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Mechanism and Selectivity of Aryltrimethylgermane Cation Radical Fragmentations

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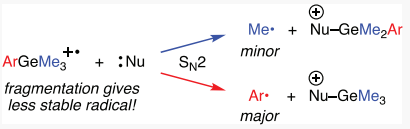
ABSTRACT: Aryltrimethylgermane cation radicals were generated by nanosecond transient absorption spectroscopy. Transient kinetics experiments show that the aryltrimethylgermane cation radicals react with added nucleophiles in reactions that are first-order in both the cation radicals and the nucleophiles. Preparative photo-oxidation experiments demonstrate that the intermediate cation radicals react with nucleophiles, resulting in aryl−Ge or Me−Ge nucleophile-assisted fragmentations. The aryltrimethylgermane cation radicals were found to react more slowly than analogous stannane cation radicals; however, loss of the thermodynamically disfavored aryl radicals remains competitive with methyl radical loss.



INTRODUCTION

Aryltrialkylstannane cation radicals generated in solution have recently been shown to undergo C−Sn bond fragmentation by a nucleophile-assisted mechanism (S_N2).[1,2] An interesting feature of these reactions is that the stannane cation radicals show a remarkable preference for loss of the (less stable) aryl radicals over methyl radicals, a result hitherto unprecedented for cation radical bond fragmentations. These curious results prompted us to study the fragmentations of analogous germane cation radicals to determine if they showed fragmentation selectivities similar to their stannane cation radical analogues. The work described herein seeks answers to three key questions. First, do aryltrialkylgermane cation radicals generated in solution undergo efficient C−Ge bond fragmentation? Second, if so, are these fragmentations unimolecular or nucleophile-assisted processes? Third, are the unusual aryl/methyl fragmentation selectivities observed for aryltrimethylstannane cation radicals also observed for related germane cation radicals?

Fragmentation reactions of unsymmetrically substituted germane cation radicals in solution have rarely been studied before. Allyl- or benzyl-trialkylgermane cation radicals are known to have a strong bias for fragmentation to form the more stable allyl or benzyl radicals.[3] The oxidation of several aryltrimethylgermanes using $AlCl_3$ in CH_2Cl_2 monitored by EPR spectroscopy has previously been shown to result in the formation of substituted biphenyl cation radicals.[4] Although the mechanism of these latter reactions and the identification of EPR-silent products have not been investigated, the results could be consistent with aryl radical formation followed by dimerization and subsequent one-electron oxidation. In the gas phase, not surprisingly, fragmentation of phenyltrimethylgermane cation radical leads to nearly exclusive loss of methyl over phenyl radical.[5]

RESULTS AND DISCUSSION

In analogy to the previously studied aryltrimethylstannane cation radicals,[1,2] we first chose to attempt the generation of the (4-methoxyphenyl)trimethylgermane cation radical ($\mathbf{1}^{+\bullet}$). Nanosecond transient absorption spectroscopy (NTAS) using a cosensitized photo-oxidation method described previously[6] was used to generate $\mathbf{1}^{+\bullet}$. Briefly, a dioxygen-saturated dichloromethane (CH_2Cl_2) solution containing 1 mM *N*-methylquinolinium hexafluorophosphate (NMQ^+), toluene (0.5 M), and 10 mM **1** was excited with a nanosecond laser (10 ns, 343 nm). Excitation of NMQ^+ produces its singlet excited state ($^1NMQ^{+}*$), which is rapidly intercepted by toluene to efficiently produce toluene$^{+\bullet}$ and the *N*-methylquinolinyl radical (NMQ•) by photoinduced electron transfer. NMQ• is scavenged by dioxygen in <100 ns leading to $O_2^{-\bullet}$, which does not have interfering absorptions in the visible region where aromatic radical cations typically absorb. Interception of toluene$^{+\bullet}$ by good electron donors such as **1** efficiently produces their cation radicals. The transient absorption spectrum collected 500 ns after the laser pulse is shown in Figure 1a. This absorption spectrum was tentatively assigned to $\mathbf{1}^{+\bullet}$ by analogy to the absorption spectrum of anisole cation radical ($\lambda_{max} \approx 430$ nm).[7] The transient was found to rapidly react ($k = 6.7 \times 10^9$ M^{-1} s^{-1}) with the good electron donor 4,4′-dimethoxybiphenyl (**2**) to give $\mathbf{2}^{+\bullet}$ ($\lambda_{max} \approx 420$ nm)[8] by monitoring the growth of $\mathbf{2}^{+\bullet}$ at 415 nm or the decay of $\mathbf{1}^{+\bullet}$ at 460 nm [see Figure 1b]. The reaction of the

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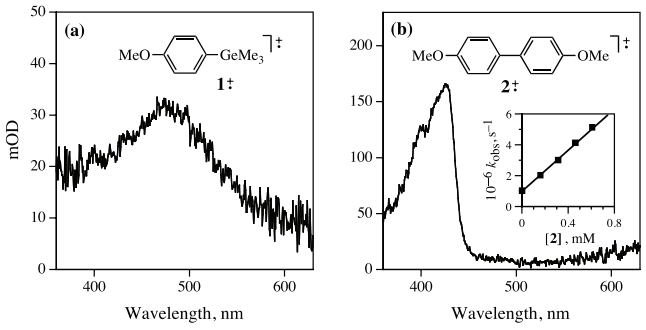


Figure 1. (a) Transient absorption spectra assigned to $1^{+\bullet}$ ($\lambda_{max} \approx$ 470 nm) recorded in CH_2Cl_2 500 ns after the laser pulse. (b) Transient spectrum of $2^{+\bullet}$ generated by the reaction of $1^{+\bullet}$ and **2** in CH_2Cl_2. The inset shows a plot of the pseudo-first-order rate constant for the reaction of $1^{+\bullet}$ with **2** vs [**2**], determined by monitoring the decay of $1^{+\bullet}$ at 460 nm.

transient with **2** to produce $2^{+\bullet}$ provides strong support to the assignment of the transient spectrum in Figure 1a to $1^{+\bullet}$.

Possible reactions of $1^{+\bullet}$ in the presence of added nucleophiles were next probed by NTAS. The kinetics of $1^{+\bullet}$ decay were monitored at 460 nm in the presence of varying concentrations of methanol (HOMe), *tert*-butyl alcohol ($HOBu^t$), and acetonitrile (MeCN). $1^{+\bullet}$ was found to react with all of the nucleophiles in reactions that were first-order in both $1^{+\bullet}$ and the nucleophile (Figure 2). Bimolecular rate

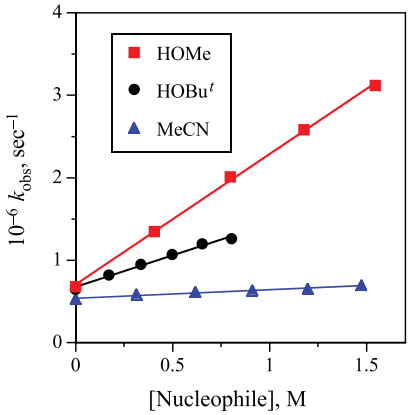


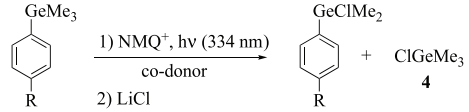
Figure 2. Pseudo-first-order rate constant plots for the reactions of $1^{+\bullet}$ with added methanol (red squares), *tert*-butyl alcohol (black circles), and acetonitrile (blue triangles).

constants for the reaction of $1^{+\bullet}$ with HOMe and $HOBu^t$ are 1.6×10^6 and 8.2×10^5 M^{-1} s^{-1}, respectively. That the more sterically encumbered $HOBu^t$ reacts less rapidly than HOMe is consistent with nucleophile-assisted fragmentation. While MeCN was observed to react with $1^{+\bullet}$, the rate constant is comparable to the background decay of $1^{+\bullet}$, and the bimolecular rate constant can only be estimated to be $\sim 1 \times 10^5$ M^{-1} s^{-1}.

The NTAS kinetics for $1^{+\bullet}$ strongly suggest a nucleophile-assisted decay pathway but do not establish the exact nature of the reaction. Toward this end, preparative photo-oxidations of **1** were conducted to identify the products for the reaction of $1^{+\bullet}$ in the presence of nucleophiles. Preparative photo-oxidations (343 nm) of **1** were carried out in CH_2Cl_2 containing 1 mM NMQ^+, 0.5 M toluene, and the nucleophiles. Products were determined at partial conversion (≤25%).

Fragmentation of $1^{+\bullet}$ was anticipated to produce nucleophile-germylium cation adducts. The reaction workup was designed to convert these adducts to germyl chlorides by treatment with LiCl, following the analogous procedure previously used for aryltrialkylstannane photo-oxidations (Scheme 1).[1,2] The two

Scheme 1. Conditions for Photo-oxidation of Aryltrimethylgermanes



1 (R = OCH_3)
5 (R = Bu^t)

3 (R = OCH_3)
7 (R = Bu^t)

expected products are (4-methoxyphenyl)dimethylgermyl chloride (**3**), indicative of methyl radical loss, and trimethylgermyl chloride (**4**), indicative of aryl radical loss. In practice, these were the only products formed as revealed by ^1H NMR spectroscopy. The product ratios were determined by integrating the germyl-methyl protons of **3** versus **4**, and the overall mass balance was determined using an internal standard.

The preparative photo-oxidations of **1** in the presence of nucleophiles resulted in the formation of **3** and **4** with typical mass balances of >95%. The statistically corrected aryl/Me loss ratios determined from the product ratios are summarized in Table 1. Remarkably, the selectivity for the aryl/Me loss ratio,

Table 1. Comparison of Statistically Corrected Aryl/Me Loss Ratios from Photo-oxidation of 1 in CH_2Cl_2 with Methanol, *tert*-Butyl Alcohol, and Acetonitrile as Nucleophiles without and with Added Base (K_2CO_3) to Aryl/Me Loss Ratios from Photo-oxidation of *p*-$MeOPhSnMe_3$

	p-MeOPh/Me loss ratios		
	1[a]		
nucleophile	without base	with base	*p*-$MeOPhSnMe_3$[b]
methanol	60	53	13.6
t-butyl alcohol	360	370	6.8
acetonitrile	2.1	1.9	0.5

[a]Errors ± 10%. [b]Reference 1.

indicative of aryl versus methyl radical loss, was ~55:1 for the reaction with HOMe and ~365:1 for the reaction with $HOBu^t$—significantly greater selectivities than those observed in analogous stannane cation radical fragmentations (see Table 1).[1,2] Addition of acetonitrile resulted in more competitive aryl and methyl radical cleavages but still showed a small preference for aryl radical loss. To test whether aryl loss could, in part, be due to protodegermylation, the photo-oxidations were also conducted in the presence of anhydrous K_2CO_3 as an acid scavenger. The addition of the base did not affect the product ratios within the experimental error, supporting the conclusion that the products are the result of nucleophile-assisted cation radical fragmentations.

The combined NTAS and product studies provide strong support for the hypothesis that the C−Ge bond fragmentations of $1^{+\bullet}$ proceed by a nucleophile-assisted mechanism that shows a higher preference for substitution to form the less stable aryl radical than aryltrimethylstannane cation radicals.[1,2] A Bent's

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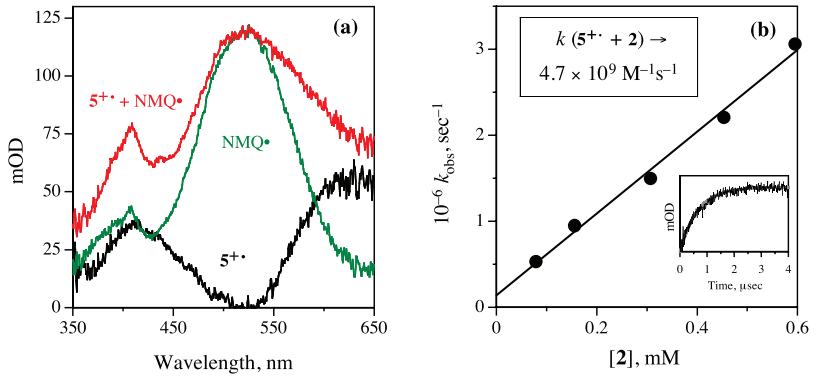

Figure 3. (a) Red trace: transient spectrum recorded 500 ns after laser excitation (343 nm) of an argon-saturated HFIP solution containing **5** (10 mM), NMQ^+ (1 mM), and benzene (0.5 M). Green trace: transient spectrum recorded 500 ns after laser excitation (343 nm) of an argon-saturated HFIP solution containing **5** (10 mM), NMQ^+ (1 mM), $PhCH_2SiMe_3$ (0.5 mM), and benzene (0.5 M). Black trace: subtraction of the green trace from the red trace (spectrum assigned to $5^{+\bullet}$). (b) Plot of the pseudo-first-order rate constant for the reaction of $5^{+\bullet}$ with **2** vs [**2**], determined by monitoring the appearance of $2^{+\bullet}$ at 415 nm. The inset shows typical rise of $2^{+\bullet}$ (black line) and the first-order fit to the experimental data (gray line).

rule explanation has previously been proposed to explain the fragmentation selectivities for the reaction of aryltrimethylstannane cation radicals with nucleophiles, where the more electronegative aryl substituent prefers to be in an apical, leaving group position of a trigonal bipyramidal transition state for nucleophilic substitution.[1] If the same effect applies to the fragmentation of germane cation radicals, the lower reactivity of $1^{+\bullet}$ versus its stannane cation radical analogue could result in a more advanced (later) transition state for the reaction of $1^{+\bullet}$ with nucleophiles, which could lead to the difference in electronegativities of the departing radicals playing a greater role in determining the fragmentation selectivities for $1^{+\bullet}$.

$1^{+\bullet}$ is ~20−30 times less reactive with nucleophiles than its comparably substituted stannane cation radical counterpart.[1] In search of a more reactive germane cation radical, we next chose to examine that of (4-*tert*-butylphenyl)trimethyl germane (**5**), which was expected to be significantly more reactive than $1^{+\bullet}$. Indeed, $5^{+\bullet}$ proved to be too reactive to study in CH_2Cl_2 solution by NTAS. Even in the absence of added nucleophiles, **5** rapidly reacts with toluene$^{+\bullet}$, but no follow-up transient attributable to $5^{+\bullet}$ could be detected in CH_2Cl_2.

Fortunately, it was possible to generate and observe $5^{+\bullet}$ in 1,1,1,3,3,3-hexafluoroisopropanol (HFIP), a solvent known to stabilize cation radicals in comparison to other polar solvents.[9] Optimal conditions for recording the absorption spectrum of $5^{+\bullet}$ used a solution of **5**/NMQ^+/benzene in argon-saturated HFIP. Under these conditions, the transient spectrum shown in red in Figure 3a is observed. This spectrum contains contributions from the NMQ• radical (λ_{max} ≈ 540 nm),[10] which is long-lived in the absence of dioxygen. The contribution of NMQ• was readily determined by performing the transient absorption experiment in the presence of 0.5 mM benzyltrimethylsilane (**6**). Under these conditions, $5^{+\bullet}$ is expected to rapidly react with **6** by electron transfer to produce $6^{+\bullet}$, which is known to rapidly undergo the benzylic C−Si bond to give benzyl radicals and a trimethylsilyl cation/nucleophile adduct,[6] both of which are spectroscopically silent in the wavelength region examined here. Thus, **6** acts as a cation radical scavenger, effectively removing $5^{+\bullet}$ from the transient spectrum. The transient absorption spectrum recorded in the presence of **6** is shown in green in Figure 3a. Subtraction of the green spectrum (due to NMQ•) from the red spectrum leads to the black spectrum in Figure 3a, which was tentatively assigned to $5^{+\bullet}$. This hypothesis was tested by determining if the transient assigned to $5^{+\bullet}$ reacted with a good electron donor by electron transfer. As shown in Figure 3b, the transient species was found to rapidly react with 4,4′-dimethoxybiphenyl (**2**) (k = 4.7 × 10^9 M^{-1} s^{-1}) to produce $2^{+\bullet}$, supporting the assignment of the transient spectrum attributed to $5^{+\bullet}$. The spectrum of $5^{+\bullet}$ in HFIP shows some similarities and some differences relative to that of the *tert*-butylbenzene cation radical, previously determined in CH_3CN (λ_{max} ≈ 450 nm).[7] The short wavelength band for $5^{+\bullet}$ in HFIP (λ_{max} ≈ 420 nm) is somewhat hypsochromically shifted relative to the *tert*-butylbenzene cation radical. The long wavelength band at ~640 nm is not present in the *tert*-butylbenzene cation radical and is presumably associated with an electronic transition involving the trimethylgermyl group. Although the assignment of the spectrum for $5^{+\bullet}$ seems secure, further work will be required to determine the precise nature of these spectral transitions.

Having confirmed the generation of $5^{+\bullet}$ in HFIP, reactions of the cation radical with nucleophiles were next investigated. As with $1^{+\bullet}$, $5^{+\bullet}$ was found to react with added nucleophiles in reactions that are first-order in both $5^{+\bullet}$ and the nucleophiles (Figure 4). The rate constants for the reaction of CH_3CN,

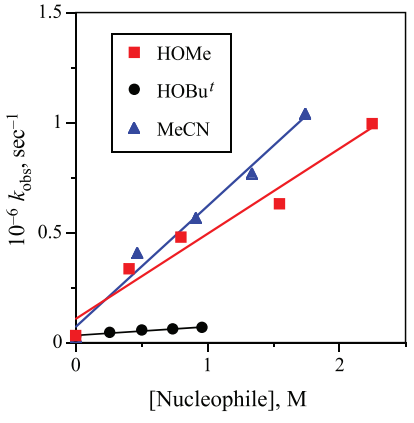

Figure 4. Pseudo-first-order rate constant plots for the reactions of $5^{+\bullet}$ with added methanol (red squares), *tert*-butyl alcohol (black circles), and acetonitrile (blue triangles).

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HOMe, and HOBu^t are 6.0×10^5, 3.9×10^5, and 4.0×10^4 M^{-1} s^{-1}, respectively. The HOMe/HOBu^t rate constant ratio (≈10) shows a clear steric effect on the nucleophile, consistent with a nucleophile-assisted fragmentation mechanism. Despite the high reactivity of $\mathbf{5}^{+\bullet}$ in CH_2Cl_2, the rate constants for the reaction of $\mathbf{5}^{+\bullet}$ with nucleophiles in HFIP are lower than those of $\mathbf{1}^{+\bullet}$ in CH_2Cl_2. This can be accounted for by the differences in reactivity between these solvents for nucleophilic substitutions on cation radicals. For example, the rate constants for the S_N2 reactions of benzyltrialkylsilane cation radicals with methanol are ~100 times lower in HFIP than in CH_2Cl_2.[6] We note that the enhanced reactivity of CH_3CN versus HOMe with $\mathbf{5}^{+\bullet}$ in HFIP versus the reversed reactivity of these nucleophiles with $\mathbf{1}^{+\bullet}$ in CH_2Cl_2 is consistent with earlier results on the reactions of benzylsilane cation radicals, where the decreased relative reactivity of HOMe versus CH_3CN in HFIP was attributed to differential effects of hydrogen bonding.[6]

As described for **1**, preparative photolyses of **5** in the presence of nucleophiles were used to determine if the reactions of $\mathbf{5}^{+\bullet}$ observed by NTAS were due to cation radical fragmentations. The conditions for the photolysis with **5** were similar to those used for **1**, with the exception that HFIP was used as the solvent and benzene as the co-donor in order to match the NTAS conditions with **5**. The products of photo-oxidation of **5** with CH_3CN and HOMe were studied. The relatively low bimolecular rate constant for the reaction of $\mathbf{5}^{+\bullet}$ with HOBu^t precluded product studies for this nucleophile because a sufficiently high concentration of HOBu^t could not be used to ensure that the majority of cation radical decay was due to the reaction with the nucleophile. The aryl/methyl loss ratios were determined as described above for **1**. Stirring of the photo-oxidized samples of **5** with LiCl resulted in the formation of the expected germyl chlorides, (4-*tert*-butylphenyl)dimethylgermyl chloride (**7**), and trimethylgermyl chloride (**4**), corresponding to methyl and aryl radical cleavage, respectively. Product ratios were quantified by ^{1}H NMR integration of the germyl-methyl proton signals in **4** and **7**. As shown in Table 2, photo-oxidation of $\mathbf{5}^{+\bullet}$ in the presence of CH_3CN or HOMe resulted in competitive aryl and methyl radical cleavage. As with **1**, the addition of a base did not substantially alter the product ratios within the experimental error.

Table 2. Statistically Corrected Aryl/Me Loss Ratios for Photo-oxidation of 5 in HFIP with Methanol and Acetonitrile as Nucleophiles without and with Added Base

	t-BuPh/Me loss ratios[a]	
nucleophile	without base	with base
methanol	0.57	0.50
acetonitrile	0.77	0.60

[a]Errors ± 10%.

The aryl/Me fragmentation selectivities for **5** are both lower than those observed with **1**, with the HOMe selectivity being substantially more affected. At present, the reasons for the relative changes are not clear. Further work will be required to determine whether the differences are dependent on the structures of the germane cation radicals and/or the reaction solvents. It was not possible to determine the fragmentation selectivites for $\mathbf{1}^{+\bullet}$ in HFIP for comparison with $\mathbf{5}^{+\bullet}$ because in this solvent $\mathbf{1}^{+\bullet}$ is too unreactive with nucleophiles.

CONCLUSIONS

Aryltrimethylgermane cation radicals have been generated by NTAS. Kinetic studies show that the germane cation radicals react with nucleophiles in reactions that are first-order in both the cation radicals and the nucleophiles. Product studies show that the reactions of the germane cation radicals lead to aryl−Ge and Me−Ge bond fragmentations. The kinetic and product studies are consistent with a nucleophile-assisted (S_N2) fragmentation process, in direct analogy to the previous reported reactions of aryltrimethylstannane cation radicals. Nucleophile-assisted fragmentations of the (4-methoxyphenyl)trimethylgermane cation radical occur with lower bimolecular rate constants than those for the corresponding stannane cation radical in CH_2Cl_2 but with higher aryl versus methyl radical cleavage selectivities. The more reactive cation radical of (4-*tert*-butylphenyl)trimethylgermane also exhibits competitive aryl/methyl radical fragmentation but with lower aryl/methyl selectivities in HFIP as a solvent. The distinctly different reactivity and selectivity resulting from simple substitution of the aryl ring affords potentially tunable reaction parameters for future development.

EXPERIMENTAL SECTION

General Experimental Procedures and Techniques. Unless otherwise noted, the following conditions were used for all nonaqueous reactions. Reactions were conducted at room temperature in oven-dried glassware (125 °C) under a nitrogen atmosphere, and the solutions were stirred magnetically using Teflon-coated magnetic stir-bars. Air- and moisture-sensitive reagents and solutions were transferred via a syringe or cannula and were introduced to the apparatus through rubber septa or three-way stopcocks under a vigorous nitrogen purge.

Routine ^{1}H NMR spectra were recorded at 400 or 500 MHz. Chemical shifts (δ) are reported in ppm relative to tetramethylsilane using the residual proton in the solvent as an internal standard. Proton−proton coupling constants are measured using line spacings. The following abbreviations were used: s (singlet), d (doublet), t (triplet), pent (pentet), and m (multiplet). ^{13}C NMR spectra were recorded at 100 MHz; chemical shifts were referenced to the solvent as an internal standard.

Steady state photolysis reactions at 334 nm were performed using a 200 W or 500 W mercury arc lamp equipped with a liquid filter filled with deionized water to absorb IR light. The emitted light was successively filtered through an Oriel 56521 cutoff filter and an Oriel 56421 interference filter (334 nm).

Materials. Unless otherwise noted, all materials were obtained from commercial sources. Bis(4-methoxyphenyl)dimethylgermane was prepared by a literature method.[11]

Nanosecond Transient Absorption Spectroscopy. A XeCl excimer laser (308 nm) was used to pump a dye laser containing *p*-terphenyl laser dye for 343 nm excitation. Transient spectral absorptions were monitored at a right angle to the laser excitation by using a home-built, xenon flashlamp system equipped with a Perkin-Elmer FX-193 flashlamp to generate the analyzing light. The analyzing light was focused into the end of a fiber optic cable and onto the entrance slit of a monochromator equipped with an intensified CCD. A pulsed xenon arc lamp was used as the monitoring light source for kinetics analyses. The monitoring light was passed through a monochromator and detected using a photomultiplier tube (PMT). The signal from the PMT was directed into a digitizing oscilloscope and then to a computer for viewing, storage, and data analysis. All transient experiments were conducted at room temperature (22 °C).

*Preparation of (4-Methoxyphenyl)trimethylgermane (**1**).* **1** is a known compound; its ^{1}H NMR spectral data were compared to the literature values.[12] A three-neck 100 mL round-bottomed flask was charged with magnesium turnings (0.68 g, 27.8 mmol), followed by a

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small crystal of I_2 and 5 mL of tetrahydrofuran (THF). The mixture was heated to reflux using a heat gun and allowed to stir until reflux subsided. After heating again to reflux, a solution of 4-bromoanisole (3.33 mL, 26.6 mmol) in THF (20 mL) was added dropwise at a rate sufficient to maintain reflux. After 2 h, bromotrimethylgermane (3.25 mL, 25.3 mmol) in THF (10 mL) was added dropwise, and the mixture was heated to reflux with an oil bath for an additional 8 h. After cooling to room temperature, a saturated aqueous ammonium chloride solution (25 mL) was added to the reaction mixture, and the organic layer was extracted with diethyl ether (3 × 50 mL). The combined organic layers were washed with water (3 × 15 mL), dried over anhydrous Na_2SO_4, and concentrated to give a clear, yellow oil. Column chromatography (hexanes, SiO_2) followed by vacuum distillation (bp 98 °C, 8 torr) afforded a clear, colorless oil (5.1 g, 78%).

^{1}H NMR ($CDCl_3$): δ 7.39 (d, J = 8.4 Hz, 2.0 H), 6.92 (d, J = 8.4 Hz, 2.0 H), 3.81 (s, 3.0 H), 0.36 (s, 9.0 H).

Lit:[12] ^{1}H NMR (acetone-d_6): δ 7.12 (m, 4 H), 3.46 (s, 3 H), 0.38 (s, 9 H).

HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{10}H_{16}OGe$, 226.0413; found, 226.0411.

*Preparation of Chloro(4-methoxyphenyl)dimethylgermane (**3**).* A 5 mL round-bottomed flask containing bis(4-methoxyphenyl)-dimethylgermane (50 mg, 0.15 mmol) and dry CH_2Cl_2 (1.0 mL) was cooled in a dry-ice/isopropanol bath. Methanesulfonic acid (10 μL, 0.15 mmol) was added via a syringe in one portion, and the reaction was warmed to room temperature. After stirring for 1 h, the reaction solution was again cooled in a dry-ice/isopropanol bath. Lithium chloride (42 mg, 1 mmol) was added under a vigorous flow of nitrogen, and the mixture was stirred for 3 h. After warming to room temperature, the mixture was filtered and concentrated under reduced pressure to give a clear oil (26 mg, 71%) that contained ∼10% of the starting material. The crude product did not require further purification to be used as a chemical shift reference for product studies.

^{1}H NMR ($CDCl_3$): δ 7.51 (d, J = 8.4 Hz 1.9 H), 6.97 (d, J = 8.4 Hz, 1.9 H), 3.83 (s, 3.0 H), 0.92 (s, 6.2 H).

^{13}C{^{1}H} NMR ($CDCl_3$): δ 161.2, 133.8, 129.5, 114.2, 55.2, 3.4.

HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_9H_{13}ClGeO$, 245.9876; found, 245.9876.

*Preparation of (4-tert-Butylphenyl)trimethylgermane (**5**).* A three-neck, 100 mL round-bottomed flask was charged with magnesium turnings (0.67 g, 27.5 mmol) followed by a small crystal of I_2 and 5 mL of THF. The mixture was heated to reflux using a heat gun and allowed to stir until reflux subsided. After heating to reflux with an oil bath, a solution of 4-*tert*-butylbromobenzene (4.34 mL, 25 mmol) in THF (20 mL) was added dropwise at a rate sufficient to maintain reflux. After 2 h, bromotrimethylgermane (3.21 mL, 25 mmol) in THF (10 mL) was added dropwise, and the mixture was heated to reflux with an oil bath for an additional 12 h. After cooling to room temperature, a saturated aqueous ammonium chloride solution (25 mL) was added to the reaction mixture, and the organic layer was extracted with diethyl ether (3 × 50 mL). The combined organic layers were washed with water (3 × 15 mL), dried over anhydrous Na_2SO_4, and concentrated to give a clear, yellow oil. Column chromatography (hexanes, SiO_2) afforded a clear, colorless oil (5.8 g, 93%).

^{1}H NMR ($CDCl_3$): δ 7.43 + 7.38 (d + d, J = 8.2 Hz, 3.9 H), 1.33 (s, 9.2 H), 0.37 (s, 8.9 H).

^{13}C{^{1}H} NMR ($CDCl_3$): δ 151.1, 139.0, 132.8, 124.9, 34.6, 31.3, −1.8.

HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{13}H_{22}Ge$, 252.0933; found, 252.0931.

Preparation of Bis(4-tert-butylphenyl)dimethylgermane. A 50 mL round-bottomed flask was charged with diethyl ether (15 mL) and 4-*tert*-butylbromobenzene (0.511 mL, 3.0 mmol). The flask was cooled in a dry-ice/isopropanol bath. A 1.7 M solution of *tert*-butyllithium in pentane (3.82 mL, 6.5 mmol) was added via a syringe pump over 30 min, and the reaction mixture was warmed to room temperature for 1 h. The flask was again cooled in a dry-ice/isopropanol bath, and dichlorodimethylgermane (0.15 mL, 1.3 mmol) was added via a syringe in one portion. The reaction was warmed to room temperature and stirred for 12 h. Distilled water (10 mL) was added, and the reaction mixture was extracted with diethyl ether (3 × 10 mL). The combined organic layers were washed with water (2 × 10 mL) and saturated brine (25 mL), dried over anhydrous Na_2SO_4, and concentrated under reduced pressure to give a colorless oil (0.30 g, 73%). The material was used without further purification.

^{1}H NMR ($CDCl_3$): δ 7.43 (d, J = 8.0 Hz, 3.7 H), 7.38 (d, J = 8.0 Hz, 4.0 H), 1.32 (s, 18.4 H), 0.62 (s, 5.9 H).

^{13}C{^{1}H} NMR ($CDCl_3$): δ 151.2, 136.7, 133.3, 124.9, 34.4, 31.1, −3.2.

HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{22}H_{32}Ge$, 370.1716; found, 370.1702.

*Preparation of Chloro(4-tert-butylphenyl)dimethylgermane (**7**).* A 5 mL round-bottomed flask was charged with bis(4-*tert*-butylphenyl)dimethylgermane (50 mg, 0.135 mmol) and dry CH_2Cl_2 (2.0 mL). The flask was cooled in a dry-ice/isopropanol bath. Methanesulfonic acid (9 μL, 0.135 mmol) was added via a syringe in one portion, and the reaction flask was warmed to room temperature. After stirring for 1 h, the reaction flask was again cooled in a dry-ice/isopropanol bath, and lithium chloride (42 mg, 1 mmol) was added under a vigorous flow of nitrogen. The resulting mixture was stirred for 3 h. After warming to room temperature, the mixture was filtered and concentrated under reduced pressure to afford a clear oil (14 mg, 38%) that contained ∼10% of the starting material. The crude product did not require further purification to be used as a chemical shift reference for product studies.

^{1}H NMR ($CDCl_3$): δ 7.54 (d, J = 8.4 Hz 1.9 H), 7.46 (d, J = 8.4 Hz, 1.9 H), 1.33 (s, 9.5 H), 0.93 (s, 5.8 H).

^{13}C{^{1}H} NMR (CD_2Cl_2): δ 133.7, 132.5, 125.9, 125.4, 35.1, 31.3, 3.3.

HRMS (ESI-TOF) m/z: $[M]^+$ calcd for $C_{12}H_{19}GeCl$, 272.0387; found, 272.0378.

*Representative Procedure for Photo-oxidations of (4-Methoxyphenyl)-trimethylgermane (**1**).* A stopcocked cuvette was charged with 4.0 mL of dichloromethane solution containing 0.020 M **1**, 1 mM *N*-methylquinolinium hexafluorophosphate[6], 0.5 M toluene, and 1.0 M methanol. The reaction solution was purged for 20 min with dioxygen that was passed through a bubbler containing a frit immersed in CH_2Cl_2. After removal of a 0.5 mL of aliquot, the cuvette was then irradiated for 60 min at 334 nm. After irradiation, a second 0.5 mL of aliquot was removed and stirred over powdered LiCl (∼25 mg) for 3 h. To each aliquot was added 0.5 mL of 10 mM 1,4-dioxane standard solution in dichloromethane. The samples were dried over Na_2SO_4, filtered through glass wool into an NMR tube, and doped with 200 μL of CD_2Cl_2. Samples were analyzed by ^{1}H NMR spectroscopy. The germyl-methyl group hydrogens of the starting material and germyl chlorides (**3** and **4**) were integrated against the methylene proton resonance of the 1,4-dioxane internal standard to determine the mass balance and aryl/Me fragmentation ratio.

*Representative Procedure for Photo-oxidations of (4-tert-Butylphenyl)-trimethylgermane (**5**).* A stopcocked cuvette was charged with 4.0 mL of an HFIP solution containing 0.020 M **5**, 1 mM *N*-methylquinolinium hexafluorophosphate, 0.5 M benzene, and 1.0 M methanol. The reaction solution was purged with dioxygen for 20 min, and a 0.5 mL of aliquot was removed. The cuvette was then irradiated for 15 min at 334 nm. After irradiation, a second 0.5 mL of aliquot was removed and stirred over powdered LiCl (∼25 mg) for 3 h. To each aliquot was added 1.0 mL of a solution of 5 mM hexamethyldisiloxane (HMDS) in dichloromethane. The samples were dried over Na_2SO_4, filtered through glass wool into an NMR tube, and doped with 200 μL of CD_2Cl_2. Samples were analyzed by ^{1}H NMR spectroscopy. The germyl-methyl group hydrogens of the starting material and resulting germyl chlorides (**4** and **7**) were integrated against the methylene proton resonance of the HMDS internal standard to determine the mass balance and aryl/Me fragmentation ratio.

Representative Procedure for the Generation and Observation of Cation Radicals. A 10 mL volumetric flask was charged with 0.54

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mL of toluene (0.5 M) and 23 mg of (4-methoxyphenyl)-trimethylgermane (0.01 M). The flask was filled to the mark with a solution of *N*-methylquinolinium hexafluorophosphate (1.0 mM) in CH_2Cl_2. Using a volumetric pipette, 3 mL of this solution was transferred to a stopcocked cuvette and gently purged for 15 min with dioxygen that was passed through a bubbler containing a frit immersed in CH_2Cl_2. The cuvette was then photolyzed on the nanosecond transient absorption system. The resulting transient UV−vis spectrum was collected at least 100 ns after the laser pulse; the time required to ensure that NMQ• is scavenged by O_2.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.joc.0c01032.

NMR spectra (^1H and ^{13}C); representative kinetic plots for bimolecular rate constants; and representative ^1H NMR spectra from preparative photo-oxidations (PDF)

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) Luo, P.; Dinnocenzo, J. P. Mechanism and Unusual Fragmentation Selectivities of Aryltrialkylstannane Cation Radicals. *J. Org. Chem.* **2015**, *80*, 9240−9246.

(2) Luo, P.; Dinnocenzo, J. P. Aryltrimethylstannane Cation Radical Fragmentation Selectivities that Depend on Co-Donor: Evidence for Reactions from Hetero-Dimer Cation Radicals. *J. Org. Chem.* **2017**, *82*, 11052−11055.

(3) (a) Kyushin, S.; Masuda, Y.; Matsushita, K.; Nakadaira, Y.; Ohashi, M. Novel Alkylation of Aromatic Nitriles via Photo-induced Electron Transfer of Group 14 Metal-carbon σ Donors. *Tetrahedron Lett.* **1990**, *31*, 6395−6398. (b) Nakanishi, K.; Mizuno, K.; Otsuji, Y. Photosubstitution of Dicyanobenzenes by Allylic Silanes, Germanes, and Stannanes via Photoinduced Electron Transfer. *Bull. Chem. Soc. Jpn.* **1993**, *66*, 2371−2379. (c) Lenczewski, M. S.; de Lijser, H. J. P.; Turner, D. M.; Dinnocenzo, J. P. Stereochemistry of Nucleophilic Substitutions on Benzyl-silane and -germane Cation Radicals: Application of the Endocyclic Restriction Test. *J. Org. Chem.* **2017**, *82*, 12112−12118.

(4) Klaukien, H.; Lehnig, M.; Reiche, T.; Reiß, S.; Such, P. Radical Cations from Aryl-silanes, -germanes and -digermanes. *J. Chem. Soc., Perkin Trans. 2* **1995**, 2115−2119.

(5) Belokon, A. V.; Klimova, T. V.; Nakrasov, Yu. S.; Stanko, V. I. Mass-Spectrometric Study of a Series of Carborane and Benzene Derivatives of Group IV Elements. *Dokl. Akad. Nauk SSSR* **1979**, *245*, 363−366.

(6) Dockery, K. P.; Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R.; Todd, W. P. Nucleophile-Assisted Cleavage of Benzyltrialkylsilane Cation Radicals. *J. Am. Chem. Soc.* **1997**, *119*, 1876−1883.

(7) Merkel, P. B.; Luo, P.; Dinnocenzo, J. P.; Farid, S. Accurate Oxidation Potentials of Benzene and Biphenyl Derivatives via Electron Transfer Equilibria and Transient Kinetics. *J. Org. Chem.* **2009**, *74*, 5163−5173.

(8) Luo, P.; Feinberg, A. M.; Guirado, G.; Farid, S.; Dinnocenzo, J. P. Accurate Oxidation Potentials of Forty Benzene and Biphenyl Derivatives with Heteroatom Substituents. *J. Org. Chem.* **2014**, *79*, 9297−9304.

(9) Eberson, L.; Hartshorn, M. P.; Persson, O. 1,1,1,3,3,3-Hexafluoropropan-2-ol as a Solvent for the Generation of Highly Persistent Radical Cations. *J. Chem. Soc., Perkin Trans. 2* **1995**, 1735−1744.

(10) Guirado, G.; Fleming, C. N.; Lingenfelter, T. G.; Williams, M. L.; Zuilhof, H.; Dinnocenzo, J. P. Nanosecond Redox Equilibrium Method for Determining Oxidation Potentials in Organic Media. *J. Am. Chem. Soc.* **2004**, *126*, 14086−14094.

(11) Katz, S. M.; Reichl, J. A.; Berry, D. H. Catalytic Synthesis of Poly(arylmethylgermanes) by Demethanative Coupling: A Mild Route to σ-Conjugated Polymers. *J. Am. Chem. Soc.* **1998**, *120*, 9844−9849.

(12) Moerlein, S. M. Use of Aryltrimethylgermanium Substrates for Facile Aromatic Chlorination, Bromination, and Iodination. *J. Org. Chem.* **1987**, *52*, 664−667.