# Nucleophilic Vinylic Substitutions of (*Z*)-(*β*-Haloalkenyl)phenyliodonium Salts with Sodium Benzenesulfinate: First Evidence of a Michael Addition of Nucleophiles to Alkenyliodonium Salts at the $C_\beta$ Atom

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Evidence for a Michael addition of a nucleophile to alkenyl(phenyl)iodonium salts at the $C_\beta$ atom is reported here for the first time. Nucleophilic vinylic substitutions of (*Z*)-(*β*-chloroalkenyl)- **2b** and (*Z*)-(*β*-bromoalkenyl)iodonium tetrafluoroborates **3b** with sodium benzenesulfinate in THF afforded stereoselectively (*Z*)-1,2-bis(benzenesulfonyl)alkene **5b** with retention of configuration. Intermediate formation of (*Z*)-(*β*-(benzenesulfonyl)alkenyl)iodonium salt **9b** in these reactions was established by $^1$H NMR experiments in $CDCl_3$. The formation of (*Z*)-**9b** involves a hitherto unobserved Michael addition of benzenesulfinate anion to the alkenyliodonium salts at the $C_\beta$ atom, followed by halogen extrusion. The formation of a stereoisomeric mixture of (*Z*)- and (*E*)-bis-sulfones **5b**, and 1-(benzenesulfonyl)cyclopentene **11** that was observed in the reaction of (*Z*)-(*β*-fluoroalkenyl)-iodonium salt **4b** in $CDCl_3$, strongly suggests the intermediacy of **9b** in this nucleophilic vinylic substitution.

Alkynyl(phenyl)iodonium salts are highly electron-deficient species[2] and act as good Michael acceptors for a variety of soft nucleophiles, including stable enolates of 1,3-dicarbonyl compounds, and oxygen (carboxylates and phenoxides), nitrogen (azide and amide), and sulfur nucleophiles (sulfinates and thiocyanates).[3] Michael addition of nucleophiles to the *β*-carbon of alkynyliodonium salts constitutes a key step for efficient cyclopentene annulation of alkynyliodonium salts via the tandem Michael−carbene insertion (MCI) reaction.[3] In contrast, Michael addition to alkenyl(phenyl)iodonium salts at the $C_\beta$ atom has never been reported.[2]

Because of the excellent nucleofugality of the phenyliodonio group, which shows a leaving group ability about $10^6$ times greater than triflate,[4] alkenyl(phenyl)iodonium salts serve as the highly activated species of alkenyl halides in nucleophilic vinylic substitution reactions with a number of nucleophiles, such as organocuprates, sulfinates, thiolates, nitrites, halides, cyanides, azides, and phosphines.[5−7] These nucleophilic vinylic substitutions of alkenyliodonium salts occur regioselectively at the ipso positions under mild conditions.

Here, for the first time, we report evidence of a nucleophilic vinylic substitution of (*Z*)-(*β*-haloalkenyl)-iodonium tetrafluoroborates **2**−**4** with sodium benzenesulfinate that involves a Michael addition to the *β*-carbon atom as the first step of the reaction.[8] Nucleophilic vinylic substitutions of *β*-chloro- **2** and *β*-bromoiodonium tetrafluoroborates **3** with sodium benzenesulfinate afforded (*Z*)-1,2-bis(benzenesulfonyl)alkene **5** stereoselectively in high yields with retention of configuration, whereas formation of a stereoisomeric mixture of (*Z*)- and (*E*)-bis-sulfones **5** was observed in the reaction of (*Z*)-(*β*-fluoroalkenyl)iodonium salt **4**.

## Results and Discussion

**Synthesis of (*Z*)-(*β*-Haloalkenyl)phenyliodonium Tetrafluoroborates.** Conjugate addition of halide ions

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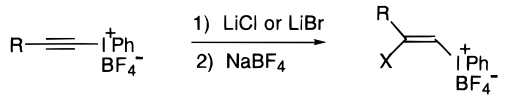
**Scheme 1**




**1** **2**; X = Cl, **3**; X = Br, **4**; X = F

**a**; R = Me, **b**; R = *n*-$C_8H_{17}$, **c**; R = $Me_2CH(CH_2)_2$, **d**; R = $Ph(CH_2)_2$, **e**; R = $Ph(CH_2)_3$, **f**; R = $Cl(CH_2)_3$, **g**; R = *c*-$C_5H_{11}CH_2$, **h**; R = *t*-Bu

**Table 1. Synthesis of (*Z*)-(*β*-Haloalkenyl)iodonium Salts 2 and 3[a]**

| entry | iodonium salt **1** | LiX[b] | time, h | product (yield,[c] %) |
|---|---|---|---|---|
| 1 | **1a** | LiCl | 12 | **2a** (81) |
| 2 | **1b** | LiCl | 9 | **2b** (91) |
| 3 | **1c** | LiCl | 12 | **2c** (85) |
| 4 | **1d** | LiCl | 11 | **2d** (70) |
| 5 | **1e** | LiCl | 10 | **2e** (88) |
| 6 | **1f** | LiCl | 12 | **2f** (80) |
| 7 | **1g** | LiCl | 20 | **2g** (84) |
| 8 | **1h** | LiCl | 4.5 | **2h** (84) |
| 9 | **1b** | LiBr | 12 | **3b** (71) |
| 10 | **1c** | LiBr | 11 | **3c** (81) |

[a] Reactions were carried out at room temperature. [b] 10 equiv of LiX were used. [c] Isolated yields.

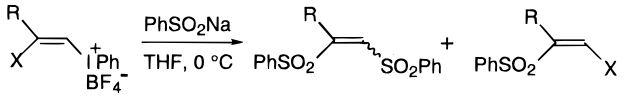
($Cl^-$ or $Br^-$) to alkynyl(phenyl)iodonium salts **1**[9] using LiCl or LiBr (10 equiv) in acetic acid at room temperature, followed by ligand exchange with $NaBF_4$, gave (*Z*)-(*β*-haloalkenyl)phenyliodonium tetrafluoroborates **2** or **3** in high yields (Scheme 1).[10] The results of synthesizing **2** and **3** are summarized in Table 1. The addition reactions were stereoselective, and no formation of the corresponding (*E*)-isomers was detected. The (*Z*)-stereochemistry of these iodonium salts was established by observation of an NOE enhancement between the vinylic and allylic protons.

Our attempt at conjugate addition of fluoride ion under similar conditions (LiF in acetic acid at room temperature) resulted in the recovery of the alkynyliodonium salt **1**. Use of CsF instead of LiF, and of water as an additive, however, led to the formation of (*Z*)-(*β*-fluoroalkenyl)-iodonium tetrafluoroborates **4**, albeit in a low yield: thus, treatment of **1b** with CsF (2 equiv) in acetone−dichloromethane (1:1) in the presence of water (20 equiv) at room temperature, followed by ligand exchange with $NaBF_4$, afforded (*Z*)-(*β*-fluoro-1-decenyl)phenyliodonium tetrafluoroborate (**4b**) in 20% yield.[11] Similarly, **4c** was prepared from **1c** in 15% yield by reaction with CsF.

**Reaction of (*Z*)−(*β*-Haloalkenyl)iodonium Salts with Sodium Benzenesulfinate.** Exposure of (*Z*)-(2-chloro-1-decenyl)iodonium tetrafluoroborate (**2b**) to sodium benzenesulfinate (2.5 equiv) in THF at 0 °C for 2 h resulted in double nucleophilic vinylic substitutions of a phenyliodonio group and a *β*-chlorine atom, giving (*Z*)-1,2-bis(benzenesulfonyl)alkene **5b**[7b] in 92% yield, along with (*Z*)-chlorosulfone **6b** in trace amounts (Scheme 2).[7a] Similarly, the reaction with (*β*-chlorovinyl)iodonium salts **2a** and **2c**−**g** afforded the corresponding (*Z*)-bis(benzenesulfonyl)alkenes **5** in high yields (Table 2). All of these reactions were exclusively stereoselective (by $^1H$ NMR) with retention of configuration. The alkenyliodonium salt **2h** with a sterically demanding *tert*-butyl group at the *β*-position took a different reaction course, i.e., monosubstitution at the α-position (Table 2, entry 8). The reaction was very slow and, after 70 h at room temperature, gave (*Z*)-2-chloro-3,3-dimethyl-1-butenyl phenyl sulfone (**8**) in 78% yield. Yield of the normal product, (*Z*)-1,2-bis(benzenesulfonyl)alkene **5h** is low (6%).

In marked contrast to the reaction of (*Z*)-(*β*-chloroalkenyl)iodonium salts **2**, the rate of substitutions of (*Z*)−(*β*-bromoalkenyl)iodonium tetrafluoroborates **3** with sodium benzenesulfinate was slow, and the reaction resulted in formation of a large amount of the (*Z*)-bromovinyl sulfone **7**: thus, *β*-bromoiodonium salt **3b** afforded a mixture of the (*Z*)-1,2-bis(benzenesulfonyl)alkene **5b** and the (*Z*)-bromovinyl sulfone **7b**[7a] in 52 and 30% yields, respectively (Table 2, entry 9). Similarly, **3c** gave a mixture of (*Z*)-**5c** (53%) and **7c** (35%). Interestingly, with (*Z*)-(2-fluoro-1-decenyl)phenyliodonium tetrafluoroborate (**4b**), we observed exclusive substitution with sodium benzenesulfinate yielding 1,2-bis(benzenesulfonyl)alkene **5**, but we obtained a mixture of stereoisomers with (*E*)-isomer as a major product. This reaction afforded a 25:75 mixture of (*Z*)- and (*E*)-**5b** in a quantitative yield (Table 2, entry 11). The reaction with **4c** also afforded a mixture of (*Z*)- (12%) and (*E*)-**5c** (68%).

**Scheme 2**




**2-4** **5** **6**; X = Cl, **7**; X = Br

**Table 2. Reaction of (*Z*)-(*β*-Haloalkenyl)iodonium Salts with Sodium Benzenesulfinate[a]**

| entry | iodonium salt | time, h | product (yield,[b] (*Z*)-**5** | (*E*)-**5** | **7** |
|---|---|---|---|---|---|
| 1 | **2a** | 8 | (*Z*)-**5a** (95) | | |
| 2 | **2b** | 2 | (*Z*)-**5b** (92)[c] | | |
| 3 | **2c** | 3.5 | (*Z*)-**5c** (89) | | |
| 4 | **2d** | 4 | (*Z*)-**5d** (93) | | |
| 5 | **2e** | 8 | (*Z*)-**5e** (86) | | |
| 6 | **2f** | 2 | (*Z*)-**5f** (83) | | |
| 7 | **2g** | 2.5 | (*Z*)-**5g** (87) | | |
| 8 | **2h** | 70 | (*Z*)-**5h** (6)[d] | | |
| 9 | **3b** | 64 | (*Z*)-**5b** (52) | | **7b** (30) |
| 10 | **3c** | 82 | (*Z*)-**5c** (53) | | **7c** (35) |
| 11 | **4b** | 49 | (*Z*)-**5b** (25) | (*E*)-**5b** (75) | |
| 12 | **4c** | 65 | (*Z*)-**5c** (12) | (*E*)-**5c** (68) | |

[a] Reactions were carried out using 2.5 equiv of sodium benzenesulfinate in THF at 0 °C. [b] Isolated yields. [c] A trace amount of **6b** was detected. [d] (*Z*)-2-Chloro-3,3-dimethyl-1-butenyl phenyl sulfone (**8**) was obtained in 78% yield.

**Stereochemistry of 1,2-Bis(benzenesulfonyl)alkenes 5.** NOE studies of **5** indicate that both of the double nucleophilic vinylic substitutions of a phenyliodonio group and a *β*-halogen atom (Cl or Br) of **2** or **3** with sodium benzenesulfinate occur with retention of config-

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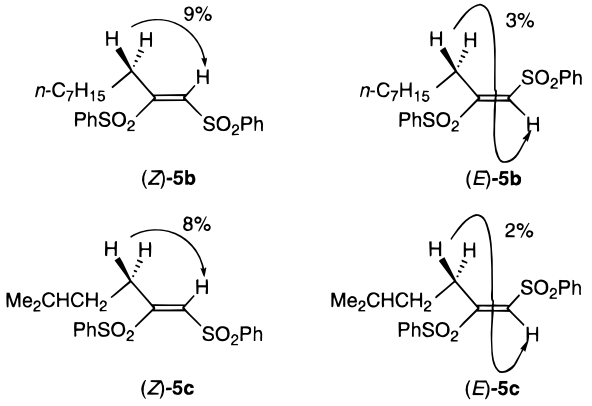



**Figure 1.** NOE measurements of **5**.

uration. The results of measurements of an NOE enhancement between the vinylic and allylic protons of **5** are shown in Figure 1. Irradiation of the allylic protons in (*Z*)-**5b**,**c** resulted in 8−9% enhancements in the vinylic proton integration whereas only 2−3% enhancements were observed with (*E*)-**5b**,**c**,[12] which is in good agreement with their assigned stereochemistry. The observed chemical shifts of vinylic protons in **5** support their stereochemical assignments: vinylic proton signals of (*Z*)-**5b**,**c** appeared at $\delta$ 6.76 whereas those of (*E*)-**5b**,**c** appeared at $\delta$ 7.38.[13] The structure of (*E*)-**5b** was established by a single-crystal X-ray analysis[22] (see Supporting Information).

**Time Courses of Nucleophilic Vinylic Substitution. A. Reaction of $\beta$-Chloroiodonium Salt 2b.** To gain insight into the mechanism of this nucleophilic vinylic substitution of (*Z*)-($\beta$-haloalkenyl)iodonium salts with sodium benzenesulfinate, we investigated the time courses of the reactions by $^1$H NMR in $CDCl_3$ at room temperature. Changing the solvent from THF to $CDCl_3$ was found to slow the rate of the reaction of (*Z*)-(2-chloro-1-decenyl)iodonium salt **2b** (Figure 2a). Most importantly, formation of considerable amounts (up to 18%) of the (*Z*)-($\beta$-(benzenesulfonyl)alkenyl)iodonium salt **9b** (X = $BF_4$, $PhSO_2$, or Cl) was detected by $^1$H NMR, especially at the early stages of the reaction. The amounts of (*Z*)-**9b** gradually decrease with an increase in the yields of the (*Z*)-1,2-bis(benzenesulfonyl)alkene **5b**, indicating that the $\beta$-sulfonyliodonium salt (*Z*)-**9b** would be an intermediate leading to the formation of (*Z*)-**5b**. Furthermore, formation of a small amount of the (*Z*)-chlorovinyl sulfone **6b** was observed during the late stages of the reaction.

It was possible to isolate the intermediate (*Z*)-**9b** (X = $BF_4$). When the reaction of **2b** was carried out using one equiv of sodium benzenesulfinate in THF at 0 °C for 12 h and quenched with an aqueous $NaBF_4$ solution, a mixture of **2b** (54%), (*Z*)-**9b** (X = $BF_4$, 11%),[3d] (*Z*)-**5b** (34%), and **6b** (1%) was produced (Scheme 3). For purification, the $\beta$-sulfonyliodonium salt (*Z*)-**9b** (X = $BF_4$) could not be applied to silica gel column chromatography, because it readily decomposes to generate an alkylidenecarbene **10b** via α-elimination yielding 1-(benzenesulfonyl)cyclopentene **11**. Repeated recrystallization (more than 10 times) of a mixture of **2b** and (*Z*)-**9b** from hexane−diethyl ether−dichloromethane permitted isolation of the pure (*Z*)-**9b** (X = $BF_4$). The intermediate

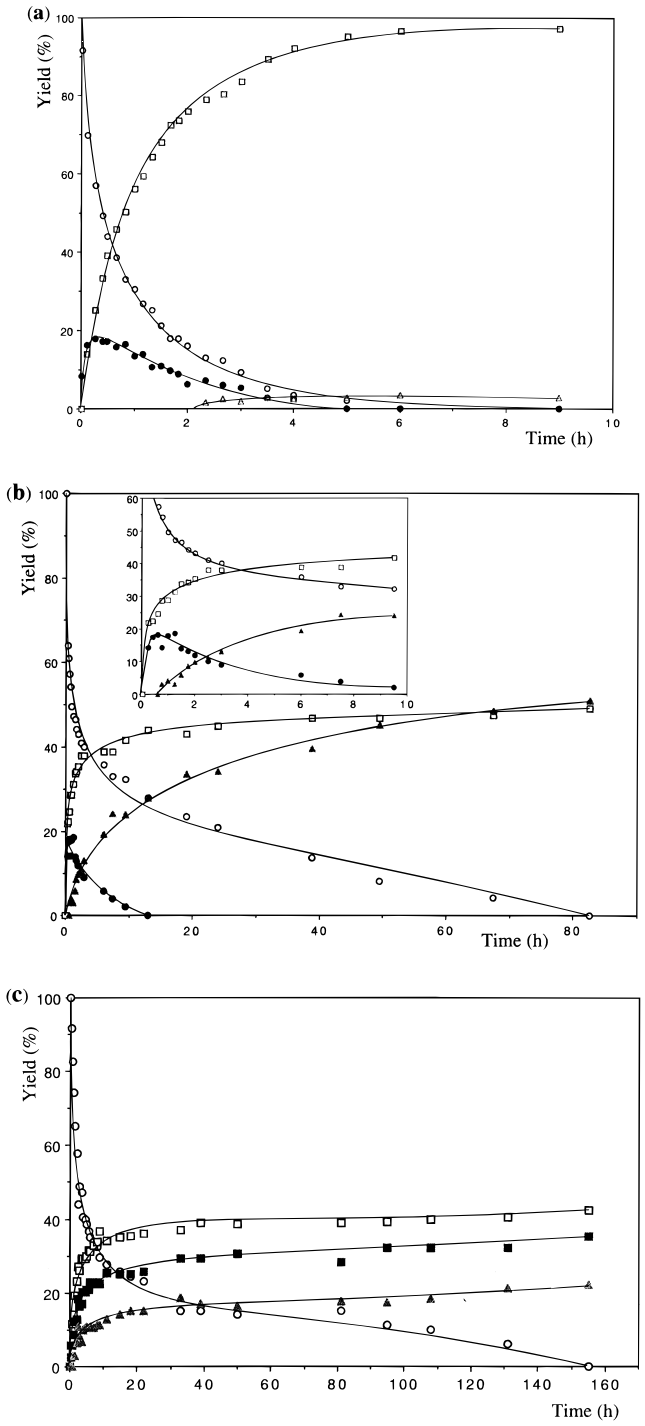
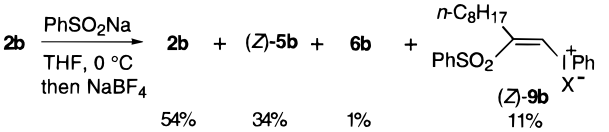



**Figure 2.** Time courses for the reaction of (*Z*)-(2-halo-1-decenyl)iodonium tetrafluoroborates with sodium benzenesulfinate (2.5 equiv) in $CDCl_3$ at room temperature. Yields were determined by $^1$H NMR. (a) Reaction of **2b**. Symbols are % recovered **2b** (○), (*Z*)-**5b** (□), **6b** (△), and (*Z*)-**9b** (●). (b) Reaction of **3b**. Symbols are % recovered **3b** (○), (*Z*)-**5b** (□), **7b** (▲), and (*Z*)-**9b** (●). (c) Reaction of **4b**. Symbols are % recovered **4b** (○), (*E*)-**5b** (□), (*Z*)-**5b** (■), and **11** (▲).

**Scheme 3**

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formation of the β-sulfonyliodonium salt (*Z*)-**9b** from the β-chloroiodonium salt **2b** clearly indicates that these nucleophilic vinylic substitutions involve a Michael addition of a nucleophile ($PhSO_2^-$) to the alkenyliodonium salt **2b** at the $C_\beta$ atom, followed by elimination of a chloride anion yielding (*Z*)-**9b**. Such a Michael addition has not been reported previously.

It has been shown that nucleophilic vinylic substitutions of (*Z*)-**9b** (X = $BF_4$) with sodium benzenesulfinate proceed at 0 °C in THF with retention of configuration and afford (*Z*)-**5b** stereoselectively in high yields.[7b] Hypothesizing that the substitution of (*Z*)-**9b** with sodium benzenesulfinate would compete with the attack of a chloride ion, liberated upon the formation of (*Z*)-**9b** from **2b**, we anticipated the formation of a small amount of the (*Z*)-chlorovinyl sulfone **6b**, produced by nucleophilic substitution of (*Z*)-**9b** with a chloride ion (with retention of configuration).[7a]

**B. Reaction of β-Bromoiodonium Salt 3b.** The time course of the nucleophilic substitution of (*Z*)-(2-bromo-1-decenyl)iodonium salt **3b** in $CDCl_3$ at room temperature is shown in Figure 2b. As in the case of the β-chloroiodonium salt **2b**, at the early stages of the reaction of **3b**, formation of considerable amounts (up to 19%) of the (*Z*)-β-sulfonyliodonium salt **9b** (X = $BF_4$, $PhSO_2$, or Br) was observed by $^1H$ NMR. The amounts of (*Z*)-**9b** gradually decrease with an increase in the yields of the (*Z*)-1,2-bis-sulfone **5b** and with formation of the (*Z*)-bromovinyl sulfone **7b**. These results suggest that the β-sulfonyliodonium salt (*Z*)-**9b** might be a common intermediate leading to the formation of (*Z*)-**5b** as well as **7b**. The intermediate formation of (*Z*)-**9b** provides additional evidence for a Michael addition of a nucleophile ($PhSO_2^-$) to the alkenyliodonium salt at the $C_\beta$ atom.

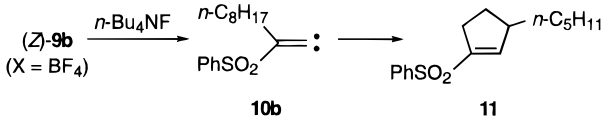
It is generally accepted that the order of nucleophilic reactivities of halide anions in dipolar aprotic solvents such as DMF, DMSO, and acetone, where solvation due to hydrogen bonding is negligible, is $Cl^- > Br^- > I^-$.[14] This reactivity sequence would suggest that the formation of the (*Z*)-chlorosulfone **6b** would be larger than that of the (*Z*)-bromosulfone **7b**, but this was not the case. Compared to **6b**, a large amount of **7b** was produced in the reaction of **3b** both in THF (compare Table 2, entries 2 and 9) and in $CDCl_3$ (compare Figures 2a and 2b). For this reason, we measured the relative reactivities of halide ($Cl^-$ and $Br^-$) and benzenesulfinate anions ($PhSO_2^-$) toward nucleophilic substitutions of the intermediate β-sulfonyliodonium salt (*Z*)-**9b** (X = $BF_4$). Competitive reactions were carried out using 20-fold excess each of two competing nucleophiles at 0 °C. The relative nucleophilic reactivities of these anions are summarized in Table 3. The rates of substitution of (*Z*)-**9b** with tetrabutylammonium salts in THF−dichloromethane (10:1) decrease in the order of *n*-$Bu_4NSO_2Ph \gg$ *n*-$Bu_4NCl >$ *n*-$Bu_4NBr$. This order of nucleophilic reactivities is in a good agreement with the one previously reported,[14] but not with our results obtained in the reactions of **2b** and **3b**. Reverse order of the rates in the substitution of (*Z*)-**9b** with halides, however, was observed, when sodium halides were used instead of tetrabutylammonium halides in THF (Table 3, entries 4−6). The relative reactivities decrease in the order of $PhSO_2Na >$ NaBr > NaCl, which is compatible with the results shown in Table 2 and Figure 2. In the reactions of **2b** or **3b** with sodium benzenesulfinate, formation of (*Z*)-**9b** will be accompanied by generation of NaCl or NaBr via Michael addition followed by halide ion extrusion. The high degree of ion pair dissociation expected for NaBr compared to NaCl in THF probably accounts for this reversal in reactivity order.[15] No interconversion among (*Z*)-**5b**, **6b**, and **7b** in the presence of these nucleophiles ($PhSO_2Na$, NaBr, or NaCl) in THF at room temperature was observed.

**Table 3. Competitive Reaction of (*Z*)-β-Sulfonyliodonium Salt (*Z*)-9b (X = $BF_4$) with Halide and Benzenesulfinate Anions[a]**

| | | | product (yield,[b] %) | | |
|---|---|---|---|---|---|
| entry | nucleophile | time, h | (*Z*)-**5b** | **6b** | **7b** |
| 1 | *n*-$Bu_4NSO_2Ph$, *n*-$Bu_4NCl$ | 9 | (93) | | |
| 2 | *n*-$Bu_4NSO_2Ph$, *n*-$Bu_4NBr$ | 7 | (92) | | |
| 3 | *n*-$Bu_4NCl$, *n*-$Bu_4NBr$ | 14 | (6) | (77) | (9) |
| 4 | $PhSO_2Na$, NaCl | 2 | (82) | | |
| 5 | $PhSO_2Na$, NaBr | 2 | (71) | | (19) |
| 6 | NaCl, NaBr | 12 | | | (88) |

[a] Reactions were carried out using 20 equiv each of two competing nucleophiles at 0 °C. Solvent: THF-dichloromethane (10:1) for entries 1 to 3; THF for entries 4 to 6. [b] Isolated yields.

**Scheme 4**




**C. Reaction of β-Fluoroiodonium Salt 4b.** The time course of the nucleophilic vinylic substitution of (*Z*)-(β-fluoro-1-decenyl)iodonium salt **4b** with sodium benzenesulfinate is shown in Figure 2c. In this reaction, no intermediate formation of the (*Z*)-β-sulfonyliodonium salt **9b** was detected by $^1H$ NMR. The reaction in $CDCl_3$ is slow and takes more than 150 h at room temperature. The major product of this reaction was found to be a stereoisomeric mixture of (*Z*)- and (*E*)-bis-sulfones **5b**, but, unexpectedly, we observed formation of a considerable amount of the 1-(benzenesulfonyl)cyclopentene **11**, which was not detected in the reaction in THF (Table 2, entry 11).

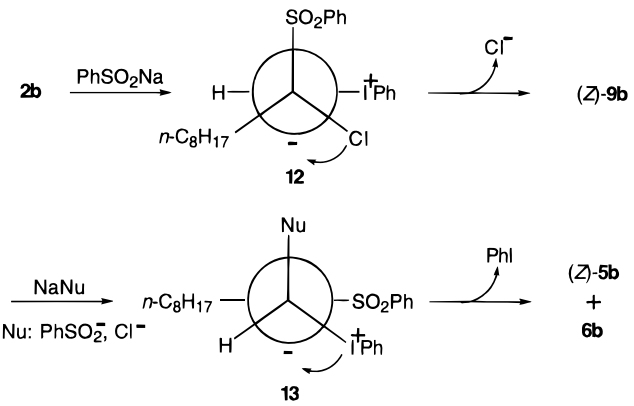
Formation of the β-sulfonyliodonium salt (*Z*)-**9b** was not detected directly, but isolation of the 1-(benzenesulfonyl)cyclopentene **11** strongly suggests the intermediacy of **9b** in the nucleophilic vinylic substitution of **4b**, since it has been shown that (*Z*)-**9b** (X = $BF_4$) reacts with *n*-$Bu_4NF$ in dichloromethane at room temperature, undergoing α-elimination to generate the alkylidenecarbene **10b** that affords the sulfonylcyclopentene **11** via intramolecular 1,5-carbon−hydrogen insertion (Scheme 4).[7a]

**Reaction Mechanism.** As illustrated in Scheme 5, a reaction mechanism for the double nucleophilic vinylic substitutions of (*Z*)-(2-chloro-1-decenyl)iodonium salt **2b** with sodium benzenesulfinate might be assumed to involve the following addition−elimination process two times: (a) Michael addition of benzenesulfinate anion to the β-chloroiodonium salt **2b** at the $C_\beta$ atom, followed by elimination of chloride anion yielding (*Z*)-**9b**, (b) Michael

(14) (a) Puar, M. S. *J. Chem. Educ.* **1970**, *47*, 473. (b) Winstein, S.; Savedoff, L. G.; Smith, S.; Stevens, I. D. R.; Gall, J. S. *Tetrahedron Lett.* **1960**, 24. (c) Weaver, W. M.; Hutchison, J. D. *J. Am. Chem. Soc.* **1964**, *86*, 261.

(15) It has been shown that the extent of ion pairing decreases with increasing ionic size.[14a]

**Scheme 5**




addition of benzenesulfinate or chloride anion to the $\beta$-(benzenesulfonyl)iodonium salt (*Z*)-**9b** at the $C_\alpha$ atom, followed by reductive elimination of the phenyliodonio group yielding (*Z*)-**5b** or **6b**, respectively.

Perpendicular attack of benzenesulfinate anion to the $\pi^*$ orbital of the $\beta$-chloroiodonium salt **2b** will produce the iodonium ylide **12**. Effects of negative hyperconjugation between the leaving group (Cl) and the carbanionic electron pair in the iodonium ylide **12** account for the preference of the internal 60° clockwise rotation over the 120° counterclockwise rotation of **12**, thereby yielding (*Z*)-**9b** stereoselectively with retention of configuration via the expulsion of the good nucleofuge (Cl).[16,17] In the reaction of the alkenyliodonium salt **2h**, the perpendicular attack of benzenesulfinate anion will be hindered by a sterically demanding *tert*-butyl group at the $\beta$-position, which slows down the rate of the reaction and makes the nucleophilic vinylic substitution at the $C_\alpha$ atom, yielding **8** a preferred reaction course.

The latter Michael addition of benzenesulfinate or chloride anion to the $\beta$-sulfonyliodonium salt (*Z*)-**9b** at the $C_\alpha$ atom has been reported.[7a,b] This substitution also proceeds with retention of stereochemistry, because of hyperconjugative stabilization of the intermediate α-sulfonyl-stabilized carbanion **13** by the C−I(III) orbital. Alternatively, a ligand coupling mechanism of (*Z*)-**9b** (X = $PhSO_2$, or Cl) yielding (*Z*)-**5b** or **6b** is also compatible with the stereochemical outcome observed in this nucleophilic vinylic substitution.[18]

As an alternative mechanism for the reaction of **2b**, an anti $\beta$-elimination pathway[19] of HCl involving intermediacy of 1-decynyl(phenyl)iodonium salt **1b**, followed by the Michael addition of sodium benzenesulfinate, should be considered. This pathway does not seem to be important, however, given that the reaction of 1-decynyl(phenyl)iodonium salt **1b** with sodium benzenesulfinate will directly generate an α-(phenylsulfonyl)alkylidenecarbene **10b**, but will not produce (*Z*)-**5b**.[3d]

Nucleophilic vinylic substitutions of the $\beta$-bromoiodonium salt **3b** will involve the same reaction pathway as that of **2b**. Although formation of the $\beta$-sulfonyliodonium salt **9b** was not detected directly by $^1$H NMR, we assumed that a similar Michael addition of benzenesulfinate anion to the $C_\beta$ atom generating the iodonium ylide **14**, shown in Scheme 6, was involved in the nucleophilic vinylic substitutions of the $\beta$-fluoroiodonium salt **4b**. Because of the poor nucleofugality of the fluorine atom,[20] the iodonium ylide **14** seems to be relatively long-lived, and, therefore, the conformer **15** formed by 60° clockwise rotation and the conformer **16** formed by 120° counterclockwise rotation will have enough time to equilibrate to some extent, thereby leading to formation of (*Z*)- and (*E*)-**9b**, respectively. Similar dependence on halogen nucleofuges has been reported in the nucleophilic substitution of *p*-nitro-$\beta$-bromo- and *p*-nitro-$\beta$-fluorostyrenes with thiophenoxide ion: (*E*)- and (*Z*)-$\beta$-bromostyrenes with a good nucleofuge give the retained 4-nitrostyryl phenyl sulfides, whereas (*E*)- and (*Z*)-$\beta$-fluorostyrenes with a poor nucleofuge result in stereoconvergence.[16b,21]

As described above, isolation of the 1-(benzenesulfonyl)-cyclopentene **11** in the reaction of **4b** in $CDCl_3$ strongly suggests the intermediacy of the $\beta$-sulfonyliodonium salt **9b**. Although there is no firm evidence, it is reasonable to assume that (*E*)-**9b** will produce the (*E*)-1,2-bis-sulfone **5b** by reacting with the benzenesulfinate anion and to generate the alkylidenecarbene **10b** via fluoride anion-induced α-elimination, as shown in Scheme 6.

## Conclusions

Reaction of (*Z*)-($\beta$-haloalkenyl)phenyliodonium tetrafluoroborates with sodium benzenesulfinate in THF predominantly undergoes double nucleophilic vinylic substitution of a phenyliodonio group and a $\beta$-halogen atom and affords (*Z*)-1,2-bis(benzenesulfonyl)alkene, its (*E*)-isomer, and/or (*Z*)-halovinyl sulfone, depending on the nature of a $\beta$-halogen atom (nucleophilicity and nucleofugality). Isolation and characterization of the intermediate (*Z*)-($\beta$-(benzenesulfonyl)alkenyl)iodonium salt strongly suggest that the double nucleophilic vinylic substitution involves a hitherto unobserved Michael addition of benzenesulfinate anion to ($\beta$-haloalkenyl)-iodonium salts at the $C_\beta$ atom as a first step of the reactions.

## Experimental Section

**General.** For general experimental detail, see ref 4. Preparative thin-layer chromatography (TLC) was carried out on precoated plates of silica gel (Merck, silica gel F-254). Kieselgel 60 (Merck, 230−400 mesh) was used for flash chromatography. Sodium benzenesulfinate dihydrate and lithium halides are commercially available and were used as received. 1-Alkynyl(phenyl)iodonium tetrafluoroborates **1** were prepared from the corresponding alkynyltrimethylsilanes by the reaction with iodosylbenzene and $BF_3$−$Et_2O$ in dichloromethane according to literature procedure.[9]

**General Procedure for Synthesis of (*Z*)−($\beta$-Chloroalkenyl)- 2 and (*Z*)-($\beta$-Bromoalkenyl)phenyliodonium Tetrafluoroborates 3.**[10] To a stirred solution of lithium chloride or lithium bromide (5 mmol) in acetic acid (20 mL) was added

(16) For reviews of nucleophilic vinylic substitutions, see: (a) Rappoport, Z. *Adv. Phys. Org. Chem.* **1969**, *7*, 1. (b) Modena, G. *Acc. Chem. Res.* **1971**, *4*, 73. (c) Miller, S. I. *Tetrahedron* **1977**, *33*, 1211. (d) Rappoport, Z. *Acc. Chem. Res.* **1981**, *14*, 7. (e) Rappoport, Z. *Recl. Trav. Chim. Pays-Bas* **1985**, *104*, 309. (f) Shainyan, B. A. *Usp. Khim.* **1986**, *55*, 942. (g) Rappoport, Z. *Acc. Chem. Res.* **1992**, *25*, 474.

(17) Apeloig, Y.; Rappoport, Z. *J. Am. Chem. Soc.* **1979**, *101*, 5095.

(18) (a) Oae, S.; Uchida, Y. *Acc. Chem. Res.* **1991**, *24*, 202. (b) Furukawa, N.; Ogawa, S.; Matsumura, K.; Fujihara, H. *J. Org. Chem.* **1991**, *56*, 6341.

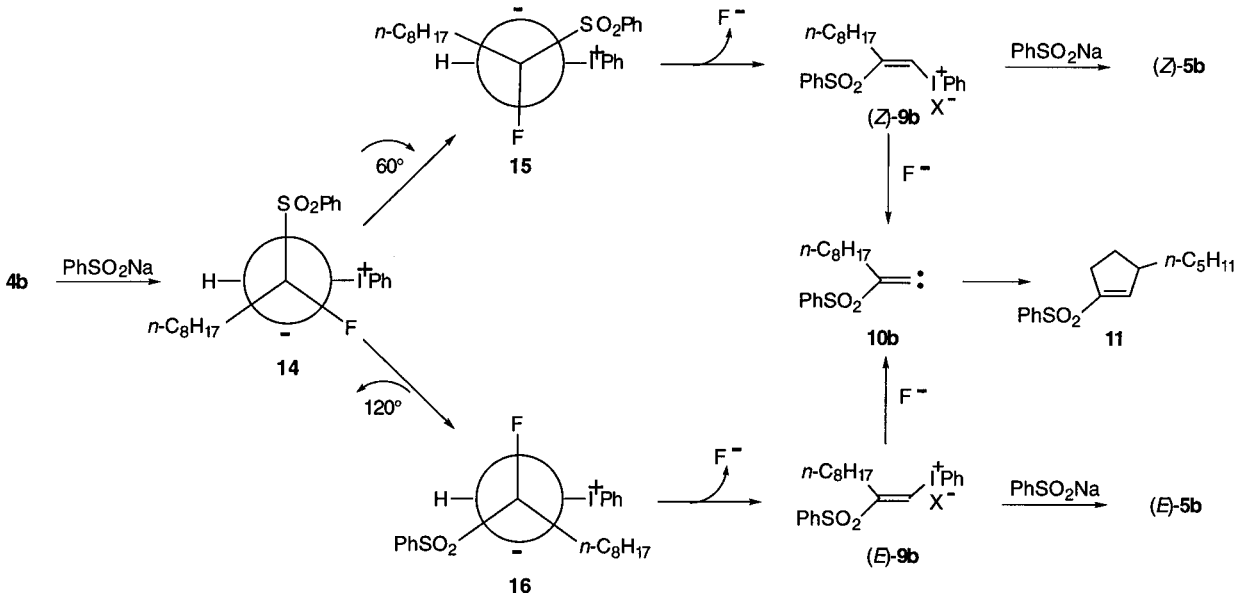
(19) Ochiai, M.; Uemura, K.; Masaki, Y. *J. Am. Chem. Soc.* **1993**, *115*, 2528.

(20) Stang, P. J.; Hanack, M.; Subramanian, L. R. *Synthesis* **1982**, 85.

(21) (a) Marchese, G.; Modena, G.; Naso, F. *Tetrahedron* **1968**, *24*, 663. (b) Marchese, G.; Modena, G.; Naso, F. *J. Chem. Soc.* (*B*) **1969**, 290.

(22) The author has deposited atomic coordinates for this structure with the Cambridge Crystallographic Data Centre. The coordinates can be obtained, on request, from the Director, Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK.

**Scheme 6**




1-alkynyl(phenyl)iodonium tetrafluoroborate **1** (0.5 mmol) at room temperature, and the solution was stirred for the periods shown in Table 1. The solvent was evaporated under reduced pressure. After addition of water, the mixture was extracted with dichloromethane two times. The combined organic extracts were vigorously shaken with a saturated aqueous sodium tetrafluoroborate solution (10 mL) two times. The organic layer was filtered and concentrated under aspirator vacuum to give an oil, which was washed several times with hexane and/or diethyl ether by decantation at −78 °C. Further purification of (*Z*)-(*β*-haloalkenyl)iodonium tetrafluoroborates **2** and **3** was accomplished by recrystallization from dichloromethane−hexane. The yields of pure products are given in Table 1.

**(*Z*)−(2-Chloro-1-propenyl)phenyliodonium tetrafluoroborate (2a):** colorless needles; mp 118−123 °C; IR (KBr) 3072, 1595, 1564, 1471, 1444, 1084, 742 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 8.04 (br d, $J$ = 8.3 Hz, 2H), 7.64 (br t, $J$ = 7.3 Hz, 1H), 7.49 (br dd, $J$ = 8.3, 7.3 Hz, 2H), 7.23 (q, $J$ = 1.2 Hz, 1H), 2.54 (d, $J$ = 1.2 Hz, 3H); FAB MS *m/z* 279 [(M − $BF_4$)$^+$]; HRMS (FAB) calcd for $C_9H_9ClI$ [(M − $BF_4$)$^+$] 278.9438, found 278.9448.

**(*Z*)−(2-Chloro-1-decenyl)phenyliodonium tetrafluoroborate (2b):**[19] colorless needles; mp 73−76 °C; IR (Nujol) 3070, 1595, 1565, 1285, 1165, 1045, 985, 735 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 8.04 (br d, $J$ = 8.0 Hz, 2H), 7.66 (br t, $J$ = 7.0 Hz, 1H), 7.50 (br dd, $J$ = 8.0, 7.0 Hz, 2H), 7.15 (s 1H), 2.72 (t, $J$ = 7.6 Hz, 2H), 1.71−1.52 (m, 2H), 1.34−1.13 (m, 12H), 0.87 (t, $J$ = 6.8 Hz, 3H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 157.8 (s), 135.4 (d), 132.7 (d), 132.3 (d), 111.6 (s), 96.0 (d), 39.8 (t), 31.7 (t), 29.0 (t), 28.3 (t), 27.5 (t), 22.5 (t), 14.0 (q); MS *m/z* (relative intensity) 300 [7, (M − $BF_4$)$^+$], 204 (87), 77 (100). Anal. Calcd for $C_{16}H_{23}BClF_4I$: C, 41.37; H, 4.99. Found: C, 41.39; H, 4.96.

**(*Z*)−(2-Chloro-5-methyl-1-hexenyl)phenyliodonium tetrafluoroborate (2c):** colorless needles; mp 57−58 °C; IR (KBr) 2957, 1599, 1471, 1441, 1063, 736 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 8.04 (br d, $J$ = 7.7 Hz, 2H), 7.66 (br t, $J$ = 7.3 Hz, 1H), 7.50 (br dd, $J$ = 7.7, 7.3 Hz, 2H), 7.20 (s, 1H), 2.73 (t, $J$ =6.6 Hz, 2H), 1.61−1.45 (m, 3H), 0.88 (d, $J$ =5.8 Hz, 6H); FAB MS *m/z* 335 [(M − $BF_4$)$^+$]; HRMS (FAB) calcd for $C_{13}H_{17}ClI$ [(M − $BF_4$)$^+$] 335.0064, found 335.0074. Anal. Calcd for $C_{13}H_{17}BClF_4I$: C, 36.96; H, 4.06. Found: C, 37.00; H, 4.06.

**(*Z*)−(2-Chloro-4-phenyl-1-butenyl)phenyliodonium tetrafluoroborate (2d):** colorless leaflets; mp 85−86 °C; IR (KBr) 3090, 1595, 1471, 1450, 1084, 740 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.81 (br d, $J$ = 7.6 Hz, 2H), 7.64 (br t, $J$ = 7.3 Hz, 1H), 7.45 (br dd, $J$ = 7.6, 7.3 Hz, 2H), 7.25−7.06 (m, 5H), 6.98 (s, 1H), 3.13−3.00 (m, 2H), 3.00−2.87 (m, 2H); FAB MS *m/z* 369 [(M − $BF_4$)$^+$]; HRMS (FAB) calcd for $C_{16}H_{15}ClI$ [(M − $BF_4$)$^+$] 368.9907, found 368.9920. Anal. Calcd for $C_{16}H_{15}BClF_4I$: C, 42.10; H, 3.31. Found: C, 42.06; H, 3.29.

**(*Z*)−(2-Chloro-5-phenyl-1-pentenyl)phenyliodonium tetrafluoroborate (2e):** colorless leaflets; mp 103−104 °C; IR (KBr) 3071, 1586, 1442, 1085, 737 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 8.02 (br d, $J$ = 7.7 Hz, 2H), 7.63 (br t, $J$ = 7.3 Hz, 1H), 7.47 (br dd, $J$ = 7.7, 7.3 Hz, 2H), 7.31−7.09 (6H), 2.73 (t, $J$ = 7.6 Hz, 2H), 2.60 (t, $J$ = 7.3 Hz, 2H), 1.95 (m, 2H); FAB MS *m/z* 383 [(M − $BF_4$)$^+$]; HRMS (FAB) calcd for $C_{17}H_{17}ClI$ [(M − $BF_4$)$^+$] 383.0064, found 383.0074. Anal. Calcd for $C_{17}H_{17}BClF_4I$: C, 43.40; H, 3.64. Found: C, 43.17; H, 3.57.

**(*Z*)−(2,5-Dichloro-1-pentenyl)phenyliodonium tetrafluoroborate (2f):** oil; IR (Nujol) 1580, 1455, 1035 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 8.05 (br d, $J$ = 8.3 Hz, 2H), 7.66 (br t, $J$ = 7.5 Hz, 1H), 7.50 (br dd, $J$ = 8.3, 7.5 Hz, 2H), 7.32 (s, 1H), 3.53 (t, $J$ = 6.2 Hz, 2H), 2.94 (t, $J$ = 7.1 Hz, 2H), 2.11 (m, 2H); FAB MS *m/z* 341 [(M − $BF_4$)$^+$]; HRMS (FAB) calcd for $C_{11}H_{12}Cl_2I$ [(M − $BF_4$)$^+$] 340.9361, found 340.9379. Anal. Calcd for $C_{11}H_{12}BCl_2F_4I$: C, 30.81; H, 2.82. Found: C, 31.26; H, 2.82.

**(*Z*)−(2-Chloro-3-cyclopentyl-1-propenyl)phenyliodonium tetrafluoroborate (2 g):**[19] pale yellow crystals; mp 68−70 °C; IR (Nujol) 2720, 1585, 1560, 1145, 1040, 965, 715 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 8.04 (br d, $J$ = 7.8 Hz, 2H), 7.62 (br t, $J$ = 7.3 Hz, 1H), 7.47 (br dd, $J$ = 7.8, 7.3 Hz, 2H), 7.23 (s, 1H), 2.69 (d, $J$ = 7.3 Hz, 2H), 2.16 (septet, $J$ = 7.7 Hz, 1H), 1.80−1.41 (m, 6H), 1.19−0.95 (m, 2H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 156.5 (s), 135.3 (d), 132.4 (d), 132.1 (d), 113.1 (s), 97.8 (d), 45.7 (t), 38.2 (d), 31.7 (t), 24.9 (t). Anal. Calcd for $C_{14}H_{17}BClF_4I$: C, 38.70; H, 3.94. Found: C, 38.98; H, 4.00.

**(*Z*)−(2-Chloro-3,3-dimethyl-1-butenyl)phenyliodonium tetrafluoroborate (2h):** colorless crystals; mp 124−125 °C; IR (KBr) 2981, 1578, 1474, 1445, 1239, 1085, 739 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 8.05 (br d, $J$ = 7.7 Hz, 2H), 7.64 (br t, $J$ = 7.3 Hz, 1H), 7.49 (br dd, $J$ = 7.7, 7.3 Hz, 2H), 7.14 (s, 1H), 1.32 (s, 9H); FAB MS *m/z* 321 [(M − $BF_4$)$^+$]; HRMS (FAB) calcd for $C_{12}H_{15}ClI$ [(M − $BF_4$)$^+$] 320.9907, found 320.9926. Anal. Calcd for $C_{12}H_{15}BClF_4I$: C, 35.29; H, 3.70. Found: C, 35.28; H, 3.46.

**(*Z*)−(2-Bromo-1-decenyl)phenyliodonium tetrafluoroborate (3b):**[19] colorless crystals; mp 70−71 °C; IR (Nujol) 2720, 1580, 1560, 1160, 1030, 980, 715 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 8.07 (br d, $J$ = 8.0 Hz, 2H), 7.68 (br t, $J$ = 7.1 Hz, 1H), 7.52 (br dd, $J$ = 8.0, 7.1 Hz, 2H), 7.43 (s, 1H), 2.79 (t, $J$ = 7.1 Hz, 2H), 1.7−1.5 (m, 2H), 1.34−1.15 (m, 10H), 0.87 (t, $J$ = 6.6 Hz, 3H). Anal. Calcd for $C_{16}H_{23}BBrF_4I$: C, 37.76; H, 4.55. Found: C, 37.68; H, 4.56.

**(*Z*)−(2-Bromo-5-methyl-1-hexenyl)phenyliodonium tetrafluoroborate (3c):** oil; IR (Nujol) 3045, 1630, 1580, 1465, 1050 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 8.07 (br d, $J$ = 8.5 Hz, 2H), 7.61 (br t, $J$ = 7.0 Hz, 1H), 7.54−7.47 (m, 3H), 2.78 (t, $J$ = 7.3 Hz, 2H), 1.79−1.47 (m, 3H), 0.88 (d, $J$ = 6.0 Hz, 6H); FAB MS *m/z* 381, 379 [(M − $BF_4$)$^+$]; HRMS (FAB) calcd for $C_{13}H_{17}BrI$ [(M − $BF_4$)$^+$] 378.9558, found 378.9564.

**Synthesis of (*Z*)−(2-Fluoro-1-decenyl)phenyliodonium Tetrafluoroborate (4b).**[11] To a stirred solution of (1-decynyl)phenyliodonium tetrafluoroborate (**1b**) (699 mg, 1.63 mmol) in acetone (2 mL) and dichloromethane (2 mL) was added a solution of CsF (496 mg, 3.27 mmol) in $H_2O$ (0.59 mL, 33 mmol) at room temperature, and the solution was stirred for 9 h. After addition of water, the mixture was extracted with dichloromethane, and the combined organic extracts were washed with water and brine (× 3). The organic layer was filtered and concentrated under aspirator vacuum to give an oil, which was washed several times with hexane by decantation at −78 °C to give (*Z*)-(2-fluoro-1-decenyl)phenyliodonium chloride (157 mg, 24%) as colorless crystals: mp 114−117 °C (recrystallized from dichloromethane−hexane); IR (Nujol) 1640, 1560, 1150, 1105, 985, 730 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 8.03 (br d, $J$ = 7.9 Hz, 2H), 7.52 (br t, $J$ = 6.9 Hz, 1H), 7.39 (br dd, $J$ = 7.9, 6.9 Hz, 2H), 6.16 (d, $J_{HF}$ = 35.5 Hz, 1H), 2.47 (dt, $J$ = 6.9 Hz, $J_{HF}$ = 15.5 Hz, 2H), 1.72−1.45 (m, 2H), 1.40−1.10 (m, 10H), 0.87 (t, $J$ = 6.4 Hz, 3H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 170.2 ($J_{CF}$ = 274 Hz), 134.4, 131.0, 130.7, 119.6, 82.8 ($J_{CF}$ = 24 Hz), 32.2 ($J_{CF}$ = 24 Hz), 31.6, 28.9, 28.5, 25.5, 22.5, 13.9; MS *m*/*z* (relative intensity) 284 [30, $(M - Ph\text{-}Cl)^+$], 204 (66), 112 (83), 77 (100). Anal. Calcd for $C_{16}H_{23}ClFI$: C, 48.44; H, 5.84. Found: C, 48.16; H, 5.76.

This ($\beta$-fluorovinyl)iodonium chloride (30 mg, 0.076 mmol) was dissolved in dichloromethane (15 mL), and the solution was vigorously shaken with a saturated aqueous sodium tetrafluoroborate solution (5 mL) four times. The organic layer was filtered and concentrated under aspirator vacuum to give an oil, which was washed several times with hexane by decantation at −78 °C to give the ($\beta$-fluorovinyl)iodonium tetrafluoroborate **4b** (29 mg, 86%) as white solids: IR (KBr) 2929, 1651, 1472, 1440, 1084, 738 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 8.02 (br d, $J$ = 7.9 Hz, 2H), 7.60 (br t, $J$ = 7.6 Hz, 1H), 7.48 (br dd, $J$ = 7.9, 7.6 Hz, 2H), 6.53 (d, $J_{HF}$ = 33.2 Hz, 1H), 2.53 (dt, $J$ = 7.7 Hz, $J_{HF}$ = 16.9 Hz, 2H), 1.62−1.16 (m, 12H), 0.87 (t, $J$ = 6.8 Hz, 3H); FAB MS *m*/*z* 361 $[(M - BF_4)^+]$; HRMS (FAB) calcd for $C_{16}H_{23}FI$ $[(M - BF_4)^+]$ 361.0829, found 361.0837. Anal. Calcd for $C_{16}H_{23}BF_5I$: C, 42.89; H, 5.17. Found: C, 42.92; H, 5.07.

**Synthesis of (*Z*)−(2-Fluoro-5-methyl-1-hexenyl)phenyliodonium Tetrafluoroborate (4c).** In a similar manner, (*Z*)-(2-fluoro-5-methyl-1-hexenyl)phenyliodonium chloride was prepared in 15% yield from (5-methyl-1-hexynyl)phenyliodonium tetrafluoroborate (**1c**) (500 mg, 1.30 mmol), CsF (394 mg, 2.60 mmol), and $H_2O$ (0.47 mL, 26 mmol) in acetone (1 mL) and dichloromethane (1 mL): white powder: mp 137−141 °C; IR (KBr) 2958, 1657, 1567, 1472, 1441, 1368, 739 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 8.02 (br d, $J$ = 8.2 Hz, 2H), 7.52 (br t, $J$ = 7.0 Hz, 1H), 7.38 (br dd, $J$ = 8.2, 7.0 Hz, 2H), 6.17 (d, $J_{HF}$ = 35.9 Hz, 1H), 2.47 (dt, $J$ = 7.7 Hz, $J_{HF}$ = 15.5 Hz, 2H), 1.57−1.39 (m, 3H), 0.86 (d, $J$ = 6.1 Hz, 6H); FAB MS *m*/*z* 319 $[(M - Cl)^+]$. Anal. Calcd for $C_{13}H_{17}ClFI \bullet {}^1/_4H_2O$: C, 43.48; H, 4.91. Found: C, 43.51; H, 4.62.

This ($\beta$-fluorovinyl)iodonium chloride (22 mg, 0.062 mmol) was dissolved in dichloromethane (15 mL), and the solution was vigorously shaken with a saturated aqueous sodium tetrafluoroborate solution (5 mL) four times. The organic layer was filtered and concentrated under aspirator vacuum to give an oil, which was washed several times with hexane by decantation at −78 °C to give the ($\beta$-fluorovinyl)iodonium tetrafluoroborate **4c** (25 mg, 99%) as an oil: IR (neat) 1646, 1472, 1446, 1050, 742 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 8.02 (br d, $J$ = 7.6 Hz, 2H), 7.65 (br t, $J$ = 7.3 Hz, 1H), 7.48 (br dd, $J$ = 7.6, 7.3 Hz, 2H), 6.48 (d, $J_{HF}$ = 33.7 Hz, 1H), 2.59 (dt, $J$ = 7.5 Hz, $J_{HF}$ = 16.2 Hz, 2H), 1.70−1.36 (m, 3H), 0.88 (d, $J$ = 6.1 Hz, 6H); FAB MS *m*/*z* 319 $[(M - BF_4)^+]$; HRMS (FAB) calcd for $C_{13}H_{17}FI$ $[(M - BF_4)^+]$ 319.0359, found 319.0356.

**General Procedure for Reaction of (*Z*)−(β-Haloalkenyl)iodonium Tetrafluoroborates 2−4 with Sodium Benzenesulfinate.** To a stirred solution of a (Z)-($\beta$-halovinyl)-iodonium salt **2**, **3**, or **4** (0.05 mmol) in THF (1 mL) was added sodium benzenesulfinate dihydrate (25 mg, 0.13 mmol) under atmosphere at 0 °C, and the mixture was stirred for the periods shown in Table 2. Water was added, the mixture was extracted with dichloromethane three times, and the combined organic phase was washed with water and brine. The solution was dried over anhydrous $Na_2SO_4$ and concentrated to give an oil, which was purified by preparative TLC. The yields of pure products are given in Table 2.

**(*Z*)-1,2-Bis(benzenesulfonyl)-1-propene (5a):** colorless needles; mp 113−115 °C (recrystallized from dichloromethane-hexane) (lit.[13a] mp 113−114.5 °C); IR (KBr) 3007, 1583, 1447, 1323, 1163, 1084, 723, 690 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 8.11−8.03 (m, 4H), 7.74−7.54 (m, 6H), 6.82 (q, $J$ = 1.3 Hz, 1H), 2.12 (d, $J$ = 1.3 Hz, 3H); MS *m*/*z* (relative intensity) 322 (2, $M^+$), 258 (5), 218 (66), 141 (51), 125 (100), 77 (98).

**(*Z*)-1,2-Bis(benzenesulfonyl)-1-decene (5b):**[7b] colorless needles; mp 91.8−92.2 °C (recrystallized from dichloromethane−hexane); IR (KBr) 2930, 2850, 1450, 1325, 1150, 720, 630 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 8.09 (br d, $J$ = 7.5 Hz, 2H), 8.03 (br d, $J$ = 7.5 Hz, 2H), 7.72−7.64 (m, 2H), 7.62−7.55 (m, 4H), 6.76 (t, $J$ = 1.4 Hz, 1H), 2.40 (dt, $J$ = 1.4, 7.7 Hz, 2H), 1.45−1.36 (m, 2H), 1.30−1.14 (m, 10H), 0.87 (t, $J$ = 6.8 Hz, 3H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 154.2, 141.4, 138.6, 138.4, 134.4, 133.8, 129.3, 129.0, 129.0, 128.2, 33.5, 31.7, 29.0, 28.7, 28.2, 22.5, 14.0; MS *m*/*z* (relative intensity) 420 (1, $M^+$), 279 (80), 218 (18), 143 (82), 137 (60), 125 (100), 77 (74); HRMS calcd for $C_{22}H_{28}O_4S_2$ ($M^+$) 420.1429, found 420.1458. Anal. Calcd for $C_{22}H_{28}O_4S_2$: C, 62.82; H, 6.71. Found: C, 62.78; H, 6.73.

**(*E*)-1,2-Bis(benzenesulfonyl)-1-decene (5b):** colorless plates; mp 76−78 °C (recrystallized from dichloromethane−hexane); IR ($CHCl_3$) 2925, 2850, 1720, 1325, 1155, 1085 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.94 (br d, $J$ = 7.7 Hz, 2H), 7.85 (br d, $J$ = 7.0 Hz, 2H), 7.81−7.54 (m, 6H), 7.38 (s, 1H), 2.75−2.67 (m, 2H), 1.52−1.16 (m, 12H), 0.88 (t, $J$ = 6.8 Hz, 3H); $^{13}C$ NMR ($CDCl_3$) $\delta$ 155.0, 139.7, 137.3, 135.2, 134.5, 129.7, 129.6, 128.8, 127.9, 31.8, 29.9, 29.0, 28.9, 27.1, 22.6, 14.1; MS *m*/*z* (relative intensity) 420 (0.2, $M^+$), 279 (100), 143 (45), 137 (30), 77 (45); HRMS calcd for $C_{22}H_{28}O_4S_2$ ($M^+$) 420.1429, found 420.1437. Anal. Calcd for $C_{22}H_{28}O_4S_2$: C, 62.82; H, 6.71. Found: C, 62.54; H, 6.77.

**(*Z*)-1,2-Bis(benzenesulfonyl)-5-methyl-1-hexene (5c):** colorless plates; mp 103−104 °C (recrystallized from dichloromethane−hexane); IR ($CHCl_3$) 2960, 2880, 1595, 1450, 1330, 1155, 1090 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 8.12−8.01 (m, 4H), 7.81−7.53 (m, 6H), 6.76 (t, $J$ = 1.5 Hz, 1H), 2.41 (br dt, $J$ = 1.5, 7.7 Hz, 2H), 1.57−1.22 (m, 3H), 0.82 (d, $J$ = 6.5 Hz, 6H); MS *m*/*z* (relative intensity) 378 (0.6, $M^+$), 237 (59), 218 (32), 143 (61), 125 (98), 95 (70), 77 (100); HRMS calcd for $C_{19}H_{22}O_4S_2$ ($M^+$) 378.0960, found 378.0941. Anal. Calcd for $C_{19}H_{22}O_4S_2$: C, 60.29; H, 5.86. Found: C, 60.55; H, 6.07.

**(*E*)-1,2-Bis(benzenesulfonyl)-5-methyl-1-hexene (5c):** colorless plates; mp 87−88 °C (recrystallized from dichloromethane−hexane); IR ($CHCl_3$) 2950, 2875, 1615, 1590, 1450, 1325, 1155, 1085 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.94 (br d, $J$ = 7.7 Hz, 2H), 7.85 (br d, $J$ = 7.7 Hz, 2H), 7.75−7.55 (m, 6H), 7.38 (s, 1H), 2.75−2.66 (m, 2H), 1.61−1.20 (m, 3H), 0.83 (d, $J$ = 6.6 Hz, 6H); MS *m*/*z* (relative intensity) 378 (0.1, $M^+$), 237 (100), 143 (43), 95 (26), 77(50); HRMS calcd for $C_{19}H_{22}O_4S_2$ ($M^+$) 378.0960, found 378.0941. Anal. Calcd for $C_{19}H_{22}O_4S_2$: C, 60.29; H, 5.86. Found: C, 60.03; H, 5.74.

**(*Z*)-1,2-Bis(benzenesulfonyl)-4-phenyl-1-butene (5d):** colorless oil; IR ($CHCl_3$) 1735, 1595, 1450, 1330, 1155, 1085 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 8.11 (br d, $J$ = 7.7 Hz, 2H), 7.88 (br d, $J$ = 7.7 Hz, 2H), 7.70−7.50 (m, 6H), 7.25−7.15 (m, 3H), 7.01−6.92 (m, 2H), 6.48 (t, $J$ = 1.4 Hz, 1H), 2.84−2.62 (m, 4H); MS *m*/*z* (relative intensity) 412 (0.1, $M^+$), 271 (44), 129 (100), 91 (78), 77 (41); HRMS calcd for $C_{22}H_{20}O_4S_2$ ($M^+$) 412.0803, found 412.0798. Anal. Calcd for $C_{22}H_{20}O_4S_2$: C, 64.05; H, 4.89. Found: C, 64.36; H, 5.19.

**(Z)-1,2-Bis(benzenesulfonyl)-5-phenyl-1-pentene (5e):** colorless needles; mp 93−94 °C (recrystallized from dichloromethane−hexane); IR ($CHCl_3$) 2930, 1720, 1585, 1450, 1325, 1155, 1090 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 8.10−8.00 (m, 4H), 7.75−7.51 (m, 6H), 7.30−7.15 (m, 3H), 7.10−7.00 (m, 2H), 6.73 (t, $J$ = 1.2 Hz, 1H), 2.56 (t, $J$ = 7.6 Hz, 2H), 2.42 (dt, $J$ = 1.2, 7.6 Hz, 2H), 1.75 (quint, $J$ = 7.6 Hz, 2H); MS *m*/*z* (relative intensity) 426 (0.7, $M^+$), 285 (80), 181 (30), 142 (99), 128 (58), 91 (100), 77 (78); HRMS calcd for $C_{23}H_{22}O_4S_2$ ($M^+$) 426.0960, found 426.0953. Anal. Calcd for $C_{23}H_{22}O_4S_2$: C, 64.76; H, 5.20. Found: C, 64.37; H, 5.22.

**(*Z*)-1,2-Bis(benzenesulfonyl)-5-chloro-1-pentene (5f):** colorless oil; IR ($CHCl_3$) 1450, 1325, 1150, 1085 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 8.16−8.00 (m, 4H), 7.71−7.51 (m, 6H), 6.84 (t, $J$ = 1.2 Hz, 1H), 3.48 (t, $J$ = 6.1 Hz, 2H), 2.56 (br dt, $J$ = 1.2, 7.3 Hz, 2H), 2.04−1.89 (m, 2H); MS *m*/*z* (relative intensity) 384 (0.4, $M^+$), 243 (11), 183 (24), 149 (53), 125 (93), 77 (100); HRMS calcd for $C_{17}H_{17}O_4ClS_2$ ($M^+$) 384.0257, found 384.0232.

**(*Z*)-1,2-Bis(benzenesulfonyl)-3-cyclopentyl-1-propene (5g):**[7b] colorless oil; IR ($CHCl_3$) 2950, 1450, 1325, 1150, 1085 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 8.09 (br d, $J$ = 7.5 Hz, 2H), 8.03 (br d, $J$ = 7.5 Hz, 2H), 7.71−7.64 (m, 2H), 7.63−7.54 (m, 4H), 6.81 (t, $J$ = 1.3 Hz, 1H), 2.41 (dd, $J$ = 7.5, 1.3 Hz, 2H), 2.01 (septet, $J$ = 7.5 Hz, 1H), 1.73−1.64 (m, 2H), 1.60−1.42 (m, 4H), 1.03−0.93 (m, 2H); MS *m*/*z* (relative intensity) 390 (0.1, $M^+$), 249 (37), 218 (32), 143 (33), 125 (88), 107 (61), 77 (100); HRMS calcd for $C_{20}H_{22}O_4S_2$ ($M^+$) 390.0960, found 390.0976. Anal. Calcd for $C_{20}H_{22}O_4S_2$: C, 61.51; H, 5.68. Found: C, 61.28; H, 5.71.

**(*Z*)-1,2-Bis(benzenesulfonyl)-3,3-dimethyl-1-butene (5h):**[7b] colorless needles; mp 138−139 °C (recrystallized from dichloromethane−hexane); IR ($CHCl_3$) 2945, 1580, 1445, 1320, 1150, 1080 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 8.16 (br d, $J$ = 8.0 Hz, 2H), 7.97 (br d, $J$ = 8.0 Hz, 2H), 7.71−7.49 (m, 6H), 7.11 (s, 1H), 1.26 (s, 9H). Anal. Calcd for $C_{18}H_{20}O_4S_2$: C, 59.32; H, 5.53. Found: C, 59.13; H, 5.53.

**(*Z*)-2-(Benzenesulfonyl)-1-bromo-1-decene (7b):**[7a] colorless oil; IR ($CHCl_3$) 2920, 2845, 1715, 1580, 1445, 1315, 1150, 1085 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 8.00 (br d, $J$ = 7.3 Hz, 2H), 7.65 (br t, $J$ = 6.8 Hz, 1H), 7.55 (br dd, $J$ = 7.3, 6.8 Hz, 2H), 6.79 (t, $J$ = 1.2 Hz, 1H), 2.54 (dt, $J$ = 1.2, 7.3 Hz, 2H), 1.66−1.46 (m, 2H), 1.36−1.14 (m, 10H), 0.88 (t, $J$ = 6.8 Hz, 3H); MS (CI, isobutane) *m*/*z* (relative intensity) 361 (100), 359 (97, $M^+ + 1$), 317 (10); HRMS calcd for $C_{16}H_{24}BrO_2S$ ($M^+ + 1$) 359.0680, found 359.0663. Anal. Calcd for $C_{16}H_{23}BrO_2S$: C, 53.48; H, 6.45. Found: C, 52.98; H, 6.40.

**(*Z*)-2-(Benzenesulfonyl)-5-methyl-1-bromo-1-hexene (7c):** colorless oil; IR ($CHCl_3$) 2945, 1585, 1440, 1315, 1150, 1085 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 8.00 (br d, $J$ = 7.7 Hz, 2H), 7.68−7.50 (m, 3H), 6.80 (t, $J$ = 1.3 Hz, 1H), 2.55 (br dt, $J$ = 1.3, 7.6 Hz, 2H), 1.62−1.41 (m, 3H), 0.91 (d, $J$ = 6.3 Hz, 6H); MS *m*/*z* (relative intensity) 318 (0.3), 316 (0.3, $M^+$), 303 (2), 301 (2), 237 (98), 143 (100), 125 (57), 95 (72), 77 (62); HRMS calcd for $C_{13}H_{17}BrO_2S$ ($M^+$) 316.0133, found 316.0115.

**(*Z*)-1-(Benzenesulfonyl)-2-chloro-3,3-dimethyl-1-butene (8):** colorless plates; mp 67−68 °C (recrystallized from dichloromethane−hexane); IR ($CHCl_3$) 2970, 1595, 1320, 1200, 1150, 1090 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.98 (br d, $J$ = 7.3 Hz, 2H), 7.64 (br t, $J$ = 7.3 Hz, 1H), 7.55 (br t, $J$ = 7.3 Hz, 2H), 6.69 (s, 1H), 1.19 (s, 9H); MS *m*/*z* (relative intensity) 258 (9, $M^+$), 223 (100), 125 (84), 117 (88), 81 (50), 77 (81); HRMS calcd for $C_{12}H_{15}ClO_2S$ ($M^+$) 258.0481, found 258.0466. Anal. Calcd for $C_{12}H_{15}ClO_2S$: C, 55.70; H, 5.84. Found: C, 55.95; H, 6.01. The structure and stereochemistry of **8** were deduced by the observed NOE enhancements between the vinylic proton and both the ortho protons and the methyl groups. Synthesis of the regioisomer, (*Z*)-2-(benzenesulfonyl)-1-chloro-3,3-dimethyl-1-butene, has been reported.[7a]

**Time Course for the Reaction of (*Z*)−(*β*-Chlorodecenyl)iodonium Salt 2b with Sodium Benzenesulfinate.** To a solution of (*Z*)-(*β*-chlorodecenyl)iodonium salt **2b** (10 mg, 0.022 mmol) in $CDCl_3$ (0.5 mL) in an NMR tube was added sodium benzenesulfinate dihydrate (11 mg, 0.054 mmol) at room temperature. $^1H$ NMR monitoring of the reaction mixture was performed over 9 h, and the results are shown in Figure 2 (a). Quenching of the reaction mixture with water followed by standard workup gave (*Z*)-1,2-bis(benzenesulfonyl)-1-decene (**5b**) (8.2 mg, 91%) and (*Z*)-2-(benzenesulfonyl)-1-chloro-1-decene (**6b**) (0.2 mg, 3%). **6b**:[7a] colorless oil; IR ($CHCl_3$) 2915, 1590, 1445, 1315, 1155, 1085 $cm^{-1}$; $^1H$ NMR ($CDCl_3$) $\delta$ 7.98 (br d, $J$ = 7.8 Hz, 2H), 7.65 (br t, $J$ = 7.5 Hz, 1H), 7.55 (br dd, $J$ = 7.8, 7.5 Hz, 2H), 6.52 (t, $J$ = 1.2 Hz, 1H), 2.54 (dt, $J$ = 1.2, 7.5 Hz, 2H), 1.70−1.50 (m, 2H), 1.43−1.18 (m, 10H), 0.88 (t, $J$ = 6.8 Hz, 3H);, 2.54 (dt, $J$ = 1.2, 7.3 Hz, 2H), 1.66−1.46 (m, 2H), 1.36−1.14 (m, 10H), 0.88 (t, $J$ = 6.8 Hz, 3H); MS (CI, isobutane) *m*/*z* (relative intensity) 629 (20), 317 (45), 315 (100, $M^+ + 1$); HRMS calcd for $C_{16}H_{24}ClO_2S$ ($M^+ + 1$) 315.1186, found 315.1200.

**Reaction Intermediate (*Z*)-[2-(Benzenesulfonyl)-1-decenyl]phenyliodonium Tetrafluoroborate (*Z*)−(9b).** To a stirred solution of (*Z*)-(*β*-chlorovinyl)iodonium salt **2b** (80 mg, 0.17 mmol) in THF (3 mL) was added sodium benzenesulfinate dihydrate (35 mg, 0.17 mmol) under atmosphere at 0 °C, and the mixture was stirred for 12 h. The mixture was vigorously shaken with a saturated aqueous sodium tetrafluoroborate solution (10 mL) four times. The organic layer was filtered and concentrated under aspirator vacuum to give an oil, which was analyzed by $^1H$ NMR and the results are shown in Scheme 3. Decantation using hexane at −78 °C several times followed by repeated fractional recrystallization using dichloromethane−hexane−diethyl ether gave pure (*Z*)-(2-sulfonyldecenyl)iodonium salt (*Z*)-**9b** (X = $BF_4$) (1.2 mg) as colorless plates (mp 118−121 °C). The structure of this iodonium salt was determined by comparison of its spectral data ($^1H$ NMR, IR, and FAB MS) with those of the authentic samples.[3d]

**Time Course for the Reaction of (*Z*)−(*β*-Bromodecenyl)iodonium Salt 3b with Sodium Benzenesulfinate.** To a solution of (*Z*)-(*β*-bromodecenyl)iodonium salt **3b** (11 mg, 0.022 mmol) in $CDCl_3$ (0.5 mL) in an NMR tube was added sodium benzenesulfinate dihydrate (11 mg, 0.054 mmol) at room temperature. $^1H$ NMR monitoring of the reaction mixture was performed over 84 h and the results are shown in Figure 2 (b). Quenching of the reaction mixture with water followed by standard workup gave (*Z*)-**5b** (3.3 mg, 43%) and (*Z*)-2-(benzenesulfonyl)-1-bromo-1-decene (**7b**) (3 mg, 33%).

**General Procedure for Competitive Reaction of (*Z*)-9b (X = $BF_4$) with Halide and Benzenesulfinate Anions.** To a stirred solution of two competing tetrabutylammonium salts (each 0.70 mmol) in THF (10 mL) and dichloromethane (1 mL) was added (*Z*)-(2-sulfonyldecenyl)iodonium salt (*Z*)-**9b** (X = $BF_4$) (20 mg, 0.035 mmol) under atmosphere at 0 °C, and the mixture was stirred for the periods shown in Table 3. Water was added, the mixture was extracted with diethyl ether three times, and the combined organic phase was washed with water and brine. The solution was dried over anhydrous $Na_2SO_4$ and concentrated to give an oil, which was purified by preparative TLC (hexane−ethyl acetate). The yields of pure products are given in Table 3, entries 1−3.

In a similar manner, competitive reactions of (*Z*)-**9b** (X = $BF_4$) with sodium salts were carried out in THF under atmosphere at 0 °C. The yields of pure products are given in Table 3, entries 4−6.

**Time Course for the Reaction of (*Z*)−(*β*-Fluorodecenyl)iodonium Salt 4b with Sodium Benzenesulfinate.** To a solution of (*Z*)-(*β*-fluorodecenyl)iodonium salt **4b** (13 mg, 0.029 mmol) in $CDCl_3$ (0.5 mL) in an NMR tube was added sodium benzenesulfinate dihydrate (14 mg, 0.071 mmol) at room temperature. $^1H$ NMR monitoring of the reaction mixture was performed over 154 h, and the results are shown in Figure 2 c. Quenching of the reaction mixture with water followed by standard workup gave (*Z*)-**5b** (2.2 mg, 18%), (*E*)-**5b** (3.6 mg, 30%), and 1-(benzenesulfonyl)cyclopentene **11**[3d] (1.8 mg, 23%).

**Supporting Information Available:** ORTEP drawing of (*E*)-**5b**; $^1H$ NMR spectra for (*Z*)-**5f**, **6b**, and **7c**; NOE data of **2b**, **2g**, **3b**, and **4b** (5 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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