JOC The Journal of Organic Chemistry

Article

pubs.acs.org/joc

Mechanism and Unusual Fragmentation Selectivities of Aryltrialkylstannane Cation Radicals

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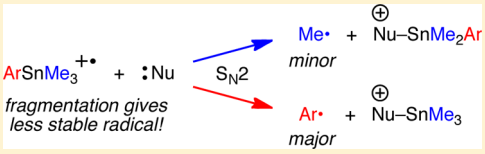
Supporting Information

ABSTRACT: Aryltrialkylstannane cation radicals were generated and characterized by nanosecond transient absorption spectroscopy. Kinetics show the fragmentations of the stannane cation radicals occur by a bimolecular, nucleophile-assisted mechanism (S_N2). Consistent with this hypothesis, steric effects on both the nucleophile and the stannane cation radicals were observed. Steady-state, preparative photooxidation experiments show that aryltrimethylstannane cation radicals have an unusual preference for loss of aryl radicals over methyl radicals and that the selectivity for aryl vs methyl radical loss is dependent on the identity of the nucleophile. The preference for loss of aryl radicals is rationalized by a hypothesis based on Bent's rules.



INTRODUCTION

Organostannanes have long been known to undergo bond fragmentation upon one-electron oxidation to give an organic radical and a stannylium cation fragment.[1,2] Not surprisingly, when the stannanes are unsymmetrically substituted, these oxidative fragmentation reactions generally lead to formation of the more stable organic radical. For example, the fragmentation of alkyltrimethylstannane cation radicals ($RSnMe_3^{+\bullet}$) generated in the gas phase by electron impact uniformly showed preferential formation of the more substituted (and more stable) alkyl radicals.[1] Fragmentation selectivities for oxidation of unsymmetrically substituted tetraalkylstannanes determined in solution similarly show that losses of the more stable alkyl radicals are strongly preferred.[2] In contrast to these trends, Shine and co-workers reported that the reaction of phenyltrimethylstannane (**1**) with thianthrene perchlorate (**2**) in acetonitrile led to oxidative fragmentation with predominant loss of the less stable phenyl radical over the methyl radical.[3] The reaction of **1** with **2** was proposed to proceed by initial one-electron oxidation and subsequent unimolecular fragmentation of $\mathbf{1}^{+\bullet}$ to primarily give phenyl radical. This seemingly contrathermodynamic outcome was rationalized by proposing preferential solvent stabilization of the Me_3Sn^+ fragment, resulting from $Ph^\bullet$ loss, over the larger $PhMe_2Sn^+$, resulting from $Me^\bullet$ loss. An alternative mechanistic hypothesis is that the fragmentation of $\mathbf{1}^{+\bullet}$ in acetonitrile is nucleophile-assisted, presumably with the solvent acting as the nucleophile. This latter mechanism is well precedented in the fragmentation reactions of organosilane cation radicals.[4] Described herein are our experiments to generate aryltrialkylstannane cation radicals, elucidate their fragmentation mechanism, and determine their fragmentation selectivities.

RESULTS AND DISCUSSION

In principle, it is possible to distinguish between the mechanisms discussed above for the fragmentation of $\mathbf{1}^{+\bullet}$ by generating the cation radical and examining its reaction kinetics in the presence and absence of nucleophiles. Generation of $\mathbf{1}^{+\bullet}$ was attempted by nanosecond transient absorption spectroscopy (NTAS) using cosensitized photooxidation of **1** in acetonitrile or dichloromethane with *N*-methylquinolinium hexafluorophosphate ($NMQ^+PF_6^-$) as a photooxidant and toluene (PhMe, 0.5 M) as a codonor.[5,6] Under these conditions, $PhMe^{+\bullet}$ (λ_{max} 430 nm) is generated within the laser pulse (10 ns). Addition of **1** (up to 0.01 M) results in a diffusion-controlled reaction with $PhMe^{+\bullet}$; however, no transient spectrum could be subsequently detected in the 350−700 nm spectral range. Because $\mathbf{1}^{+\bullet}$ is expected to absorb in this region, the simplest way to explain this result is that $\mathbf{1}^{+\bullet}$ is formed by reaction of **1** with $PhMe^{+\bullet}$ but the resulting stannane cation radical decays more rapidly than it is formed. Attempted generation of $\mathbf{1}^{+\bullet}$ in hexafluoroisopropyl alcohol (HFIP), which often stabilizes cation radicals,[7] was foiled by the rapid, thermal destannylation of **1** in HFIP. Unable to directly observe $\mathbf{1}^{+\bullet}$ by NTAS, we next sought to examine the chemistry of similar stannane cation radicals that might be longer lived. (4-Biphenyl)trimethylstannane (**3**) turned out to be a suitable candidate.

Preparative photooxidation of **3** was first carried out to determine the aryl/Me loss selectivity for comparison to that from reaction of **1** with **2**. Using 1,2,4,5-tetracyanobenzene (TCB) as a photooxidant in CD_3CN and a variety of codonors (0.1−0.5 M PhMe, $PhBu^t$, PhCl, and *o*-PhF_2), the aryl/Me loss ratios were determined at partial conversion (<30%) after irradiation at 313 nm. Following the method of Wong and Kochi,[2b] treatment of the crude reaction mixtures with LiCl gave stannyl chlorides Me_3SnCl and 4-$BPMe_2SnCl$, whose ratios were determined by ^1H NMR. Mass balance, determined by addition of an internal standard, was >95% in all cases. The

Received: July 21, 2015
Published: September 2, 2015

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DOI: 10.1021/acs.joc.5b01690
J. Org. Chem. 2015, 80, 9240−9246

average, statistically corrected aryl/Me ratio determined from the Me_3SnCl/4-$BPMe_2SnCl$ ratios was found to be 11.8 ± 0.3 and was independent of the codonor used. It is interesting to note that this ratio is remarkably similar to that reported by Shine for the oxidation of **1** by **2** (Ph/Me = 14).[3] Encouraged by these results, we next sought to generate $\mathbf{3}^{+\bullet}$ by NTAS.

Photolysis (343 nm; 10 ns) of a solution containing 1 mM NMQ, 0.5 M PhMe, and 0.01 M **3** in dioxygen-saturated CH_3CN gave the transient spectrum shown in Figure 1a after

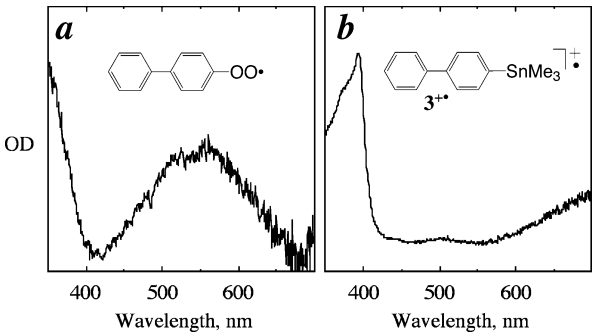

Figure 1. Transient spectra assigned to (a) the 4-biphenyl peroxyl radical in CH_3CN and (b) $\mathbf{3}^{+\bullet}$ in CH_2Cl_2.

100 ns. This spectrum is *not* due to $\mathbf{3}^{+\bullet}$, as the transient does not react with good electron donors such as 1,2,4,5-tetramethoxybenzene (TMB). Importantly, the transient is not observed in the absence of O_2. The transient spectrum is in good agreement with that of the 4-biphenyl peroxyl radical (4-BPOO•), which was independently generated by photolysis of 4-iodobiphenyl in O_2-saturated CH_3CN.[8] The formation of 4-BPOO• is consistent with initial generation of $\mathbf{3}^{+\bullet}$ and its subsequent fragmentation in CH_3CN to give 4-BP•, which rapidly reacts with O_2. If this is correct, we reasoned that $\mathbf{3}^{+\bullet}$ might be directly observed by NTAS in a less nucleophilic solvent. This was indeed the case. Laser flash photolysis as described above but in CH_2Cl_2 produced the transient spectrum shown in Figure 1b. This transient species reacted rapidly with TMB ($k = 2.1 \times 10^{10}$ M^{-1} s^{-1}) to produce $TMB^{\bullet+}$ (λ_{max} 450 nm). On the basis of this result and the similarity of the transient spectrum to that of biphenyl$^{+\bullet}$ (λ_{max} ~380 and 670 nm),[9] we assign the transient species to $\mathbf{3}^{+\bullet}$. Importantly, the transient was found to rapidly react with added nucleophiles in reactions that were first order in $\mathbf{3}^{+\bullet}$ and first order in nucleophile. For example, $\mathbf{3}^{+\bullet}$ reacts with CH_3CN with a rate constant of 1.5×10^8 M^{-1} s^{-1} (see the Supporting Information for representative, pseudo-first-order rate plots). This large rate constant readily explains why $\mathbf{3}^{+\bullet}$ was not observed in CH_3CN by NTAS. The stannane cation radical $\mathbf{3}^{+\bullet}$ also reacts with alcohols. The rate constants for reaction with HOMe and $HOBu^t$ are 1.9×10^8 and 5.9×10^7 M^{-1} s^{-1}, respectively, consistent with a steric effect on the nucleophile.

Results similar to those with **3** were obtained with (4-methoxyphenyl)trimethylstannane (**4**). Preparative photooxidation of **4** with TCB in CH_3CN using the same four codonors used with **3** gave an average, statistically corrected aryl/Me loss ratio of 1.1 ± 0.1, with mass balances of >95%. Although this ratio is lower than that observed for **3**, it is still noteworthy that loss of the less stable aryl radical is competitive with methyl radical loss. Photooxidation of **4** by NTAS using NMQ/PhMe in dioxygen-saturated CH_3CN gave the transient spectrum shown in Figure 2a after 100 ns. This spectrum matches well

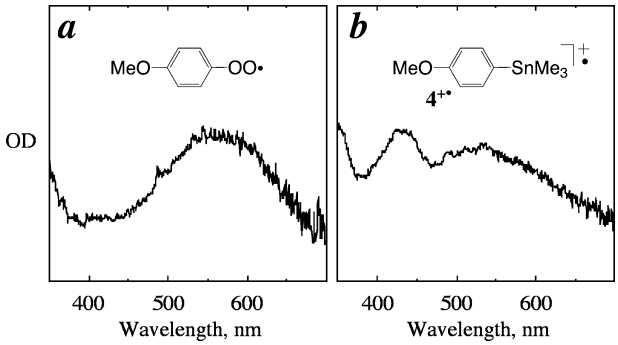

Figure 2. Transient spectra assigned to (a) the 4-methoxyphenyl peroxyl radical in CH_3CN and (b) $\mathbf{4}^{+\bullet}$ in CH_2Cl_2.

that of the 4-methoxyphenyl peroxyl radical, which was independently generated by photolysis of 4-iodoanisiole in O_2-saturated CH_3CN.[10] The transient spectrum generated by photooxidation in CH_2Cl_2 is shown in Figure 2b. This species reacts rapidly ($k = 1 \times 10^{10}$ M^{-1} s^{-1}) with the good electron donor 4,4′-dimethoxybiphenyl (DMBP) to produce $DMBP^{+\bullet}$ (λ_{max} ~425 nm).[11] We accordingly assign the transient species to $\mathbf{4}^{+\bullet}$. As with $\mathbf{3}^{+\bullet}$, $\mathbf{4}^{+\bullet}$ reacts rapidly with added nucleophiles. The rate constants for reaction with CH_3CN, HOMe, and $HOBu^t$ in CH_2Cl_2 are 1.1×10^7, 6.4×10^7, and 1.5×10^7 M^{-1} s^{-1}, respectively. The HOMe/$HOBu^t$ rate constant ratio again shows a clear steric effect on the nucleophile. As shown in Figure 2b, the absorption spectrum of $\mathbf{4}^{+\bullet}$ shows two bands in the visible region (λ_{max} ~430 and 550 nm). Rate constants measured at both 430 and 550 nm were indistinguishable (±10%), consistent with both absorption bands in Figure 2b belonging to $\mathbf{4}^{+\bullet}$. We note that the short-wavelength band is similar to that found in anisole cation radical (λ_{max} ~425 nm).[12] The long-wavelength band is presumably associated with an electronic transition involving the trimethylstannyl group. Although the assignment of the spectrum for $\mathbf{4}^{+\bullet}$ seems secure, further work will be required to determine the precise nature of these spectral transitions.

Although the kinetic experiments clearly show that $\mathbf{3}^{+\bullet}$ and $\mathbf{4}^{+\bullet}$ react with added nucleophiles, it is worth noting that the experiments do not unequivocally demonstrate that the reactions lead to fragmentation of the stannane cation radicals. If a nucleophile-assisted mechanism is operative, the aryl/Me loss ratio is predicted to be nucleophile-dependent. This prediction was tested experimentally by performing preparative photooxidations of **3** and **4** in CH_2Cl_2/NMQ/$PhCH_3$ with relatively high concentrations (~1 M) of added nucleophiles to ensure that >95% of $\mathbf{3}^{+\bullet}$ and $\mathbf{4}^{+\bullet}$ react with the targeted nucleophiles instead of adventitious nucleophiles in the solvent. The Ar/Me loss ratios were determined after photooxidation with HOMe, $HOBu^t$, and CH_3CN as nucleophiles from the stannyl chloride products after treatment with LiCl, as described above. The statistically corrected fragmentation selectivities are shown in Table 1 and demonstrate that the aryl/Me loss ratios are indeed dependent on the nucleophile for both **3** and **4**. It is noteworthy that the Ar/Me loss ratios measured for CH_3CN in CH_2Cl_2 for **3** and **4** (14.4 and 0.5) are reasonably similar to those found in CH_3CN (11.8 and 1.1). Interestingly, the fragmentation selectivities for $\mathbf{4}^{+\bullet}$ with HOMe and $HOBu^t$ as nucleophiles show that, as with $\mathbf{3}^{+\bullet}$, aryl radical loss can also predominate in the fragmentation of $\mathbf{4}^{+\bullet}$. Finally, we note that the fragmentation selectivities for **4** show variation greater than that for **3**. The origin of this subtle effect is, as yet,

DOI: 10.1021/acs.joc.5b01690
J. Org. Chem. 2015, 80, 9240−9246

Table 1. Statistically Corrected Aryl/Me Loss Ratios for Photooxidations of 3 and 4 in CH_2Cl_2 with Methanol, *tert*-Butyl Alcohol, and Acetonitrile as Nucleophiles

nucleophile	aryl/Me loss ratios[a]	
	3	4
methanol	8.9 ± 0.2	13.6 ± 0.2
tert-butyl alcohol	7.0 ± 0.2	6.8 ± 0.1
acetonitrile	14.4 ± 0.1	0.5 ± 0.1

[a]Average of at least two determinations.

unclear. Most important, however, is that the combined data show that the Ar/Me loss ratios for these stannane cation radical fragmentations clearly depend on the identity of the nucleophile and the departing radical, consistent with the nucleophile-assisted fragmentation mechanism.

The nucleophile-assisted fragmentation mechanism also predicts that the rate constants for reaction of aryltrialkylstannane cation radicals with nucleophiles should be dependent on the steric environment around the tin atom. To test this prediction, we sought aryltrialkylstannanes with alkyl groups that had comparable leaving group ability (i.e., radical stability) but that differed sterically. Stannanes **5** and **6** (Np = neopentyl) were found to be suitable substrates. These stannanes had the additional virtue that preparative photooxidation experiments demonstrated that they both led to exclusive loss of the alkyl groups, showing that the aryl/alkyl loss selectivity is quite sensitive to the relative stabilities of the aryl and alkyl groups. Photooxidation of **5** and **6** with NMQ/PhMe in CH_2Cl_2 led to similar transients (Figure 3). Both species rapidly reacted with

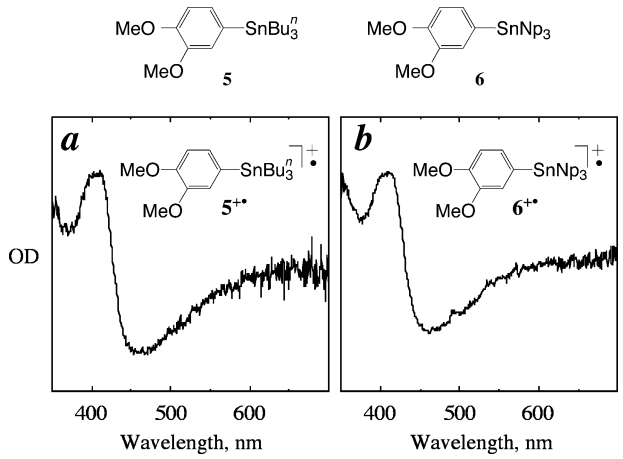

Figure 3. Transient spectra assigned to (a) $5^{+\bullet}$ and (b) $6^{+\bullet}$ in CH_2Cl_2.

TMB ($k \approx 4 \times 10^9$ M^{-1} s^{-1}) to give $TMB^{+\bullet}$, consistent with their assignment to $5^{+\bullet}$ and $6^{+\bullet}$. Both cation radicals reacted with added nucleophiles, but with significantly different rate constants. For example, with HOMe as nucleophile, the rate constant for reaction with $5^{+\bullet}$ is ~15 times greater than that with $6^{+\bullet}$ ($k = 6.1 \times 10^6$ vs 4.0×10^5 M^{-1} s^{-1}). The rate constant ratio is ~30 with acetonitrile as nucleophile ($k = 2.2 \times 10^6$ vs 7.5×10^4 M^{-1} s^{-1}). These experiments provide a final piece of evidence consistent with a nucleophile-assisted fragmentation mechanism.

Having established that the fragmentation mechanism of aryltrialkylstannanes is nucleophile-assisted, one can now speculate with more confidence on the origin of the unusual selectivity for aryl radical loss from the aryltrimethylstannane cation radicals. A plausible and simple explanation is based on Bent's rules,[13] one of which states that trigonal-bipyramidal species are generally more stable when the more electronegative substituents are located in the apical positions. Because an aryl group is significantly more electronegative than a methyl group, one might plausibly expect a transition state where the aryl group is in the apical position would be energetically favored,[14] leading to aryl radical loss, despite this transition state leading to loss of the less stable radical. This could explain the nucleophile-assisted fragmentation selectivities for $3^{+\bullet}$ and $4^{+\bullet}$. However, the fragmentation reactions of $5^{+\bullet}$ and $6^{+\bullet}$ clearly demonstrate that radical stability also plays an important role in determining the fragmentation selectivities of stannane cation radicals.

Reaction of Phenyltrimethylstannane with Thianthrene Perchlorate. As mentioned in the Introduction, our investigation of the mechanism and fragmentation selectivities of aryltrialkylstannane cation radicals was originally motivated by the report of Shine et al. on the oxidation of phenyltrimethylstannane (**1**) by thianthrene perchlorate (**2**).[3] While examining this reaction further, we made an interesting and mechanistically revealing discovery. The reaction of **1** with **2** in Shine's study was done by adding **1** to a solution of **2** in CH_3CN and monitoring the reaction by the disappearance of the intense color of **2**, which we found took >24 h at 22 °C. Interestingly, when several drops of a solution containing **2** were instead added to a stirred solution containing excess **1** (0.056 M), the color of **2** disappeared immediately (<1 s), demonstrating that the reaction of **1** with **2** is, in fact, quite rapid. As explained below, on the basis of the reactivity data and an estimate of the free energy for electron transfer from **1** to **2**, an electron transfer mechanism for the reaction of **1** and **2** can be confidently excluded by a simple kinetic competence test.

The free energy for electron transfer from **1** to **2** can be determined from the difference in the oxidation potentials of **1** and thianthrene. Literature oxidation potentials for thianthrene in CH_3CN vary from 1.22 to 1.30 V vs SCE.[15] Although the oxidation potential of **1** has not been determined electrochemically, its ionization potential (8.83 ± 0.05 eV)[16] is indistinguishable from that of toluene (8.8228 ± 0.0001 eV),[17] whose oxidation potential has recently been accurately determined to be 2.26 ± 0.02 V vs SCE in CH_3CN.[9] Given their comparable ionization potentials and structural similarities, the oxidation potential of toluene should be a reasonable estimate for that of **1**.

A conservative way to estimate the *maximum* rate constant for electron transfer from **1** to **2** is to equate the free energy of electron transfer (ΔG_{et}) to the activation free energy ($\Delta G_{et}^{\ddagger}$). Using the largest, literature oxidation potential for **2** (1.30 V vs SCE)[15a] and 2.26 V for the oxidation potential of **1**, ΔG_{et} is estimated to be 22 kcal/mol. Using the Eyring equation and substituting ΔG_{et} for $\Delta G_{et}^{\ddagger}$ gives a *maximum* rate constant for electron transfer of 2.4×10^{-4} s^{-1} at 22 °C for the species *in contact*. Using the rate constants for diffusional encounter and separation of **1** and **2** in CH_3CN,[18] and the concentration of **1** in the experiment described above (0.056 M), the rate constant for electron transfer from **1** to **2** is calculated to be $\lesssim 8 \times 10^{-6}$ s^{-1}, which corresponds to a half-life of $\gtrsim$90000 s: i.e., ~10^5 times greater than that observed experimentally! Given that this conservative model does not take into account the reorganization energies for electron transfer, which will increase in the estimated reaction half-life, one can confidently exclude an electron transfer mechanism for the reaction of **1** with **2**. A

DOI: 10.1021/acs.joc.5b01690
J. Org. Chem. 2015, 80, 9240−9246

more likely hypothesis is that **2** reacts with **1** by a polar mechanism, in analogy with examples of stannane oxidations with other electron-deficient species.[2b,19,20] With some irony, now two things are clear. First, the similar Ar/Me fragmentation selectivities observed in the reaction of **1** with **2** and for the authentic stannane cation radicals reported herein must now be considered fortuitous. Second, the reaction of **1** with **2**, which was the original motivation for the present work on aryltrialkylstannane cation radical fragmentations, does *not* proceed via stannane cation radical $\mathbf{1}^{+\bullet}$ as an intermediate.

■ CONCLUSIONS

In conclusion, several aryltrialkylstannane cation radicals have been generated and spectroscopically characterized in solution at room temperature for the first time. Nanosecond transient absorption experiments demonstrated that the stannane cation radicals undergo rapid fragmentation by a bimolecular, nucleophile-assisted mechanism. Consistent with this hypothesis, steric effects on both the nucleophile and the stannane cation radicals were observed. Preparative photooxidation experiments show that aryltrimethylstannane cation radicals have an unusual preference for loss of aryl radicals over methyl radicals and that the aryl/methyl selectivities are dependent on the identity of the nucleophile. Finally, we note that the selective generation of aryl radicals from stannane cation radicals may find utility in organic synthesis.

■ 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 solutions were stirred magnetically using Teflon-coated magnetic stir bars. Air- and moisture-sensitive reagents and solutions were transferred via 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 either 400 or 500 MHz. Chemical shifts (δ) are given in ppm relative to tetramethylsilane using the residual proton in the solvent as an internal standard (CHD_2CN, δ 1.95; $CHDCl_2$, δ 5.35; $CHCl_3$, δ 7.27). Proton−proton coupling constants reflect assumed first-order behavior. The following abbreviations were used: s (singlet), d (doublet), t (triplet), q (quartet), pent (pentet), dd (doublet of doublets), dt (doublet of triplets), m (multiplet), and br (broad). Peak integrations were normalized by multiplying the fractional peak area (area peak/sum of all peak areas) by the total number of protons in the proposed structure. ^{13}C NMR spectra were recorded at either 100 or 125 MHz; chemical shifts are referenced to internal chloroform-*d* ($CDCl_3$, δ 78.0 ppm) unless otherwise stated. ^{119}Sn NMR spectra were recorded at 186.5 MHz on a 500 MHz NMR spectrometer; chemical shifts (δ) in ppm are relative to tetramethyltin.

High-resolution electron impact mass spectra were obtained on a double-focusing magnetic sector instrument.

Analytical gas chromatography was performed on a chromatograph equipped with a flame ionization detector and a Restek Rtx-1 column (60 m × 0.25 mm column with a 0.5 μm film thickness). Preparative gas chromatography separations were performed on a chromatograph equipped with a thermal conductivity detector using helium as the carrier gas.

Steady-state photolysis reactions were performed using a 200 or 500 W mercury arc lamp equipped with a liquid filter filled with deionized water to absorb IR light. For 334 nm irradiation the light was filtered by an Oreil No. 56521 cutoff filter and a No. 56421 334 nm interference filter. For 313 nm irradiation the light was filtered by an Oreil No. 59450 cutoff filter and No. 56511 313 nm interference filter.

Reactions utilizing microwave heating were conducted in sealed Teflon-capped pressure tubes in an Explore 48 model 909480 microwave reactor.

Purifications by column chromatography were performed using 230−400 mesh silica gel.

Solvents. Reagent grade solvents were used for all extraction and workup procedures. Hexanes and acetone were distilled before use. Diethyl ether, tetrahydrofuran, and acetonitrile were purified by passing through a column of activated alumina from a solvent purification system.[21] Dichloromethane was distilled from phosphorus pentoxide before use.

Materials. Toluene, 1,2-difluorobenzene, *tert*-butylbenzene, and chlorobenzene were distilled before use. Spectral grade methanol, ethanol, and *tert*-butyl alcohol were distilled before use. 1,2,4,5-Tetracyanobenzene (TCB) was recrystallized from chloroform. 1,2,4,5-Tetramethoxybenzene was generously provided by the Kodak Co. Trimethylphenylstannane,[22] bis(4-methoxyphenyl)-dimethylstannane,[23] (4-methoxyphenyl)trimethylstannane,[24] tri-*n*-butyl(3,4-dimethoxyphenyl)stannane,[25] and dineopentyltin dichloride[26] were prepared by literature procedures.

The following materials were purchased from commercial sources and used as received: trimethyltin chloride (1.0 M solution in THF), 4-bromoanisole, 4-bromoveratrole, lithium chloride, tri-*n*-butyltin chloride, di-*n*-butyltin dichloride, iodobenzene, 4-iodoanisole, 4-bromobiphenyl, phenyltin trichloride, 4-iodobiphenyl, neopentyl chloride, dichlorodimethyltin, and di-*n*-butyltin dibromide.

Nanosecond Transient Absorption Spectrosopy. 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 PerkinElmer 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. The signal from the PMT was directed into a digitizing oscilloscope and then to a computer for viewing, storage, and data analysis.

Preparation of (4-Biphenyl)trimethylstannane (3). A 25 mL flask was charged with 0.130 g (5.4 mmol) of magnesium turnings, 3 mL of THF, and a small crystal of iodine. After gentle warming with a heat gun, 2 mL of THF was added, followed by the addition of 1.16 g (4.98 mmol) of 4-bromobiphenyl in 8 mL of THF at a rate sufficient to maintain reflux. After reflux for 1 h, a trimethyltin chloride solution (5 mmol, 5 mL of 1 M in THF) was added to the reaction mixture. The resulting mixture was refluxed for 1 h and stirred at room temperature for 10 h. After treatment with aqueous saturated ammonium chloride, the reaction mixture was extracted with diethyl ether (30 mL × 4). The combined organic layers were dried over $MgSO_4$ and concentrated to give a yellow solid. Purification by column chromatography (hexanes, SiO_2) gave white crystals (1.43 g, 90%). Further recrystallization from methanol gave colorless plates.

^{1}H NMR ($CDCl_3$ 400 MHz): δ 7.66−7.53 (m, 6.0 H), 7.45 (t, J = 7.6 Hz, 2.0 H), 7.36 (t, J = 7.6 Hz, 1.0 H), 0.33 (s + d, J^{117}_{Sn-H} = 53.2 Hz, J^{119}_{Sn-H} = 55.2 Hz, 9.0 H). ^{13}C NMR ($CDCl_3$ 125 MHz): 142.2, 142.12, 142.09, 137.3 (J_{Sn-C} = 36.4 Hz), 129.7, 128.2, 128.1, 127.8 (J_{Sn-C} = 45.6 Hz), −8.5 (J^{117}_{Sn-C} = 334.2, J^{119}_{Sn-C} = 349.6 Hz). ^{119}Sn NMR ($CDCl_3$ 186.5 MHz): δ −27.50. EI-HSMS: m/z 318.0427 $[M]^+$, calcd for $C_{15}H_{18}Sn$ 318.0430.

Preparation of Bis(4-biphenyl)dimethylstannane. A 50 mL flask was charged with 0.2 g (8 mmol) of magnesium turnings, 5 mL of THF, and a small crystal of iodine. After gentle warming with a heat gun, 5 mL more of THF was added, followed by the addition of 1.8 g (7.7 mmol) of 4-bromobiphenyl in 8 mL of THF at a rate sufficient to maintain reflux. After reflux for 1 h, 0.845 g (3.85 mmol) of dimethyltin dichloride in 5 mL of THF was added to the reaction mixture. The resulting mixture was refluxed for 1 h and stirred at room temperature for 10 h. After treatment with aqueous saturated ammonium chloride, the reaction mixture was extracted with diethyl

DOI: 10.1021/acs.joc.5b01690
J. Org. Chem. 2015, 80, 9240−9246

ether (50 mL × 4). The combined organic layers were dried over $MgSO_4$ and concentrated to give a white solid. Purification by recrystallization (charcoal) from ethyl acetate gave white needles (1.1 g, 63%).

^{1}H NMR ($CDCl_3$ 500 MHz): δ 7.69−7.60 (m, 12.0 H), 7.45 (t, J = 7.5 Hz, 4.0 H), 7.36 (tt, J = 1.0 Hz, 7.5 Hz, 1.9 H), 0.58 (s + d + d, J^{117}_{Sn-H} = 53.5, J^{119}_{Sn-H} = 56.0 Hz, 6.0 H). ^{13}C NMR ($CDCl_3$ 100 MHz): 142.5, 142.1, 140.4, 137.7 (J_{Sn-C} = 38.0 Hz), 129.8, 128.3, 128.1, 128.0 (J_{Sn-C} = 48.0 Hz), −9.0 (J_{Sn-C} = 348.9 Hz). ^{119}Sn NMR ($CDCl_3$ 186.5 MHz): δ −57.39. EI-HSMS: m/z 456.0891 [M]$^+$, calcd for $C_{26}H_{24}Sn$ 456.0900.

Preparation of (4-Biphenyl)dimethyltin Chloride. A 100 mL flask was charged with 0.42 g (0.92 mmol) of bis(4-biphenyl)-dimethylstannane and 30 mL of diethyl ether. To the resulting white suspension was added dropwise 2.4 mL of a 0.38 M HCl solution (0.92 mmol) in diethyl ether to give a clear solution. The volatiles were removed under reduced pressure to give a yellow powder that was recrystallized from hexanes to give colorless crystals (0.11 g, 35%).

^{1}H NMR ($CDCl_3$ 400 MHz): δ 7.76−7.65 (m, 4.1 H), 7.61 (d, J = 7.2 Hz, 1.9 H), 7.48 (t, J = 7.2 Hz, 2.0 H), 7.39 (t, J = 7.2, 0.9 H), 0.90 (s + d, J_{Sn-H} = 56.8 Hz, 6.0 H). ^{1}H NMR (CD_3CN 400 MHz): δ 7.77 (d + d + d, J = 8.4 Hz, J_{Sn-H} = 55.2 Hz, 2.0 H), 7.74−7.65 (m, 4.0 H), 7.49 (t, J = 7.2 Hz, 2.1 H), 7.40 (t, J = 7.6, 1.0 H), 0.88 (s + d, J_{Sn-H} = 65.8 Hz, 5.9 H). ^{1}H NMR (CD_2Cl_2 400 MHz): δ 7.79−7.64 (m, 6.0 H), 7.49 (t, J = 7.2 Hz, 2.1 H), 7.41 (t, J = 7.2 Hz, 1.0 H), 0.92 (s + d + d, J^{117}_{Sn-H} = 58.8, J^{119}_{Sn-H} = 60.0 Hz, 5.9 H). ^{13}C NMR ($CDCl_3$ 125 MHz): 143.9, 141.6, 140.1, 136.5 (J_{Sn-C} = 49.9 Hz), 129.9, 128.7, 128.5, 128.2, −1.1 (J^{117}_{Sn-C} = 377.5, J^{119}_{Sn-C} = 395.0 Hz). ^{119}Sn NMR ($CDCl_3$ 186.5 MHz): δ 99.60. EI-HSMS: m/z 337.9872 [M]$^+$, calcd for $C_{14}H_{15}ClSn$: 337.9884.

Preparation of (4-Methoxyphenyl)dimethyltin Chloride. A 100 mL round-bottom flask was charged with 5.4 g (15 mmol) of bis(4-methoxyphenyl)dimethylstannane and 20 mL of diethyl ether, followed by dropwise addition of 23 mL of a 0.65 M HCl solution (15 mmol) in diethyl ether over 2 h. The reaction mixture was concentrated, and the yellow residue was purified by column chromatography (10/1 hexanes/EtOAc, SiO_2) to give a yellow oil (3.15 g, 73%).

^{1}H NMR ($CDCl_3$ 400 MHz) 7.51 (d + d + d, J = 8.4 Hz, J_{Sn-H} = 54.8 Hz, 2.0 H), 7.00 (d, J = 8.4 Hz, 2.0 H), 3.84 (s, 6.0 H), 0.84 (s + d + d, J^{117}_{Sn-H} = 56.8 Hz, J^{119}_{Sn-H} = 59.2 Hz, 6.0 H). ^{1}H NMR (CD_3CN 400 MHz) 7.59 (d + d + d, J = 8.8 Hz, J_{Sn-H} = 55.2 Hz, 2.0 H), 7.02 (d, J = 8.8 Hz, 2.0 H), 3.81 (s, 6.0 H), 0.82 (s + d + d, J^{117}_{Sn-H} = 63.6 Hz, J^{119}_{Sn-H} = 66.4 Hz, 6.0 H). ^{1}H NMR (CD_2Cl_2 400 MHz) 7.55 (d + d + d, J = 8.4 Hz, J_{Sn-H} = 53.6 Hz, 2.0 H), 7.03 (d, J = 8.8 Hz, 2.0 H), 3.85 (s, 6.0 H), 0.87 (s+ d + d, J^{117}_{Sn-H} = 57.2 Hz, J^{119}_{Sn-H} = 60.0 Hz, 6.0 H). ^{13}C NMR ($CDCl_3$ 125 MHz): δ 162.0, 137.3 (J_{Sn-C} = 55.3 Hz), 131.9 (J^{117}_{Sn-C} = 555.0 Hz, J^{119}_{Sn-C} = 580.9), 115.5 (J_{Sn-C} = 63.4 Hz), 56.0, −1.2 (J_{Sn-C} = 396.6 Hz). ^{119}Sn NMR ($CDCl_3$ 186.5 MHz): δ 101.67. EI-HRMS m/z: [M]$^+$, 291.9675, calcd for $C_9H_{13}ClOSn$ 291.9677.

Preparation of Trineopentylphenylstannane. Trineopentylphenylstannane was prepared by modification of a literature procedure.[27] A 100 mL three-necked flask was charged with 1.7 g (70 mmol) of magnesium powder, 0.27 g (1.51 mmol) of anthracene, 50 mL of THF, and 0.10 mL of methyl iodide (1.6 mmol).[28] The reaction mixture was placed in a sonication bath for 6 h. To the resulting yellow suspension was added 5.0 g (47 mmol) of neopentyl chloride in 6 mL of THF over 0.5 h. The reaction mixture was heated at 70 °C for 12 h. Titration[29] showed that the solution contained 0.55 M active Grignard reagent. Phenyltin trichloride (1.65 mL; 10 mmol) was slowly added to this solution. The resulting mixture was heated to reflux for 8 h and sequentially treated with 50 mL of water and 50 mL of saturated aqueous ammonium chloride. The aqueous layer was extracted with diethyl ether (100 mL × 4). The combined organic layers were dried over $MgSO_4$ and then concentrated to give a yellow oil. Purification by column chromatography (hexanes, SiO_2) gave colorless crystals (3.8 g, 60%).

^{1}H NMR[27] ($CDCl_3$ 500 MHz): δ 7.63 (dd + d + d, J = 1.5 Hz, 7.5 Hz, J_{Sn-H} = 39.5 Hz, 1.9 H), 7.36−7.27 (m, 2.9 H), 1.42 (s + d, J_{Sn-H} = 51.5 Hz, 6.0 H), 1.07 (s, 27.2 H). ^{13}C NMR ($CDCl_3$ 125 MHz): δ 146.0 (J^{117}_{Sn-C} = 360.9 Hz, J^{119}_{Sn-C} = 378.5), 137.6 (J_{Sn-C} = 31.1 Hz), 128.8 (J_{Sn-C} = 40.0 Hz), 128.6, 34.7 (J_{Sn-C} = 32.5 Hz), 33.8 (J^{117}_{Sn-C} = 314.8 Hz, J^{119}_{Sn-C} = 329.2 Hz), 33.2 (J_{Sn-C} = 19.4 Hz). ^{119}Sn NMR ($CDCl_3$ 186.5 MHz): δ −79.49.

Preparation of (3,4-Dimethoxyphenyl)trineopentylstannane (6). In a 100 mL round-bottom flask containing 4.26 g (10.4 mmol) of trineopentylphenylstannane and 10 mL of diethyl ether was slowly placed 17 mL (11.3 mmol) of a 0.67 M HCl solution in diethyl ether over 1 h. The volatiles were removed under reduced pressure to give white crystals (trineopentyltin chloride),[30] which were used without purification. The crystals were transferred into a 50 mL three-necked flask and dissolved in 15 mL of THF. A (3,4-dimethoxyphenyl) magnesium bromide solution (14 mmol, 23 mL of a 0.6 M in THF) was added dropwise. The resulting red solution was heated to reflux for 10 h and then treated with a saturated aqueous ammonium chloride solution. The reaction mixture was extracted with diethyl ether (100 mL × 4). The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo to give a green oil that was purified twice by column chromatography (20/1 hexanes/EtOAc, SiO_2) to give a colorless oil (4.5 g, 92%). A small portion of the purified product was distilled under reduced pressure to give a colorless oil (bp 117 °C, 0.05 Torr).

^{1}H NMR ($CDCl_3$ 400 MHz) δ 7.17−7.03 (m, 2.0 H), 6.88 (d, 7.6 Hz, 1.0 H), 3.90 (s, 3.0 H), 3.88 (s, 3.0 H), 1.35 (s + d, J_{Sn-H} = 50.4 Hz, 5.9 H), 1.02 (s, 27.2 H). ^{13}C NMR ($CDCl_3$ 125 MHz): δ 149.8, 149.4, 136.4, 130.3 (J_{Sn-C} = 32.9 Hz), 120.2 (J_{Sn-C} = 40.1 Hz), 112.0 (J_{Sn-C} = 49.8 Hz), 56.8, 56.5, 34.6 (J_{Sn-C} = 32.3 Hz), 33.9 (J^{117}_{Sn-C} = 315.5 Hz, J^{119}_{Sn-C} = 330.2 Hz), 33.2 (J_{Sn-C} = 19.4 Hz). ^{119}Sn NMR ($CDCl_3$ 186.5 MHz): δ −75.33. EI-HSMS: m/z 470.2205 [M]$^+$, calcd for $C_{23}H_{42}O_2Sn$ 470.2207.

Preparation of Di-*n*-butylbis(3,4-dimethoxyphenyl)-stannane. A 50 mL two-necked flask was charged with 25 mL of a 0.73 M (3,4-dimethoxyphenyl)magnesium bromide solution (18.3 mmol) in THF. Di-*n*-butyltin dibromide (2.0 mL, 3.5 g, 8.9 mmol) in 8 mL of THF was then added dropwise. The resulting reaction mixture was stirred for 10 h and then treated with aqueous ammonium chloride solution. After extraction with diethyl ether (100 mL × 4) the combined organic layers were dried over $MgSO_4$ and concentrated to give a purple oil. Purification by column chromatography (97/3 hexanes/EtOAc, SiO_2) gave a colorless oil (4.0 g, 88%).

^{1}H NMR ($CDCl_3$ 500 MHz): δ 7.05 (dd, J = 1.0 Hz, 7.5 Hz, 1.9 H), 7.00 (d, J = 1.0 Hz, 1.9 H), 6.92 (d, J = 7.5 Hz, 2.1 H), 3.89, 3.86 (s, s, 11.9 H combined), 1.64 (pent, $J \approx$ 7.5 Hz, 4.0 H), 1.39 (sext, $J \approx$ 6.8 Hz, 4.1 H), 1.30−1.27 (m, 4.0 H), 0.91 (t, J = 7.0 Hz, 5.8 H). ^{13}C NMR ($CDCl_3$ 125 MHz): δ 150.4, 149.8 (J_{Sn-C} = 53.8 Hz), 132.0, 130.5 (J_{Sn-C} = 34.4 Hz), 119.8 (J_{Sn-C} = 41.2 Hz), 112.3 (J_{Sn-C} = 53.9 Hz), 56.7, 56.5, 29.8 (J_{Sn-C} = 20.8 Hz), 28.2 (J_{Sn-C} = 58.2 Hz), 14.6, 11.4 (J^{117}_{Sn-C} = 350.9 Hz, J^{119}_{Sn-C} = 367.4 Hz). ^{119}Sn NMR ($CDCl_3$ 186.5 MHz): δ −63.32. EI-HSMS: m/z 508.1628 [M]$^+$, calcd for $C_{24}H_{36}O_4Sn$ 508.1636.

Preparation of Di-*n*-butyl(3,4-dimethoxyphenyl)tin Chloride. In a glovebox, a 10 mL microwave reaction vessel was charged with 1.2 g (4.0 mmol) of di-*n*-butyltin dichloride and capped with a snap-on septum cap. After removal from the glovebox, 1.1 g (2.2 mmol) of di-*n*-butylbis(3,4-dimethoxyphenyl)stannane was added. The reaction mixture was heated at 100 °C in a microwave reactor with stirring for 1 h and then passed through a short, acidic alumina column with diethyl ether as eluent. Removal of the volatiles in vacuo gave a colorless oil (1.1 g, 60%), which was contaminated with ∼5% 1,2-dimethoxybenzene. This material was purified before use by preparative gas chromatography (10% OV-1 8020 GAS-CHROM, 1/4 in. × 6 ft, 250 °C).

^{1}H NMR ($CDCl_3$ 400 MHz) 7.15−7.01 (m, 2.0 H), 6.96 (d, J = 8.0 Hz, 1.0 H), 3.92 (s, 3.0 H), 3.90 (s, 2.9 H), 1.82−1.69 (m, 3.9 H), 1.54−1.36 (m, 7.9 H), 0.93 (t, J = 7.6 Hz, 6.2 H). ^{13}C NMR ($CDCl_3$ 125 MHz): δ 151.5, 150.4, 132.4, 129.4, 118.5, 112.6, 56.9, 56.7, 28.8 (J_{Sn-C} = 24.5 Hz), 27.8 (J_{Sn-C} = 66.2 Hz), 18.8 (J^{117}_{Sn-C} = 363.4 Hz, J^{119}_{Sn-C} = 379.5 Hz), 14.6. ^{119}Sn NMR ($CDCl_3$ 186.5 MHz): δ 87.56. EI-HSMS: m/z 406.0707 [M]$^+$, calcd for $C_{16}H_{27}ClO_2Sn$ 406.0722.

DOI: 10.1021/acs.joc.5b01690
J. Org. Chem. 2015, 80, 9240−9246

Preparation of Bis(3,4-dimethoxyphenyl)-dineopentylstannane. A 25 mL three-necked flask was charged with 0.30 g (0.90 mmol) of dineopentyltin dichloride in 5 mL of THF. A (3,4-dimethoxyphenyl)magnesium bromide solution (2.28 mmol, 4.0 mL of a 0.57 M solution in THF) was added dropwise. The resulting red mixture was heated to reflux for 12 h and then stirred at room temperature for 12 h. After treatment with aqueous ammonium chloride solution, the reaction mixture was extracted with diethyl ether (50 mL × 4). The combined organic layers were dried over $MgSO_4$ and concentrated in vacuo to give a yellow oil. Purification by column chromatography (10/1 hexanes/EtOAc, SiO_2) gave a colorless oil (0.25 g, 52%).

^{1}H NMR ($CDCl_3$ 400 MHz): 7.11 (d + d + d, J = 6.8 Hz, J_{Sn-H} = 43.2 Hz, 2.0 H), 7.04 (s + d, J_{Sn-H} = 44.0 Hz, 2.0 H), 6.91 (d + d, J = 7.6 Hz, J_{Sn-H} = 11.2 Hz, 2.0 H), 3.89, 3.84 (s, s, combined for 12.0 H), 1.48 (s + d, J_{Sn-H} = 53.6 Hz, 4.0 H), 0.97 (s, 18.0 H). ^{13}C NMR ($CDCl_3$ 125 MHz): δ 150.2, 149.8 (J_{Sn-C} = 54.4 Hz), 133.9, ($J^{117}{}_{Sn-C}$ = 421.5 Hz, $J^{117}{}_{Sn-C}$ = 441.6 Hz), 130.8 (J_{Sn-C} = 35.5 Hz), 120.2 (J_{Sn-C} = 42.1 Hz), 112.3 (J_{Sn-C} = 54.4 Hz), 56.9, 56.6, 34.4 (J_{Sn-C} = 19.6 Hz), 33.2 ($J^{117}{}_{Sn-C}$ = 346.5 Hz, $J^{119}{}_{Sn-C}$ = 362.25 Hz), 33.0 (J_{Sn-C} = 19.6 Hz). ^{119}Sn NMR ($CDCl_3$ 186.5 MHz): δ −86.00. EI-HSMS: m/z 536.1929 [M]$^+$, calcd for $C_{26}H_{40}O_4Sn$ 536.1949.

Preparation of (3,4-Dimethoxyphenyl)dineopentyltin Chloride. A 10 mL flask was charged with 0.15 g (0.4 mmol) of bis(3,4-dimethoxyphenyl)dineopentylstannane in 2 mL of diethyl ether. An HCl solution (0.42 mmol, 0.62 mL of a 0.67 M solution in diethyl ether) was slowly added over 20 min. The resulting mixture was concentrated in vacuo to give a yellow oil (0.21 g). Purification by preparative gas chromatography (column 10% OV-1 8020 GAS-CHROM 1/4 in. × 6 ft, 206 °C) gave a colorless oil (0.050 g, 29%).

^{1}H NMR ($CDCl_3$ 400 MHz) 7.18 (s + d, J_{Sn-H} = 54.4 Hz, 1.0 H), 7.13 (dd + d + d, J = 0.8 Hz, 8.0 Hz, J_{Sn-H} = 54.4 Hz, 1.0 H), 6.95 (d + d + d, J = 8.0 Hz, J_{Sn-H} = 16.0 Hz, 1.0 H), 3.92, 3.90 (s, s, combined for 6.0 H), 1.70 (s + d, J_{Sn-H} = 52.4 Hz, 4.0 H), 1.07 (s, 18.0 H). ^{13}C NMR ($CDCl_3$ 100 MHz): δ 151.1, 150.3, 134.8, 129.1 (J_{Sn-C} = 54.6 Hz), 118.4 (J_{Sn-C} = 53.3 Hz), 112.5 (J_{Sn-C} = 69.5 Hz), 57.0, 56.7, 40.6 ($J^{117}{}_{Sn-C}$ = 352.0 Hz, $J^{119}{}_{Sn-C}$ = 368.5 Hz), 34.2 (J_{Sn-C} = 43.0 Hz), 33.2 (J_{Sn-C} = 23.2 Hz). ^{119}Sn NMR ($CDCl_3$ 186.5 MHz): δ 68.73. EI-HSMS: m/z 434.1019 [M]$^+$, calcd for $C_{18}H_{31}ClO_2Sn$ 434.1035.

Representative Procedure for Photooxidations of Aryltrimethylstannanes in CD_3CN. A stopcocked quartz cuvette containing a Teflon-coated magnetic stir bar was charged with 0.5 mL of a 0.0225 M 1,2,4,5-tetracyanobenzene solution in CD_3CN, 40 μL of a 0.13 M solution of stannane in CD_3CN, 0.4 mL of CD_3CN, and an aromatic codonor (0.1−0.5 M). The solution was purged with argon for ∼15 min and then photolyzed with stirring at 313 nm for 10 min. To the resulting solution was added 30 μL of a 0.17 M dioxane solution (internal standard) in CD_3CN and 20 μL of a 4 M aqueous LiCl solution. After it was stirred for 10 min, the solution was quickly dried over $MgSO_4$, filtered into a NMR tube, and analyzed by ^{1}H NMR spectroscopy. Integrations of the methyl group hydrogens of the tin chlorides were used to calculate the aryl/Me fragmentation ratio and the mass balance (vs the internal standard).

Representative Procedure for Photooxidations of Aryltrimethylstannanes in CH_2Cl_2. A stopcocked quartz cuvette containing a Teflon-coated magnetic stir bar was charged with 2 mL of a 0.0133 M stannane solution in 9/1 CH_2Cl_2/CD_2Cl_2 containing 4 mM $NMQ^+PF_6^-$, 0.5 M toluene, and 1 M nucleophile. The reaction solution was photolyzed at 334 nm with stirring for ∼60 min, and then 25 μL of a 0.282 M dioxane solution (internal standard) in CH_2Cl_2 was added. The reaction mixture was stirred over dry LiCl powder for 3 h, filtered through a plug of glass wool, and then analyzed by ^{1}H NMR spectroscopy. Integrations of the methyl group hydrogens of the tin chlorides were used to calculate the aryl/Me fragmentation ratio and the mass balance (vs the internal standard).

Procedure for the Photooxidation of Tri-*n*-butyl(3,4-dimethoxyphenyl)stannane (5) in CH_3CN. **5** was purified by preparative GC (10% OV-1 8020 GAS-CHROM 1/4 in. × 6 ft, oven temperature 250 °C) immediately before use, because photooxidations carried out without purification by preparative GC resulted in low conversions. A stopcocked quartz cuvette containing a Teflon-coated magnetic stir bar was charged with 1.5 mL of a 0.0164 M solution of **5** in dioxygen-saturated acetonitrile containing 1.6 mM $NMQ^+PF_6^-$ and 0.5 M toluene. The solution was photolyzed at 334 nm with stirring for 80 min. To the resulting solution was added 100 μL of a 0.362 M dibenzyl ether (internal standard) solution in CD_3CN, which was stirred over 0.080 g of dry LiCl powder for 3 h. The mixture was then concentrated under reduced pressure, triturated with $CDCl_3$, filtered through a plug of glass wool, and analyzed by ^{1}H NMR spectroscopy, which showed that di-*n*-butyl(3,4-dimethoxyphenyl)tin chloride was formed in near-quantitative yield. ^{119}Sn NMR spectroscopy confirmed that di-*n*-butyl(3,4-dimethoxyphenyl)tin chloride was the only tin chloride product formed.

Procedure for the Photooxidation of (3,4-Dimethoxyphenyl)trineopentylstannane (6) in CH_3CN. **6** was purified by preparative GC (10% OV-1 8020 GAS-CHROM 1/4 in. × 6 ft, oven temperature 250 °C) immediately before use, because photooxidations carried out without purification by preparative GC resulted in low conversions. A stopcocked quartz cuvette was charged with 0.021 g (0.045 mmol) of **6** and 2 mL of a dioxygen-saturated acetonitrile solution containing 1.6 mM $NMQ^+PF_6^-$ and 0.5 M toluene. The solution was photolyzed at 334 nm with stirring for 90 min. To the resulting solution was added 100 μL of a 0.208 M dibenzyl ether (internal standard) solution in CD_3CN, which was stirred over 0.080 g of dry LiCl powder for 3 h. The mixture was then concentrated under reduced pressure, triturated with $CDCl_3$, filtered through a plug of glass wool, and analyzed by ^{1}H NMR spectroscopy, which showed that (3,4-dimethoxyphenyl)dineopentyltin chloride was formed in near quantitative yield. ^{119}Sn NMR spectroscopy confirmed that (3,4-dimethoxyphenyl)dineopentyltin chloride was the only tin chloride product formed.

General Procedure for the Generation and Observation of Stannane Cation Radicals by Nanosecond Transient Absorption Spectroscopy. Transient absorption experiments were typically performed in quartz stopcocked cuvettes containing solutions with ∼1 mM $NMQ^+PF_6^-$ (OD ≈ 1 at 343 nm), 0.5 M toluene, and ∼0.01 M stannane in either dioxygen-saturated acetonitrile or dichloromethane. Transient spectra were generally recorded after 100 ns so as to avoid interference from the *N*-methylquinolyl radical.[31] For this reason, fitting of transient decays or growths for kinetic experiments were only done after 100 ns.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.5b01690.

NMR spectra (^{1}H, ^{13}C, and ^{119}Sn) and representative kinetic plots for bimolecular rate constants (PDF)

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

The NSF (CHE-1464629) is gratefully acknowledged for financial support.

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DOI: 10.1021/acs.joc.5b01690
J. Org. Chem. 2015, 80, 9240−9246