sub>2</sub>	88	82
Me <sub>3</sub> SiCl	Me <sub>3</sub> SiSiMe <sub>3</sub>	76	60
Et <sub>3</sub> SiCl	Et <sub>3</sub> SiSiEt <sub>3</sub>	77	67
CH <sub>2</sub> =CHMe <sub>2</sub> SiCl	(CH <sub>2</sub> =CHMe <sub>2</sub> Si) <sub>2</sub>	83	73
PhMe <sub>2</sub> SiCl	PhMe <sub>2</sub> SiSiMe <sub>2</sub> Ph	90	79
Ph <sub>2</sub> HSiCl	Ph <sub>2</sub> HSiSiHPh <sub>2</sub>	90	70
Mes <sub>2</sub> SiCl <sub>2</sub>	Mes <sub>2</sub> Si=SiMes <sub>2</sub> **	20	<20

\* yields based on GLC peak integration of all products formed and unreacted starting material

† current efficiencies calculated as:  $\frac{\text{\#coulombs calculated}}{\text{\#coulombs actual}} \times \% \text{ yield of dimer}$

\*\* isolated as the MeOH adduct Mes<sub>2</sub>SiH-SiMes<sub>2</sub>OMe

With prototype compounds like those listed in the Table successfully coupled, we hope to go on to more novel systems containing Si-Si bonds:

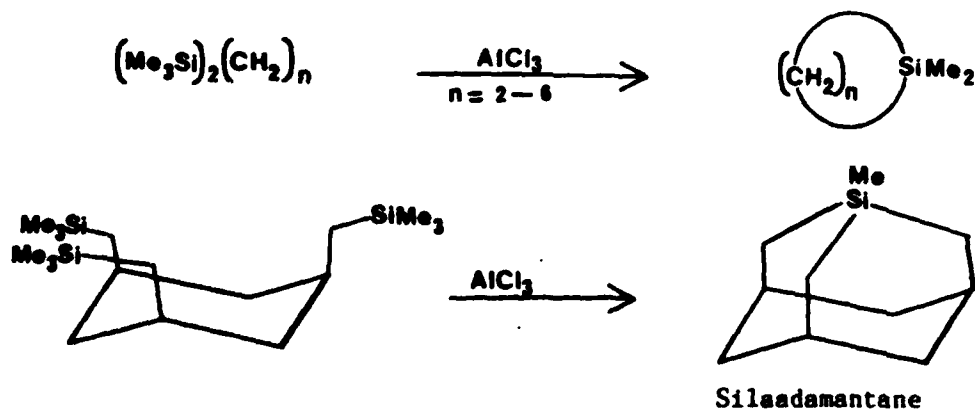


This technique is not without its difficulties, however, some of which were mentioned earlier, and a major challenge to this research program will be to circumvent the problems of the very high reduction potentials and the voracious reactivity of the electrogenerated reactive intermediates.

#### LEWIS ACID CATALYZED REDISTRIBUTION REACTIONS OF ORGANOSILANES

Although redistribution reactions of organosilanes are well-known and have been investigated in detail [3] nearly all of the systems studied have been simple aliphatic silanes and much of the work was in the gas phase. Our goal was to extend the utility of this reaction in the condensed phases by investigating the possibility of using the reaction type to prepare complex organosilanes by design.

This project enjoyed success right from the start. We found that organosilanes reacted with strong Lewis acids under mild conditions and, if the conditions were carefully controlled, useful synthetic schemes could be realized. We studied cyclization reactions in particular and discovered that aluminum chloride was particularly effective in promoting silicon-carbon bond cleavage and reformation to give cyclic and cage compounds readily and in good yields:



## SONOCHEMISTRY

During the course of the work on our original objectives in electrochemistry and redistribution reactions we needed better ways to make some of feedstock and standard materials. There was some literature precedent for ultrasonic acceleration of chemical reactions although the history was sparse and somewhat confusing. We elected to study the effects of ultrasonic waves on the reactions of organosilicon chlorides with lithium to give disilanes, compounds that we required in our laboratory as standards for spectroscopic and chromatographic techniques.

The effects of ultrasound on these, as well as other reactions, exceeded our expectations. In summary, we have found that ultrasonic irradiation using a simple laboratory cleaner, accelerates a wide variety of reactions. While we are still in the early stages of our investigations we do see some trends:

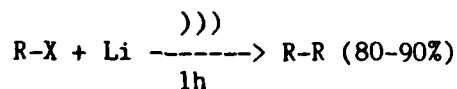
1-heterogeneous reactions are more greatly accelerated by ultrasonic waves than homogeneous reactions,

2-reactions involving the softer, more electropositive metals appear to respond better to ultrasonic irradiation than metals of the transition series, for example, and

3-reactions involving metals appear to be more responsive than those involving nonmetals.

Listed below are the reactions we examined during the tenure of this grant period and found to be accelerated by ultrasonic waves:

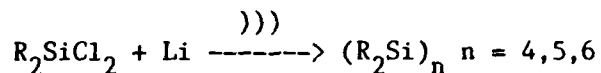
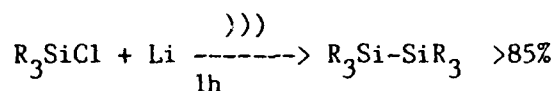
1)The Wurtz Reaction: reductive coupling of halocarbons by lithium is accelerated to give symmetrical hydrocarbons in high yield and excellent purity.[4]



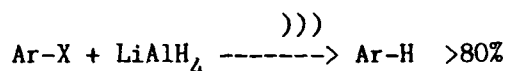
R=alkyl, aryl, benzoyl; X = Cl, Br; lithium dispersion

2)Reductive Coupling of Chlorosilanes: essentially the Wurtz reaction applied to silicon. We found this very useful for preparing small and large quantities of linear and cyclic di-, tri-, and

polysilanes.[5]

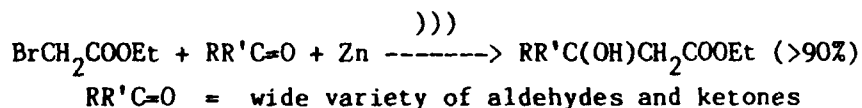


3)Lithium Aluminum Hydride Reduction of Aromatic Halocarbons: this is normally an inefficient process requiring high temperatures to give moderate to low yields. Ultrasonic waves permit the reaction to go in high yields in a few hours at room temperature.[6]

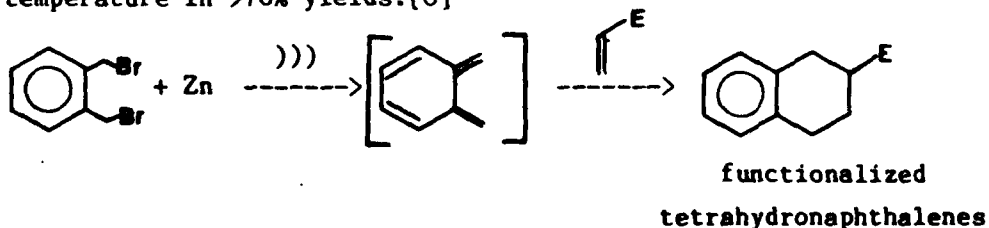


This reaction is now under study by the National Center for Disease Control in Atlanta, Georgia as a potential method for reducing the toxicity of polyhalogenated aromatics such as PCB's and PBB's.

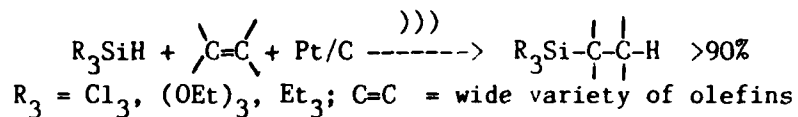
3)The Reformatsky Reaction: this is the most general method for the synthesis of beta hydroxyesters, valuable intermediates in organic synthesis with particularly important applications in the drug industry. This reaction can now be executed in a manner of a few minutes at room temperature to give nearly quantitative yields of the desired ester. Typically, several hours at >70 deg. are required.[7]



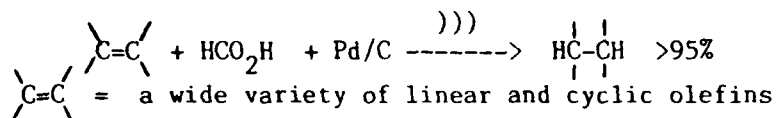
4)The Generation of o-Xylylene: this reactive intermediate, normally only available via a low yield pyrolysis reaction at >200 degrees, is very useful in cycloaddition reactions to produce functionalized tetrahydronaphthalenes, key intermediates in the synthesis of antibiotics. We can now generate o-xylylene at room temperature in >70% yields.[8]



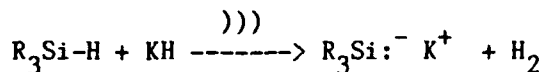
5) The Hydrosilation Reaction: this reaction is one of the most useful methods for making silicon to carbon bonds and has broad based applications in research and industrial labs. The increase in reaction rate and yield with ultrasonic waves permits the use of a recoverable catalyst such as platinum on carbon.[9]



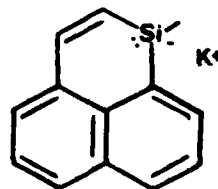
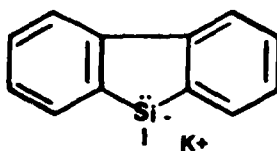
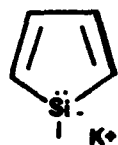
6) Hydrogenation of Olefins: This classic reaction is of enormous importance to a broad spectrum of chemists and the discovery that ultrasound greatly facilitates the saturation of double and triple bonds at room temperature using a convenient, inexpensive and readily available source of hydrogen like formic acid in the presence of palladium on carbon catalyst should be very helpful to the practicing chemist.[9]



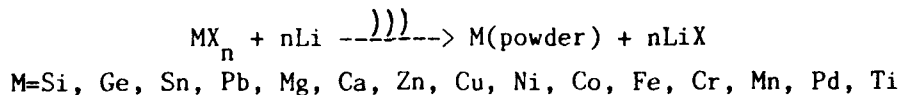
7) Preparation of Silyl Anions: While carbanions play a very important role in organic chemistry, the silicon counterparts have not yet contributed substantially to organosilicon chemistry. Part of the reason for this has been the difficulty encountered when preparing them. Normally, these are produced in highly toxic media, hexamethylphosphorotriamide, for example. We have been able to generate silyl anions in good yields in a common solvent (tetrahydrofuran) at room temperature when we irradiate the reaction mixture with ultrasonic waves.[10]



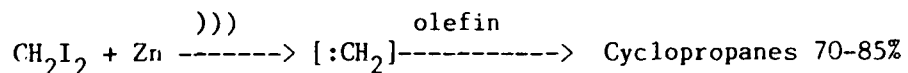
This approach has permitted us to investigate the chemistry of the potentially aromatic silyl anions below:



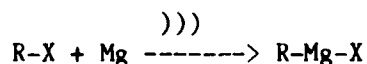
8) Reduction of Metal Halides to Metal Powders: Freshly prepared metal powders are very active reagents and quite useful in organic synthesis. Using ultrasound we have shortened the time and greatly reduced the severity of conditions required to produce these metal powders. Rather than heat metal halides and molten potassium or sodium in boiling solvent for twenty hours we can produce the same powders in less than ten minutes with lithium (a much easier metal to work with) at room temperature. [12]



9) Generation of Carbenes: Carbenes are among the most important reactive intermediates in organic chemistry having significant impact on the synthetic, structural and theoretical branches of the discipline. One of the most useful methods of preparing carbenes is by the techniques developed by Simmons and Smith at DuPont utilizing special zinc catalysts and geminal dihalides. Normally these reactions require heating to about 70 degrees and the yields are quite variable. When the reactions are carried out in the presence of ultrasonic waves consistently good yields are obtained at room temperature. [13]



10) Formation of Grignard Reagents: Ultrasound greatly facilitates this reaction and this particular application of ultrasonic waves is enjoying widespread use. In our laboratories we have examined a number of organic halides that are typically quite reluctant to react with magnesium and form the Grignard and found that, when ultrasound is used, the reaction proceeds smoothly and in high yield. Among the most dramatic examples are the formation of adamantylmagnesium bromide and an assortment of vinylmagnesium halides. [12]



We have investigated a wide variety of reactions using ultrasonic waves and find that the accelerating affect, while not applicable to all reactions, is so general that we are increasing our efforts in the area.

#### SUMMARY

Three major efforts in organosilicon chemistry were initiated during the tenure of this grant: 1) synthetic organosilicon electrochemistry; 2) synthetic applications of the Lewis Acid catalyzed redistribution reaction; and, 3) synthetic applications of ultrasonic waves. All three projects were successful to varying degrees.

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