The photochemistry of trimethylsilyltriphenylgermane (Ph₃GeSiMe₃), triphenylsilyltrime-
thylgermane (Ph₃SiGeMe₃), and 1,1,1-trimethyl-2,2,2-triphenyldigermane (Ph₃GeGeMe₃) has been studied in hydrocarbon solution by steady state and laser flash photolysis methods and is compared to previously reported data for the homologous disilane Ph₃SiSiMe₃. A variety of products are formed upon photolysis of the three compounds in the presence of 2,3-dimethyl-1,3-butadiene or chloroform, but in each case the major ones are derived from M–M′ bond homolysis and dimethyl- or diphenylgermylene extrusion. The trapping products of the 1,3,5-(1-metalla)hexatriene derivatives formed by [1,3]-MMe₃ migration into the ortho-
position of one of the phenyl rings are formed as well, in yields of 9–30%. While these experiments indicate that germylenes are formed in at least twice the yield of the 1,3,5-(1-
metalla)hexatrienes, only the latter and triphenylsilyl or triphenylgermyl radicals can be detected by laser flash photolysis techniques. The metallaenes have been identified on the basis of their time-resolved UV absorption spectra and absolute rate constants for reaction with 2,3-dimethylbutadiene, methanol, acetone, acetic acid, oxygen, and carbon tetrachloride and can be distinguished from germylenes by their lack of reactivity toward triethylsilane and chloroform. Radical formation is shown to result from reaction of the triplet states of these compounds, and a triplet lifetime is estimated for Ph₃GeSiMe₃ and compared to that of the disilane homologue. The results of time-resolved experiments on other, related compounds are discussed in light of these results.

Introduction

The photochemistry of arylsilanes has been extensively investigated over the past 25 years. In general, photolysis of these compounds leads to the formation of three distinct types of reactive intermediates, in relative yields that vary markedly depending on the degree of aryl substitution in the disilane and on the solvent. This complexity is most aptly demonstrated by the photochemistry of methylpentaphenylsilane (1), which yields silenes 2 and 3 by [1,3]-SiPh₂Me migration and dehydrosilylation (elimination of H–SiPh₃ (4)), respectively, and the silyl free radicals 5 and 6 by Si–Si bond homolysis (Scheme 1). The (1-sila)hexatriene 2 by concerted [1,3]-silyl migration is relatively minor in 1, but is quite frequently the major photoreaction of arylsilanes in solution.

1,1,1-Trimethyl-2,2,2-triphenyldimetallanes (Ph₃MM′Me₃; M, M′ = Si, Ge). Direct Detection and Characterization of Silene and Germene Reactive Intermediates

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The opposite is true of the dehydrodisilylation reaction to produce silene 3. Both these reaction pathways are singlet-derived; silyl free radical formation results from the triplet state of the disilane and hence can be made to predominate either by enhancing intersystem crossing through adjustment of the solvent polarity or by slowing down the singlet-derived reaction pathways by attaching sterically bulky substituents.

Disilanes are the simplest congeners of higher oligosilanes and polysilanes, whose photochemical and photophysical behavior has also been of considerable interest. The photochemistry of trisilanes and higher oligosilanes is usually characterized by predominant extrusion of silylene reactive intermediates, a process of relatively minor importance in aryldisilanes except in the presence of special structural constraints.

Laser flash photolysis studies of aryldisilanes have provided a wealth of mechanistic information on the reactions of transient silenes with various "silenophiles" such as alcohols, ketones and aldehydes, carboxylic acids, dienes, and oxygen, as well as important insight into various aspects of disilane photochemistry and the effects of substrates on disilane photochemistry. In this paper, we report the results of a study of the photochemistry of the Si

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\text{Ph}_3\text{MMMe}_3
\]

and of 1,1,1-trimethyl-2,2,2-triphenyl-digermesilylene (7d) by steady state and laser flash photolysis techniques. Our intent was to examine, in a systematic way, the changes induced in the photochemistry of 7a as a result of replacement of first one and then both of the silicon atoms with germanium. We anticipated (based on literature precedent; vide infra) that photolysis of these compounds might afford the corresponding (1-metalla)hexatriene reactive intermediates in high enough yields that they might be detected by flash photolysis methods, thus affording the opportunity to broaden the scope of our studies of the differences in the reactivity of silicon- and germanium-carbon double bonds.

Previously reported work on 7a, and a related series of compounds (9b–d) by Mochida and Gaspar and their co-workers suggests that reactive intermediates of this type are formed in significant yields in the photolysis of arylgermasilanes, but in minor amounts relative to silyl and/or germyl radicals and dimethylgermylene. Germylene formation is even more dominant in the photochemistry of FeII-germasilane and -silagermane complexes, where the efficiency of the reaction appears not to depend greatly on which of the two group 14 atoms is attached to the metal center.

Photochemistry of the trimethyltriphenylgermasilane (8a) yields cleanly and in high yield the (transient) 1,1-diphenyl-(1-sila)hexatriene derivative 8b, which can easily be detected and studied by such methods. In contrast, photolysis in more polar solvents leads to high yields of the corresponding silyl free radicals, with 8b being formed in low (but still detectable) amounts. The remarkable sensitivity of the photochemistry of this compound to solvent polarity provided the impetus for the discovery that silyl free radicals are formed via the triplet state of the disilane and hence can be made to predominate either by enhancing intersystem crossing through adjustment of the solvent polarity or by slowing down the singlet-derived reaction pathways by attaching sterically bulky substituents.

In this paper, we report the results of a study of the photochemistry of the trimethyltriphenylgermasilane derivatives 7b,c and of 1,1,1-trimethyl-2,2,2-triphenyl-digermesilylene (7d) by steady state and laser flash photolysis techniques. The compound to solvent polarity provided the impetus for the discovery that silyl free radicals are formed via the triplet state of the disilane and hence can be made to predominate either by enhancing intersystem crossing through adjustment of the solvent polarity or by slowing down the singlet-derived reaction pathways by attaching sterically bulky substituents.

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Photolyzed amount of 7 is one of the Ph₃M-rM e₃M factors. This method underestimates the yields of the as simple percentages of the total detectable products, J. Organomet. Chem. P. P.

The product yields listed were determined by ¹H NMR spectroscopy on crude photolysis mixtures in C₆D₁₂ solution, which showed the yields of 12 and 13 to be relatively low molecular weight products (13Me and 16) because they elute much earlier than the starting material and other products. This was verified by ¹H NMR spectroscopy on crude photolysis mixtures in C₆D₁₂ solution, which showed the yields of 12 to be similar to those of 13 in the photolyses of 7b-d; the same was found to be true of the relative yields of 13 and 16 in the photolyses of 7c,d. The three photolyses also contained several other minor products, each of which was formed in yields of less than ~3%. The material balances (starting material + identified products) were determined to be on the order of 65–75% after ca. 50% conversion of starting material in all three cases.

Compounds 11b and 11c, which were isolated, exhibited spectroscopic data similar to those reported previously for 11a⁹ and the DMB adducts of 10b,c.⁴³,⁴² A pure sample of 11d could not be isolated in sufficient quantities for rigorous characterization and so was obtained by ³¹P NMR spectroscopy of the dimeric free radicals consistent with disproportionation of Ph₃M⁺ radicals from the molecular ion, a fragmentation pathway that is relatively minor in compounds 11a,b. The product mixtures also contained four isomeric compounds with similar but slightly lower GC retention times than the precursors (7); these are collectively identified in eqs 1–3 as 15Ge (from 7b,d), 15Si (from 7c). They were tentatively identified on the basis of their mass spectra as dimers of the carbon-centered free radicals (17) derived from addition of Me₃M⁺ to the diene, as shown in eq 4. The mass spectra of the four (C₉H₁₉Si)₂ isomers (15Si) are identical and exhibit a weak molecular ion (M⁺ = 310), prominent (M/2)⁺ ions, and a (M⁺ = 73) parent ion due to Me₃Si. The spectra of the germanium analogues (15Ge) are also identical to one another and contain the M⁺ = 119 (Me₃Ge) parent ion, but show only the (M/2)⁺ ion in the higher mass range. The relative yields of the four isomeric products were the same from 7b and 7d. The corresponding products from trapping of Ph₃M⁺ radicals were not detected in the photolyses, not unexpectedly considering their very high molecular weights.

The mechanism for formation of Ph₃M-H (14Si and 14Ge) is not clear. The mass spectra of these compounds formed in the photolyses of 7b-d in C₆H₁₂ and C₆D₁₂ indicated that no deuterium was incorporated in either of these products in the deuterated solvent, indicating that they are not formed from reaction of Ph₃M⁺ radicals with the solvent. Furthermore, no evidence could be obtained for the presence of products that might be consistent with disproportionation of Ph₃M⁺ and 17 in any of the three cases. Since these products would have the same molecular formula as those derived from trapping of Me₃M=CH₂ by the diene (C₆H₁₂M⁵⁺), we can similarly rule out the possibility that 14 is formed by either Ph₃M⁺/Me₃M⁺ disproportionation or concerted dehydrometalation. At an early point in the study, photolyses of 7b-d were carried out in hexane containing m-decalin (0.1 M), to probe for the formation of Me₃M=CH₂ by trapping with the alcohol. The expected alkoxymetallanes (18) are indeed formed under these conditions, but are accompanied by increased yields of 14 in all three cases. Thus, the most likely mechanism for formation of 18 in these experiments is direct reaction of the alcohol with the excited singlet states of 7b-d, a reaction that is particularly well established to occur with arylsilanes.²⁶,⁴⁰ We have not explored the point further.

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(39) Product yields are listed as simple percentages of the total photolyzed amount of 7, although the majority of them contained only one of the Ph₃M or Me₃M groups of the precursors. This was taken into account for determination of material balances.
formation of 19M and 22M is ascribed to reaction of Ph3M+ and Me3M+ radicals with the halocarbon. The resulting dichromyl radicals then dimerize to yield 20 or abstract hydrogen (most likely from the triphenylmetallanes (14), which could not be detected in the photolysis by either GC or NMR) to yield CH2Cl2 (21). The much higher relative yields of radical-derived products in these experiments, compared to those in the presence of 0.5 M DMB, provide good evidence that they are formed predominantly (if not completely; vide infra) via the triplet states of 7b–d.

These results suggest that the lowest excited singlet states of the three molecules react via two competing pathways to form reactive intermediates which are subsequently trapped by DMB: [1,3]-SiMe3 or [1,3]GeMe3 migration to yield the (1-metallal)hexatriene species 8b–d (trapped by DMB as 11) and extrusion of dimethyl- or diphenylgermylene (trapped by DMB as 13) with the concomitant formation of Ph3MC2H (12M) or PhM′(C1H2)3 (16M). Germylene extrusion is the dominant excited singlet state reaction pathway in each case and particularly prominent in the case of 7d. This process does not occur in significant yields upon photolysis of the disilane analogue 7a13,19,20 Free radical formation occurs in much higher yields from 7b–d than it does from 7a,13 perhaps indicating that intersystem crossing is enhanced in the germanium-containing compounds compared to the disilane.

Direct Detection and Identification of Reactive Intermediates by Laser Flash Photolysis. Laser flash photolysis experiments employed continuously flowing, deoxygenated hexane solutions of 7b–d (5 × 10−4 M) and a KrF excimer laser as excitation source (248 nm, 20 ns pulses, 50 mJ). Transient absorption spectra recorded 0.2–1.0 μs after the laser pulse are shown in Figure 1 for 7b and 7c, along with typical transient decay traces recorded at short (320–300 nm) and long (480–490 nm) wavelengths. In both cases, the spectra consist of absorptions due mainly to two transient species. The 330 nm wavelength transient absorptions are readily identifiable as due to triphenylsilylethyl (from 7b) and triphenylgermyl (from 7c) radicals, on the basis of comparisons to the published spectra41,42 and the fact that they are quenched by chloroform with rate constants on the order of kq ∼ (1.7 ± 0.2) × 106 M−1 s−1, which is also in excellent agreement with literature data.41 The published spectra of these radicals also show evidence for a weaker absorption band centered at ~450 nm,41 which is obscured in the spectra of 7b,c by the long wavelength bands due to the second transient species. However, the lifetime of the latter can be shortened to <20 ns upon addition of methanol to the solution (vide infra), and under these conditions spectra that are in excellent agreement with the literature spectra of these radicals are obtained.

Addition of trans-1,3-octadiene to the solutions of 7b–d caused reductions in the initial ΔOD’s at 330 nm, indicating that free radical formation is suppressed upon addition of the diene. This is consistent with the process being derived from the triplet states of 7b–d, as suggested above. On the other hand, the initial ΔOD’s at 480–490 nm were unaffected by the addition of diene (beyond the slight reductions expected due to screening of the excitation light by the diene), indicating these products to be singlet-derived. Quenching of radical formation by the diene was investigated quantitatively in the case of 7c, by monitoring the ΔOD330 as a function of diene concentration. To correct for screening of the excitation light by the diene and minor variations in laser intensity, the ΔOD330 value at each diene concentration was normalized against the ΔOD at 490 nm; the resulting Δ OD330 Δ OD490 ratios are thus proportional to the quantum yield for radical formation (relative to that for formation of the 490 nm species) at each diene concentration. A plot of the data according to the Stern–Volmer expression of eq 6 is shown in Figure 2. The slope is the product of the lifetime and rate constant for quenching by diene of the triplet state of the germasilane (kqTR = 21.4 ± 1.3 M−1) and affords an estimate of 2.7 ± 0.3 ns for the lifetime of the triplet state of 7c, assuming a value of kq = 8 × 109 M−1 s−1.43 This compares favorably with our previously reported estimate of τR = 6 ± 3 ns for the triplet lifetime of 7a, determined under similar conditions.17

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(\Phi_3/\Phi)_{Ph3Ge} = (\Delta OD_{330}/\Delta OD_{490})/(\Delta OD_{330}/\Delta OD_{490}) = 1 + k_{qTR}(\text{diene})
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The value of the Stern–Volmer constant determined above for 7c is large enough that under the conditions of our steady state photolysis experiments in the presence of 0.5 M DMB (vide supra), the triplet state of this compound should be quenched with more than 90% efficiency. The fact that significant yields of radical-derived products are still observed thus indicates that radical formation is probably both singlet- and triplet-derived in 7b–d. While photolysis of the disilylethyl derivative (7a) leads to Si–Si bond homolysis only in polar solvents via reaction of the lowest triplet state,17,19 we really cannot rule out the possibility that some portion of the reaction may be derived from the lowest excited singlet state in this case as well.


Addition of methanol (MeOH), DMB, acetone, acetic acid, carbon tetrachloride, or oxygen to the solutions of Ph₃SiGeMe₃ (7b) resulted in an increase in the pseudo-first-order rate constant for decay of the long-wave-length transient absorption. Plots of $k_{\text{decay}}$ versus concentration of added reagent were curved for methanol (Figure 3a), but fit acceptably to the second-order polynomial expression shown in eq 7, where $k_{d0}$ is the decay rate constant in the absence of methanol, and $k_{\text{MeOH}}$ and $k_{2\text{MeOH}}$ are the overall second- and third-order rate constants for reaction of the transient with the alcohol. Similar plots for the other reagents were linear in concentration and were thus analyzed according to eq 8. Representative plots of $k_{\text{decay}}$ vs concentration for the quenching of the long wavelength transient from 7b by MeOH, acetic acid, DMB, and acetone are shown in Figure 3. Of the six reagents examined, only oxygen, DMB, and carbon tetrachloride affected the lifetime of the triphenylsilyl radical absorption at 330 nm as well as that of the longer wavelength transient. In contrast, addition of chloroform to the solution had no effect on the lifetime of the long wavelength transient absorption within the concentration range examined ([CHCl₃] < 0.02 M), but quenched that of the radical efficiently (vide supra).

The lifetime of the 480 nm transient absorption from photolysis of Ph₃GeSiMe₃ (7c) was also quenched upon addition of DMB, HOAc, acetone, carbon tetrachloride, or oxygen, but with the exception of the halocarbon, quenching was much less efficient than with the analogous transient from 7b. The decay rate constants varied in direct proportion to concentration of added reagent in each case, as is illustrated by the quenching plots shown in Figure 4 for reaction of the transient with acetic acid, DMB, and acetone. Again, addition of up to ~0.06 M chloroform had no effect on the lifetime of the long wavelength absorption, but quenched the radical absorption at shorter wavelengths. Addition of up to 1.7 M MeOH had no discernible effect on the lifetimes at either monitoring wavelength.

The transient absorption spectrum recorded by flash photolysis of a deoxygenated hexane solution of Ph₃GeGeMe₃ (7d) showed similarities to those from the other two compounds (Figure 5a), but the long wavelength absorption band was significantly less intense than the short wavelength absorption at 330 nm. Still, transient decays recorded at the two wavelengths showed marked differences in lifetime, indicating that two different transient species are being observed. As with 7c, addition of 0.065 M chloroform to the solution shortens the lifetime of the 330 nm transient to <25 ns (consistent with its assignment to triphenylgermyl radicals) but has little effect on that of the 480 nm transient ($\tau \approx 2.5 \mu$s). This allows isolation of the spectrum due to the long-wavelength-absorbing species, as is shown in Figure 5b. Addition of DMB, carbon tetrachloride, or oxygen to the chloroform/hexane solutions of 7d resulted in shortening of the lifetime of this transient, and the transient decay rate varied linearly with concentration. Quenching by HOAc, acetone, and MeOH was not investigated in this case.
spectra and reactivity of hexatriene derivative assigned to the 7-trimethylgermyl-substituted 1-silahexatriene of the quenchers examined, suggesting it should be strikingly similar rate constants for reaction with all of the transient 1-silahexatriene (solid lines represent the best fits of the data to eq 8). The similarities in the UV absorption spectrum nearly identical to that of 7b, 1,1-diphenylgermene, on the basis of experiments in which the two compounds can be expected to react rapidly with Me$_2$Ge:. Finally, the extinction coefficient of the long wavelength (325 nm, 28,29,47) of the transient obtained from germasilane (8b) can be expected to be at least an order of magnitude larger than that of the (n,p) absorption of dimethylgermylene; this leads to the expectation that the absorption due to 8b should be at least 5 times greater than for the germylene, given they are formed in relative yields of 1:2.46

Similarly, we assign the 480 nm transient products observed by flash photolysis of 7c,d to the 1-germahexatrienes 8c,d. These two compounds can be expected to exhibit absorption maxima and extinction coefficients similar to the silicon analogues 8a,b, since 1,1-diphenylsilane (23a) and 1,1-diphenylgermene (23b) exhibit nearly identical UV absorption spectra in hydrocarbon solvents ($\kappa_{\text{max}} = 325$ nm, 28,29). The transient assigned as 8c also exhibits the expected decrease in reactivity compared to 8a,b toward the nucleophilic quenchers MeOH, HOAc, and acetone, judging from a comparison of the absolute reactivities of 23a and 23b toward these same reagents.28,29 While assignment of this transient to Me$_2$Ge:, which our product studies show is formed in roughly twice the yield of 8b (eq 1), can be ruled out on the basis of several arguments. First, dimethylgermylene has been reported to exhibit an absorption maximum in the 420-450 nm range in hydrocarbon solvents at room temperature,23,36,37,44 significantly lower than the absorption maximum of the transient obtained from germasilane 7b. Second, the transient shows the same high reactivity toward methanol (and the other five reagents) as 8a; dimethylgermylene is known to be relatively unreactive toward alcohols ($k_{\text{ROH}} \ll 10^3$ M$^{-1}$ s$^{-1}$).37,45 Third, the transient shows no detectable reactivity toward triethylsilane and chloroform, reagents which are known or can be expected to react rapidly with Me$_2$Ge:. 23a and 23b exhibit absorption maxima and extinction coefficients nearly identical to that of 7b, 1,1-diphenylgermene, on the basis of experiments in which the two compounds can be expected to react rapidly with Me$_2$Ge:. 23a and 23b exhibit absorption maxima and extinction coefficients nearly identical to that of 7b, 1,1-diphenylgermene, on the basis of experiments in which the two compounds can be expected to react rapidly with Me$_2$Ge:.
nucleophilic quenching of 8d was not investigated, the similarities in the rate constants for quenching by DMB, oxygen, and CCl4 to those for 8c provides reasonably compelling support for its assignment. Again, the alternative assignment of these transients to diphenyl- or dimethylgermylene can be ruled out by their lack of reactivity toward triethylsilane and/or chloroform; furthermore, the product studies indicate that their yields relative to those of 8c,d are too low (when the differences in extinction coefficient are factored in) for them to dominate the observed transient absorption spectra.

Attempts to obtain direct evidence for germylene formation from 7b,c by laser flash photolysis have been unsuccessful in both cases. Flash photolysis of 7b in hexane containing 0.1 M MeOH, to shorten the lifetime of the (1-sila)hexatriene 8b to <100 ns, afforded a transient absorption spectrum assignable to only Ph3Si+. The long wavelength absorption band in the spectrum of the radical is expected to overlap with that due to dimethylgermylene, yet the decay kinetics in this monitoring wavelength range were identical to those measured at the maximum of the short wavelength absorption band of the radical at ~330 nm. Furthermore, addition of triethylsilane or n-bromohexane had no effect on the lifetime at either wavelength. Since product studies indicate that the yield of Me2Ge: from 7b is in fact fairly high (vide supra), our failure to detect the germylene by flash photolysis is presumably due to its low expected extinction coefficient compared to that of the radical. Similar results were obtained in flash photolysis experiments with 7c in methanolic hexane solution.

Steady state photolysis of a hexane solution of 7b containing 0.5 M DMB and up to 4 M triethylsilane led to the formation of no new products and no reduction in the yield of 13Me relative to that of 12Si compared to that obtained in the absence of silane. This is surprising, since Me2Ge: has been reported to be only 5 times less reactive toward hydridosilanes than DMB on the basis of time-resolved quenching experiments using permethylcyclopolygermanes as germylene precursors.36,37,44 We do not understand the reasons for this, although it should be pointed out that the published kinetic results were not actually accompanied by supporting product studies.

It is interesting to note that the trends in the absolute reactivity of (1-germa)hexatriene 8c toward O2, CCl4, DMB, and MeOH are very similar to those reported by Mochida and co-workers for Me2Ge:, using permethylcyclopolygermanes as germylene precursors.37,44 We believe that these unanticipated similarities have led to erroneous assignments in some of the time-resolved studies of Me2Ge: and Ph2Ge: in solution which have been reported, in particular, those that have employed arylgermasilanes (e.g., 9c31,32) or aryl(disila)germanes (e.g., 2438) as germylene precursors. While steady state

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Table 1. Absolute Rate Constants (in units of 10⁻⁸ M⁻¹ s⁻¹) for Quenching of Transient 1-Metallahexatrienes (8a–d) by 2,3-Dimethyl-1,3-butadiene (DMB), Acetone, Acetic Acid, Methanol, Oxygen, Carbon Tetrachloride, and Triethylsilane in Hexane Solution at 23 °C

<table>
<thead>
<tr>
<th>Quencher</th>
<th>8a</th>
<th>8b</th>
<th>8c</th>
<th>8d</th>
</tr>
</thead>
<tbody>
<tr>
<td>DMB</td>
<td>0.30 ± 0.01</td>
<td>0.34 ± 0.03</td>
<td>0.030 ± 0.003</td>
<td>0.027 ± 0.002</td>
</tr>
<tr>
<td>acetone</td>
<td>5.42 ± 0.05</td>
<td>5.68 ± 0.06</td>
<td>0.0021 ± 0.0005</td>
<td>b</td>
</tr>
<tr>
<td>acetic acid</td>
<td>3.49 ± 0.48</td>
<td>2.21 ± 0.20</td>
<td>0.0039 ± 0.0005</td>
<td>b</td>
</tr>
<tr>
<td>MeOH</td>
<td>(1.1 ± 0.4)⁺</td>
<td>(1.5 ± 0.8)⁺</td>
<td>&lt; 0.001⁺</td>
<td>b</td>
</tr>
<tr>
<td>(5 ± 12)[MeOH]</td>
<td>(55 ± 13)[MeOH]</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>O₂</td>
<td>1.9 ± 0.2</td>
<td>1.6 ± 0.10</td>
<td>0.961 ± 0.045</td>
<td>0.94 ± 0.05</td>
</tr>
<tr>
<td>CCl₄</td>
<td>1.1 ± 0.1</td>
<td>1.2 ± 0.1</td>
<td>0.29 ± 0.03</td>
<td>0.35 ± 0.03</td>
</tr>
<tr>
<td>HSiEt₃</td>
<td>&lt; 0.0001</td>
<td>&lt; 0.0004⁺</td>
<td>&lt; 0.0004⁺</td>
<td>b</td>
</tr>
</tbody>
</table>

* From polynomial least-squares fitting of kₜₚ decay vs [Q] data according to eqs 7 or 8. Errors are quoted as ±2σ. *b Not determined. *c Addition of up to 1.7 M MeOH had no effect on the lifetime in deoxygenated solution. *d Addition of up to 4 M HSiEt₃ had no effect on the lifetime in deoxygenated solution.
trapping experiments clearly demonstrate that in both cases Me₂Ge: and Ph₂Ge: (respectively) are the major products of photolysis of these compounds in solution, they also show that the corresponding (1-germa)hexatriene derivatives are formed as well in significant yields. Flash photolysis of 9c and 24 was reported to lead to the formation of transients absorbing in the 420–460 nm region, which were assigned to the germylenes on the basis of their absorption maxima, the fact that in the absence of trapping agents they decay with second-order kinetics (consistent with dimerization to the corresponding digermene, whose second-order growth was also observed), and on the basis of absolute rate constants for reaction with reagents such as O₂, DMB, CCl₄, MeOH, and Et₃SiH. However, several of these rate constants (in particular, those for reaction with Et₃SiH) are in clear disagreement with those determined using other Me₂Ge:36,37,45 and Ph₂Ge:36 precursors. On the basis of what we now know of the effects of substituents on the UV spectra and reactivity of transient silenes and germenes of homologous structure in solution,19,28,29,47–49 information that was not available at the time of the original studies, the data reported are more in line with those expected for the (1-germa)hexatriene analogues 10c and 25, respectively.

Comparison of the Reactivities of the Si–C and Ge=C Bonds in 8a–d. As mentioned earlier, the (1-sila)hexatriene derivatives 8a,b are roughly 3 orders of magnitude more reactive than the germanium analogues 8c,d toward methanol, acetic acid, and acetone (Table 1), a difference that is also mirrored in the simpler M=C derivatives 23a,b.9 Both silenes and germenes react with alcoholic reagents (and probably acetic acid as well50) via a mechanism involving initial complexation of the nucleophile at the heteroatom, followed by proton transfer,7,26,51,52 In the case of silenes, the proton-transfer step occurs by two competing mechanisms, one involving unimolecular migration of the proton from oxygen to carbon and one involving catalysis by a second molecule of alcohol. Kinetically, the result of this is a mixed first- and second-order dependence of the silene/germene decay rate constant on alcohol concentration.7,26 The much lower reactivity of germenes compared to silenes toward nucleophiles can be explained as due primarily to the higher electronegativity of germanium relative to silicon, which leads to a less polar M=C bond.28,29 This has the effect of slowing down the initial complexation step of these reactions and, because the complex is weaker, of reducing the rate at which it collapses to product by intramolecular proton transfer relative to reverting to starting materials.

On the other hand, the reactivities of these compounds toward the diene, oxygen, and carbon tetrachloride are much less dependent on the identity of the group 14 heteroatom than is the case with nucleophilic quenchers. These three reagents do not react with silene 23a at measurable rates in solution (k ≤ 10⁷ M⁻¹ s⁻¹),53 from which it can be concluded that their unusually high reactivity toward 8a,b is due to the unique structure of the (1-sila)hexatriene system, which appears to accentuate reactivity (compared to simpler metalloene systems) via biradical or biradicaloid mechanisms.19

The reaction of simple silenes and germenes with aliphatic dienes proceeds nonconcertedly, generally to yield a mixture of ene-, [2+2]-, and [4+2]-cycloaddition products.54–58 In contrast, the reaction of 8a with DMB proceeds largely via ene-addition, although there is at least one other minor product formed in yields that are too low to allow isolation.19 The same is true of 8b–d, according to GC/MS analysis of the reaction mixtures. We thus conclude that the reaction of dienes with 8 is also nonconcerted, most likely involving the biradical intermediate (26) shown in eq 9. The enhanced reactivity of 8 compared to simpler silenes and germenes presumably results from the facts that the initial step involves formation of a biradical with significantly greater resonance stabilization and that collapse of the biradical to the ene-adduct 11 enjoys an additional driving force due to aromatization. In this reaction, the germanium analogues 8c,d are roughly 10 times less reactive than the silicon analogues 8a,b.

Reaction of oxygen with arylsilane-derived 1-(sila)hexatrienes such as 10a and 8a proceeds with bimolecular rate constants on the order of 10⁹ M⁻¹ s⁻¹ and yields phenyltrimethylsilane (16Si) and silane oligomers (eq 9; M = M = Si).19 The reaction presumably must proceed via a triplet biradical intermediate (27) such as that shown in eq 10, although the mechanism for collapse of the biradical to the observed products is not well understood. It is interesting to note that the products correspond formally to those of R₂Si: extrusion of

from the disilane. Similar products are known to be formed upon reaction of silenes of this type with dimethyl sulfoxide. To verify that quenching of the 480–490 nm transients from flash photolysis of 7b and 7c with oxygen results in the same chemistry (and to provide further evidence consistent with their assignment), the two germasilanes were photolyzed in oxygen-saturated cyclodexane solution. As expected, photolysis of 7b under these conditions led to the formation of phenyltrimethylgermane (16Ge, 7%), a product that is not formed in the absence of oxygen. Similarly, photolysis of 7c under these conditions led to an enhancement in the yield of 16Si, relative to that obtained in experiments in nitrogen-saturated solution.

Presumably, reaction of 8 with CCl4 also proceeds via a radical mechanism, which would explain the similar reactivities of 8a,b and 8c,d, as well as the fact that simpler silenes and germenes such as 23a,b show much lower reactivity toward this reagent. It seems most likely that the reaction is initiated by electron transfer, on the basis that quenching of 8a–d by CCl4 is at least 100 times faster than by chloroform. The mechanistic details are extremely difficult to ascertain, because CCl4 reacts rapidly with the excited singlet states of arylsilyl or arylgermyl radicals (including 7a) by electron transfer, which ultimately results in Si–Si bond cleavage and the formation of the corresponding chlorosilanes. Similar behavior can be expected for 7b–d.

Summary and Conclusions

The direct irradiation in solution of arylgermasilanes and -digermes of the general structure Ph3GeMe3 (7b–d) leads mainly to M–M' bond homolysis, at least partially via the lowest excited triplet state which is partially via the lowest excited triplet state which is in competition with the formation of a mixture of germene, silene, and germene reactive intermediates. The latter are formed in similar yields and can be trapped by aliphatic dienes. This same general behavior has been reported previously for other arylgermasilanes and -digermes,30–32 as well as aryl-silasgermanes38 and aryltrigermes.36,45 As with the disilane analogue 7a, flash photolysis of 7b–d results in the formation of strong transient absorptions due to arylsilyl or arylgermyl radicals (λmax = 330–355 nm), superimposed on absorptions due to a second transient species which absorbs at longer wavelengths (λmax = 480–490 nm).

In the case of Ph3SiGeMe3 (7b), this transient reacts with MeOH, AcOH, acetone, DMB, O2, and CCl4 in hydrocarbon solution with rate constants nearly identical to that of the (1-sila)hexatriene (8a) observed under similar conditions from Ph3SiSiMe3 (7a) and can thus be identified as the (1-sila)hexatriene derivative 8b. Neither the absorption maximum nor the reactivity of the transient is consistent with a possible alternative assignmen to Me2Ge, on the basis of the various studies of this transient germene that have been previously reported. This is not unexpected, since product studies indicate that the germene is formed in only ca. twice the yield of 8b, and the extinction coefficient of the long wavelength n,p absorption band of the germene can be expected to be at least an order of magnitude lower than that of the π,π* absorption band of the silene.46

The long wavelength transient from flash photolysis of Ph3GeSiMe3 (7c) absorbs with λmax ≈ 480 nm and reacts with nucleophilic quenchers (HOAc, MeOH, and acetone) with rate constants that are on the order of 104 lower than those for reaction of 8a,b with the same reagents. Much higher reactivity is observed toward O2, CCl4, and dienes, with absolute rate constants that are only 2–10 times lower than the corresponding values for reaction of 8a,b. The transient has been assigned to the (1-germa)hexatriene 8c on the basis of these data. Again, an alternative assignment to Ph3Ge:, which product studies suggest is formed in roughly twice the yield of 8c, can be ruled out on the basis of the extinction coefficient arguments discussed earlier, its low reactivity toward triethylsilane and chloroform, and the fact that Ph3Ge: has been reported to absorb at somewhat shorter wavelengths (λmax, 445–460 nm29,35,36,38,60) than the transient observed from 8c. A transient with the same absorption maximum and identical reactivity toward O2, CCl4, and DMB is observed in the case of the digermane 7d and is identified as (1-germa)-hexatriene 8d.

The 1000-fold lower reactivity of 8c,d compared to 8a,b toward oxygen-containing nucleophilic trapping agents such as alcohols, carboxylic acids, and ketones parallels the differences reported previously for 1,1-diphenylsilene (23a) and 1,1-diphenylgermene (23b).28,29 Much smaller differences in reaction rate are observed for DMB, O2, and CCl4 reagents that are normally relatively unreactive toward either silenes or germenes of simpler structure (e.g., 23a,b). This unusually high, relatively indiscriminate reactivity is presumably due to the presence of the cyclohexasilanyl substituent at the metallaene carbon atoms in 8a–d, which would clearly be expected to promote reactions that proceed through radical or biradical intermediates.

Experimental Section

1H and 13C NMR spectra were recorded on Bruker AC200 or DRX500 NMR spectrometers in deuterated chloroform solution and are referenced to tetramethylsilane. Ultraviolet absorption spectra were recorded on Hewlett-Packard HP8451 or Perkin-Elmer Lambda 9 spectrometers. Low-resolution mass spectra and GC/MS analyses were determined using a Hewlett-Packard 5890 gas chromatograph equipped with a HP-5971A mass selective detector and a DB-5 fused silica capillary column (30 m × 0.25 mm; Chromatographic Specialties, Inc.). High-resolution desorption electron impact (DEI) mass spectra and exact masses were recorded on a VGH ZAB-E mass spectrometer. Exact masses employed a mass of 12.000000 for carbon. Infrared spectra were recorded on a BioRad FTS-40 FTIR spectrometer and are reported in wavenumbers (cm⁻¹).

Analytical gas chromatographic analyses were carried out by GC/MS or using a Hewlett-Packard 5890 gas chromatograph equipped with a flame ionization detector, a Hewlett-Packard 3396A recording integrator, conventional heated splitless injector, and a DB-1 fused silica capillary column (15 m × 0.20 mm; Chromatographic Specialties, Inc.). Semi-preparative GC separations employed a Varian 3300 gas chromatograph equipped with a thermal conductivity detector and a 6 × 0.25” stainless steel OV-101 packed column.
(Chromatographic Specialties). Radial chromatographic separations employed a Chromatotron (Harrison Research, Inc.), 2- or 4-mm silica gel 60 thick-layer plates, and hexane/ethyl acetate mixtures as eluant.

Hexane (BDH Omnisolv) was used as received without additional purification or drying. Methanol, 2,3-dimethyl-1,3-butadiene, acetone (HPLC grade), acetic acid, chloroform, and carbon tetrachloride were used as received from Cambridge Isotope Labs. Compounds 7b–d were prepared and purified as previously reported.61 Solutions of 7b–d (0.1 g, 3.66 × 10⁻⁴ mol) in hexane (15 mL) containing 2,3-dimethyl-1,3-butadiene (0.5 M) were placed in quartz tubes, which were then sealed with rubber septa and deoxygenated with a stream of dry argon. The samples were then photolyzed for 1 h in a Rayonet reactor equipped with a merry-go-round and six RPR2537 lamps, with periodic monitoring of the course of the photolysis by GC. Methyltriphenylsilane (12αi), triphenylsilane (14αi), trimethylphenylsilane (16αi), methyldiphenylgermylene (12αe), trimethylgermylene (16αe), and trimethylphenylgermane (16αg) were identified by GC and/or GC/MS co-injection with authentic samples obtained from Aldrich or synthesized by known routes. The germylene-diene adducts 13αe and 13αg were isolated by semipreparative GC, from the photolysis mixtures from 7b and 7c, respectively, after evaporation of the solvent and dissolution of the resulting colorless oils in a small amount of pentane. The two compounds were identified by comparison of their 1H NMR and mass spectra to previously reported data.32 The (1-metalla)hexatriene retentions time and mass spectral comparisons to previously reported data.32 The (1-metalla)hexatriene silane (7b) was identified on the basis of GC co-injection with authentic solutions, which were synthesized under a nitrogen atmosphere and were identified by GC/MS and by GC co-injection with authentic samples. The (1-metalla)hexatriene silane (7b) was identified on the basis of GC co-injection with authentic samples. The (1-metalla)hexatriene silane (7b) was identified on the basis of GC co-injection with authentic samples. The (1-metalla)hexatriene silane (7b) was identified on the basis of GC co-injection with authentic samples. The (1-metalla)hexatriene silane (7b) was identified on the basis of GC co-injection with authentic samples. The two compounds exhibited the following NMR and mass spectral data.

1-Trimethylsilylarenecane (18αi). 1H NMR: δ 0.11 (s, 9H), 0.88 (t, 3H, δ = 7.0 Hz), 1.27 (bd, s, 14H), 1.53 (t, 2H, δ = 6.5 Hz), 3.57 (t, 2H, δ = 6.7 Hz). 13C NMR: δ -0.13, 14.5, 23.1, 26.2, 29.7, 29.8, 30.0, 30.2, 32.3, 33.1, 63.1. ²⁵Si NMR: δ 17.1. MS (EI): m/z (I) 230 (5), 215 (100), 199 (5), 187 (5), 157 (10), 143 (10), 129 (115), 105 (20), 73 (50), 75 (50).

1-Trimethylgermylene (18αi). 1H NMR: δ 0.39 (s, 9H), 0.89 (3H, t, δ = 6.9 Hz), 1.27 (bd s, 14H), 1.53 (t, 2H, δ = 6.9 Hz), 3.55 (2H, t, δ = 6.7 Hz). 13C NMR: δ 0.78, 14.5, 23.1, 26.2, 29.7, 29.8, 30.0, 30.2, 33.1, 34.0, 64.9. MS (EI): m/z (I) 276 (5), 261 (10), 231 (5), 203 (5), 189 (5), 173 (7), 149 (75), 119 (100), 105 (30), 89 (30), 75 (5).

Nanosecond laser flash photolysis experiments employed the pulses (248 nm; ca. 16 ns; ca. 50 mJ) from a Lambda-Physik Compex 120 excimer laser filled with F₂/Kr/H₂ mixtures and a microcomputer-controlled detection system.64 Solutions were prepared at concentrations such that the absorbance at the excitation wavelength (248 nm) was ca. 0.7 (4.4 × 10⁻³ M) and were flowed continuously through a 3 × 7 mm Suprasil flow cell connected to a calibrated 100 mL reservoir. Solution temperatures were measured with a Teflon-coated copper/constantan thermocouple, which was inserted directly into the flow cell, and are accurate to within 0.1 °C. Quenchers were added directly to the reservoir by microtiter syringe as aliquots of standard solutions. Rate constants were calculated by linear least-squares analysis of decay rate-concentration data (6–15 points, depending on whether the plots were linear or curved), which spanned over 1 order of magnitude in the transient decay rate. Errors are quoted as twice the standard deviation obtained from the least-squares analysis in each case.

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