# Free-Radical Chain Substitution Reactions ($S_H2'$) of Alkenyl-, Alkynyl-, and (Alkenyloxy)stannanes[1]

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Free-radical chain substitution reactions of allyltributylstannane were observed with PhSSPh, $PhCH_2SSCH_2Ph$, PhSeSePh, $PhSO_2Cl$, $n$-$PrSO_2Cl$, or $CCl_3SO_2Cl$, where the attacking radicals leading to allylic rearrangement with displacement of $Bu_3Sn\cdot$ were $PhS\cdot$, $PhCH_2S\cdot$, $PhSe\cdot$, $PhSO_2\cdot$, $n$-$PrSO_2\cdot$, and $CCl_3\cdot$, respectively. Allylic rearrangement was also observed in the $S_H2'$ reaction of crotyltributylstannane with PhSSPh, $PhCH_2SSCH_2Ph$, $PhSO_2Cl$, or $n$-$PrSO_2Cl$. Propargyltriphenylstannane underwent $S_H2'$ substitution to form the allenic substitution products with $PhSO_2Cl$, $n$-$PrSO_2Cl$, $CCl_4$, and $CHCl_3$ while 2-butynyltriphenylstannane formed the 1,2-butadiene with $PhSO_2Cl$ or $n$-$PrSO_2Cl$. Reaction of (1-cyclohexenyloxy)tributylstannane with $CCl_4$ or $BrCCl_3$ formed $\alpha$-(trichloromethyl)cyclohexanone. With $HCBr_3$ the initially formed $\alpha$-(dibromomethyl)cyclohexanone readily underwent dehydrobromination to form $\alpha$-(bromomethylene)cyclohexanone. [(2-Methyl-1-propenyl)oxy]tributylstannane formed $\alpha$-(trichloromethyl)isobutyraldehyde with $CCl_4$ or $BrCCl_3$. Reaction with $HCBr_3$ gave a mixture of $\alpha$-(dibromomethyl)isobutyraldehyde and 1-(dibromomethyl)-2,2-dimethyloxirane.

## Introduction

Allylstannanes are recognized to undergo $S_H2'$ substitution with a variety of alkyl halides (reactions 1 and 2).[2]

$$R\cdot + CH_2{=}CHC^*H_2SnR'_3 \xrightarrow{S_H2'} RCH_2CH{=}C^*H_2 + R'_3Sn\cdot \quad (1)$$

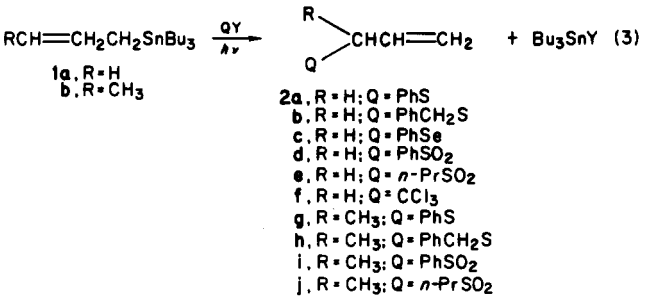
$$R'_3Sn\cdot + RX \rightarrow R'_3SnX + R\cdot \quad (2)$$

Similar reaction are known for allyl or propadienyl derivatives of Co, Ir, and Rh with both carbon-centered[3] and heteroatom-centered radicals.[4] We have extended this free-radical chain substitution to include propargyl[5] and alkenyloxy tin derivatives. We have also demonstrated $S_H2'$ substitutions using hetero-centered radicals ($RS\cdot$, $RSO_2\cdot$, and $PhSe\cdot$) with allylstannanes.

## Results and Discussion

**Allylstannanes.** Table I summarizes results of photostimulated substitutions of allyl- and crotyltributylstannane (reaction 3). The reactions did not occur in the dark but could be initiated by azobis(isobutyronitrile) (AIBN) at 70 °C. The photostimulated reactions were completely inhibited for up to 4 h by 10 mol % of $(t\text{-}Bu)_2NO\cdot$ or galvinoxyl.

The 1-butenyl derivatives **2g** and **2i** rearranged readily under the reaction conditions to give 2-butenyl derivatives.[6] This rearrangement was much faster for Q = PhS than for

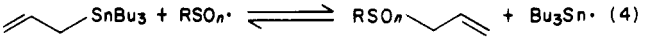



Q = $PhCH_2S$ and for Q = $PhSO_2$ than for Q = $n$-$PrSO_2$. Thus, after 2 h of irradiation in the presence of PhSSPh, **1b** gave a 1:1 mixture of **2**(Q = PhS) and **3**(Q = PhS).

$$\underset{\mathbf{2}}{QCH(CH_3)CH{=}CH} \xrightarrow[QY]{h\nu} \underset{\mathbf{3}}{CH_3CH{=}CHCH_2Q} \quad (3a)$$

However, with short irradiation times the 1-butenyl derivatives **2h–j** could be formed without significant rearrangement to **3**. The sulfonyl radicals $PhSO_2\cdot$ or $n$-$PrSO_2\cdot$ reacted with **1** without loss of $SO_2$. However, with $Cl_3C\text{-}SO_2\cdot$ loss of $SO_2$ occurred to form the $CCl_3\cdot$ which underwent $S_H2'$ substitution with **1a** to yield **2f**. A similar process has been observed in the reaction of $CCl_3SO_2Cl$ with allylcobaloxime.[4]

The displacement of $R_3Sn\cdot$ by $RSO_2\cdot$ or $RS\cdot$ radicals must be a reversible reaction because Ueno has observed that allylic sulfides or sulfones will react with $Bu_3SnH$ to form allylic stannanes.[7] The equilibrium of reaction 4 can




be driven to the left by the reactions of $RSO_n\cdot$ with $Bu_3SnH$ or to the right by the reactions of $R_3Sn\cdot$ with RSSR or $RSO_2Cl$. Under the conditions employed in Table I the isomerization of 1-butenyl- to 2-butenyltributylstannanes (via $Bu_3Sn\cdot$ attack) was not a complicating factor.

*N*-Bromosuccinimide failed to undergo a free-radical chain reaction with **1a**. Only allyl bromide was formed, presumably from an $S_E$ substitution process.

**Propargylstannanes.** Reactions of propargyltriphenylstannane with $PhSO_2Cl$, $n$-$PrSO_2Cl$, $CCl_4$, or $CHCl_3$

(1) Supported by Grant CHE-8119343 from the National Science Foundation.

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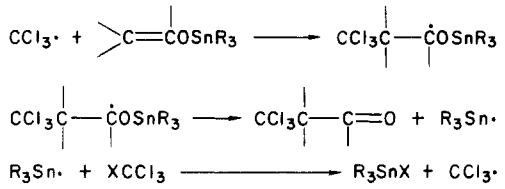
**Table I. Photostimulated Reaction of Allylstannanes[a]**

$$RCH{=}CHCH_2SnBu_3 + QY \xrightarrow[C_6H_6]{h\nu} RC(Q)HCH{=}CH_2 + Bu_3SnY$$

| R | QY | conditn | product (% yield)[b] |
|---|---|---|---|
| H | PhSSPh | 6 h | **2a** (85, 77[c]) |
| H | PhSSPh | 4 h, 10 mol % $(t\text{-Bu})_2NO\cdot$ | **2a** (0) |
| H | PhSSPh | 4 h, 10 mol % galvinoxyl | **2a** (0) |
| H | $PhCH_2SSCH_2Ph$ | 6 h | **2b** (77[c]) |
| H | PhSeSePh | 6 h | **2c** (94) |
| H | $PhSO_2Cl$ | 6 h | **2d** (76[c]) |
| H | $n\text{-}PrSO_2Cl$ | 6 h | **2e** (74[c]) |
| H | $CCl_3SO_2Cl$ | 6 h | **2f** (31) |
| $CH_3$ | PhSSPh | 2 h | **2g**:**3a** (1:1) |
| $CH_3$ | $PhCH_2SSCH_2Ph$ | 1.5 h | **2h** (34) |
| $CH_3$ | $PhSO_2Cl$ | 9 min | **2i** (72) |
| $CH_3$ | $n\text{-}PrSO_2Cl$ | 3 min | **2j** (46) |

[a] General procedure involved 3 mmol of stannane and 3 mmol of QY in 10 mL of deoxygenated $C_6H_6$ or $C_6D_6$. Solutions were stirred in a round-bottomed Pyrex flask ca. 15 cm from a 275-W sunlamp. [b] $^1H$ NMR yields in $C_6D_6$. [c] Isolated yields.

**Scheme I**



were complicated by rearrangement to the propadienylstannane (reaction 5). The complete rearrangement of

$$HC{\equiv}CCH_2SnPh_3 + Ph_3Sn\cdot \rightarrow Ph_3SnCH{=}\dot{C}CH_2SnPh_3$$
**4a**

$$\rightarrow Ph_3SnCH{=}C{=}CH_2 + Ph_3Sn\cdot \quad (5)$$
**5**

**4a** to **5** occurred upon irradiation at 40 °C or with AIBN at 70 °C. Thermal rearrangement at 70 °C was not observed in 8 h. This rearrangement was not observed for the 2-butynylstannane **4b**. Apparently **4a** is more reactive than **5** toward attack by $RSO_2\cdot$, $CCl_3\cdot$, or $CHCl_2\cdot$ because reactions of **4a** with $RSO_2Cl$, $CCl_4$, or $CHCl_3$ led to a mixture of **5** and the substitution product **6**. Table II summarizes results obtained using AIBN and $h\nu$ to stimulate reaction 6. Better yields of **6a–d** were obtained with

$$RC{\equiv}CCH_2SnPh_3 \xrightarrow[h\nu]{QY} QC(R){=}C{=}CH_2 + Ph_3SnY \quad (6)$$

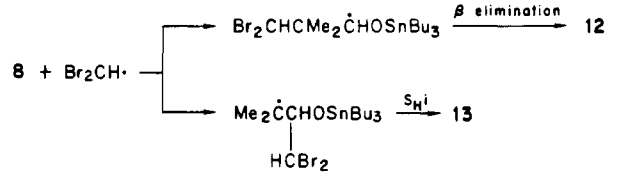
**4a**, R = H
**b**, R = $CH_3$

**6a**, R = H; Q = $PhSO_2$
**b**, R = H; Q = $n\text{-}PrSO_2$
**c**, R = H; Q = $CCl_3$
**d**, R = H; Q = $CHCl_2$
**e**, R = $CH_3$; Q = $PhSO_2$
**f**, R = $CH_3$; Q = $n\text{-}PrSO_2$

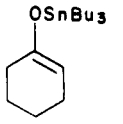
AIBN at 70 °C while $h\nu$ at 35–40 °C gave better yields in the reations of **4b**. The allenic stannane **5** was unreactive to attack by $RSO_2\cdot$, $CCl_3\cdot$, or $CHCl_2\cdot$ radicals since the products of $S_H2'$ substitution ($QCH_2C{\equiv}CH$) were not observed. Attack of radicals ($S_H2'$) upon allenic groups have been observed in the case of cobaloxime, iridium, and rhodium derivatives.[3,4]

**(Alkenyloxy)stannanes.** (Alkenyloxy)stannanes are known to undergo electrophilic attack at the β-position by alkyl halides.[8] Arylation reactions employing Pd(0) are also known to occur.[9] We have examined the free-radical

**Scheme II**



$S_H2'$ substitution of **7** and **8** with $CCl_4$, $BrCCl_3$, and $CHBr_3$ (Scheme I).



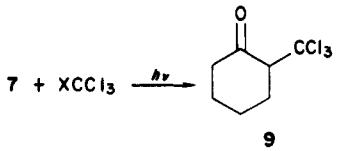
**7**

$(CH_3)_2C{=}CHOSnBu_3$

**8**

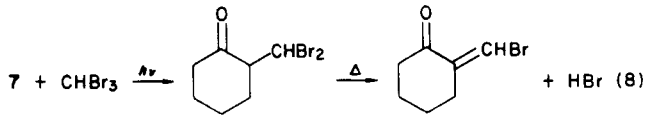
Stannanes **7** and **8** were chosen because they are reported to exist solely in the oxy form and not as a mixture of two equilibrating metallotropic isomers.[10]

α-(Trichloromethyl)cyclohexanone (**9**) was prepared in good yield from **7** upon photostimulated reaction with $CCl_4$ or $BrCCl_3$ (reaction 7). The reaactions did not occur in the dark and were inhibited by 10 mol % $(t\text{-Bu})_2NO\cdot$ (Table III). Reaction of **7** with tribromomethane ($h\nu$, 1 h) formed the corresponding α-(dibromomethyl)cyclohexanone (29%) which upon distillation underwent dehydrobromination to form **10** (reaction 8). Reaction of **8** with $CCl_4$ or $BrCCl_3$ produced the α-trichloromethyl aldehyde **11** (reaction 9, Table III).



(7)

**9**

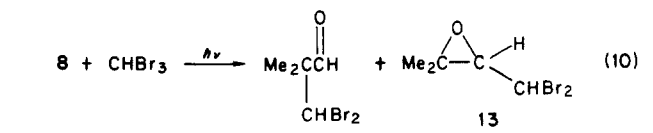


(8)

**10**

$$CCl_3X + Me_2C{=}CHOSnBu_3 \xrightarrow{h\nu} CCl_3CMe_2CHO + Bu_3SnX \quad (9)$$
**11**

Reaction of **8** with $CHBr_3$ gave not only the expected dibromomethyl aldehyde **12** (formally $S_H2'$ substitution) but also the epoxide **13** in a 3:1 ratio (reaction 10). Formation of the epoxide most likely involves α-addition of $Br_2CH\cdot$ followed by an internal ($S_Hi$) displacement of $Bu_3Sn\cdot$ (Scheme II).



(10)

**12** **13**

Reaction products of $CBr_4$ or PhSSPh with **7** or **8** were not observed and only traces of reaction occurred with $CHCl_3$. The chloro sulfones $PhSO_2Cl$ or $CCl_3SO_2Cl$ reacted with **7** in the presence or absence of irradiation to form α-chlorocyclohexanone by an $S_E2'$ reaction (reaction 11).

## Experimental Section

**Reagents.** Allyltri-*n*-butylstannane was prepared by the Grignard route using THF as solvent:[11] bp 106 °C (0.1 torr); $^1H$

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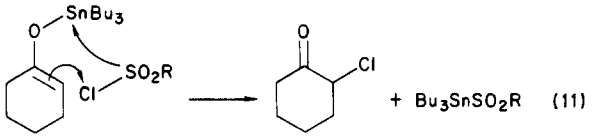


NMR ($C_6D_6$) δ 0.7–2.4 (m, 29), 4.8 (m, 2), 5.9 (m, 1). Crotyltri-*n*-butylstannane was prepared from $Bu_3SnNa$ and crotyl chloride:[12] bp 99 °C (0.1 torr); $^1H$ NMR ($C_6D_6$) δ 0.9–2.5 (m, 32), 5.2 (m, 2). Propargyltriphenylstannane was prepared by the Grignard route.[12] Recrystallized material from hexane: mp 80–82 °C; $^1H$ NMR ($C_6D_6$) δ 1.35 (t, 1, $J$ = 3 Hz), 1.55 (d, 2, $J$ = 3 Hz), 6.8–7.5 (m, 15); IR ($CCl_4$) 3290, 2110 $cm^{-1}$. Propadienyltriphenylstannane was prepared from the propargyl isomer by refluxing in EtOH for 15 min:[13] mp 58–59 °C; $^1H$ NMR ($CCl_4$) δ 4.45 (d, 2, $J$ = 7 Hz), 5.51 (t, 1, $J$ = 7 Hz), 7.7 (m, 15). 2-Butynyltriphenylstannane was prepared from the Grignard of 4-bromo-2-butyne[14] (bp 72 °C (100 torr); $^1H$ NMR δ 1.91 (t, 3), 4.0 (q, 1)). Recrystallization of the stannane from hexane gave material: mp 68–69 °C; $^1H$ NMR ($CCl_4$) δ 1.69 (t, 3, $J$ = 4 Hz), 2.16 (q, 2, $J$ = 4 Hz); IR ($CCl_4$) 2223 $cm^{-1}$. (1-Cyclohexenyloxy)tri-*n*-butylstannane was prepared from 1-cyclohexenyl acetate and tri-*n*-butylethoxystannane:[15] $^1H$ NMR ($CCl_4$) δ 0.5–2.0 (m, 35), 4.5 (m, 1). [(2-Methyl-1-propenyl)oxy]tri-*n*-butylstannane was prepared in a similar fashion from 2-methylpropenyl acetate:[16] bp 115 °C (8 torr); $^1H$ NMR ($CCl_4$) δ 0.5–2.0 (m, 33), 6.5 (m, 1).

**Photostimulated Reactions of Organostannanes.** Equal molar amounts (~3 mmol) of substrate and organostannane were mixed in 10 mL of $C_6H_6$ (or $C_6D_6$ if the reaction was to be followed by $^1H$ NMR) in a Pyrex flask fitted with a rubber septum. The solution was deoxygenated by nitrogen bubbling for 15 min and then magnetically stirred ca. 15 cm from a 275-W sunlamp. Reactions employing halomethanes as the substrate used a large excess of the halomethane as the reaction solvent. At the end of the reaction the solvent was removed by rotatory evaporation and the product isolated by kugelrohr distillation. For reactions followed by $^1H$ NMR the substrates were mixed in $C_6D_6$ or polyhalomethane solvent, transferred to a 6-mm NMR tube capped with a septum, and irradiated by the sunlamp. For dark reactions the flask or NMR tube was wrapped with aluminum foil. Reactions catalyzed by AIBN were performed in an oil bath at 70 °C.

**Reactions of Allyltri-*n*-butylstannane.** Analysis by $^1H$ NMR for **2a-f** was based on the doublet methylene absorption at δ 3.0–3.5. The following products were isolated. Allyl phenyl sulfide (**2a**): bp 95–140 °C (38 torr); $^1H$ NMR ($C_6D_6$) δ 3.45 (d, 2, $J$ = 6.5 Hz), 4.85–6.22 (m, 3), 7.2 (m, 5). Allyl benzyl sulfide (**2b**); bp 140–150 °C (0.5 torr); $^1H$ NMR ($C_6D_6$) δ 2.95 (d, 2, $J$ = 6 Hz), 3.58 (s, 2), 4.8–6.1 (m, 3), 7.35 (m, 5). Allyl phenyl selenide (**2c**): $^1H$ NMR ($C_6D_6$) δ 3.35 (d, $J$ = 6H). Allyl phenyl sulfone (**2d**): bp 80–120 °C (0.3 torr); $^1H$ NMR ($C_6D_6$) δ 3.77 (d, 2, $J$ = 6.5 Hz), 4.8–6.1 (m, 3), 7.4–8.0 (m, 5). Allyl *n*-propyl sulfone (**2e**): bp 110–150 °C (39 torr); $^1H$ NMR ($C_6D_6$) δ 1.1 (t, 3), 1.8 (m, 2), 2.95 (m, 2), 3.75 (d, 2, $J$ = 6 Hz), 5.25–6.35 (m, 3). 4,4,4-Trichloro-1-butene (**2f**): bp 30–50 °C (100 torr); $^1H$ NMR ($C_6D_6$) δ 3.2 (d, 2, $J$ = 6 Hz).

Reactions of crotyltri-*n*-butylstannane were followed by $^1H$ NMR by observing the characteristic PhSCH proton which displayed a pentet splitting for **2h-j** and a doublet splitting for **3**.

**Reactions of Propargyltriphenylstannane (4a).** Irradiation of **4a** in $C_6D_6$ for 19 h showed by $^1H$ NMR that isomerization to **5** was complete. No isomerization was observed in the dark at 70 °C for 7 h. However, in the presence of 10 mol % of AIBN at 70 °C for 7 h isomerization to **5** was complete. No reaction of **4a** was observed with $PhSO_2Cl$ or *n*-$PrSO_2Cl$ in $C_6D_6$ for 7 h at 70 °C. In the presence of AIBN at 70 °C a mixture of **5** and the rearranged sulfones **6a,b** was observed. Following kugelrohr distillation **6a** and **6b** were isolated by preparative GC by using a 5 ft × $^1/_4$ in. 15 % OV-3 column at 180 (**6a**) or 140 °C (**6b**). 1-(Phenylsulfonyl)propadiene (**6a**): bp 130 °C (0.8 torr); $^1H$ NMR ($C_6D_6$) δ 4.65 (d, 2, $J$ = 6.5 Hz), 5.85 (t, 1, $J$ = 6.5 Hz), 6.75–7.95 (m, 5); $^{13}C$ NMR δ 101.39 (C-1) 209.15 (C-2), 83.16 (C-3), 142.22, 136.00 (ortho), 132.71 (meta), 128.71 (para); IR 1975, 1940 $cm^{-1}$; GCMS (relative intensity) 180 (1.5), 141 (25), 116 (12), 77 (100); HRMS 180.02391, calcd for $C_9H_8SO_2$ 180.0245. 1-(*n*-Propylsulfonyl)propadiene (**6b**): bp 60–105 °C (1.3 torr); $^1H$ NMR ($C_6D_6$) δ 0.55 (t, 3). 1.6 (m, 2), 2.9 (m, 2), 4.95 (d, 2, $J$ = 6.5 Hz), 6.05 (t, 1, $J$ = 6.5 Hz); $^{13}C$ NMR (proton coupled) δ 98.32 (d × t, $J_{CH}$ = 8.4, 0.35 Hz, C-1), 209.95 (s, C-2), 82.87 (t × d, $J_{CH}$ = 7.7, 0.15 Hz, C-3), 57.37 (t, $C_\alpha$), 16.37 (t, $c_\beta$), 13.01 (q, $C_\gamma$): IR 1985, 1940 $cm^{-1}$; GCMS (relative intensity) 104 (100), 103 (11), 81 (25), 79 (20), 76 (71), 75 (13), 67 (99), 63 (12), 55 (30), 54 (30), 53 (31), 47 (14); HRMs 146.0415, calcd for $C_6H_{10}SO_2$ 146.04016.

Reactions of **4a** with $CCl_4$ and $CHCl_3$ were performed by using the chlorocarbon as the solvent. Distillation yielded mixtures of **6c** with $CCl_4$ and **6d** with $CHCl_3$ which were analyzed by $^1H$ NMR and GCMS. 4,4,4-Trichloro-1,2-butadiene (**6c**):[17] collected at 35–40 °C (100 torr); $^1H$ NMR ($CCl_4$) δ 5.35 (d, 2, $J$ = 6.5 Hz), 6.1 (t, 1, $J$ = 6.5 Hz); IR 1960, 1550 $cm^{-1}$; GCMS (relative intensity) 162 (0.2), 161 (0.04), 160 (2.2), 159 (0.3) 158 (7), 157 (0.4), 156 (7.8), 125 (10), 123 (63), 121 (100) 87 (10), 86 (10), 85 (50). 4,4-Dichloro-1,2-butadiene (**6d**): collected at 25 °C (1.5 torr); $^1H$ NMR (double irradiation at 300 MHz) δ 5.8 (d × t, 1 (H-4), $J_{3,4}$ = 8, $J_{1,4}$ = 1 Hz), 5.4 (q, 1 (H-3), $J_{4,3}$ = $J_{1,3}$ = 8 Hz), 4.6 (d × d, 2 (H-1), $J_{3,1}$ = 8, $J_{4,1}$ = 1 Hz); IR (neat) 1980, 1950 $cm^{-1}$; GCMs (relative intensity) 126 (0.86), 124 (6), 122 (10), 89 (28), 87 (100), 61 (9).

**Reactions of 2-Butynyltriphenylstannane (4b).** Benzenesulfonyl chloride or *n*-$PrSO_2Cl$ and **4b** in a 1:1 mol ratio (7.4 mmol in 10 mL $C_6H_6$) were irradiated with a sunlamp. The solvent was evaporated under reduced pressure and 25 mL of 10% aqueous KF added to the residue. After the reaction was stirred for 10 min and filtered, the residue was extracted with $Et_2O$ and the extract stirred for 1 day with 40 mL of 10% aqueous NaOH. The ether layer was separated and kugelrohr distilled to give **6e,f** and a residue of **4b**. The sulfones **6e,f** were further purified by preparative GC by using a 5 ft × $^1/_4$ in. 15% OV-3 column at 180 (**6e**) or 140 °C (**6f**). 1-Methyl-1-(phenylsulfonyl)propadiene (**6e**): collected at 70–110 °C (1.5 torr); $^1H$ NMR ($C_6D_6$) δ 1.58 (t, 3, $J$ = 4 Hz), 4.55 (q, 2, $J$ = 4 Hz), 6.5–7.8 (m, 5); $^{13}C$ NMR δ 108.61 (C-1), 207.80 (C-2), 82.01 (C-3), 135.11 ($CH_3$), 140.86, 132.64 (ortho), 128.56 (meta), 128.8 (para); IR 1980, 1955 $cm^{-1}$; GCMS (relative intensity) 194 (1), 130 (18), 125 (18), 123 (12), 109 (10), 78 (20), 77 (50), 53 (100); HRMS 194.04033, calcd for $C_{10}H_{10}SO_2$ 194.04016.

1-Methyl-1-(*n*-propylsulfonyl)propadiene (**6f**): collected at 130–140 °C (1.5 torr); $^1H$ NMR ($C_6D_6$) δ 0.53 (m, 3), 1.13 (t, 3, $J$ = 4 Hz), 1.35 (m, 2), 2.50 (m, 2), 4.55 (q, 2, $J$ = 4 Hz); $^{13}C$ NMR δ 106.76 (C-1), 207.65 (C-2), 81.44 (C-3), 13.01 ($CH_3$), 13.30 ($C_\gamma$), 54.84 ($C_\alpha$), 16.17 ($C_\beta$); IR 1970, 1940 $cm^{-1}$; GCMS (relative intensity) 161 (0.07), 160 (0.9), 118 (4) 90 (1.6), 89 (2.5), 81 (3.1), 75 (6), 74 (15), 58 (3), 54 (12), 53 (100); HRMS 160.05609, calcd for $C_7H_{12}SO_2$ 160.00581.

**Reactions of (Alkenyloxy)stannanes.** No reaction was observed in the dark between **7** or **8** and halomethanes while the photostimulated reaction of **7** with $CCl_4$ to form **9** was drastically retarded by 10 mol % $(t\text{-Bu})_2NO\cdot$ for periods up to 85 min (in the absence of the nitroxide, **7** was completely consumed in less than 1 h). Benzenesulfonyl chloride or *n*-$PrSO_2Cl$ reacted readily with **7** in the dark to form α-chlorocyclohexanone.

The (alkenyloxy)stannanes (freshly prepared **7** or **8**) were dissolved in 10 mL of the halocarbon (Table III) in a round-bottomed Pyrex flask equipped with a septum. The stirred solution was deoxygenated by nitrogen bubbling for 5 min before irrdiation with a 275-W sunlamp which maintained a reaction temperature of ~35 °C. Products were isolated by short-path or kugelrohr distillation and by recrystallization of **9** from hexane.

α-(Trichloromethyl)cyclohexanone (**9**): mp 92–93 °C; $^1H$ NMR ($C_6D_6$) δ 1.6–2.9 (m, 8), 3.3 (m, 1); IR ($CCl_4$) 1720 $cm^{-1}$; GCMS

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**Table II. Reactions of Propargylstannanes with QY Reagents**[a]

$RC{\equiv}CCH_2SnPh_3 + QY \rightarrow QC(R){=}C{=}CH_2 + Ph_3SnY$

| R | QY | conditn | % yield[b] $QC(R){=}C{=}CH_2$ (6) | % yield[b] $Ph_3SnC(H){=}C{=}CH_2$ (5) |
|---|---|---|---|---|
| H | $PhSO_2Cl$ | 70 °C, $C_6H_6$, 8 h, 10 mol % AIBN | 36[c] | 36 |
| H | $n$-$PrSO_2Cl$ | 70 °C, $C_6H_6$, 8 h, 10 mol % AIBN | 31 | 43 |
| H | $CCl_4$ | 70 °C, $CCl_4$, 8 h, 10 mol % AIBN | 46 | 24 |
| H | $CHCl_3$ | 70 °C, $CHCl_3$, 8 h, 10 mol % AIBN | 31 | 12 |
| $CH_3$ | $PhSO_2Cl$ | 35 °C, 35 h, $h\nu$ | 42 | 0 |
| $CH_3$ | $n$-$PrSO_2Cl$ | 35 °C, 38 h, $h\nu$ | 31 | 0 |

[a] Reaction of 1:1 mole ratio of stannane with QY (1-7 mmol) in 10 mL of solvent. Photostimulated reactions were irradiated with a 275-W sunlamp ca. 15 cm from the Pyrex reaction flask. [b] $^1H$ NMR yield. [c] Isolated yield.

**Table III. Photostimulated Reaction of (Alkenyloxy)stannanes with Alkyl Halides**[a]

| stannane | RX | conditn | product (% yield)[b] |
|---|---|---|---|
| 7 | $CCl_4$ | 35 °C, 1 h | **9** (59) |
| 7 | $BrCCl_3$ | 35 °C, 3 h | **9** (64) |
| 7 | $CHBr_3$ | 35 °C, 1 h | **10** (30) |
| 8 | $CCl_4$ | 35 °C, 2 h | **11** (54) |
| 8 | $BrCCl_3$ | 35 °C, 5 min | **11** (48) |
| 8 | $CHBr_3$ | 35 °C, 3 h | **12** (18) |
| | | | **13** (6) |

[a] The stannane (7 mmol) in 10 mL of the halocarbon (solvent) was irradiated with a 275-W sunlamp ca. 15 cm from the Pyrex reaction flask. [b] Yield by $^1H$ NMR.

(relative intensity) 218 (1), 216 (4), 214 (4), 179 (12), 178 (10), 137 (17), 135 (26), 124 (14), 122 (22), 117 (21), 115 (66) 114 (14), 113 (14), 111 (65), 109 (100), 101 (9), 87 (16), 85 (11), 84 (59), 83 (26), 79 (53), 77 (14), 75 (13), 73 (16), 67 (13), 65 (12), 55 (65), 53 (15), 51 (31), 49 (11).

The photostimulated reaction of $HCBr_3$ with **7** gave the unstable $\alpha$-(dibromomethyl)cyclohexanone which could be detected by GCMS or $^1H$ NMR but which underwent dehydrobromination to $\alpha$-(bromomethylene)cyclohexanone (**10**) upon distillation. Compound **10**: bp 40–55 °C (4 torr); $^1H$ NMR ($C_6D_6$) $\delta$ 0.8–2.2 (m, 8), 7.3 (t, 1, $J$ = 2 Hz); IR ($CCl_4$) 3085, 1709, 1589, 1442, 1288, 1137 $cm^{-1}$; GCMS (relative intensity) 190 (13), 188 (12), 81 (100), 79 (34), 53 (50), 51 (14). Surprisingly **7** failed to react with $CBr_4$.

Reactions of **8** with $CCl_4$ or $BrCCl_3$ gave $\alpha$-(trichloromethyl)-isobutyraldehyde (**11**) isolated by kugelrohr distillation at 30–50 °C (0.2 torr): $^1H$ NMR ($C_6D_6$) $\delta$ 1.09 (s, 6), 9.8 (s, 1); IR ($CCl_4$) 2840, 2720, 1745, 650 $cm^{-1}$; GCMS (relative intensity) 194 (0.05), 192 (0.5), 190 (2), 189 (0.1), 188 (2), 161 (4), 159 (4), 127 (11), 126 (26), 125 (20), 124 (40), 123 (9), 119 (6), 117 (8), 111 (8), 109 (13), 91 (29), 89 (96), 87 (16), 63 (13), 53 (100), 51 (28), 50 (9), 49 (11).

The photostimulated reaction of **8** with $CBr_4$ failed to occur while $HCBr_3$ gave a mixture of **12** and **13** which distilled at 46–51 °C (3.5 torr). The mixture was analyzed by GC–FT-IR and GCMS as well as by $^1H$ NMR. $\alpha$-(Dibromomethyl)isobutyraldehyde (**12**) : $^1H$ NMR ($C_6D_6$) $\delta$ 1.1 (s, 6), 5.65 (s, 1), 9.3 (s, 1); IR (vapor) 2985, 2947, 2885, 2815, 2707, 1743, 1465, 1400, 1373, 1465, 1400, 1373, 1272, 1157, 991, 883 $cm^{-1}$; GCMs (relative intensity) 246 (0.4), 244 (1.0), 242 (0.4), 217 (13), 215 (26), 213 (13), 165 (11), 163 (12), 137 (14), 136 (96), 134 (100), 133 (20), 109 (8), 107 (9), 95 (4), 93 (5). 1-(Dibromomethyl)-2,2-dimethyloxirane (**13**): $^1H$ NMR ($C_6D_6$) $\delta$ 1.1 (s, 6), 3.35 (d, 1, $J$ = 8 Hz), 5.25 (d, 1, $J$ = 8 Hz); IR (vapor) 2993, 2978, 2939, 2889, 1508, 1458, 1423, 1384, 1315, 1245, 1192, 1138, 1091, 1034, 914 $cm^{-1}$; GCMS (relative intesnity, 20 eV) 247 (0.01), 246 (0.003), 245 (0.03), 244 (0.01), 243 (0.01), 242 (0.002), 219 (0.3), 188 (1.7), 186 (3.4), 184 (1.8), 166 (1.8), 165 (43), 163 (45), 137 (0.4), 135 (0.4), 137 (0.4), 135 (0.4), 134 (0.02), 133 (0.06), 125 (0.1), 124 (0.2), 123 (0.5), 122 (0.3), 121 (0.5), 109 (0.3), 107 (0.8), 105 (0.5), 84 (0.1), 83 (0.5), 82 (0.1), 59 (14), 56 (3.4), 55 (100), 53 (0.3); GCMS (CI, isobutane) (relative intensity) 247 (52), 245 (100), 243 (52), 241 (0.2), 167 (1.8), 166 (3.4), 165 (30), 163 (28), 151 (45), 149 (47), 141 (3.5), 139 (4.8), 137 (4.6), 135 (4.7), 125 (2.2), 125 (2.2), 123 (1.1), 122 (1.0), 121 (8.3), 113 (9.9), 111 (4.4), 109 (1.3), 101 (1.7), 100 (1.1), 99 (5.6), 97 (7.5), 95 (3.9), 93 (1.6), 91 (1.4), 87 (2.3), 86 (1.7), 85 (16), 83 (7.7), 81 (9.6), 80 (4.5), 75 (2.78), 73 (6), 72 (6.9), 71 (27), 69 (14), 67 (11).

**Registry No.** **1a**, 24850-33-7; **1b**, 31197-41-8; **2a**, 5296-64-0; **2b**, 6937-97-9; **2c**, 14370-82-2; **2d**, 16212-05-8; **2e**, 95019-49-1; **2f**, 13279-84-0; **2g**, 701-75-7; **2h**, 75238-62-9; **2i**, 54897-36-8; **2j**, 95019-50-4; **3**, 702-04-5; **4a**, 4104-89-6; **4b**, 4104-93-2; **5**, 4104-90-9; **6a**, 2525-42-0; **6b**, 95019-51-5; **6c**, 34819-62-0; **6d**, 83682-41-1; **6e**, 13603-90-2; **6f**, 95019-52-6; **7**, 17851-97-7; **8**, 17198-92-4; **9**, 95019-53-7; **10**, 95019-54-8; **11**, 16630-97-0; **12**, 95019-55-9; **13**, 95019-56-0; PhSSPh, 882-33-7; $PhCH_2SSCH_2Ph$, 150-60-7; PhSeSePh, 1666-13-3; $PhSO_2Cl$, 98-09-9; $n$-$PrSO_2Cl$, 10147-36-1; $CCl_3SO_2Cl$, 2547-61-7; $CCl_4$, 56-23-5; $CHCl_3$, 67-66-3; $BrCCl_3$, 75-62-7; $CHBr_3$, 75-25-2.