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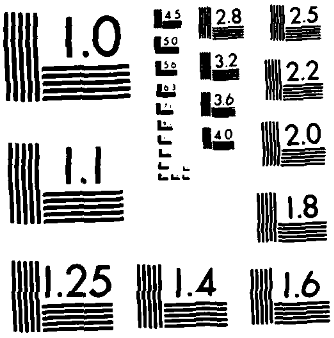

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FINAL REPORT

STRUCTURAL AND SYNTHETIC ORGANOSILICON CHEMISTRY

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AFOSR-81-0185

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The use of organosilicon compounds in synthesis is described. In particular the use of trimethylsilyl iodide, silyloxydienes, and vinyl iodides are highlighted. Several structural organosilicon studies are also described.

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STRUCTURAL AND SYNTHETIC ORGANOSILICON CHEMISTRY

AFOSR-81-0185

Final Scientific Report

July 23, 1984

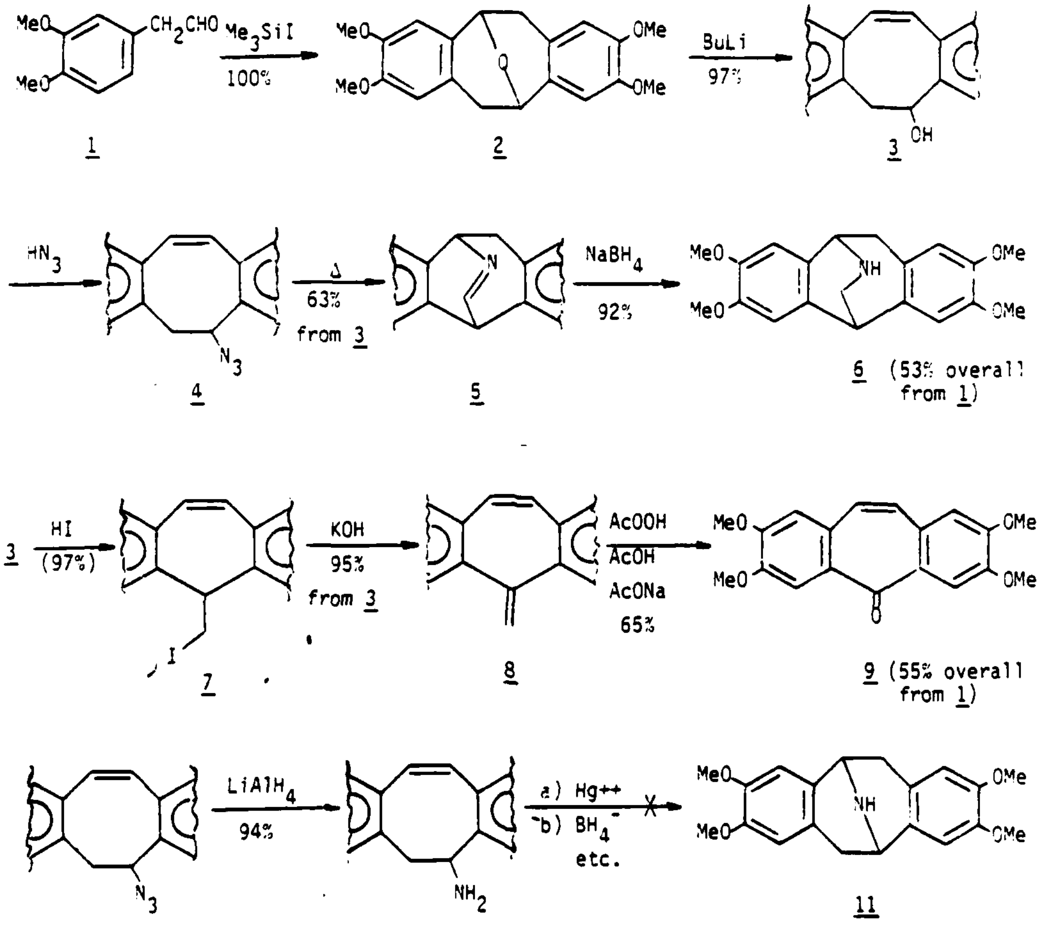
Introduction

This grant was funded for three years rather than the four requested and we have not been able to accomplish some of our originally stated goals. However, many of our major objectives have been achieved as described below. In addition many of the results obtained have permitted us to modify our approach to organosilicon research in the future. Besides the results described here, we have also published extensively prior to this grant on the use of trimethylsilyl iodide,[1] silyloxydienes and silyldienes,[2] and silyl enol ethers[3] in synthesis. The results obtained during this grant are divided into two areas, synthetic and structural.

1) Synthetic Studies

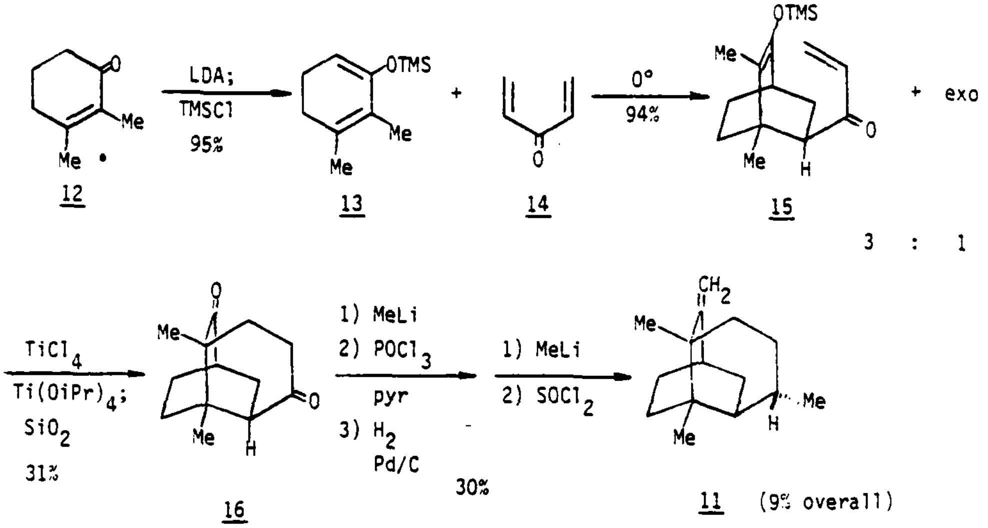
Nearly all of our successes came from the synthetic portion of our proposal. This was due to two reasons: first, our background was more strongly synthetic; and second, it was originally somewhat difficult to get time on the low temperature apparatus.

a) Dibenzocycloheptatriene and -octatriene Synthesis: Our initial work was on the use of trialkylsilyl iodides for aldehyde condensations. We initially investigated the use of the α-iodo silyl ethers formed from the addition of trimethylsilyl iodide to phenylacetaldehyde derivatives in intramolecular Friedel-Crafts alkylations. As proposed, we were able to extend this reaction sequence to homoveratraldehyde 1 in order to prepare the tetramethoxy cyclic ether 2 in quantitative yield. Opening of the ether with butyllithium gave a 97% yield of the alcohol 3, the key intermediate in these syntheses. Our first target was the alkaloid isopavine 6. The alcohol 3 was converted without rearrangement into the azide 4 which was then thermolyzed to produce, via loss of nitrogen and rearrangement, dehydroisopavine 5 in 63% yield from 3. Hydride reduction afforded isopavine 6 in 92% yield, thereby ending a four-step synthesis from 1 in 53% overall yield. Intermediates for the preparation of substituted amitriptyline analogues, e.g., the ketone 9, were also readily available by this scheme. The alcohol 3 was converted in excellent yield into the rearranged iodide 7 which was eliminated to the exocyclic methylene compound 8 in 95% yield from 3. A very novel oxidative cleavage of the methylene group was effected with peracetic acid to give the desired ketone 9 in 65% yield, thus making it available from 1 in four steps in 55% overall yield. However, we were not able to prepare the final target compound in this series; namely, the alkaloid pavine 11. Reduction of the azide 4 produced the amine 10, but all attempts at cyclizing this amine, e.g., aminomercuration or aminopalladation followed by reduction, were unsuccessful. This work has been published[4] as has the earlier work in this area.[1c]

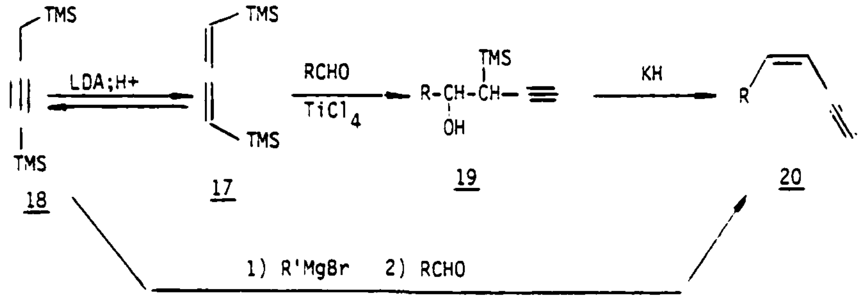


b) <u>Silyloxydienes and the Synthesis of Seychellene</u>: We finished the development of a very efficient two-step procedure for the preparation of substituted tricyclo[5.3.1.0^{3,8}]undecane systems from cyclic silyloxydienes and divinyl ketone. The utility of this synthetic process was shown by the total synthesis of the sesquiterpene seychellene 11. Silylation of the kinetic enolate of dimethylcyclohexenone 12 gave the 2-silyloxycyclohexadiene 13 in 95% yield.

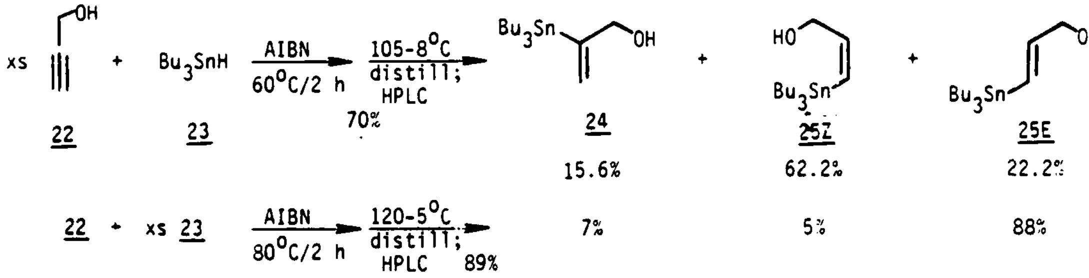
Diels-Alder reaction of 13 with divinyl ketone 14 afforded a 94% yield of a mixture of stereoisomers in which the endo isomer 15 predominated. Cyclization to the tricyclic diketone 16 was effected under carefully controlled conditions using 1:1 $TiCl_4/Ti(OiPr)_4$ to give a 31% yield of 16 (29% from 13). This diketone was then converted into seychellene 11 in five steps in 30% yield, thus ending a seven-step synthesis of 11 from 12 and 14 in 9% overall yield. This work has been published,[5] following our earlier reports in this area.[2ab]



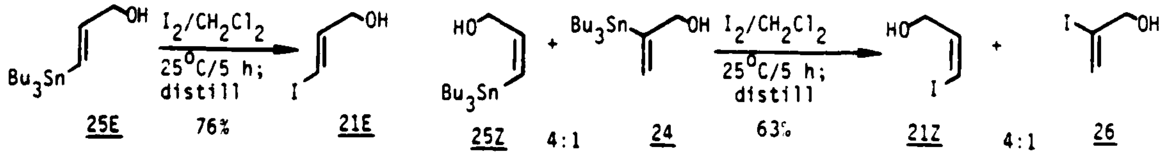
c) Allenic Silanes-Enyne Synthesis: We began investigating the use of 1,3-bis(trimethylsilyl)allene 17 for the conversion of aldehydes into cis- and trans-enynes, a process which would be quite useful for the synthesis of the neurotoxin histrionicotoxin. We were able to prepare the disilylallene 17 from the known 1,3-bis(trimethylsilyl)propyne 18 by formation of the anion (LDA) of 18 at low temperature followed by quenching. A 1:1 mixture of 17:18 was produced which could be chromatographed to give pure 17. This is the first reasonable preparation of 17, which promises to be an interesting compound. We began studying the $TiCl_4$-catalyzed condensation of 17 with various aldehydes and acetals, e.g., benzaldehyde and its dimethyl acetal, to give the silyl alcohols 19, which could then be converted with base to the cis-enynes 20. We had begun to get modest yields of stereochemical mixtures of the enynes in which the cis isomer 20 predominated, when a report[6] appeared based on exactly the same general idea. This publication described the predominant formation of Z-enynes by the condensation of the magnesium salt of the bissilylpropyne 18 with aldehydes in good yields. Since this work accomplished completely what we had intended to do in this area of enyne synthesis, we have terminated our work in this area.



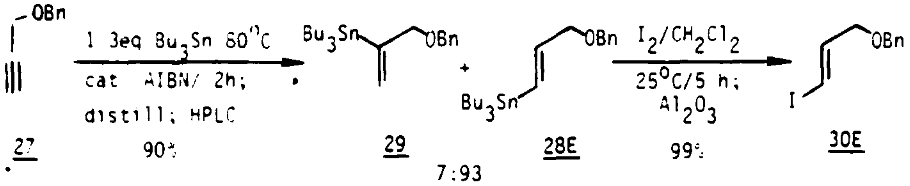
d) Stereoselective Acetylene to Vinyl Iodide Conversion: Vinyl halides are rapidly becoming important synthetic intermediates in organic chemistry since they can be used to generate vinyl anions and vinyl radicals under mild conditions. We decided to prepare these compounds by a new method, namely by hydrosilylation of the alkyne followed by electrophilic desilylative halogenation to give the desired vinyl halide. Although this general process was successful, the yields were somewhat low. We then turned our attention to the analogous process using the tin derivatives. Hydrostannylation of propargyl alcohol 22 with tributylstannane 23 catalyzed by azobisisobutyronitrile (AIBN) can be forced to give either the E- or Z-isomer of 3-tributylstannylprop-2-en-1-ol 25E or 25Z in high yield. When the stannane is used in excess, the E-isomer 25E is the major product (88%), while the Z-isomer 25Z is the predominant product (62%) using excess alcohol (some of the 2-stannyl-2-propenol 24 is also formed in each reaction).



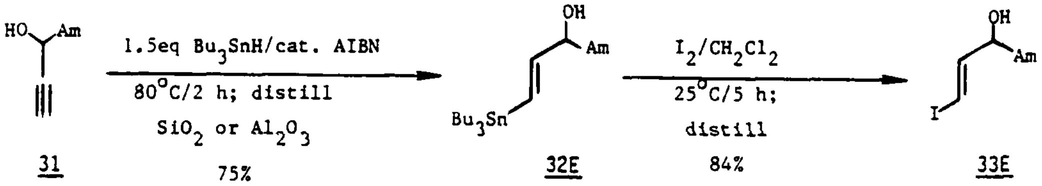
Iodination is easily accomplished in good yield by simple treatment with iodine in dichloromethane to give the iodopropenols, 21EZ. Thus, the two-step process



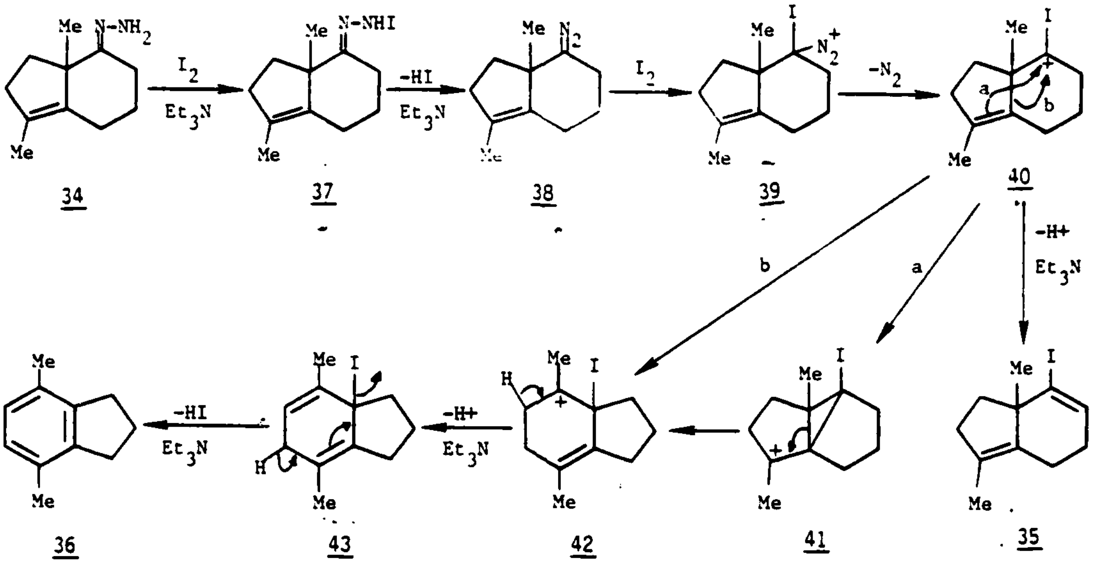
occurs stereoselectively in good overall yield (60% for the E-isomer, 27% for the Z-isomer). This process has been extended to other compounds. For example, propargyl benzyl ether 27 was converted into E-3-iodoallyl benzyl ether 30E in



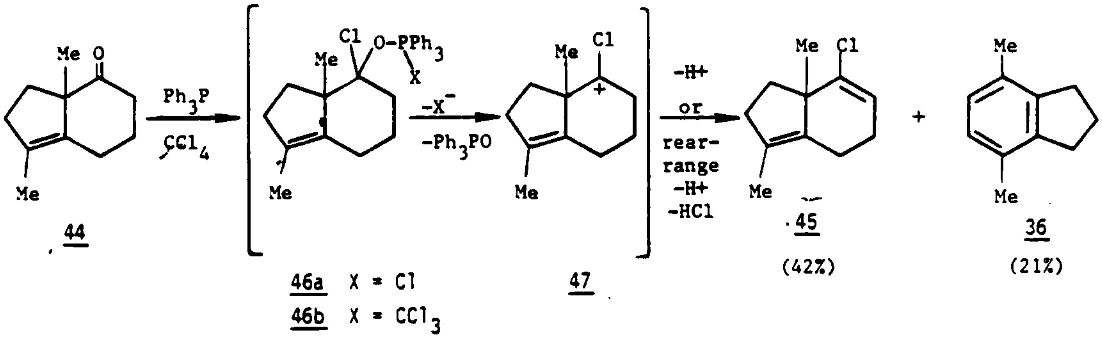
83% overall yield, and the important prostaglandin intermediate E 1-iodo-1-octen-3-ol 33E was prepared from the corresponding alkynol 31 in 63% overall yield. We have also assigned all of the peaks in both the ^1H and ^{13}C NMR of all compounds by high field NMR and europium shift studies. This material has been published.[7]



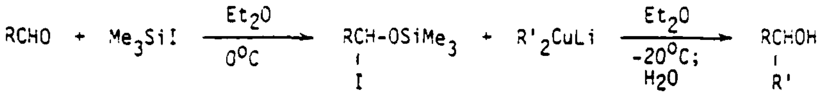
e) Rearrangement in Iodination of Hydrazones in Base: In connection with the above project, we examined another method[8] for the preparation of vinyl iodides, namely the treatment of ketone hydrazones with iodide in base. This reaction works reasonably well in most cases but in applying it to a particular example, namely a β,γ-unsaturated ketone, we observed a very unusual and intriguing rearrangement. Thus treatment of the β,γ-enone hydrazone 34 with two equivalents of iodine in excess triethylamine gave 7% of the desired vinyl iodide 35 and 28% of the hydrocarbon 36, shown by its spectral data to be 4,7-dimethylindane. We have proposed a reasonable mechanism to account for the unusual rearrangement in the formation of 36 which provides further evidence for the intermediacy of an iodocarbonium ion (e.g., 40) in the mechanism.



A similar reaction could be effected by treatment of <u>44</u> with triphenylphosphine and carbon tetrachloride to give the corresponding vinyl chloride <u>45</u> in 42% yield along with the indane <u>36</u> in 21% yield. A similar mechanism involving the analogous chlorocarbonium ion <u>47</u> was proposed. This material has been published.[9]



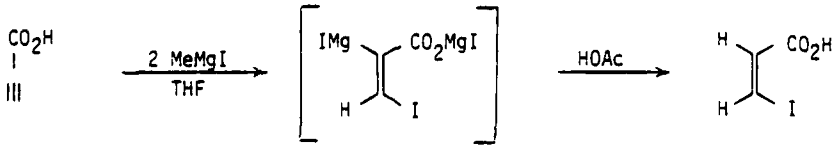
f) <u>Addition of Organocuprates to α-Iodoalkyl Trimethylsilyl Ethers</u>: With this reaction, we have completed nearly all of the work of the original proposal in the area of aldehyde condensations. Addition of trimethylsilyl iodide <u>49</u> to aldehydes <u>48ab</u> occurs essentially instantaneously even in diethyl ether solution to give the corresponding α-iodoalkyl trimethylsilyl ethers <u>50ab</u>.[1c] When these iodoethers are treated with ethereal solutions of lithium dialkylcuprates <u>51ab</u> followed by aqueous workup, the secondary alcohols <u>52a-d</u> are isolated in good yield. This material has been published.[10]



$$\mathrm{RCHO} + \mathrm{Me_3SiI} \xrightarrow[0^{\circ}\mathrm{C}]{\mathrm{Et_2O}} \underset{\mathrm{I}}{\mathrm{RCH}}\text{-}\mathrm{OSiMe_3} + \mathrm{R'_2CuLi} \xrightarrow[-20^{\circ}\mathrm{C};\ \mathrm{H_2O}]{\mathrm{Et_2O}} \underset{\mathrm{R'}}{\mathrm{RCHOH}}$$

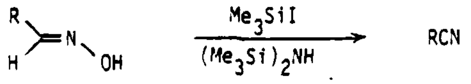
48a R=Et	49	50a R=Et	51a R'=Bu	52a R=Et; R'=Bu
48b R=Hx		50b R=Hx	51b R'=Me	52b R=Et; R'=Me
				52c R=Hx; R'=Bu
				52d R=Hx; R'=Me

g) Z-3-Iodoacrylic Acid Synthesis: In conjunction with the projects described in d and e above, we investigated a very novel method for the preparation of Z-3-iodoacrylic acid 54Z, a compound useful for the preparation of the thermodynamically less stable Z-isomers of 3-iodoallylic systems. We found[11] that addition of propiolic acid 53 to a THF solution of methylmagnesium iodide (prepared in the usual way) followed by workup with glacial acetic acid produces the crystalline acid 54Z in 80% yield. Mechanistic studies have shown that an anion is formed at the position α to the acid, presumably by addition of magnesium iodide at the β-position, which is then quenched on workup (i.e., quenching with D_2O gives the Z-α-deuterio-β-iodoacrylic acid). This result is contrary to that reported in the literature[12] for this reaction. This work has been published.[11]



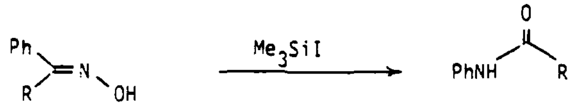
53 80% 54Z

h) Conversion of Aldehydes into Nitriles: As proposed, we investigated the dehydration of aldoximes 55 with trimethylsilyl iodide and hexamethyldisilazane to give the nitriles 56. The reaction works in good yield and is simple to perform. The material has been published.[13]



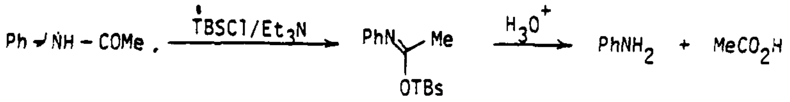
55a	R = $PhCH_2$	84%	36a
55b	n-C_8H_{17}	88%	36b
55c	$3,4(OMe)_2C_6H_3CH_2$	86%	36c

i) Beckmann Rearrangement of Aryl Ketoximes: As an extension of the above reaction, we investigated the reaction of ketoximes with trimethylsilyl iodide. Ketoximes of aryl ketones rearrange smoothly to give the corresponding amides. For example, benzophenone oxime 57a and acetophenone oxime 57b give high yields of benzanilide and acetanilide, 58ab, respectively. Curiously, the reaction does not occur with aliphatic ketoximes, such as acetoxime and cyclohexanone oxime. This material has been published.[13]



57a R = Ph 75% 58a R = Ph
57b R = Me 55% 58b R = Me

j) Cleavage of N-CO Bond of Amides: We obtained some encouraging preliminary results in this area. Formation of the t-butyldimethylsilyl imino ether from acetanilide followed by mild acidic hydrolysis produced aniline in 40% yield. Control studies have shown that the hydrolysis conditions do not cleave acetanilide itself to any extent and thus the silyl imino ether has activated the amide bond for hydrolysis. Clearly much more work must be done on this reaction before it is useful. We hope to investigate soon three hindered silyl iodides--t-butyldimethylsilyl iodide, triethylsilyl iodide, and (2,4,6-tri-t-butylphenoxy)-dimethylsilyl iodide--in this process.[14]

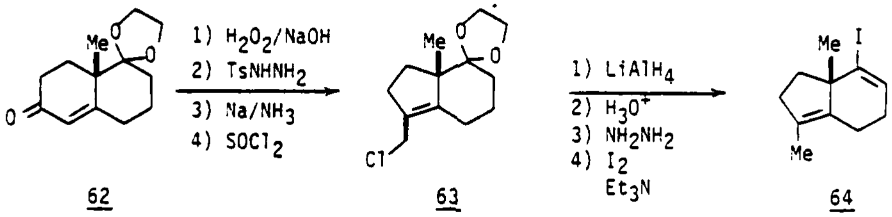


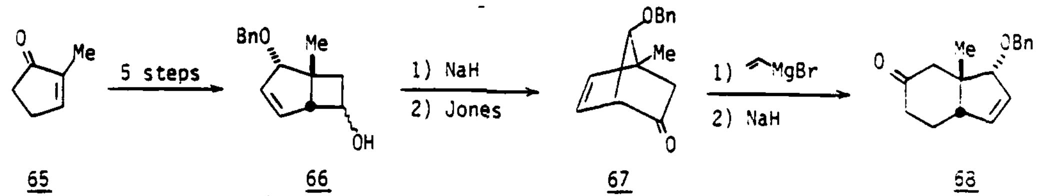
k) Iodomethyl Benzyl Ether: We were partially successful in achieving our goal in this area. Reaction of the benzyl acetal of formaldehyde 59 with trimethylsilyl iodide produced benzyl trimethylsilyl ether 60 and the desired iodomethyl benzyl ether 61. However, we were not able to completely purify the iodo ether away from the silyl ether.[15] We hope to do so in the near future.

$$(PhCH_2O)_2CH_2 \xrightarrow{Me_3SiI} Me_3SiOCH_2Ph + PhCH_2OCH_2I$$

59 60 61

1) Steroid Synthesis: Finally, two other synthetic projects were partially funded from this grant. They involved the preparation of the optically active vinyl iodide 64 from the chiral enone ketal 62 in eight steps. This was an extension of our earlier work on the preparation of vinyl iodides (d and e above) and permits the steroid intermediate 64 to be easily prepared in optically active form.[16] The other intermediate for steroid synthesis is the enone benzyl ether 67 prepared from 65 in seven steps via 66 in good yield. Enone 67 can be converted into the bicyclic steroid analogue 68 in two easy steps using an anionic oxy-Cope rearrangement as the key step.[17]

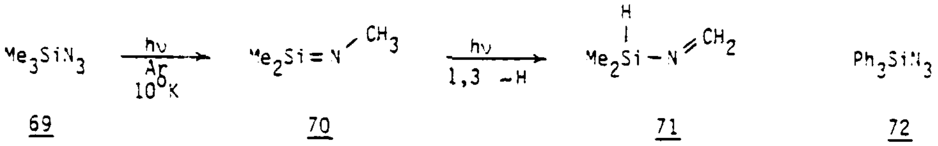




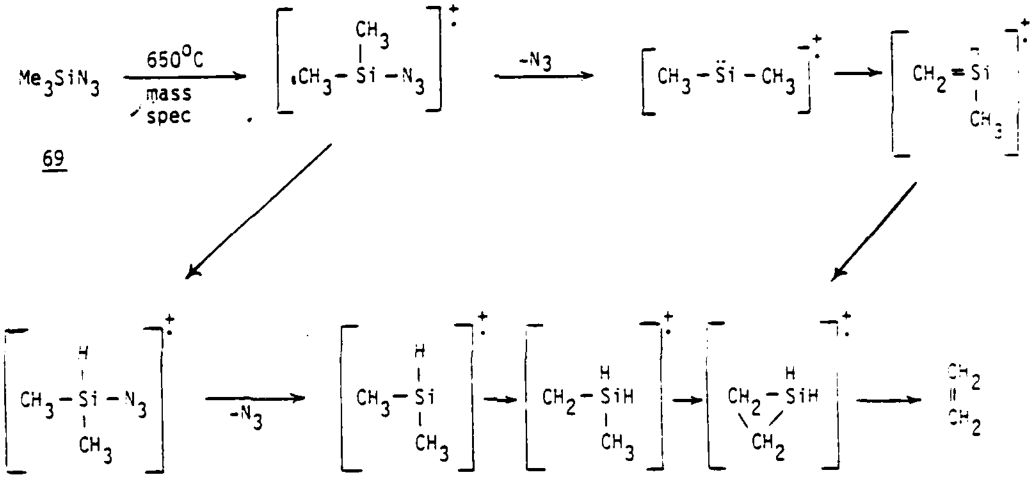
2) Structural Studies

The results here have come more slowly than in the synthetic area due to our decision to study the synthetic projects initially. However, our investigations in this area have begun to bear fruit.

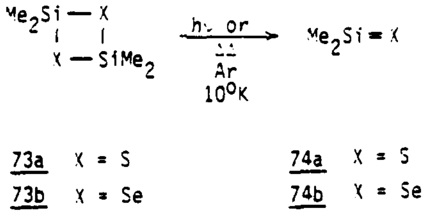
a) sp^2 Hybridization: We examined (with the help of Orville Chapman and his low temperature equipment) the generation of several systems with silicon in sp^2 hybridization. For example, trimethylsilyl azide 69 has been photolyzed in an argon matrix to give the silyl imine 71 as reported by Perutz.[18a] We assume that the reaction proceeds by initial formation of the silaimine 70 (from the nitrene) which is then photolyzed further to give 71 by a 1,3 hydride shift. Since this step is photochemically but not thermally allowed (at 10°K), we have tried to adjust the wavelength of irradiation to allow 70 to be isolated. Also we have prepared triphenylsilyl azide 72 in order to try to produce the silaimine from it by photolysis.[18bc]



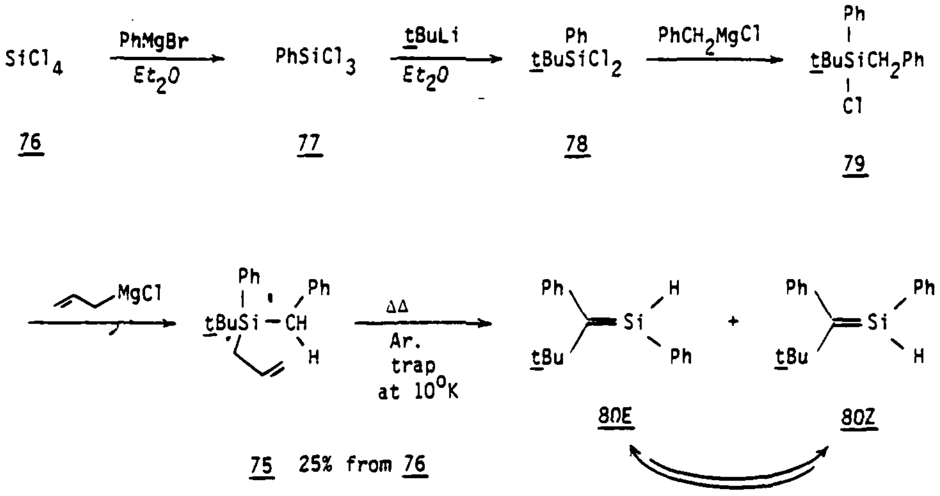
Some extremely intriguing results have been obtained from the thermal decomposition of the azide 69 at high temperatures just before the inlet port of a high resolution mass spectrometer. At a temperature of 30°C, the major high molecular weight fragment corresponds to loss of methyl rather than loss of azide ($M-CH_3$ is base, $M-N_3$ is 19%). More interesting is the fact that at a pyrolysis temperature of 650°C, the major fragmentation product is ethylene (100%, shown not to be N_2 by high resolution mass spec). The production of ethylene could occur by one of several pathways, all of which are quite unusual in organosilicon chemistry. Examples are given below, for which there is some evidence in the mass spectral fragmentation pattern. We hope to investigate in the future the flash thermolysis of 69 followed by deposition on a CsI window at 20°K in order to see if the mass spectral results can be duplicated in a bulk sample.



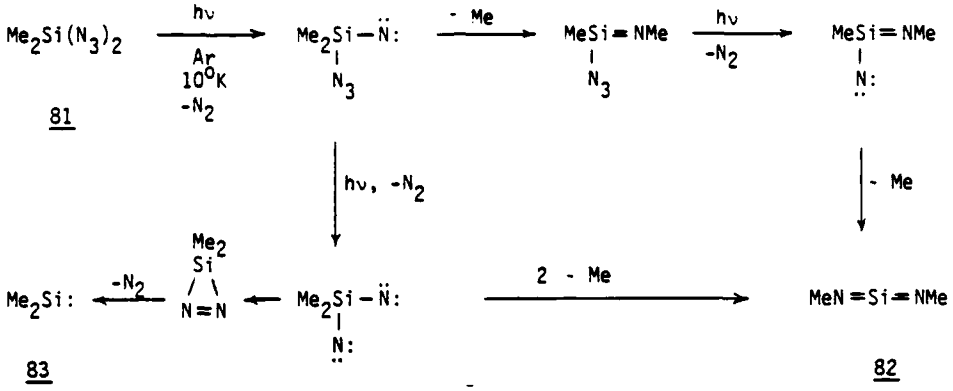
We have studied the low-temperature photochemistry of the tetramethylcyclodisilathiane 73a and the selenium analogue 73b in hopes of obtaining the silathione and silaselenone 74ab. Although the original experiments were not encouraging, we are planning to look at them in more detail at some future date.



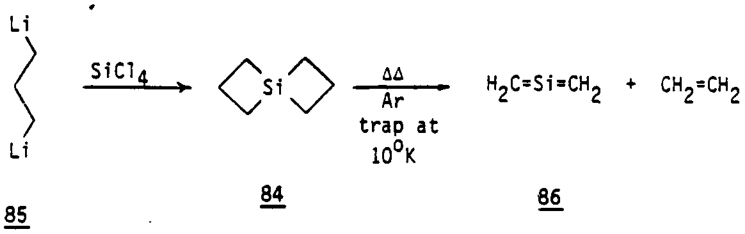
b) Carbon-Silicon π-Bond Energy: We prepared the key tetrasubstituted silane 75, required for the measurement of the carbon-silicon π-bond energy. Beginning with silicon tetrachloride 76, we prepared the benzyl-t-butylphenylsilyl chloride 79 via the trichloro and dichloro intermediates 77 and 78. Coupling of 79 with allyl Grignard reagent gave a very high yield of the desired compound 75. We hope to thermolyze 75 soon and trap the products in an argon matrix to produce the silastilbene isomers 80EZ and study their subsequent equilibration.



c) sp Hybridization: We studied the behavior of two derivatives which may yield, at low temperature, the first isolable compounds with silicon in sp hybridization. The diazidosilane 81 was prepared from the readily available dichlorodimethylsilane. We attempted its photochemical decomposition to give the sila analogue of a carbodiimide 82. The photolysis was not clean and several intermediates were produced. We hope to clean up this photolysis in order to prove the intermediacy of the siladiimide 82 (conjectured to be present at high temperature by Ando[19]) and gather some information about the other intermediates present in this transformation. Also we seem to have produced a large amount of the silylene 83 under certain conditions. This may constitute a new method of generating silylenes (and from them disilenes) which would be greatly superior to other known methods. From the silylenes, e.g., 83, one could prepare large numbers of other multiply-bonded silicon species (e.g., $Me_3Si{=}O$, $Me_2Si{=}S$, $Me_2Si{=}C{=}O$, etc.).



Finally we are attempting to improve the preparation of silaspiro[3,3]hexane 84 by reacting the newly reported[20] 1,3-dilithiopropane 85 with silicon tetrachloride. We then plan to crack two moles of ethylene from 84 to give the silaallene 86 but did not have time to try this reaction.



3) Conclusion

We have accomplished nearly all of the original goals in the synthetic area and some in the structural area. We hope to concentrate on more structural work in the future.

To date, nine papers have been published on work supported by this grant with several more still waiting to be written. With additional funding, all of the goals of our original four-year proposal could have been completed. As it now stands, this additional work must be funded elsewhere.

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