Organogermanium chemistry:
Germacyclobutanes and digermane additions to acetylenes

by

Andrew Michael Chubb

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Program of Study Committee:
Thomas J. Barton, Major Professor
William S. Jenks
Valerie V. Sheares Ashby
Mark S. Gordon
Constance P. Hargrave

Iowa State University

Ames, Iowa

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Graduate College
Iowa State University

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Andrew Michael Chubb
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Major Professor

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ABSTRACT

This dissertation comprises two main research projects. The first project, presented in Chapter 1, involves the synthesis and thermochemistry of germacyclobutanes (germetanes). Four new germetanes (spirodigermetane, diallylgermetane, dichlorogermetane, and germacyclobutane) have been synthesized using a modified di-Grignard synthesis. Diallylgermetane is shown to be a useful starting material for obtaining other germetanes, particularly the parent germetane, germacyclobutane. The gas-phase thermochemistries of spirodigermetane, diallylgermetane and germacyclobutane have been explored *via* pulsed stirred-flow reactor (SFR) studies, showing remarkable differences in decomposition, depending on the substitution at the germanium atom.

The second project investigates the thermochemical, photochemical, and catalytic additions of several digermanes to acetylenes. The first examples of thermo- and photochemical additions of Ge-Ge bonds to $C\equiv C$ are demonstrated. Mechanistic investigations are described and comparisons are made to analogous disilane addition reactions, previously studied in our group.

GENERAL INTRODUCTION

This dissertation is divided into two chapters, each dealing with a separate project in the area of organogermanium chemistry. Each chapter is self-contained, with its own introduction, results and discussion, conclusions, experimental, and references sections. Four appendices are included and contain ancillary data that is important for reference purposes, but was deemed unnecessarily bulky to include in the main body of the dissertation.

The first chapter describes the synthesis and thermochemistry of germacyclobutanes (germetanes). Four new germetanes (spirodigermetane, diallylgermetane, germacyclobutane, and dichlorogermetane) have been synthesized using a modified di-Grignard synthesis. The gas-phase thermal rearrangements of the first three germetanes were investigated *via* pulsed stirred-flow reactor (SFR) studies and possible mechanisms were proposed and explored.

The second chapter involves the thermochemical, photochemical, and catalytic additions of several digermanes to acetylenes. This work is based on analogous disilane addition reactions, previously studied in our group. The first examples of thermo- and photochemical additions of Ge-Ge bonds to $C\equiv C$ are demonstrated and mechanistic investigations are described with comparisons being made to the aforementioned disilane addition reactions.

I. SYNTHESIS AND THERMOCHEMISTRY OF GERMACYCLOBUTANES

A. Introduction

1. Cyclobutane. Since the first report¹ of its synthesis from cyclobutene in 1907, cyclobutane (**1**) has been the subject of considerable interest over the years.²⁻⁹ In particular, the thermochemistry of this deceptively simple molecule has engendered a rather vigorous debate.^{2,3,10-18} As a result, the attempted elucidation of the mechanism of thermal decomposition of cyclobutane has produced some very excellent examples of physical and mechanistic organic chemistry for nearly a century.

The first reported thermolysis of cyclobutane is a 1951 communication by Genaux and Walters (Scheme 1).² The authors monitored the change in pressure in the thermal decomposition of cyclobutane from 430 to 480 °C. In each of the thermolyses, the pressure increase was a first order process and the final pressures were twice the initial pressures, consistent with a fragmentation of cyclobutane into two molecules. Infrared spectroscopy confirmed that the thermolysis of cyclobutane is quite clean, with ethylene being formed almost exclusively.

Scheme 1. Thermolysis of cyclobutane.

Further investigations by the Walters group confirmed the first order nature of the decomposition and Arrhenius treatment of their data yielded an activation energy (E_a) of 62.5 kcal/mol and $\log A$ of 15.6.^{19,20} A free radical chain mechanism was ruled out by the results of several experiments. First, no decrease in reaction rate was observed upon addition of the free radical inhibitors nitric oxide, propene, and toluene. Second, dimethyl ether, which reacts with free radicals, did not undergo decomposition when added to the thermolysis mixture. Third, two reactions whose rates increase in the presence of free radicals,

formaldehyde decomposition and ethylene polymerization, did not have an appreciable difference in rate upon thermolysis in the presence of cyclobutane. Although attempts to trap a 1,4-diradical intermediate (3) with added hydrogen failed, the authors proposed that the decomposition occurred *via* initial homolytic cleavage of a carbon-carbon bond (Scheme 2). Such a mechanism is consistent with the calculated Arrhenius parameters and the failure to trap the proposed intermediate does not rule out its formation, particularly if it is short-lived.

Scheme 2. Decomposition of cyclobutane *via* sequential homolytic cleavages.

Likewise, the thermolysis of ethylcyclobutane (4) also was found to be clean, yielding ethylene and butene in a first order process (Scheme 3).²¹ The Arrhenius parameters reported for ethylcyclobutane decomposition were nearly identical to those obtained for cyclobutane thermolysis: $E_a = 62.0$ kcal/mol and $\log A = 15.6$. Again, as in the case of cyclobutane thermolysis, no inhibition was observed upon addition of propylene, toluene or nitric oxide, ruling out a free radical chain mechanism.

Scheme 3. Thermolysis of ethylcyclobutane.

Experiments by Trotman-Dickenson's group also showed a first order decomposition upon thermolysis of cyclobutane.³ However, Trotman-Dickenson noted several similarities between the thermolyses of cyclobutane and cyclopropane. In particular, the plots of $\log k/k_{\infty}$ vs. $\log P$ for the two decompositions were quite similar in shape and magnitude, with the curve for cyclobutane being shifted to lower pressures. This shifting of the cyclobutane curve relative to that of cyclopropane was not unexpected due to the greater complexity of

the cyclobutane molecule. These similarities led the authors to propose a more concerted-type mechanism similar to that proposed²² for the thermal isomerization of cyclopropane.

Using thermochemical arguments, Trotman-Dickenson's group estimated that cyclobutane has around 26 kcal/mol of ring strain.³ This ring strain, assuming a typical C–C bond energy on the order of 85 kcal/mol, would lead to an E_a for homolytic bond cleavage in cyclobutane around 59 kcal/mol. Although this estimated E_a is close to the experimental value, the authors argued that, as in Slater's cyclopropane mechanism, the sequential homolytic cleavage mechanism does not occur in the thermolysis of cyclobutane. Instead, they proposed a concerted mechanism involving alternate stretching and contracting of opposite C–C bonds (Scheme 4). Since two concerted C–C homolyses would cost 144 kcal/mol in total (85 kcal/mol per C–C bond, less 26 kcal/mol ring strain), a fairly late transition state involving substantial double-bond character was assumed. The larger than expected $\log A$ value then could be explained by the increased entropy due to the formation of nearly free ethylene molecules.

Scheme 4. Concerted mechanism for cyclobutane thermolysis.

Genaux, Kern and Walters argued, however, that the higher $\log A$ was more indicative of a homolytic ring cleavage.²⁰ Using the experimental A factor, they calculated an entropy of activation ($\Delta S^\ddagger$ at 449 °C) of +9 cal/mol·K. Further thermodynamic calculations using experimental and literature data yielded an overall entropy change (ΔS_{rxn}) of +43 cal/mol·K for the reaction. Since ΔS_{rxn} is considerably larger than $\Delta S^\ddagger$, the authors concluded that the structure of the transition state is much more reactantlike than productlike. Realizing that the diradical formed upon homolytic ring cleavage could be an intermediate, rather than a transition state, Walters and coworkers compared the calculated entropy change (ΔS_{rad}) upon diradical formation with the calculated entropy of activation. Calculations gave a value of $\Delta S_{\text{rad}} \geq 15$ cal/mol·K, which is larger than $\Delta S^\ddagger$. The transition state, therefore,

most likely lies somewhere between cyclobutane and the fully-formed diradical (Scheme 5). The authors point out that, although attempts at trapping a diradical intermediate have failed, estimates of the E_a for decomposition of the diradical to two molecules of ethylene are on the order of 15 kcal/mol, well within the experimental conditions for favoring unimolecular decomposition before bimolecular trapping.

Scheme 5. Formation of the tetramethylene diradical from cyclobutane.

Further support for the diradical mechanism appeared to come in 1961 with studies of the thermolysis of *cis*- and *trans*-1,2-dimethylcyclobutane (*cis*-6 and *trans*-6).^{11,23} Two modes of cleavage, symmetrical (route A) and asymmetrical (route B), are possible for both dimethylcyclobutanes (Scheme 6). In fact, products corresponding to both cleavages were detected upon thermolysis of either the *cis* or *trans* stereoisomer, though symmetrical cleavage was favored in both cases (83% for *cis* and 78% for *trans*). These results are not surprising, considering that steric repulsion between the methyl groups would result in preferential cleavage of the C1–C2 bond and that these steric effects would be greater in *cis*-dimethylcyclobutane, leading to the observed greater preference for symmetrical cleavage in that stereoisomer.

Scheme 6. Modes of decomposition of *cis*- and *trans*-1,2-dimethylcyclobutane.

However, it is the stereochemical outcomes of these thermolyses that strengthened the argument for the diradical mechanism. If the decompositions occur *via* a concerted

mechanism, as in Scheme 4, only the *cis*- or *trans*-2-butene (**8**) would be formed upon thermolysis of pure *cis*- or *trans*-dimethylcyclobutane, respectively. Instead, Gerberich and Walters found that *both* 2-butene isomers were formed in each of the thermolyses (each with ~15% decomposition of the starting material), suggesting that not only was the tetramethylene diradical formed, but also that it was long-lived enough to undergo bond rotation before cleavage of the second C–C bond (Scheme 7). In addition, isomerization of the initial cyclobutanes occurred in both cases, albeit in low yields (2-3%), presumably due to ring closure of the intermediate diradical after bond homolysis and rotation.

Scheme 7. Thermolytic isomerization of *cis*-dimethylcyclobutane.

At first glance, Woodward and Hoffmann's orbital symmetry theory also appeared to support the two-step hypothesis.^{4,24} As a system with $4n$ (where $n=1$) π electrons, the *thermal* one-step cycloreversion of cyclobutane would be symmetry-forbidden. However, further elaboration of the rules governing such pericyclic reactions reveals that the situation is not quite so simple.²⁵⁻²⁷ While the $[2_s+2_s]$ cycloreversion, leading to a single 2-butene isomer in the *cis*- and *trans*-1,2-dimethylcyclobutane thermolyses, is thermally forbidden, the $[2_s+2_a]$ cycloreversion is thermally *allowed*. This complicates the interpretation of the results of the dimethylcyclobutane thermolyses because in the $[2_s+2_a]$ cycloreversion, *both* 2-butene isomers should be formed. Salem and Wright, using an expanded set of orbitals which included contributions from the σ_{C-H} orbitals on cyclohexane, backed up Woodward and Hoffmann's orbital analysis in 1969.²⁸

In order to shed some light on the nature of the proposed tetramethylene diradical intermediate, Hoffmann *et al.* used extended Hückel calculations to explore the potential energy surface (PES) for the stepwise cyclobutane decomposition.¹⁵ Interestingly, the tetramethylene diradical was not found as a true minimum on the PES for the decomposition of cyclobutane. Instead, the calculations described a large, relatively flat area corresponding to the many possible conformations adoptable by the ring-opened cyclobutane. This large region allows the “twixtyl” species, as the authors named it, to have the longer lifetime expected for a true intermediate, rather than a transition state.

A more rigorous, *ab initio* study of the cyclobutane → diradical → ethylene PES was reported by Segal in 1974.¹⁶ Segal’s calculations found that the tetramethylene diradical was in fact an intermediate with a well depth of 3.6 kcal/mol, remarkably close to that found by Benson^{29,30} (~4 kcal/mol), using thermochemical estimates. Since then, several groups have investigated, both theoretically and experimentally, the tetramethylene diradical in attempts to elucidate its nature, particularly with respect to its stability.³¹⁻³⁵

A breakthrough for the proposed diradical mechanism came in 1994 with femtosecond investigations by Zewail’s group.¹⁸ The authors directly generated the tetramethylene diradical by photo-induced decarbonylation³⁶ of cyclopentanone (**9**) and then monitored its reaction along two paths, ring closure to cyclobutane and fragmentation to ethylene (Scheme 8). The lifetime for the tetramethylene diradical was measured to be around 700 fs, much longer than that expected for a transition state (~40 fs). A later study, including DFT calculations reinforced these results and showed that the measured lifetimes are sufficient to allow internal rotation around the C2–C3 bond of the tetramethylene diradical.³⁷ While the case for nonconcerted thermolytic decomposition of cyclobutane certainly is not closed, current thinking appears to be leaning in that direction.

Scheme 8. Photochemical generation and subsequent reactions of tetramethylene diradical.

2. Silacyclobutanes (siletanes). The first reported isolation of a silacyclobutane (siletane) was the synthesis of 1,1-dimethyl-1-silacyclobutane (dimethylsiletane, **10**) in 1954 (Scheme 9).³⁸ Sommer and Baum reported an impressive yield of 66% for the siletane. This paper was followed shortly by the publication of West's synthesis of the 3,3-bisethyl ester substituted dimethylsiletane.³⁹

Scheme 9. The first synthesis of dimethylsiletane (**10**).

The thermochemistry of siletanes was to begin a little over a decade later. In 1968, Gusel'nikov and Flowers demonstrated that the gas-phase thermolysis of dimethylsiletane yields 1,1,3,3-tetramethyl-1,3-disilacyclobutane (**12**).⁴⁰ The decomposition was found to be first order with average Arrhenius parameters of $E_a = 62.5$ kcal/mol and $\log A = 15.64$. Due to the similarity of these values to those obtained¹⁰ in the thermolyses of cyclobutanes, the authors proposed that the reaction proceeded through the nonconcerted elimination of

ethylene to form 1,1-dimethylsilene (**11**). However, due to the kinetic instability of the C–Si double bond, the dimethylsilene dimerizes in a head-to-tail fashion to form the observed disilacyclobutane (Scheme 10).

Scheme 10. Thermolysis of dimethylsilacyclobutane.

Gusel'nikov and Flowers also noted that, unlike in the case of cyclobutanes, the decomposition of dimethylsiletane is inhibited by the presence of ethylene. To explain these observations, they proposed that the extrusion of ethylene is reversible. Experiments with added propene seemed to support their hypothesis, resulting in the appearance of an additional product whose mass and GC retention time were consistent with the formation of a trimethylsiletane. The authors also noted that this reversibility is not unprecedented; Butler describes just such a process (with an E_a for the back reaction of ~ 25 kcal/mol) in the octafluorocyclobutane thermolysis.⁴¹

It is important to note that, at that time, a stable Si–C doubly bonded species had not yet been identified and was a highly speculative entity.⁴² Therefore, Gusel'nikov and Flowers did not propose the intermediacy of a silene casually. Scheme 11 summarizes some of the experimental evidence that led them to propose a silene intermediate. Cycloaddition

Scheme 11. Dimethylsilene reactions.

reactions, such as the silene dimerization and reaction with ethylene or propene, were well known in 1968.⁴³ Addition of water or ammonia across the Si–C double bond is easily visualized, owing to the polarity of the Si–C bond and the purported weakness of the π bond. Indeed, such nucleophilic additions are now characteristic reactions used to trap silenes.^{44,45} The proposal of an intermediate silene proved to be quite sound as, for many years, thermolysis of silacyclobutanes became a standard method for cleanly generating silenes.⁴⁵

As in the case of cyclobutane, the question of whether the decomposition of siletanes is concerted or stepwise (*i.e.*, involving a diradical intermediate) inevitably must arise. Gusel'nikov and Flowers ruled out a concerted mechanism because they deemed the *A* factor too large to accommodate such a constrained process.⁴⁰ It wasn't until 1997 that *ab initio* calculations were performed to address this issue.^{46,47} In both papers, a cyclic transition state was found between the starting siletane and ethylene + silene products. However, this transition state is not one typical of a concerted 2+2 cycloaddition (or –reversion). Instead, the structure was quite unsymmetrical, indicating a “highly asynchronous route...along which there is considerable diradical character.”⁴⁷ The mechanism appears to involve simultaneous lengthening of opposite bonds, but with one bond (C–C, *vide infra*) broken to a greater extent in the transition state.

Due to the lower symmetry of silacyclobutanes relative to cyclobutanes, two different initial bond cleavages are possible: Si–C and C–C (Scheme 12). In the case of dimethylsiletane (**10a**), both routes lead to the same products. Thus, Gusel'nikov and Flowers, recognizing that no definitive comparison of Si–C and C–C bond energies then were known, were unable to determine which bond scission was most likely.

Scheme 12. Initial Si–C vs. C–C bond cleavage in dimethylsiletanes.

In 1975, two independent papers provided evidence for an initial C–C bond cleavage. Upon thermolysis of both 1,1,2-trimethyl-1-silacyclobutane^{48,49} (**10b**) and 1,1-dimethyl-2-phenyl-1-silacyclobutane⁴⁹ (**10c**), the majority of cleavage produced the R-substituted silene (**17b-c**). The preference for C2–C3 cleavage vs. C3–C4 cleavage was assumed, due to the formation of a more stable 2° alkyl radical in the former.⁴⁸ In the case of **10c**, the preference for C–C scission was significantly more pronounced than with **10b**, presumably due to the better ability of a phenyl vs. a methyl group to stabilize an alpha radical. This conclusion is consistent with the finding of Golino *et al.* that, under their reaction conditions, **10b** required a higher temperature (611 °C, the same as for **10a**) than **10c** (530 °C) to effect complete decomposition of the initial siletane. *Ab initio* calculations, too, confirmed the preferential C–C bond cleavage (*vide supra*).⁴⁷

Based on the thermolyses^{9,20,50} of their all-carbon predecessors, little, if any, difference between the thermolyses of dimethylsiletane and the parent silacyclobutane was expected. In fact, when 1-silacyclobutane (**18**) was thermolyzed in 1975, eight years after its first synthesis,⁵¹ very similar results were obtained (Scheme 13).⁵² However, the expected dimerization product of the intermediate silene (**19**), was not formed. Instead, more reactive trapping agents, such as benzophenone and hexamethylcyclotrisiloxane (D3), had to be used.

In the absence of a trapping agent, the thermolysis gave a high molecular weight polymer, which the authors presumed to have come from condensation of **19**.

Scheme 13. Thermolysis of 1-silacyclobutane.

Eight years later, in his own study of the thermolysis of silacyclobutane, Conlin and Gill obtained some surprising results (Scheme 14).⁵³ In addition to the expected intermediate silene (**19**), they were able to trap two other reactive intermediates, the divalent carbene analogues silylene (**21**) and methylsilylene (**22**), using the known⁵⁴ silylene trap 1,3-butadiene (**24**). Also formed, in a 1:1 ratio with silylene (**21**), was cyclopropane (**23**), which isomerized to propene (**7**) at the higher temperature ranges. Conlin's group had observed very similar results in the vacuum pyrolysis of 1-methyl-1-silacyclobutane (methylsiletane) two years earlier.⁵⁵

Scheme 14. Conlin & Gill's thermolysis of 1-silacyclobutane.

Conlin and Gill proposed that silylene and cyclopropane were formed in the same process (Scheme 15). Homolytic cleavage of a Si–C bond would yield diradical **28**, which then could undergo a C–C homolytic cleavage to silene and ethylene, much the same as in the cases of dimethylsiletane and cyclobutane. Alternatively, the diradical could decompose to silylene and cyclopropane through a second Si–C bond scission. Simultaneous formation of these two products would explain the observation that they are both formed in equal amounts.

Scheme 15. Thermolytic formation of silene, silylene and cyclopropane.

The formation of methylsilylene was much less easily explained, considering that its components are not immediately available in the starting siletane. Also adding to the remarkable character of this intermediate was the fact that it is the major silicon-containing product at every temperature investigated. In fact, the ratio of **21** to **19** increased with temperature, up to a value of 5.1 at 697 °C. To explain these data, Conlin and Gill suggested that methylsilylene is formed from a 1,2-hydrogen migration of silene (Scheme 16).

Scheme 16. Methylsilylene from a 1,2-hydrogen migration of silene.

This idea was not unprecedented; Conlin and Wood used the same 1,2-shift to explain the formation of dimethylsilylene (**30**) in the methylsiletane thermolysis.⁵⁵ They further predicted that silene would undergo this hydrogen migration more easily than methylsilene (**31**). In the article immediately following Conlin and Wood's paper, Drahnak, Michl and West provided evidence that this rearrangement is reversible.⁵⁶ Photochemically-generated dimethylsilylene⁵⁷ formed methylsilene and then disilacyclobutane **32** upon warming of the hydrocarbon matrix to 100 K (Scheme 17). The authors were careful to point out that disilacyclobutane **32** did not necessarily arise from dimerization of methylsilene. The same product had been observed by Gaspar and Conlin after dimerization of dimethylsilylene to form a disilene.⁵⁸ The mechanism for the formation of disilacyclobutanes from disilenes also had been the subject of considerable interest, but is outside the scope of the current discussion.⁵⁹⁻⁶¹

Scheme 17. Interconversion of dimethylsilylene and methylsilene.

Another possibility for the formation of methylsilylene is a 1,2-hydrogen shift of the diradical formed from initial C–C bond cleavage (Scheme 18, R=H). This mechanism initially was proposed by Barton for the formation of dimethylsilylene in the methylsiletane thermolysis (Scheme 18, R=Me).⁶² In that study, independent retro-Diels-Alder generation of methylsilene in the presence of silylene traps *did not* result in the formation of dimethylsilylene-trapped products, suggesting that silenes may not be formed as thermal decomposition products of hydridosiletanes. Comparison of bond dissociation energies reveal that Barton's mechanism is thermochemically feasible; a silicon-centered radical is ~9

kcal/mol more stable than a carbon-centered radical.⁶³ Theoretical studies, too, cast a shadow on the silene $\rightarrow$ silylene mechanism, yielding an isomerization barrier of 41-45 kcal/mol.^{64,65}

Scheme 18. Silylenes from 1,2-hydrogen migrations of diradicals.

Conlin and Gill⁵³ concluded that, both mechanisms are quite feasible, but that the entropic requirements of the key steps, namely homolysis or 1,2-H migration of the diradical, allow for a distinction. Since $\Delta S^\ddagger$ for the H migration should be lower than that for the bond homolysis to form silene, the silene route should be favored. Although it appears that this is not in fact the case, as lower silene yields were observed at higher temperatures, the high temperatures used in their study make a silene-silylene rearrangement accessible.

In 1984, the controversy surrounding the thermal decomposition of hydridosiletanes took another turn. While new experiments appeared to support the silylene-silene interconversion at higher temperatures,^{66,67} other evidence called into question the mechanism of propene formation. Conlin and Gill proposed that the propene obtained in their thermolysis of silacyclobutane (**18**) came from thermal isomerization of cyclopropane, which they detected in the lower temperature range.⁵³ However, in the hands of Davidson *et al.*, no cyclopropane was detected upon thermolysis of **18**, even at lower temperatures and conversions; propene and ethylene were the only hydrocarbon products detected.⁶⁸ Particularly intriguing was the fact that no C_3 products had ever been detected in the thermolysis of dimethylsiletane. Thus it was clear to the authors that some mechanism other than direct elimination of cyclopropane from the initially formed diradical proposed by Conlin and Gill (Scheme 16) must be operating to form propene.

Based on stirred-flow reactor⁶⁹ (SFR) kinetic studies⁶⁸ coupled with deuterium labeling experiments,⁷⁰ Barton and coworkers were able to show that propene formation is

formed in a somewhat more complex manner (Scheme 19). Their data suggest that, in addition to homolytic C–C bond cleavage, hydridosiletanes (**34**) can undergo an alternative (essentially irreversible) 1,2-H/D shift to form silylene **35**. This silylene then can insert into a β -C–H bond to yield a silacyclopropane (silirane, **36**) which then eliminates a silylene and a deuterium-labeled propene (**38**). One remarkable aspect of this mechanism is that the silylene insertion into a C–H bond is *reversible*, leading to scrambling of the deuterium and, in some cases, more than one (and even zero) deuteria incorporated in the eventual propene. Independent generation of propylsilylene⁶⁸ (**35**, R=H) as well as subsequent investigations of alkylsilylenes^{71,72} have confirmed that such an insertion does, in fact, occur.

Scheme 19. Mechanism of propene formation.

Ab initio calculations^{47,73,74} performed in 1997 also provided support for Barton's silirane mechanism and have served to help clarify the siletane decomposition mechanism. Skancke calculated⁷⁴ a barrier height of *ca.* 12 kcal/mol for **35** $\rightarrow$ **36** (R=H) and 23-26 kcal/mol for the reverse process. Any process involving diradicals (*e.g.*, ring opening) was ruled out as these species were calculated to lie significantly above the transition states for the **35** $\rightarrow$ **36** isomerization. The calculations of Gordon *et al.* confirmed Barton's hypothesis that the formation of the silylene is competitive with silene formation.

Though the history of silacyclobutane thermolysis has been short relative to that of cyclobutane, it has been no less fervid. At least for now, a consensus appears to have been reached regarding the mechanism of thermal silacyclobutane decomposition. Two characteristically different routes, summarized in Scheme 20, apparently are available to the siletanes. The first is the more "traditional" consecutive bond homolyses to yield two doubly bonded species, a silene and an alkene. The second, more exotic route is a 1,2-hydrogen

migration to form an intermediate silylene, which then reversibly inserts into a β -C-H bond until it finally decomposes to a silylene and an olefin.

Scheme 20. Silacyclobutane decomposition.

3. Germacyclobutanes (germetanes). Only a few years after his initial silacyclobutane work, Gusel'nikov investigated the thermolysis of 1,1-dimethyl-1-germacyclobutane (dimethylgermetane, **39**) in 1970.⁷⁵ He discovered that the germanium analogue gave surprisingly different results from those of the silicon analogue. In addition to ethylene, the major products of thermolysis were cyclopropane, propene, and 1,1,2,2-tetramethyl-1,2-digermacyclopentane (**40**), the product of an apparent insertion of the silylene analogue, dimethylgermylene (**42**), into a Ge-C bond of the starting material (Scheme 21). No products, namely a 1,3-digermacyclobutane, indicating the formation of a Ge-C doubly bonded species (germene) were isolated.

Scheme 21. Gusel'nikov's dimethylgermetane thermolysis.

Gusel'nikov proposed that **39** was decomposing *via* two different routes (Scheme 22). The first route is analogous to the decomposition of dimethylsilacyclobutane and cyclobutane: formation of ethylene and 1,1-dimethyl-1-germene (dimethylgermene, **41**). All attempts at trapping the purported germene were unsuccessful, though a later report by Barton *et al.* showed that pyrolytically-generated diethylgermene does dimerize to form the expected digermacyclobutane.⁷⁶ The second route, comprising the majority of the decomposition, is homolytic cleavage of both Ge–C bonds, forming dimethylgermylene (**42**) and the trimethylene diradical (**43**), which undergoes a 1,2-H shift to propene or reversibly closes to cyclopropane. Independent synthesis and subsequent thermolysis of digermacyclopentane **40** indicated that it is more stable than **39** under the reaction conditions and thus is most likely not responsible for the observed products.

Scheme 22. Gusel'nikov's proposed mechanism for dimethylgermetane decomposition.

Conlin followed up Gusel'nikov's work in 1992 with some elegant trapping and kinetics experiments.⁷⁷ Conlin thermolyzed dimethylgermetane in the presence of 1,3-butadiene and isolated products corresponding to trapped dimethylgermylene (**42**) and 1,1-dimethylgermene (**41**). Based on his findings, Conlin proposed a mechanism (Scheme 23) which involves an initial homolytic germanium-carbon bond cleavage to yield a diradical intermediate (**41**). This intermediate then can decompose in one of three ways. First, simple homolysis of a C–C bond would eliminate ethylene and yield dimethylgermene. Second, an intramolecular elimination of cyclopropane would yield dimethylgermylene. The formation of propene is a bit more complicated. Intramolecular abstraction of a hydrogen atom from a

germanium methyl results in the formation of 1-methyl-1-propyl-1-germene (**45**). A retroene-type reaction then yields dimethylgermylene and propene.

Scheme 23. Conlin's proposed mechanism for dimethylgermetane decomposition.

The only other germetane thermolysis reported in the literature is that of 1,1,3,3-tetramethylgermacyclobutane (tetramethylgermetane, **46**).⁷⁸ The vacuum pyrolysis of **46** was used to generate dimethylgermene (**41**) independently of dimethylgermetane (Scheme 24) in the hopes of providing evidence for its existence. Interestingly, the pyrolysis resulted in the formation of dimethylgermene and isobutylene (**48**), but not dimethylgermylene, dimethylcyclopropane or dimethylpropene, products expected based on the results of dimethylgermetane thermolysis. The authors concluded that tetramethylgermetane probably decomposes only by a homolytic cleavage process, as is the case with cyclobutane. This route is favored over one forming a germylene because of the relative stability of the 3° alkyl radical (**47**) formed in the initial homolysis.

Scheme 24. Vacuum pyrolysis of tetramethylgermetane.

To date, no further investigations into the kinetics or mechanism of germetane thermolysis have been reported, though several studies on the photolysis of diphenylgermetane have been performed.^{79,80} With the thermochemistries of dimethylsiletane and its parent system being so different, one must wonder if the chemistry of the parent germetane would differ as much from that of dimethylgermetane.

B. Results and discussion

1. The intramolecular cyclization strategy. Retrosynthetic analysis (Scheme 25) suggests that the most likely direct precursor of germacyclobutane would be dichlorogermacyclobutane (dichlorogermetane, **50**). As dichlorosiletane (**53**) is generally prepared *via* magnesium-induced intramolecular ring closure⁸¹ of commercially-available 3-chloropropyltrichlorosilane (**52**), the analogous route to dichlorogermetane was envisioned. In fact, such reactions are known to give germacyclobutanes, using sodium/potassium alloy (NaK) or sodium metal in place of magnesium.⁸² However, the synthesis of 3-chloropropyltrichlorogermane (**51**) would have to be undertaken due to the lack of a commercial source of this material.

Scheme 25. Retrosynthetic analysis of germacyclobutane.

The first strategy employed (Scheme 26) utilized the ability of diiodogermylene (GeI_2 , **54**) to insert into carbon-halogen bonds.⁸³ Thus, heating a mixture of GeI_2 and 1,3-diiodopropane (**55**) at 150 °C overnight yielded the intended 3-iodopropyltriiodogermene (**56**). Although attempts at isolating the product failed, its formation was demonstrated from the triphenyl derivative **57**, which was formed *in situ* in 10% yield by addition of phenylmagnesium bromide.

Scheme 26. Iodopropylgermane route.

Reduction of **56** with lithium hydride to form the trihydrido derivative **58**, which would offer an alternate route to germacyclobutane (Scheme 27), also was attempted. The reaction resulted in complete disappearance of the 1,3-diiodopropane and formation of a product whose GC-MS pattern is consistent with **58**. However, removal of the solvent from the reaction mixture resulted in complete loss of the product, possibly due to intermolecular

$$\begin{array}{ccccccc} \text{GeCl}_4 & + & \text{Et}_3\text{GeH} & \longrightarrow & \left[\text{Cl}_3\text{GeH} \right] & \xrightarrow[\text{(ref. 84)}]{\text{Me}_3\text{Ge}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}=\text{CH}_2} & \text{Me}_3\text{Ge}-\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{GeCl}_3 \\ \mathbf{60} & & \mathbf{61} & & \mathbf{62} & & \mathbf{64} \\ & & & & & & \\ & & \mathbf{62} + \text{CH}_2=\text{CHCH}_2\text{Cl} & \rightleftharpoons & \text{Cl}_3\text{Ge}-\text{CH}_2\text{CH}_2\text{CH}_2\text{Cl} \\ & & \mathbf{65} & & \mathbf{66} \end{array}$$

Dichlorogermetane precursor **66** was prepared by first reacting tetrachlorogermene with ethylmagnesium bromide to form tetraethylgermane (**67**). Aluminum chloride-catalyzed chlorination of **67** gave chlorotriethylgermane (**68**), which then was reduced with lithium aluminum hydride to the desired **61** (Scheme 29). However, all attempts at forming **66** using Mazerolles' method failed (Scheme 28). The low boiling point (45 °C) of allyl

chloride relative to the reaction temperature (50 °C) probably hinders its chances of reacting before decomposition of trichlorogermane occurs.

Scheme 29. Synthesis of triethylgermane.

2. Diaminogermane. As formation of dialkylgermacyclobutanes is generally carried out through reaction of a dialkyldichlorogermane with the di-Grignard reagent **70** (Scheme 30),^{85,86} this strategy next was considered.

Scheme 30. Di-Grignard formation of dialkylgermacyclobutanes.

There is a problem with this route, however. Retrosynthetic analysis of dichlorogermacyclobutane (Scheme 31) suggests that the desired starting material would be dichlorogermane (H_2GeCl_2 , **71**). However, the lack of commercial sources of and reliable synthetic routes to this material rendered this approach unfeasible. Instead, a strategy was envisioned that utilized the conversion of aminogermanes to chlorogermanes (Scheme 32).⁸⁷ In this method, the amino groups on germanium would serve as protecting groups on the germanium.

Scheme 31. Retrosynthesis of dichlorogermacyclobutane.

Scheme 32. Ge–N conversion to Ge–Cl.

Unfortunately, the preparation of bis(diethylamino)dichlorogermene (**72**) proved to be problematic. Reaction of tetrachlorogermene (**60**) with diethylamine (**74**) yielded a horrible mixture of aminochlorogermenes through apparent amine-catalyzed redistribution (Scheme 33).

Scheme 33. Attempted diamination of tetrachlorogermene.

3. Spirodigermene. Direct synthesis of dichlorogermene (**50**) by reacting di-Grignard **70** with tetrachlorogermene (**60**) was attempted next. The obvious problem with this strategy is that, once formed, dichlorogermene can react with another equivalent of **70** to form 4-germaspiro[3.3]heptane (spirodigermene, **75**). Therefore, careful control of reaction conditions, especially dilution, addition order and rate, and stoichiometry, must be maintained.

Scheme 34. Expected di-Grignard reaction with tetrachlorogermane.

In 1982, Bickelhaupt published a somewhat laborious procedure for the formation of 1,3-bis(bromomagnesio)propane (**70**) from 1,3-dibromopropane (**60**).⁸⁶ Two years later, he prepared dimethylgermetane (**39**) in 96% yield with the di-Grignard reagent prepared using this procedure. However, application of this method to the synthesis of dichlorogermetane **50** failed to yield the desired product (see Experimental section). Perturbations of Bickelhaupt's original procedure included increasing dilution, reversing reagent addition order, varying relative amounts of reagents, and using activated magnesium⁸⁸ (Mg^*) in place of magnesium turnings. The only Ge-containing products (Scheme 35) isolated during these reactions were spirodigermetane **75**, 1,1-diallyl-1-germacyclobutane (diallylgermetane, **76**), and tetraallylgermane (**77**). Spectroscopically pure samples of germetanes **75** and **76** could be obtained only by preparative gas chromatography (prep-GC) as attempted distillation resulted in decomposition. The ^1H NMR spectra of both **75** and **76** contained ring proton resonances in the range 1.5-2.0 ppm, consistent with those reported for the corresponding dimethylgermetane.⁸⁵ Likewise, the ^{13}C resonances for the ring carbons corresponded well to those of dimethylgermetane, with values in the 20-25 ppm range.⁸⁵ The formation of the allylgermanium species can be rationalized by a MgBr_2 -induced formation of allylmagnesium bromide (**78**) from di-Grignard **70** (Scheme 36).⁸⁶

Scheme 35. Di-Grignard reaction with tetrachlorogermane.

Scheme 36. Allylmagnesium bromide formation from di-Grignard **70**.

These two new germetanes are interesting themselves. For instance, **75** contains two strained 4-membered rings instead of just one and has the potential for some interesting thermochemistry. Diallylgermetane **76**, which will be discussed in the next section, has allyl substituents on the germanium atom instead of the alkyl substituents seen in previously-synthesized germetanes and present the possibility of very interesting retroene processes. In order to carry out the thermochemical experiments, a better method for synthesizing **75** and **76** in higher yields would have to be designed. Thus, it was determined that “delayed coaddition” (see experimental section) of dibromopropane and tetrachlorogermane followed by simple column chromatography resulted in the isolation of spirodigermetane **75** in 45% yield. With a reliable synthesis in hand, the thermochemical studies of **75** were ready to begin.

Spirodigermetane is insufficiently volatile for neat introduction into the stirred-flow reactor (SFR, see experimental section), so it was used as a solution in benzene. SFR thermolysis (see Appendix A) from 430-500 °C resulted in the formation of cyclopropane, propene, and a small amount of ethylene in a 3:10:1 ratio (GC), respectively, at 490°C (Scheme 37). The hydrocarbons were identified by comparison of GC retention times (alumina column) and MS fragmentation with those of authentic samples. These results are consistent with those obtained from thermolysis of dimethylgermetane (which, for direct comparability, also was thermolyzed in the SFR; see Appendix A). However, the activation energy (E_a) for decomposition of spirodigermetane (51 kcal/mol) is 11 kcal/mol lower than the E_a for dimethylgermetane (62 kcal/mol)! Initially, it was believed that this significant lowering of E_a can be explained by the added ring strain inherent in spirodigermetane. The

driving force for ring cleavage in germacyclobutanes is the ring strain associated with forcing the sp^3 -hybridized Ge to compress its bond angles from 109.5° to 90° . To accommodate this compression, the remaining C–Ge–C bond angle would expand to $>109.5^\circ$. Addition of the second ring to this already strained system would introduce even more strain as the remaining bonds are compressed to approach the 90° angles of 4-membered rings.

Scheme 37. SFR thermolysis of spirodigermetane.

One common method used to estimate molecular ring strain is the use of isodesmic reactions.^{89,90} Isodesmic calculations were carried out on a series of germetanes (see Appendix B); the results are summarized in Table 1. The results of the calculations confirm that, while each of the other germetanes investigated have ring strain energies around 20 kcal/mol, spirodigermetane does in fact have twice as much (*ca.* 40 kcal/mol). Therefore, **75** could have a lower E_a and faster rate of decomposition, as is observed, depending upon the mechanism of decomposition. However, this explanation could be true only if *both* rings were being cleaved simultaneously in the rate-determining step. As this is unlikely to occur, the lower E_a for spirodigermetane (compared to that for dimethylgermetane) still remains somewhat puzzling.

Table 1. Calculated ring strain energies (MP2//HF/6-31G*) of selected germetanes.

molecule	ring strain (kcal/mol)
germetane	-21.63
methylgermetane	-19.91
dimethylgermetane	-18.38
spirodigermetane	-39.79

In addition to simple ring cleavage, the formation of ethylene in the thermolysis can result from initial cleavage of one of the 4-membered rings in **75**, followed by ring expansion and subsequent decomposition to atomic germanium and two molecules of ethylene (Scheme 38). Visible germanium deposition on the inner walls of the SFR reactor after several thermolyses is consistent with such a process.

Scheme 38. A possible mechanism for thermolytic ethylene formation from **75**.

4. Diallylgermetane. Since diallylgermetane (**76**) was produced only as a byproduct in the di-Grignard reaction of tetrachlorogermane, a better synthesis was designed. The new starting material, diallyldichlorogermane (**79**), was prepared in 18% yield by a modification of a Direct Process method by Zueva *et al.* (Scheme 39).⁹¹ The diallyldichlorogermane then was used in the di-Grignard reaction developed for synthesis of spirodigermetane to give diallylgermetane (**76**) in 61% yield (Scheme 40).

Scheme 39. Direct Process synthesis of diallyldichlorogermane.

Scheme 40. Synthesis of diallylgermetane.

The thermochemistry of allylsilanes has been studied quite extensively.⁹²⁻⁹⁴ Two competing pathways were found to be operating (Scheme 41): a retroene elimination (path

A) and silicon-allyl bond homolysis (path B), with the retroene mechanism dominating the reaction. A retroene mechanism presents several interesting possibilities for the thermal decomposition of diallylgermetane, two of which are shown in Scheme 42.

Scheme 41. Thermolysis of allylsilanes.

Scheme 42. Possible thermal decomposition routes for diallylgermetane.

SFR thermolysis (see Appendix A) of diallylgermetane from 430–510 °C resulted in the formation of propene and a small amount of hexadiene (Scheme 43). In marked contrast to the thermolysis of both dimethylgermetane and spirodigermetane, no cyclopropane formation was observed, even when an alumina column was used for better separation of the hydrocarbons (the difference in retention times between cyclopropane and propene on the alumina column was confirmed to be >1 minute using authentic samples). SFR thermolysis of cyclopropane alone at these temperatures failed to yield propene, ruling out the disappearance of cyclopropane by thermal decomposition. Indeed, temperatures in excess of 600 °C were needed before significant isomerization of the cyclopropane was observed.

However, just as in the case of spirodigermetane thermolysis, the E_a for decomposition of diallylgermetane (55 kcal/mol) is lower than that for dimethylgermetane (62 kcal/mol).

Scheme 43. SFR thermolysis of diallylgermetane.

An explanation can be found in the thermochemistry of allylgermanes, such as allyltrimethylgermane. There is good evidence that allylgermanes thermally decompose *via* homolysis of the weakest bond, the allyl-germanium bond (Scheme 44).⁹⁵ In fact, SFR thermolysis of diallyldimethylgermane gave Arrhenius parameters ($E_a = 53 \text{ kcal/mol}$, $\log A = 14$) that are quite close to those of diallylgermetane (see Appendix A). Thus, homolytic cleavage of an allyl-germanium bond in diallylgermetane offers a lower-energy decomposition than the germanium-carbon ring cleavage observed for dimethylgermetane.

Scheme 44. Thermolysis of allyltrimethylgermane.⁹⁵

To test this hypothesis, flow pyrolysis of diallylgermetane (**76**) was performed in the presence of carbon tetrachloride (Scheme 45). Since carbon-chlorine bonds are efficient traps for germanium-centered radicals, the formation of chlorogermanes would suggest the formation of these intermediates. The expected products, chloro(allyl)germetane (**81**) and dichlorogermetane (**50**), were indeed formed, suggesting that homolysis of a germanium-allyl bond in diallylgermetane at least competes with ring cleavage.

Scheme 45. Flow pyrolysis of diallylgermetane in CCl_4 .

5. Germacyclobutane. Diallylgermetane had a side benefit in that it offered an alternative route to germacyclobutane. In 1968, Roberts showed that allylgermanes can be converted to chlorogermanes with mercuric chloride (Scheme 46).⁹⁶ An added attraction to this method was that HgCl_2 could be a mild enough Lewis acid that electrophilic ring opening of the germacyclobutane ring could be avoided. Indeed, reaction of diallylgermetane with an excess of HgCl_2 in acetonitrile resulted in a 47% yield of dichlorogermetane **50** (Scheme 47). Extraction of moisture-sensitive **50** from the mercury salts proved to be challenging as the solubility of the polar dichlorogermetane is limited in hydrocarbon solvents compared to polar solvents. Accordingly, the reaction was carried out in a liquid-liquid extraction apparatus (see Appendix C). Upon completion of the reaction, extraction of the product into pentanes was accomplished in three days.

Reduction of dichlorogermetane with lithium aluminum hydride then afforded the long-awaited parent germacyclobutane **49** in quantitative yield. The product was isolated as a clear colorless liquid by low pressure distillation from the reaction mixture. The boiling point of **49** was not able to be determined accurately due to its volatility; the distillation receiver had to be cooled to $-78\text{ }^\circ\text{C}$ in order to collect the distilled product at ~ 20 torr and samples were stored in a refrigerator. In addition to peaks for the germetane ring protons (1.50 and 2.20 ppm), a germanium hydride peak was detected at 4.70 ppm by ^1H NMR (Figure 1). The ^1H NMR values for the ring protons are in good agreement with those measured for dimethylgermetane (**39**): 1.46 and 2.25 ppm.⁸⁵ The ^{13}C NMR spectrum (Figure 2) showed only resonances for the two ring carbons at 15.16 and 24.59 ppm. In the IR spectrum of **49**, the Ge–H bond stretch was evident at 2066 cm^{-1} while the GeH_2 bending and wagging frequencies appeared at 865 and 881 cm^{-1} .⁸²

Figure 1. ^1H NMR spectrum of germacyclobutane (49).

Figure 2. ^{13}C NMR spectrum of germacyclobutane (49).

Scheme 46. Conversion of allylgermanes to chlorogermanes with HgCl_2 .⁹⁶

Scheme 47. Synthesis of germacyclobutane.

Upon SFR thermolysis, germacyclobutane yielded propene as the only detected hydrocarbon product (Scheme 48). The identity of propene was confirmed by MS and identification of its bromine adduct, 1,2-dibromopropane. This sole production of propene, coupled with the significantly lower (relative to the other germetanes) E_a for germacyclobutane suggests the occurrence of a different mechanism, presumably the proposed initial [1,2]-H shift, for its decomposition. If initial ring Ge-C bond homolysis were occurring, cyclopropane also should be formed, as was the case in the thermolysis of dimethylgermetane and spirodigermetane. Sequential Ge-C homolyses also should result in the formation of significant amounts of cyclopropane through ring closure of the intermediate propane-1,3-diyl diradical.⁹⁷

$$E_a = 48.2 \pm 0.3 \text{ kcal/mol}$$

$$\log A = 14.73 \pm 0.09$$

Scheme 48. SFR thermolysis of germacyclobutane.

To provide evidence for the [1,2]-H shift mechanism (Scheme 49), propylgermane (**85**) was prepared and its thermochemistry examined. If a [1,2]-H shift to form propylgermylene is occurring, then production of **82** *via* a different route also should result in the formation of propene. Propylgermane was chosen as a thermal precursor to **82** because mono- and dialkylgermanes are known to lose molecular hydrogen to yield germylenes upon thermolysis.^{98,99} SFR thermolysis of **85** indeed did generate propene, which was detected as above by bromine trapping. No other products were detected by GC.

Scheme 49. Possible mechanism for germetane decomposition.

To further investigate the proposed mechanism, dideuteriogermetane (**86**) was synthesized by the lithium aluminum deuteride reduction of dichlorogermetane. Evidence for the formation of the isotopically-labelled germetane was provided by the lack of Ge–H peaks in the ^1H NMR spectrum and the appearance of a Ge–D stretch at 1490 cm^{-1} in the IR spectrum. The results of SFR thermolysis of **86** are presented in Scheme 50; again, propene was the only hydrocarbon produced in the reaction. To determine the amount of deuterium incorporation in the propene, a second SFR reactor was prepared in which a GC-MS was used in place of an analytical (FID) GC for product detection and analysis. Nearly 80% of the propene formed contained deuterium, based on comparison of the abundances of the m/z 41, 42, and 43 peaks, which represent the base peaks for propene, propene- d , and propene- d_2 , respectively. These data are consistent with a [1,2]-migration of D from Ge to an α ring carbon. It is interesting to note that approximately 2/3 of the propene contained not just one deuterium, but *two*, consistent with a reversible migration step. Further support was provided

by comparison of the rate constants for the germacyclobutane and dideuteriogermetane thermolyses. A primary deuterium isotope effect of 1.57 (at $T=410\text{ }^{\circ}\text{C}$), also consistent with a mechanism involving cleavage of a Ge–H (or Ge–D) bond in the rate determining step, was found.¹⁰⁰

Scheme 50. Synthesis and SFR thermolysis of dideuteriogermetane.

Although these data appear to support the proposed [1,2]-H migration, they do not rule out a mechanism involving initial homolytic cleavage of a germanium-carbon bond. The intermediate diradical thus formed also could give propylgermylene upon an intramolecular hydrogen abstraction (Scheme 51). Indeed, closer inspection of the Arrhenius parameters for this reaction reveals some apparent inconsistencies. While an E_a of 48.2 kcal/mol seems too low to be consistent with Ge–C ring cleavage, especially when compared to those observed for other germacyclobutanes (*e.g.* 62 kcal/mol for dimethylgermetane), the observed $\log A$ of

Scheme 51. Possible mechanisms for thermal decomposition of germacyclobutane.

14.7 is consistent with a process requiring a less constrained transition state, such as a homolytic cleavage.^{101,102} It is quite possible that both processes are occurring in competition under these conditions and the Arrhenius parameters thus represent a combination of those for the competing reactions. However, log A values can be rather variable¹⁰² and the E_a value of 48.2 kcal/mol is much too low to be attributed to ring cleavage.

C. Conclusions

Four new germetanes have been synthesized (Figure 3) and the thermal behavior of three of them (spirodigermetane **75**, diallylgermetane **76**, and germacyclobutane **49**) has been studied. A modified di-Grignard synthesis produces **75** and **76** in moderate yields and dichlorogermetane (**50**) and diallylgermetane themselves have proven to be useful starting materials, opening the way for the study of myriad other potentially interesting germetanes.

Figure 3. New germetanes.

Gas-phase thermolysis of **75** yields the same hydrocarbon products observed in previously studies systems, though with a lower energy of activation (E_a). Isodesmic calculations indicate that the ring strain in **75**, approximately double that in other monocyclic germetanes, is the likely cause for the decreased E_a . Diallylgermetane (**76**), on the other hand, produces only propene and 1,5-hexadiene upon gas-phase thermolysis. Trapping studies and comparison to the activation parameters of acyclic allylgermanes suggest that the germanium-allyl bond is weak enough to compete with ring cleavage.

The thermochemistry of the original target of this study, the parent germetanes **49**, is quite different from dimethylgermetane, as predicted. The only hydrocarbon product detected is propene, which, along with deuterium labeling studies, indicates an intramolecular hydrogen migration, much like in the case of the parent silacyclobutane, is occurring. While it is possible that the H-migration and ring-cleavage mechanisms may be in

competition with each other, the comparatively low E_a value (48.2 kcal/mol) favors the migration.

D. Experimental

Instrumentation and General Procedures. ^1H and ^{13}C NMR spectra were acquired on Varian (VXR-300 and VXR-400) spectrometers. Chemical shifts are reported as parts per million (ppm) relative to tetramethylsilane using the given solvents as standards: CDCl_3 (^1H 7.27 ppm, ^{13}C 77.23 ppm), C_6D_6 (^1H 7.16 ppm, ^{13}C 128.39 ppm). Fourier transform infrared (FTIR) spectra were obtained on a Bio-Rad Digilab FTS-7 spectrometer using neat samples in a 0.025 mm sealed cell. Exact masses were obtained *via* high resolution mass spectrometry (HRMS) on a Kratos MS50 mass spectrometer with a resolution of 10,000. Gas chromatography-mass spectrometry (GC-MS) data were obtained using a Hewlett-Packard 5890 Series II Plus gas chromatograph connected to an electron impact (EI) 5972 Series Mass Selective Detector operating at 70 eV. Routine analytical gas chromatography was performed using a Hewlett-Packard 5890 Series II gas chromatograph (GC) equipped with a flame ionization detector. A 30 meter J&W DB-5 capillary (0.250 mm i.d.) column was used for separation in both the analytical and GC-MS gas chromatographs. Preparative gas chromatography was carried out on a Varian Aerograph Model 920 gas chromatograph using a thermal conductivity detector. Copper tubing (210x0.5 cm) packed with Alltech 14% SE-30 on Chromosorb W-HP was used for the separations and helium was used as the carrier gas.

Pulsed stirred-flow reactor (SFR) studies were performed using an apparatus modeled after that of Baldwin *et al.*⁶⁹ The system was calibrated using the gas-phase thermal isomerization of cyclopropane to propene.⁶⁹ A quartz reaction chamber with a volume of 4 mL was heated by a tube furnace controlled with a Digi-Sense temperature controller. A helium flow rate of 30 mL/min was maintained through the reaction chamber by a MKS Model 1259B mass flow controller. Reactants and products were swept directly into a Hewlett-Packard 5890 GC, where they were separated and then analyzed by a flame ionization detector (FID). FID data were recorded on a Hewlett-Packard 3392A integrator in addition to a microcomputer. The GC was equipped with either a 30 m J&W DB-5 or a 50 m

Varian Al₂O₃/Na₂SO₄ ("alumina") megabore (0.53 mm i.d.) column. Hydrocarbon products were identified by comparison of their retention times to those of authentic samples on the alumina column. A similar apparatus was connected to the GC-MS described above for additional studies.

Tetrahydrofuran (THF) was distilled over lithium aluminum hydride (LAH) and diethyl ether was distilled over sodium/benzophenone prior to use. Other solvents and reagents were obtained commercially and used without further purification, unless indicated otherwise.

Synthesis of germanium diiodide (54). The synthesis of **54** was achieved by using Garvey's modification¹⁰³ of Foster's^{104,105} route. After drying in an Abderhalden drying pistol overnight, the desired product was obtained as bright golden flakes in 90% yield.

Synthesis of 3-iodopropyltriphenylgermane (57). Germanium diiodide (5.00 g, 15.3 mmol) and diiodopropane (2.00 mL, 17.4 mmol) were placed in a 25 mL round bottom flask fitted with a magnetic stir bar and West condenser. The reaction was heated to 150 °C and stirred for 8 hours under a positive pressure of Ar. The reaction mixture turned from a pasty golden-colored liquid to a yellow-orange liquid with white precipitate. Diethyl ether (50 mL) was added, followed by 15 mL of a 3 M solution of phenylmagnesium bromide in diethyl ether (45 mmol). Stirring was continued overnight, after which the excess Grignard reagent was quenched with 10 mL water. The ether layer then was washed thrice with 10 mL saturated aqueous sodium chloride and dried over anhydrous magnesium sulfate.

Concentration *in vacuo* gave a yellow oil, which, upon column chromatography (silica gel, pentanes) yielded 0.75 g (1.6 mmol, 10% yield) white powdery **57**. ¹H NMR (300 MHz, chloroform-*d*) δ 1.60 (m, 2 H, Ge-CH₂-CH₂), 2.03 (m, 2 H, CH₂-CH₂-CH₂), 3.21 (t, *J* = 8 Hz, 2 H, I-CH₂-CH₂), 7.42 (m, 12 H, aromatic); ¹³C NMR (75 MHz, chloroform-*d*) δ 10.77 (Ge-CH₂), 15.63 (CH₂-CH₂-CH₂), 29.58 (I-CH₂), 128.40, 129.17, 134.94, 136.54; GC-MS (EI): *m/z* (% relative intensity) 397 (M⁺-Ph, 2), 355 (3), 305 (100), 227 (12), 201 (2), 151 (23), 125 (3), 99 (2), 77 (3).

Attempted synthesis of 3-iodopropylgermane (58). The reaction was performed according to the procedure for the synthesis of 3-iodopropyltriphenylgermane (57), except that LiH (10 molar equivalents, based on GeI_2) in 100 mL diethyl ether was used in place of the phenylmagnesium bromide. GC-MS analysis indicated that the starting material had disappeared and a new product with a MS pattern consistent with 58 had formed. Removal of the solvent *in vacuo* produced a small amount of white salts in yellow oil, but GC-MS analysis of the material showed that the product had disappeared. **GC-MS (EI):** m/z (% relative intensity) 245 ($\text{M}^+ - \text{H}$, 69), 201 (100), 127 (18), 119 (36), 91 (78), 77 (GeH_3 , 73).

Synthesis of tetraethylgermane (67).^{106,107} Tetraethylgermane was synthesized according to a modification of two literature procedures.^{106,107} Germanium tetrachloride (11.4 mL, 100 mmol) was dissolved in 200 mL dry diethyl ether in a 500 mL 3-neck round bottom flask fitted with a Friedrichs condenser, magnetic stir bar, septum, and 250 mL pressure-equalizing addition funnel. The apparatus had been flushed with argon prior to the addition and the reaction was run under a positive pressure of argon. A 3.0 M solution of ethylmagnesium bromide (EtMgBr) in diethyl ether (150 mL, 450 mmol) was transferred to the addition funnel and the flask was cooled in an ice bath. The EtMgBr was added dropwise while stirring, after which the reaction was stirred overnight. The flask was again cooled in an ice bath and the reaction was quenched by slow addition of water. Another portion (100 mL) of diethyl ether was added to the reaction mixture. The organic layer was washed thrice with saturated aqueous sodium chloride solution (100 mL each) and dried over anhydrous calcium chloride. Filtration and removal of the solvent *in vacuo* yielded tetraethylgermane as a clear colorless liquid in quantitative yield. **^1H NMR** (300 MHz, chloroform- d): δ 0.72 (q, $J = 9$ Hz, 3 H, $\text{Ge}-\text{CH}_2-\text{CH}_3$), 1.02 (t, $J = 9$ Hz, 4 H, $\text{Ge}-\text{CH}_2-\text{CH}_3$); **^{13}C NMR** (75 MHz, chloroform- d): δ 3.51 ($\text{Ge}-\text{CH}_2-\text{CH}_3$), 8.97 ($\text{Ge}-\text{CH}_2-\text{CH}_3$).

Synthesis of chlorotriethylgermane (68).¹⁰⁸ A modification of Mironov and Kravchenko's monochlorination of tetramethylgermane¹⁰⁹ was used. A 25 mL 2-neck round bottom flask was fitted with a septum, West condenser, and magnetic stir bar; the apparatus was flushed with argon and a positive pressure of argon kept thereafter. Tetraethylgermane (3.5 g, 19

mmol) and anhydrous aluminum chloride (0.06 g, 0.4 mmol) were added to the flask and isopropyl chloride (1.8 mL, 19 mmol) added dropwise *via* syringe. The reaction was heated to 95 °C in an oil bath for one hour. Distillation yielded 1.86 g (9.53 mmol, 50% yield) chlorotriethylgermane. ^1H NMR (300 MHz, chloroform-*d*): δ 1.14 (s, 15 H); ^{13}C NMR (75 MHz, chloroform-*d*): δ 8.02, 10.42; **b.p.** 175-178 °C (lit.¹⁰⁸ 173-177 °C).

Synthesis of triethylgermane (61).¹¹⁰ The synthesis of the title compound was based on Anderson's procedure.¹¹⁰ Lithium aluminum hydride (7.4 g, 195 mmol) was dissolved in 250 mL dry diethyl ether in an argon-purged 500 mL 3-neck round bottom flask fitted with a magnetic stir bar, Friedrichs condenser, and septum. While stirring the reaction, chlorotriethylgermane (24.0 mL, 144 mmol) was added dropwise *via* syringe. Upon completion of the addition, the reaction was heated to reflux overnight. The flask then was cooled in an ice bath and the reaction was quenched by the slow addition of 200 mL slightly acidic (H₂SO₄) water. The organic layer was washed with three 100 mL portions of water and dried over anhydrous sodium sulfate. Distillation yielded 8.06 g (50.1 mmol, 35% yield) triethylgermane. **GC-MS** (EI): *m/z* (% relative intensity) 161 (M^+ -H, 74), 133 (M^+ -Et, 100), 103 (48), 75 (17); **b.p.** 115-117 °C (lit.⁸² 122 °C, 769 torr).

Attempted synthesis of 3-chloropropyltrichlorogermane (66). This procedure was modeled after that of Huc *et al.* for hydrogermylation of terminal alkenes with HgCl₃.⁸⁴ A 25 mL 3-neck round bottom flask was fitted with a magnetic stir bar, West condenser, and a 25 mL pressure-equalizing addition funnel. The apparatus was flushed with argon and 2.5 mL (22 mmol) germanium tetrachloride was added to the flask. The flask was heated to 50 °C with an oil bath and dropwise addition of a mixture of 1.7 mL (11 mmol) triethylgermane and 0.90 mL (11 mmol) allyl chloride was begun through the addition funnel. The reaction was monitored by GC-MS. Heating was continued until no allyl chloride remained (7 days). None of the intended product was detected by GC-MS, though triethylchlorogermane (**68**) was formed in significant amounts.

Attempted synthesis of bis(diethylamino)dichlorogermane (72). Anderson's procedure for the tetraamination of tetrachlorogermane was used as a model for this reaction.⁸⁷

Diethylamine (51.75 mL, 500 mmol) was dissolved in 250 mL dry diethyl ether in an argon-flushed 500 mL 2-neck round bottom flask fitted with a 50 mL pressure-equalizing addition funnel and a magnetic stir bar. The flask was cooled with an ice bath and the tetrachlorogermane (11.4 mL, 100 mmol) in 50 mL dry diethyl ether was added dropwise through the addition funnel. White "smoke" and white precipitate immediately formed. The reaction was allowed to warm to room temperature upon completion of the addition and was stirred overnight. Filtration and removal of the solvent *in vacuo* yielded an inseparable mixture of products (*vide supra*).

Attempted synthesis of dichlorogermetane (50) using Bickelhaupt's method.^{85,86}

Magnesium turnings (2.4 g, 100 mmol) were placed in 150 mL dry diethyl ether in a 250 mL 2-neck round bottom flask fitted with a magnetic stir bar, Friedrichs condenser, and 50 mL pressure-equalizing addition funnel. 1,3-Dibromopropane (3.42 g, 17 mmol) in 50 mL dry diethyl ether was added dropwise through the addition funnel while stirring the reaction mixture. After stirring the reaction overnight, the ether was distilled off under reduced pressure and 100 mL dry tetrahydrofuran (THF) was added. The resulting mixture was stirred for 20 minutes and then filtered. The remaining residue was rinsed 4 more times in this fashion and the THF solutions were combined. Anhydrous magnesium bromide (3.13 g, 17 mmol) was dissolved in a minimum amount of 1:1 diethyl ether:THF and added to the combined THF solutions. The resulting solution was stirred overnight, after which it was cannulated into a 500 mL pressure-equalizing addition funnel connected to a 1000 mL round bottom flask containing tetrachlorogermane (5.0 mL, 44 mmol) in 500 mL dry THF and a magnetic stir bar. The contents of the addition funnel were added dropwise (very slowly) while stirring the reaction vigorously. After stirring overnight, the reaction failed to produce any **50**, as indicated by GC-MS analysis, though the amount of tetrachlorogermane remaining had noticeably decreased.

Preparation of activated magnesium (Mg*). Rieke's procedure⁸⁸ was scaled up and used as follows. Potassium chunks (7.82 g, 200 mmol) were freshly cut and added to a solution of anhydrous magnesium chloride (10.47 g, 110 mmol) in 250 mL dry THF in a 500 mL round bottom flask fitted with a West condenser and magnetic stir bar. The reaction was heated to reflux for 3 hours, forming a dark grey colored dispersion. The mixture was allowed to cool before using.

Synthesis of 4-germaspiro[3.3]heptane (spirodigermetane, 75). A 500 mL 3-neck round bottom flask was fitted with a Friedrichs condenser, magnetic stir bar, and a 50 mL pressure-equalizing addition funnel and charged with 20.0 g (0.823 mol) -50 mesh powdered magnesium. The system was evacuated and back-filled thrice with argon, after which the system was kept under a positive pressure of argon. 250 mL dry diethyl ether was added to the flask and 13.0 mL (0.128 mol) 1,3-dibromopropane in 37 mL dry diethyl ether was added to the addition funnel. The dibromopropane solution was added dropwise while stirring until bubbling of the ether was observed. 3.0 mL (0.026 mol) tetrachlorogermene then was added to the addition funnel while continuing the dropwise addition. The reaction was stirred for three hours at room temperature. Oven-dried silica gel (150 mL) was added to the reaction mixture and stirring was continued for another ½ hour. The reaction mixture then was poured onto a large (5x25 cm) chromatography column containing a small amount of silica gel and hexanes and eluted with hexanes. The solvent was removed *in vacuo* from the eluent and the resulting yellow oily residue was chromatographed (silica gel, hexanes), yielding 0.90 g (45% yield) of spirodigermetane. ¹H NMR (300 MHz, chloroform-*d*): δ 1.80 (t, *J* = 9 Hz, 8 H, Ge-CH₂), 2.22 (pentet, *J* = 9 Hz, 4 H, Ge-CH₂-CH₂); ¹³C NMR (75 MHz, chloroform-*d*): δ 21.97, 25.41; GC-MS (EI): *m/z* (% relative intensity) 158 (M⁺, 17), 130 (M⁺-C₂H₄, 5), 116 (100), 102 (35), 88 (40), 74 (41); HRMS: *m/z* 158.01551 (calc. for C₆H₁₂Ge 158.01517).

Synthesis of 1,1-dimethyl-1-germacyclobutane (dimethylgermetane, 39).⁷⁷

Dimethylgermetane was synthesized using the method described above for the synthesis of spirodigermetane. Dimethyldichlorogermene was used in place of tetrachlorogermene. GC-

MS (EI): m/z (% relative intensity) 146 (M^+ , 11), 131 ($M^+ - \text{Me}$, 9), 118 (91), 103 (42), 89 (100), 75 (19), 73 (19).

Synthesis of diallyldichlorogermane (79).⁹¹ The synthesis of **79** was performed using a modification of the procedure by Zueva and coworkers. A contact mass consisting of 13.75 g (189.4 mmol) 100 mesh germanium powder, 11.25 g (177. mmol) 200 mesh copper powder, and 0.13 g (4.8 mmol) 20 μm aluminum powder was combined with a mortar and pestle and placed in the apparatus shown in Appendix B. The tube furnace was heated at 250 °C overnight under Ar flow (220 ml/min). The furnace temperature then was increased to 350 °C and 50.0 mL (61.3 mmol) allyl chloride was added to the apparatus *via* syringe. When the allyl chloride was gone (usually 7-8 hours), the furnace was turned off and the apparatus was allowed to cool. Vacuum distillation (6 torr) of the product mixture yielded 7.8 g (18% yield) diallyldichlorogermane and 6.9 g (17% yield) allyltrichlorogermane. For *diallyldichlorogermane*, **¹H NMR** (300 MHz, chloroform-*d*): δ 2.515 (d, J = 9 Hz, 4 H), 5.19 (m, 4 H), 5.84 (m, 2 H); **¹³C NMR** (75 MHz, chloroform-*d*): δ 30.69, 119.07, 128.89; **GC-MS (EI):** m/z (% relative abundance) 185 (25), 150 (4), 109 (65), 82 (95), 74 (6), 67 (100); **b.p.** 60-63 °C, 6 torr (lit. 85 °C, 17 torr). For *allyltrichlorogermane*, **GC-MS (EI):** m/z (% relative abundance) 220 (M^+ , 44), 179 (37), 144 (18), 109 (100), 74 (18); **b.p.** 33-35 °C, 6 torr (lit.¹¹¹ 153.8 °C, 743.5 torr).

Flow pyrolysis of 79 in carbon tetrachloride. A solution of 0.1 g (0.5 mmol) **79** in 3.0 mL (31 mmol) CCl_4 was pyrolyzed at 450 °C under argon flow, yielding an inseparable mixture of decomposition products. GC-MS analysis of the pyrolysate showed that *ca.* 75% of the starting germetane had decomposed, forming a mixture of chlorinated germanes, including the major products dichlorogermetane (**50**) and chloro(allyl)germetane (**81**) in 4% and 25% conversion, respectively (GC-MS).

Synthesis of 1,1-diallyl-1-germacyclobutane (diallylgermetane, 76). A 500 mL 2-neck round bottom flask was fitted with a Friedrichs condenser, magnetic stir bar, and a 25 mL pressure-equalizing addition funnel and charged with 15.0 g (0.617 mol) -50 mesh powdered

magnesium. The system was evacuated and back-filled thrice with argon, after which the system was kept under a positive pressure of argon. 250 mL dry diethyl ether was added to the flask and 5.0 mL (0.049 mol) 1,3-dibromopropane in 20 mL dry diethyl ether was added to the addition funnel. The dibromopropane solution was added dropwise while stirring until bubbling of the ether was observed. Diallyldichlorogermane (4.0 g, 0.018 mol) then was added to the addition funnel while continuing the dropwise addition. The reaction was stirred overnight at room temperature. After quenching with distilled water (200 mL) and washing with saturated aqueous ammonium chloride (200 mL), water (200 mL), and saturated aqueous sodium chloride (200 mL), the ether layer was dried over anhydrous magnesium sulfate. Upon filtration and removal of the solvent *in vacuo*, the product was isolated by gravity column chromatography on silica gel with hexanes as eluent. The reaction afforded 2.16 g (61% yield) of **76** as a clear colorless liquid. ^1H NMR (300 MHz, chloroform-*d*): δ 1.55 (t, $J = 9$ Hz, 4 H, Ge-CH₂-CH₂), 1.985 (d, $J = 9$ Hz, 4 H, ring Ge-CH₂-CH₂), 2.18 (pentet, $J = 9$ Hz, 2 H, CH₂-CH=CH₂), 4.92 (m, 4 H, allyl Ge-CH₂), 5.91 (m, 4 H, CH₂-CH=CH₂); ^{13}C NMR (75 MHz, chloroform-*d*): δ 18.41 (ring Ge-CH₂), 21.59 (ring Ge-CH₂), 22.96 (CH₂-CH=CH₂), 113.02 (CH₂-CH=CH₂), 134.86 (CH₂-CH=CH₂); GC-MS (EI): m/z (% relative intensity) 198 (M^+ , 1), 170 ($\text{M}^+ - \text{C}_2\text{H}_4$, 3), 157 (100), 129 (38), 115 (77), 101 (32), 89 (47), 74 (8); HRMS: m/z 197.04890 (calc. for C₉H₁₆Ge 197.04866).

Synthesis of 1,1-dichloro-1-germacyclobutane (dichlorogermetane, 50). In the apparatus shown in Appendix B, 20 g (74 mmol) mercuric chloride was dissolved in 40 mL dry acetonitrile. To this solution, 3.03 g (15.4 mmol) diallylgermetane (**76**) was added, immediately forming a fluffy white precipitate. The reaction was stirred for 2½ hours, after which the flask containing 50 mL dry pentanes was heated to 50 °C. The extraction was carried out for three days. Fractional distillation of the pentanes extract under reduced pressure yielded 1.33 g (47% yield) of the title compound. ^1H NMR (300 MHz, chloroform-*d*) δ 2.27 (pentet, $J = 9$ Hz, 2 H, Ge-CH₂-CH₂), 2.98 (t, $J = 9$ Hz, 4 H, Ge-CH₂-CH₂); ^{13}C NMR (75 MHz, chloroform-*d*) δ 18.72 (Ge-CH₂), 47.02 (Ge-CH₂-CH₂); GC-MS (EI): (% relative intensity) 186 (M^+ , 2), 158 ($\text{M}^+ - \text{C}_2\text{H}_4$, 33), 150 (9), 144 (8), 123 (1), 109 (100), 99

(2), 88 (10), 74 (17); **HRMS**: m/z 185.90527 (calc. for $C_3H_6Cl_2Ge$ 185.905026); **b.p.** 67-69 °C at 23 torr.

Synthesis of 1-germacyclobutane (49). 10 mL (5 mmol LAH) of 0.5 M lithium aluminum hydride (LAH) in diglyme was added to a 25 mL side-arm round bottom flask fitted with a magnetic stir bar, rubber septum, and a short-path distillation head. A short piece of Teflon tubing was connected to the drip tip of the distillation head to extend it nearly to the inside wall of the 4 mL collection tube connected to the receiver end of the distillation head. The flask was cooled in an ice/salt bath and the collection tube was cooled in a dry ice/acetone bath. 1.42 g (7.65 mmol) dichlorogermene (**50**) was added *via* syringe to the stirring LAH solution. The reaction was stirred for ½ hour, after which vacuum, supplied by a water aspirator, was applied for 1 hour. The ice/salt bath was removed and vacuum was applied again until no more bubbling was observed in the diglyme solution. A quantitative yield of **49**, a clear colorless liquid, was obtained. 1H NMR (300 MHz, benzene- d_6): δ 1.50 (m, 4 H, Ge-CH₂-CH₂), 2.20 (m, 2 H, Ge-CH₂-CH₂), 4.70 (m, 2 H, Ge-H); ^{13}C NMR (75 MHz, benzene- d_6): δ 15.16 (Ge-CH₂), 24.59 (Ge-CH₂-CH₂); **FTIR**: $\bar{\nu}$ (cm⁻¹) 2993 (w), 2938 (w), 2873 (w), 2066 (s), 2050 (s, Ge-H), 881 (w, Ge-H), 865 (w, Ge-H); **GC-MS (EI)**: m/z (% relative intensity) 116 ($M^+ - 2H$, 18), 101 (7), 88 (41), 74 (100); **HRMS**: m/z 117.98401 (calc. for C_3H_8Ge 117.983824).

Synthesis of 1,1-dideuterio-1-germacyclobutane (86). The title compound was obtained in quantitative yield using the procedure described for **49** except that lithium aluminum deuteride was used in place of lithium aluminum hydride. 1H NMR (300 MHz, benzene- d_6): δ 1.49 (t, $J = 9$ Hz, 4 H, Ge-CH₂-CH₂), 2.20 (pentet, $J = 9$ Hz, 2 H, Ge-CH₂-CH₂); ^{13}C NMR (75 MHz, benzene- d_6): δ 14.82 (Ge-CH₂), 24.57 (Ge-CH₂-CH₂); **FTIR**: $\bar{\nu}$ (cm⁻¹) 2993 (w), 2934 (w), 2878 (w), 1506 (w), 1490 (w); **GC-MS (EI)**: m/z (% relative intensity) 116 ($M^+ - 2D$, 12), 101 (4), 90 (42), 74 (100).

Synthesis of propyltrichlorogermene.¹¹² Magnesium turnings (15.0 g, 617 mmol) were placed in a 500 mL 3-neck round bottom flask fitted with a magnetic stir bar, Friedrichs

condenser, and a 25 mL pressure-equalizing addition funnel. The system was evacuated and back-filled thrice with argon, after which the system was kept under a positive pressure of argon. Dry diethyl ether (250 mL) was added to the flask and 5.0 mL 1-bromopropane (55 mmol) was dissolved in 20 mL dry diethyl ether and placed in the addition funnel. A crystal of iodine was added to initiate the reaction, after which the 1-bromopropane solution was added dropwise while stirring. Stirring was continued for 2 hours after completion of the addition. The resulting Grignard reagent was filtered through a glass wool plug in Teflon tubing to a 250 mL pressure-equalizing addition funnel attached to a 1000 mL 3-neck round bottom flask fitted with a magnetic stir bar and Friedrichs condenser. Tetrachlorogermane (10.0 mL, 87.6 mmol) was dissolved in 250 mL dry diethyl ether and placed in the flask. The flask was cooled to 0 °C and the Grignard reagent was added dropwise while stirring. The reaction was stirred overnight. Removal of the solvent by distillation left 6.6 mL of crude propyltrichlorogermane. This mixture was used without further purification in the reduction reaction that follows. **GC-MS (EI):** m/z (% relative intensity) 222 (M^+ , 1), 207 (7), 186 (80), 184 (56), 179 (94), 150 (26), 144 (23), 109 (100), 99 (3), 87 (5), 74 (15).

Synthesis of propylgermane (85).¹¹² A 0.5 M solution (100 mL, 50 mmol) of lithium aluminum hydride (LAH) in diglyme was placed in a 250 mL round bottom flask fitted with a magnetic stir bar. A short-path distillation head with 100 mL pear flask attached was connected to the round bottom flask, which then was cooled in an ice/NaCl bath. The pear flask was cooled to -78 °C and the crude propyltrichlorogermane obtained in the previous synthesis was added dropwise *via* syringe. The reaction was stirred for 2 hours. The ice/NaCl bath was removed and the reaction was stirred for 2 more hours, after which a water aspirator was used to pull the propylgermane (0.26 g, 3% overall yield) into the pear flask trap. **¹H NMR** (300 MHz, benzene-*d*₆): δ 0.72 (m, 2 H), 0.78 (t, J = 6 Hz, 3 H), 1.29 (sextet, J = 6 Hz, 2 H), 3.51 (t, J = 3 Hz, 3 H); **¹³C NMR** (75 MHz, benzene-*d*₆): δ 10.38, 16.68, 21.29; **GC-MS (EI):** m/z (% relative intensity) 119 (M^+ -1, 16), 116 (15), 103 (12), 89 (41), 74 (100).

Trapping of propene with bromine. A needle connected to the exit port of an SFR reactor was immersed in a solution of a few drops of bromine in chloroform-*d* in an NMR tube. Propylgermane or germacyclobutane (10 total injections in each case) was introduced into the SFR (furnace T=500 °C). NMR analysis of the resulting solution revealed the formation of 1,2-dibromopropane. ¹¹³ ¹H NMR (300 MHz, chloroform-*d*): δ 1.85 (d, *J* = 6 Hz, 3 H), 3.58 (t, *J* = 9 Hz, 1 H), 3.88 (dd, *J* = 6 Hz, 1 H), 4.28 (m, 1 H).

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II. DIGERMANE ADDITIONS TO ACETYLENES

A. Introduction

1. Disilane additions to acetylenes. Woodward-Hoffmann orbital symmetry theory^{1,2} has become one of the cornerstones of organic chemistry. It's ability to predict the stereochemical outcomes of concerted reactions has made it a powerful tool for understanding the electronic aspects of pericyclic reactions. For example, a concerted [2+2] mechanism for thermal decomposition of cyclobutane, described in the previous chapter, was able to be ruled out based on orbital symmetry rules. The orbital interactions involved in [2+2] cycloadditions are shown in Figure 1.

Figure 1. Orbital interactions in [2+2] cycloadditions.

These cycloadditions recently have become of interest in organosilicon chemistry due to the reactive nature of the Si-Si single bond. It is well known that a Si-Si sigma bond behaves remarkably like a C-C pi bond.³ For example, halogens “add” across a Si-Si single

bond, cleaving it in much the same way as halogens add to alkenes (Scheme 1).⁴ The Si–Si bond $\sigma \rightarrow \sigma^*$ transition occurs around 190 nm ($\text{Me}_3\text{Si–SiMe}_3$)⁵ as compared to the $\pi \rightarrow \pi^*$ transition at 165 nm for ethylene.⁶

Scheme 1. Reaction of halogens with Si–Si and C=C bonds.

However, with the exception of recent work in the Barton group (*vide infra*), the only [2+2] cycloadditions of disilanes studied were those involving transition metal (*e.g.*, palladium) catalysis.^{7,8} The first such report was by Sakurai *et al.*, who showed that cyclic disilanes (**1**) in the presence of a Pd(0) or Pd(II) catalyst added in a *cis* fashion to substituted acetylenes to yield disilacycloalkenes (**2**) (Scheme 2).⁹ Since then, various other intra- and intermolecular catalytic Si–Si additions have been explored, including additions to both alkenes^{10,11} and alkynes.^{12–14}

Scheme 2. Catalytic Si–Si addition to substituted acetylenes.

Despite the Si–Si sigma bond's chemical similarity to C–C pi bonds, only fairly recently have their thermal and photochemical [2+2] cycloadditions been investigated.^{15–17} The first example of such a reaction was the flow pyrolysis of disilacyclooctyne **3** Scheme 3).¹⁵ The thermally-allowed $[2_s+2_a]$ cycloaddition gave bicyclic compound **4** and tetraphenylbutatriene (**5**) in 70% yield. Semiempirical (AM1) calculations showed that the

expected $[2_s+2_a]$ transition state geometry was 14 kcal/mol lower in energy than the forbidden $[2_s+2_s]$ geometry while *ab initio* calculations on an intermolecular model system gave an activation entropy ($\Delta S^\ddagger$) of -35.16 cal/mol·K. AM1 calculations on **3** also revealed that the relative orientation of the Si-Si and C≡C bonds in **3** is very close to that in the $[2_s+2_a]$ transition state. Thus, it was postulated that the main barrier for the bimolecular reaction could be due to entropic factors.

Scheme 3. Flow pyrolysis of **3**.

In order to test this hypothesis, flow pyrolyses (Scheme 4) of acyclic congener **6** and of hexamethyldisilane (**9**) with phenylacetylene (**10**) were performed. In the latter case, no reaction was observed, possibly due to the large value of $\Delta S^\ddagger$, though these data do not provide definitive proof. In the case of acyclic **6**, in which free rotation frees it from being constrained in a $[2_s+2_a]$ geometry, silane **7** and trisilane **8** were formed exclusively from a silylene extrusion and insertion.

Scheme 4. Flow pyrolyses of acyclic and intermolecular analogues of **3**.

Two different disilacyclooctynes also were pyrolyzed to test the generality of the cycloaddition (Scheme 5). Hexasilacyclooctyne **13** did not undergo an intramolecular [2+2] addition, but instead thermally extruded dimethylsilylene, as had been previously observed for this¹⁸ and other^{19,20} polysilacycloalkynes. Dibenzodisilacyclooctyne **11**, on the other hand, did yield the apparent [2_s+2_a] cycloaddition product **12** upon flow pyrolysis at 550 °C. This isomer was found to be strongly photoluminescent (emission λ_{max} = 425 nm) with a rather impressive quantum yield (Φ_f = 0.68), making it a potential material for organic light-emitting diodes (LEDs).

Scheme 5. Other disilacyclooctyne pyrolyses examined.

The photochemical Si–Si addition next was explored. However, UV (254 nm) photolysis of **3** did not result in the expected product (**16**) of a photochemically-allowed intramolecular [2_s+2_s] addition (Scheme 6). Instead, isomer **15** and tetraphenylbutatriene (**5**) were isolated in 85% and 10% yields, respectively. A diradical mechanism initiated by homolytic Si–Si bond cleavage (Scheme 7) was proposed to explain the formation of **15**. The formation of tetraphenylbutatriene is easily explained by extrusion of two equivalents of dimethylsilanone (**17**) from the expected photoadduct **16** (Scheme 6). This explanation is supported by the results of catalytic decomposition of **3**. As catalytic [2+2] cycloadditions of Si–Si single bonds to C–C triple bonds typically yield *cis* adducts (*vide supra*), the

Scheme 6. Photolysis of **3**.

reaction of **3** with a Pd(II) catalyst also should give tetraphenylbutatriene as a product. This was in fact the case; addition of catalytic amounts of Pd(OAc)₂ and 1,1,3,3-tetramethylbutyl isocyanide gave **5** as the sole product in 100% yield after column chromatography.

Scheme 7. Proposed mechanism for formation of photoisomer **15**.

Photolysis of cyclic hexasilaalkyne **13** expectedly¹⁸ yielded the same ring-contracted product **14** obtained in its thermolysis (Scheme 5). The surprising result came upon photolysis of **11** (Scheme 8). Instead of the allowed $[2_s+2_s]$ isomer **18**, only thermoisomer **12** was formed, and in 92% yield! These results were remarkable because, if the reaction indeed were a concerted process, it would be the first example of a forbidden photochemical $[2_s+2_a]$ cycloaddition.^{1,2}

Scheme 8. Photolysis of **11**.

Trapping experiments were performed in order to shed more light on the mechanism of this puzzling rearrangement (Scheme 9). The possibility of a homolysis mechanism was explored first, but photolysis of **11** in neopentyl chloride failed to yield **20**, the expected product of intermolecular reaction with diradical **19**. Likewise, a silene intermediate (**21**) formed by photochemically-induced 1,3-silyl migration, a precedented²¹ reaction, was not trapped in the methanol-solvated photolysis. Instead, methoxysilane **23** was obtained in 76% yield (24% **12**), suggesting an electron-transfer mechanism (Scheme 10), though the failure to trap both **19** or **21** does not rule out a mechanism involving either homolysis or 1,3-silyl migration.

Scheme 9. Trapping experiments in the photolysis of **11**.

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