centrated under reduced pressure and diluted with 5% HCl and the product extracted into $CHCl_3$. The combined organic layers were dried over $MgSO_4$ and concentrated by rotary evaporation. Flash chromatography ($CH_2Cl_2$) provided 0.06 g (0.28 mmol, 60%) of carboxylic acid **15**, which had a $^1H$ NMR spectrum identical with that previously reported:[7] $^1H$ NMR $\delta$ 2.03 (s, 3 H, $CH_3CO$), 2.15 (q, 2 H, $ArCH_2CH_2$), 2.69 (t, $J$ = 6 Hz, 2 H, $ArCH_2$), 3.75 (s, 1 H, OH), 4.68 (q, $J$ = 6 Hz, 1 H, NHC*H*), 7.26 (s, 5 H, Ar), 7.49 (s, 1 H, NH).

**α-[(Trifluoroacetyl)amino]-γ-phenyl-γ-butyrolactone (16).** Triethylsilane (0.38 mL, 0.28 g, 2.4 mmol) was added to a solution of 0.20 g (0.69 mmol) of keto acid **12** in 1.06 mL (1.57 g, 14 mmol) of freshly distilled trifluoroacetic acid. The solution was heated under reflux for 1 h, allowed to cool, and poured into 5 mL of cold $H_2O$. The product was extracted with $CHCl_3$ (3 × 10 mL), dried over $MgSO_4$, and evaporated under vacuum to give a white solid, which was recrystallized from $PhCH_3$ to yield 0.094 g (0.35 mmol, 50%) of pure lactone **16**: mp 168–170 °C; IR (Nujol) 3345, 1779, 1722, 1557, 1217, 1185, 1147, 752, 702 $cm^{-1}$; $^1H$ NMR ($Me_2CO$-$d_6$) $\delta$ 2.32–3.36 (m, 2 H, $CH_2$), 5.11 (m, 1 H, C*H*NH), 5.53, 5.72 (dd, $J$ = 6 Hz, 1 H, ArC*H*), 7.50 (s, 5 H, Ar), 9.17 (br s, 1 H, NH); $^{13}C$ NMR ($Me_2SO$-$d_6$) $\delta$ 35.2, 49.6, 77.6, 126.0, 128.4, 138.4, 156.0 (q, $CF_3$), 172.8, 194.4; $^{19}F$ NMR ($Me_2CO$-$d_6$) $\delta$ −13.4.

Anal. Calcd for $C_{12}H_{10}F_3NO_3$: C, 52.76; H, 3.69; N, 5.13. Found: C, 52.78; H, 3.80; N, 5.03.

**Diastereomeric Amides from Mosher's Acid and 2-Amino-6,7-dimethoxy-1,2,3,4-tetrahydronaphthalene.** To a magnetically stirred solution of 21 mg (0.10 mmol) of crude (*R*)-(+)-ADTN bis(methyl ether) (**10**) in 2 mL of $CCl_4$ at room temperature under $N_2$ was added 300 μL of dry pyridine followed by 35 mg (0.14 mmol) of the acid chloride[11] of (−)-α-methoxy-α-(trifluoromethyl)phenylacetic acid (Mosher's Acid) (Aldrich, 99+%). After 12 h (at which point the formation of precipitated pyridinium chloride was apparently complete) the solution was diluted with $CH_2Cl_2$ and washed successively with dilute aqueous HCl, saturated aqueous $NaHCO_3$, and saturated aqueous NaCl. After drying over $MgSO_4$ the solvents were removed by rotary evaporation to yield the carboxamide **17**. The same reaction was carried out with the racemic amine **2**, which was obtained by the reductive amination of 6,7-dimethoxy-2-tetralone (Aldrich) with $NaBH_3CN$ in the presence of $NH_4OAc$.[2b]

The 1:1 mixture of diastereomeric amides from the racemic amine **2** had the following $^1H$ NMR (270 MHz): $\delta$ 1.65–2.08 (m, 4 H, $ArCH_2CH_2$), 2.52 and 2.98 (2 $q_{AB}$, $J_{gem}$ = 7 Hz, 4 H, $ArCH_2CHN$), 2.75 (m, 4 H, $ArCH_2CH_2$), 3.38 (s, 6 H, $CH_3OCCO$), 3.75 (s, 12 H, $Ar(OCH_3)_2$), 4.24 (m, 2 H, NHC*H*), 6.45, 6.48, 6.49, 6.52 (s, 4 H, Ar), 6.76 (2 d, $J$ = 10 Hz, 2 H, NH), 7.11–7.66 (m, 10 H, Ph). As anticipated, the amide from the optically active amine, **10**, had a simpler spectrum under the same conditions: $\delta$ 1.65–2.08 (m, 2 H, $ArCH_2CH_2$), 2.55 and 3.00 ($q_{AB}$, $J_{gem}$ = 7 Hz, 2 H, $ArCH_2CHN$), 2.75 (m, 2 H, $ArCH_2CH_2$), 3.38 (s, 3 H, $CH_3OCCO$), 3.76 (s, 6 H, $Ar(OCH_3)_2$), 4.24 (m, 1 H, NHC*H*), 6.45 (s, 1 H, $ArH_a$), 6.52 (s, 1 H, $ArH_b$), 6.80 (d, $J$ = 10 Hz, 1 H, NH), 7.11–7.76 (m, 5 H, Ar). The best region of the spectra for analysis of the enantiomeric purity of **10** was that of the aromatic protons, $\delta$ 6.4–6.6. On this basis, **10** was estimated to have an enantiomeric excess of ≥94%, as described in the text.

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**Registry No.** (±)-**2**, 97466-04-1; **4**, 91-16-7; **5**, 75403-90-6; (±)-**5**, 97466-03-0; **6**, 97403-64-0; **7**, 97403-65-1; **8**, 97403-66-2; **9**, 97403-67-3; **10**, 97403-68-4; **10**·HCl, 97403-63-9; **11**, 71074-51-6; (±)-**12**, 97403-69-5; (±)-**13**, 97403-70-8; (±)-**14**, 97403-71-9; (±)-**15**, 5440-40-4; (±)-**16**, 97403-72-0; **17**, 97415-81-1; (2*S*)-**17**, 97403-73-1; $C_6H_6$, 71-43-2; Mosher's acid chloride, 39637-99-5.

## Olefin Synthesis by Reaction of Stabilized Carbanions with Carbene Equivalents. 1. Use of (Iodomethyl)tributylstannane for Methylenation of Sulfones

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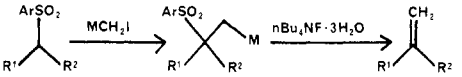
Recently, a novel method for methylenation of *sec*-alkyl aryl sulfones consisting of alkylation with $Me_3SiCH_2I$ followed by fluoride-induced desulfonylsilylation (eq 1, M = $Me_3Si$) was reported.[1] This method is effective for

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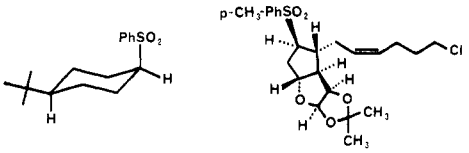
methylenation of sterically unhindered sulfones such as 3α-(phenylsulfonyl)cholestane[1] and *cis*-4-*tert*-butylcyclohexyl phenyl sulfone (**1a**).[2] However, it is ineffective for methylenation of moderately hindered sulfones such as **1b**[3] due to the slowness of the alkylation step.[4,5]




1a 1b

The purpose of this paper is to report that not only unhindered sulfones such as **1a** but also moderately hindered sulfones such as **1b** can be methylenated in excellent yield by employing the eq 1 method with either of two tin analogues of the silicon reagent (eq 1, M = *n*-$Bu_3Sn$ or $Me_3Sn$).[6] Not only does this modification solve the problem of the slowness of the alkylation, but it also results in a tremendous increase in the rate of the *n*-$Bu_4NF$·$3H_2O$-induced fragmentation.

The operating procedure is straightforward. First, the sulfone is deprotonated, by treatment of a solution in THF at −78 °C with either LDA or *n*-BuLi.[7] Next, the tin

(1) Kocienski, P. J. *Tetrahedron Lett.* **1979**, 2649.

(2) Prepared from 4-*tert*-butylcyclohexanone by successive treatments with 1.00 equiv of LAH ($Et_2O$, room temperature, 15 min; 100.0%), 1.25 equiv of TsCl (pyr, room temperature, 16 h; 100.0%), 3.4 equiv of PhSH and 3.2 equiv of NaH (THF, Δ, 10 h; 89.9%), and 3.6 equiv of MCPBA ($CH_2Cl_2$, 0 °C, 40 min; 94.8%): mp 114.5–115.5 °C.

(3) The method of preparation of this compound will be disclosed in a subsequent paper.

(4) (a) Kocienski, P. J. *J. Org. Chem.* **1980**, *45*, 2037. (b) Kocienski, P.; Todd, M. *J. Chem. Soc., Perkin Trans. 1* **1983**, 1777.

(5) (a) Kocienski, P.; Todd, M. *J. Chem. Soc., Chem. Commun.* **1982**, 1078. (b) Kocienski, P.; Todd, M. *J. Chem. Soc., Perkin Trans. 1* **1983**, 1783.

(6) After this work was essentially complete, three papers[6a–c] appeared in which the use of *n*-$Bu_3SnCH_2I$ for methylenation of sulfones was described. However, the yields (46–78%) are inferior to those afforded by the procedure described herein, presumably because a slight excess of *n*-BuLi (1.05[6a]–1.15[6c] equiv) is employed to deprotonate the sulfone.[7] Also, harsher reagents (aryllithiums)[6b] or conditions (xylene, Δ, 7 h, or $SiO_2$, $CH_2Cl_2$, Δ, 20 h)[6d] are employed to effect fragmentation. Thus, the procedure described herein is more practical. (a) Ochiai, M.; Tada, S.; Sumi, K.; Fujita, E. *Tetrahedron Lett.* **1982**, *23*, 2205. (b) Ochiai, M.; Sumi, K.; Fujita, E.; Tada, S. *Chem. Pharm. Bull.* **1983**, *31*, 3346. (c) Ochiai, M.; Ukita, T.; Fujita, E.; Tada, S. *Chem. Pharm. Bull.* **1984**, *32*, 1829. (d) Ochiai, M.; Ukita, T.; Fujita, E. *J. Chem. Soc., Chem. Commun.* **1983**, 619.

(7) Use of an excess of *n*-BuLi must be avoided since, as Fujita and co-workers have reported,[6a,c] *n*-BuLi reacts with *n*-$Bu_3SnCH_2I$ to form *n*-BuI, which then alkylates the lithiated sulfone preferentially. Since it is difficult to measure exactly 1.0 equiv, we routinely use 1.1 equiv and then quench the excess with an appropriate amount of *i*-$Pr_2NH$ (0.2 equiv, −78 °C, 8 min).

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Table I[a]

| entry | sulfone | $MCH_2I$, M | $t^{1/2}$ (1 → 2)[b] | % yield (1 → 3)[c] |
|---|---|---|---|---|
| a | **1a** | $Me_3Si$ | >5 h | 60.3 |
| b | **1a** | $n$-$Bu_3Sn$ | 30 s | 96.8 |
| c | **1b** | $Me_3Si$ | *d* | |
| d | **1b** | $n$-$Bu_3Sn$ | 1 h[e] | 77.7 |
| e | **1b** | $Me_3Sn$ | 4 min[e,f] | 85.8 |
| f | **1b** | $CH_3(CH_2)_2$ | 4 min[e,f] | |

[a] Refer to eq 1. All experiments listed in the table were performed by treating a solution of the sulfone in THF (0.20 M for **1a**, 0.12 M for **1b**) with 1.1 equiv of $n$-BuLi (−78 °C, 5 min) followed by $i$-$Pr_2NH$ (0.2–0.6 equiv, −78 °C, 10 min), followed by 1.5 equiv of alkylating agent. [b] The period of time required for the alkylation to reach 50% conversion (at −78 °C). [c] Chromatographically and spectroscopically ($^1H$ NMR and $^{13}C$ NMR) homogeneous samples of all compounds **2** and **3** were obtained by flash chromatography. Elemental composition data (high-resolution MS) consistent with the proposed structures were obtained for compounds **1a** and **2b** (M = $n$-Pr) but could not be obtained for the β-trialkylstannyl sulfones **2a** (M = $n$-$Bu_3Sn$), **2b** (M = $n$-$Bu_3Sn$), or **2b** (M = $Me_3Sn$) due to desulfonylstannylation of the molecular ion. [d] At −78 °C, alkylation is too slow to measure. At higher temperatures (−30 °C), some alkylation may occur, but unidentified side reactions predominate. [e] By $^{13}C$ NMR, all alkylated sulfones **2b** are isomerically homogeneous (presumably the configuration of the arylsulfonyl substituent is α). [f] By a competition experiment, it was determined that $Me_3SnCH_2I$ is actually 1.2 times more reactive than $n$-BuI.

reagent (1.3 equiv) is added and the reaction mixture stirred and warmed if necessary until alkylation is complete. Finally, $n$-$Bu_4NF{\cdot}3H_2O$ (3.0 equiv) is added[8,9] and the reaction mixture stirred at 0 °C for 5 min, at which time fragmentation to the olefin is complete. Workup of the reaction is simple because much of the tin is converted to $R_3SnF$, which can be precipitated from the reaction mixture by dilution with ether.[10]

Both tin reagents are considerably more reactive than the silicon reagent. The tributyltin reagent is ~600 times more reactive (see Table I, entries a vs. b), and the trimethyltin reagent is $\sim 10^4$ times more reactive.[11] Although the trimethyl reagent is more reactive than the tributyl reagent, the tributyl reagent alkylates **1b** quite rapidly (alkylation is complete within 1.5 h at −30 °C), which suggests that it should be usable for methylenation of moderately hindered sulfones in general. The two reagents are prepared by the same method (treatment of the corresponding trialkylstannyl chloride with Simmons–Smith reagent[12,13]). However, the starting material for preparation of the trimethyl reagent ($Me_3SnCl$) is relatively expensive and toxic.[14] Thus, the tributyl reagent is

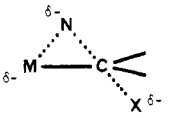


**Figure 1.**

preferable to the trimethyl reagent for methylenation of all sulfones except those that are particularly unreactive.

Although both $n$-$Bu_3SnCH_2I$ and $Me_3SnCH_2I$ are sufficiently reactive to be useful synthetically, they are not exceptionally reactive on an absolute scale. For example, the trimethyl reagent, which is the more reactive of the two, is only approximately equal in reactivity to $n$-BuI (see Table I, ref *f*).

In many previously reported cases of bimolecular[15] nucleophilic displacements at carbons bearing organometallic substituents (all those of which we are aware), the rate is either greater than[16–22] or equal to[23–25] that of the all-carbon ($n$-alkyl) analogue. For example, the rate of Finkelstein reaction of $Me_3SiCH_2Cl$ (KI, acetone) is greater than that of $n$-BuCl (by a factor of 16 at 50 °C,[16] by a factor of 26 at 20 °C[17]). Yet Eaborn has shown that the +I character of metals retards displacement.[16,25] Thus, numerous investigators[16–18,20–22,25] have concluded that displacements at metal-bearing carbons proceed through "nonclassical" transition states in which there is partial bonding between an empty orbital on the metal and an unshared lone pair on the nucleophile (as depicted in Figure 1, where M is the organometallic substituent, N the nucleophile, and X the leaving group).[26]

By contrast, in each case reported herein, the reactivity of the metal-bearing reagent is either less than or equal to that of $n$-BuI. This indicates that unusual stabilizing effects such as nonclassical bonding are absent from the transition states. The rate of displacement correlates well with the steric bulk and inductive effect of the metal. For example, the fact that $Me_3SiCH_2I$ is much less reactive than $n$-BuI can be attributed to the fact that the $Me_3Si$ group is sterically larger than $n$-Pr[27] or to the fact that the

(8) Fragmentation can also be effected cleanly (albeit more slowly) by treatment with $n$-$Bu_4NCl$ (half-life of **2b** (M = $n$-$Bu_3Sn$) at room temperature in THF, ~4 h); $n$-$Bu_4NBr$ and $n$-$Bu_4NI$ (THF, Δ) have no effect. Thus, the kinetic affinity of halogen anions for tin decreases with increasing softness of the halogen anion, which suggests that the trialkylstannyl group is a hard electrophile.

(9) The β-trialkylstannyl sulfones can be isolated and purified by flash chromatography if desired (fragmentation on the column is not a problem if the residence time is less than ~10 min). However, the yield and quality of final product are equally high if isolation and purification are omitted. Thus, in practice, it is preferable to add the $n$-$Bu_4NF{\cdot}3H_2O$ directly to the reaction mixture.

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(11) This value is an estimate, obtained by comparing each reagent to an alkylating agent of intermediate reactivity ($n$-$Bu_3SnCH_2I$), using different substrates (**1a** and **1b**); see the data contained in entries a vs. b and d vs. e of Table I. The reactivity difference is too great to be accurately measured with a common substrate at the same temperature.

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(15) Unimolecular displacements at the metal-bearing carbon are expected to be very slow because carbonium ions are greatly destabilized by organometallic substituents (for example, the rate of dehydrobromination of 2-(trimethylsilyl)-2-bromopropane under solvolysis conditions (60% $EtOH/H_2O$, 25 °C) is $3.8 \times 10^4$ times less than that of the carbon analogue, 2-*tert*-butyl-2-bromopropane, see: Cartledge, F. K.; Jones, J. P. *Tetrahedron Lett.* **1971**, 2193).

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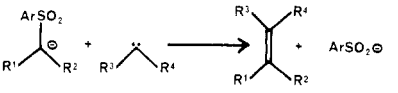
(26) In at least some of these cases, the rate acceleration could also be due to partial bonding between the leaving group and the metal in the transition state (refer to Figure 1, where N is the leaving group and X the nucleophile).

+I effect of the $Me_3Si$ group is greater than that of *n*-Pr or to both. Also, the fact that $Me_3SnCH_2I$ and *n*-BuI are about equally reactive can be attributed to the fact that the steric and inductive effects of the $Me_3Sn$ group negate each other: the $Me_3Sn$ group is sterically smaller than *n*-Pr[27] but has a greater +I effect. Thus, we hypothesize that all of the displacements reported herein proceed through "classical" $S_N2$ (Walden inversion) transition states. Evidently, the $R_3Sn$ and $Me_3Si$ groups are either too sterically hindered or insufficiently electrophilic to bond with the incoming sulfone nucleophile.

Not only the alkylation but also the fragmentation is considerably more rapid with tin than with silicon. For example, fragmentation of **2a** (M = *n*-$Bu_3Sn$) with 3.0 equiv of *n*-$Bu_4NF{\cdot}3H_2O$ in THF is complete after 5 min at 0 °C, whereas fragmentation of **2a** (M = $Me_3Si$) with 3.0 equiv of *n*-$Bu_4NF{\cdot}3H_2O$ in THF requires refluxing for 30 min.[28] The fact that fluoride ion has a great affinity for silicon is well-known;[29] however, the fact that fluoride ion has an even greater (kinetic) affinity for tin than for silicon has not been reported previously, to our knowledge.[30]

The reaction of sulfone-stabilized carbanions with reagents with latent carbene character (of which the above-described reaction is an example) is emerging as a useful class of methods for synthesis of olefins (eq 2).




Previously reported examples include the reaction of sulfone-stabilized carbanions with lithium salts of tosylhydrazones of aldehydes to form trisubstituted olefins,[31] and the reaction of sulfone-stabilized carbanions with acylsilanes to form silyl enol ethers.[32] In subsequent papers in this series, additional examples of this class of method for synthesis of olefins will be described.

## Experimental Section

**Procedure for Methylenation of 1b Using *n*-$Bu_3SnCH_2I$.** A solution of **1b** (499.6 mg, 1.099 mmol) in 5.0 mL of THF was cooled to −78 °C and treated with *n*-BuLi/hexane (0.75 mL of 1.6 M solution, 1.20 mmol). After 7 min, *i*-$Pr_2NH$ (0.62 mL of 0.356 M THF solution, 0.221 mmol) was added and the reaction mixture stirred at −78 °C for 8 min. A solution of *n*-$Bu_3SnCH_2I$ (631.3 mg, 1.466 mmol) in 2.0 mL of THF was then added and the reaction mixture warmed to −30 °C. A TLC (eluent, 20% ethyl acetate/cyclohexane) taken after 1.5 h indicated that conversion of the starting sulfone **1b** ($R_f$ 0.14) into intermediate **2b** (M = *n*-$Bu_3Sn$) ($R_f$ 0.47) was essentially complete, so after another 30 min, a solution of *n*-$Bu_4NF{\cdot}3H_2O$ (1.0506 g, 3.335 mmol) in 2.5 mL of THF was added, whereupon a solid began to precipitate. A TLC taken after 30 min indicated that formation of **3b** ($R_f$ 0.51) was only ~50% complete, so the reaction mixture was warmed to 0 °C. A TLC taken after 1.5 h indicated that fragmentation was complete, so the reaction mixture was diluted with 15 mL of ether, the precipitate filtered off, and the filtrate poured into 15 mL of 3% aqueous NaOH. The organic layer was separated and the aqueous layer extracted with ether (2 × 15 mL). The extracts were then combined, dried ($MgSO_4$), and concentrated in vacuo to leave a yellow oil, consisting of olefin **3b** contaminated by small amounts of more polar impurities and nonpolar tin byproduct(s) by TLC and $^1H$ NMR. This material was then flash chromatographed on 89 g of $SiO_2$ (eluent, 10% ethyl acetate/cyclohexane) to afford **3b** in pure form as a colorless oil. Yield: 266.7 mg (0.8534 mmol, 77.7%).

**Spectral and Analytical Data. 1a**: $^1H$ NMR ($CDCl_3$) δ 0.83 (9 H, s), 1.5–1.8 (6 H, m), 2.1–2.4 (3 H, m), 3.10 (1 H, br s), 7.5–7.7 (3 H, m), 7.8–8.0 (2 H, m); $^{13}C$ NMR ($CD_2Cl_2$) δ 22.43 (t), 25.31 (t), 27.58 (q), 32.76 (s), 47.41 (d), 59.19 (d), 128.82 (d), 129.44 (d), 133.66 (d), 139.57 (s); MS (EI), *m/e* 265 (P − $CH_3$, 1.7%), 224 (20.9%), 143 (100.%). Anal. Calcd for $C_{16}H_{24}O_2S$: C, 68.53; H, 8.63; S, 11.43. Found: C, 68.64; H, 8.58; S, 11.32.

**2a (M = $Me_3Si$)**: $^1H$ NMR ($CD_2Cl_2$) δ 0.20 (9 H, s), 0.80 (9 H, s), 1.15 (2 H, s), 0.8–1.2 (3 H, obscured m), 1.41 (2 H, td, *J* = 12.8, 3.7 Hz), 1.63 (2 H, br s), 1.92 (2 H, d, *J* = 12 Hz), 7.55 (2 H, t, *J* = 7 Hz), 7.66 (1 H, t, *J* = 7 Hz), 7.84 (2 H, d, *J* = 8 Hz); $^{13}C$ NMR ($CD_2Cl_2$) δ 1.23 (q), 18.20 (t), 22.60 (t), 27.49 (q), 32.48 (s), 33.03 (t), 47.34 (d), 66.98 (s), 128.93 (d), 131.26 (d), 133.64 (d), 136.32 (s).

**2a (M = *n*-$Bu_3Sn$)**: $^1H$ NMR ($CD_2Cl_2$) δ 0.82 (9 H, s), 0.92 (9 H, t, *J* = 7.3 Hz), 0.9–1.9 (29 H, m), 7.5–7.8 (5 H, m); $^{13}C$ NMR ($CD_2Cl_2$) δ 11.10 (t), 11.58 (t), 13.96 (q), 22.62 (t), 27.53 (q), 27.98 (t), 29.63 (t), 32.54 (s), 33.39 (t), 47.38 (d), 66.99 (s), 128.95 (d), 131.25 (d), 133.69 (d), 135.90 (s).

**2b (M = *n*-$Bu_3Sn$)**: $^1H$ NMR ($CD_2Cl_2$) δ 0.91 (9 H, t, *J* = 7.2 Hz), 1.15 (3 H, s), 1.21 (3 H, s), 1.0–2.3 (29 H, m), 2.42 (3 H, s), 2.64 (1 H, dd, *J* = 13.1, 6.8 Hz), 3.28 (1 H, td, *J* = 11.3, 6.7 Hz), 3.55 (2 h, t, *J* = 6.6 Hz), 4.35 (1 H, t, *J* = 3.4 Hz), 5.41 (2 H, m), 5.86 (1 H, d, *J* = 3.3 Hz), 7.39 (2 H, d, *J* = 8.1 Hz), 7.76 (2 H, d, *J* = 8.2 Hz); $^{13}C$ NMR ($CD_2Cl_2$) δ 11.98 (t), 13.87 (q), 15.82 (t), 21.66 (q), 25.00 (t), 25.97 (q), 26.24 (q), 27.47 (t), 27.90 (t), 29.52 (t), 32.78 (t), 39.16 (d), 39.31 (t), 45.00 (t), 58.25 (d), 77.11 (d), 78.86 (d), 79.61 (s), 112.35 (s), 113.10 (d), 128.97 (d), 129.48 (d), 130.24 (d), 130.86 (d), 133.50 (s), 145.44 (s).

**2b (M = $Me_3Sn$)**: $^1H$ NMR ($CD_2Cl_2$) δ 0.23 (9 H, s), 1.18 (3 H, s), 1.21 (3 H, s), 1.2–2.4 (11 H, m), 2.42 (3 H, s), 2.67 (1 H, dd, *J* = 13.1, 6.8 Hz), 3.34 (1 H, td, *J* = 11.4, 6.8 Hz), 3.54 (2 H, t, *J* = 6.6 Hz), 4.35 (1 H, t, *J* = 3.4 Hz), 5.35 (2 H, m), 5.86 (1 H, d, *J* = 3.3 Hz), 7.39 (2 H, d, *J* = 8.2 Hz), 7.76 (2 H, d, *J* = 8.3 Hz); $^{13}C$ NMR ($CD_2Cl_2$) δ −6.63 (q), 18.40 (t), 21.67 (q), 24.96 (t), 25.97 (q), 26.24 (q), 27.38 (t), 32.73 (t), 39.03 (t), 39.23 (d), 44.99 (t), 58.24 (d), 77.07 (d), 78.87 (d), 79.44 (s), 112.34 (s), 113.10 (d), 128.85 (d), 129.46 (d), 130.26 (d), 130.77 (d), 133.34 (s), 145.51 (s).

**2b (M = *n*-Pr)**: $^1H$ NMR ($CD_2Cl_2$) δ 0.92 (3 H, t, *J* = 7.2 Hz), 1.23 (3 H, s), 1.27 (3 H, s), 1.3–2.5 (16 H, m), 2.41 (3 H, s), 3.52 (2 H, t, *J* = 6.5 Hz), 3.72 (1 H, td, *J* = 11.3, 6.8 Hz), 4.34 (1 H, t, *J* = 3.4 Hz), 5.39 (2 H, sym. m), 5.89 (1 H, d, *J* = 3.3 Hz), 7.38 (2 H, d, *J* = 8.1 Hz), 7.75 (2 H, d, *J* = 8.3 Hz); $^{13}C$ NMR ($CD_2Cl_2$) δ 14.06 (q), 21.63 (q), 23.91 (t), 24.87 (t), 26.06 (q), 26.26 (q), 26.66 (t), 27.50 (t), 32.29 (t), 32.53 (t), 32.63 (t), 38.21 (d), 44.92 (t), 58.77 (d), 76.93 (d), 78.45 (s), 79.61 (d), 112.32 (s), 113.24 (d), 128.92 (d), 129.39 (d), 130.16 (d), 130.60 (d), 134.05 (s), 145.38 (s); MS (EI), *m/e* 495/497 (P − $CH_3$, 15.1%), 297/299 (100%). Anal. Calcd for $C_{26}H_{36}{}^{35}ClO_5S$ (P − $CH_3$): *m/e* 495.1972. Found: *m/e* 495.1979.

**Registry No.** **1a**, 97634-88-3; **1b**, 97673-24-0; **2a** (M = $Me_3Si$), 97634-89-4; **2a** (M = $Bu_3Sn$), 97634-90-7; **2b** (M = $Bu_3Sn$), 97634-91-8; **2b** (M = $Me_3Sn$), 97634-92-9; **2b** (M = *n*-Pr), 97634-93-0; **3a**, 13294-73-0; **3b**, 97466-31-4; $Me_3SiCH_2I$, 4206-67-1; $Bu_3SnCH_2I$, 66222-29-5; $Me_3SnCH_2I$, 23696-40-4; BuI, 542-69-8; PhSH, 108-98-5; 4-*tert*-butyl cyclohexanone, 98-53-3.

(27) The *A* value of the $Me_3Si$ group is 2.4–2.6 kcal/mol: Kitching, W.; Olszowy, H. A.; Drew, G. M.; Adcock, W. *J. Org. Chem.* **1982**, *47*, 5153. The *A* value of the $Me_3Sn$ group is 0.9–1.1 kcal/mol: Kitching, W.; Doddrell, D.; Grutzner, J. B. *J. Organomet. Chem.* **1976**, *107*, C5. Moder, T. I.; Hsu, C. C. K.; Jensen, F. R. *J. Org. Chem.* **1980**, *45*, 1008. Kitching, W.; Olszowy, H. A.; Harvey, K. *J. Org. Chem.* **1982**, *47*, 1893. The *A* value of the *n*-Pr group is 2.1 kcal/mol: Eliel, E. L.; Allinger, N. L.; Angyal, S. J.; Morrison, G. A. "Conformational Analysis"; Wiley: 1965; p 44.

(28) Both **2a** (M = $Me_3Si$) and **2a** (M = *n*-$Bu_3Sn$) are >90.% epimerically pure by $^{13}C$ NMR. Presumably, they have the same configuration, so it is legitimate to compare their rates of fragmentation.

(29) The fluorine–silicon bond strength is 129 kcal/mol, see: Paquette, L. A. *Science (Washington, D.C., 1883—)* **1982**, *217*, 793.

(30) The fact that fluoride-induced desulfonylstannylation is faster than desulfonylsilylation may be due either to the fact that the carbon–tin bond is weaker than the carbon–silicon bond (54 kcal vs. 60 kcal) [Davis, D. D.; Gray, C. E. *J. Org. Chem.* **1970**, *35*, 1303] or to the fact that the trialkylstannyl group is sterically smaller than the trimethylsilyl group and thus, does not imply that the tin–fluorine bond is stronger than the silicon–fluorine bond.

(31) Vedejs, E.; Dolphin, J. M.; Stolle, W. T. *J. Am. Chem. Soc.* **1979**, *101*, 249.

(32) (a) Reich, H. J.; Rusek, J. J.; Olson, R. E. *J. Am. Chem. Soc.* **1979**, *101*, 2225. (b) Reich, H. J.; Kelly, M. J. *J. Am. Chem. Soc.* **1982**, *104*, 1119. (c) Reich, H. J.; Kelly, M. J.; Olson, R. E.; Holtan, R. C. *Tetrahedron* **1983**, *39*, 949.