JOC The Journal of Organic Chemistry

Article

pubs.acs.org/joc

# Mechanistic Studies on the Generation and Properties of Superelectrophilic Singlet Carbenes from Bis(perfluoroalkanesulfonyl)bromonium Ylides

Kazunori Miyamoto,*[,†] Susumu Iwasaki,[‡] Ryusuke Doi,[‡] Taiga Ota,[‡] Yufuko Kawano,[‡] Junpei Yamashita,[‡] Yuuta Sakai,[‡] Norihiro Tada,[§] Masahito Ochiai,[‡] Satoko Hayashi,[∥] Waro Nakanishi,*[,∥] and Masanobu Uchiyama*[,†]

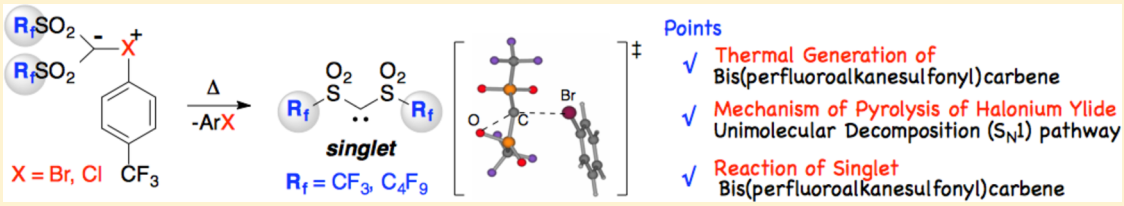
[†]Graduate School of Pharmaceutical Sciences, The University of Tokyo, 7-3-1 Hongo Bunkyo-ku, Tokyo 113-0033, Japan

[‡]Graduate School of Pharmaceutical Sciences, The University of Tokushima, 30-8 Shomachi, Tokushima 770-8505, Japan

[§]Gifu Pharmaceutical University, 1-25-4, Daigaku-nishi, Gifu 501-1196, Japan

[∥]Department of Materials Science and Chemistry, Faculty of Systems Engineering, Wakayama University, 930 Sakaedani, Wakayama 640-8510, Japan

Supporting Information




**ABSTRACT:** Pyrolysis of bis(perfluoroalkanesulfonyl)bromonium ylides in various olefins results in highly stereospecific formation of cyclopropanes via unimolecular decomposition. Product analysis, kinetic study, substituent effects, and theoretical study revealed the generation of singlet bis(perfluoroalkanesulfonyl)carbenes stabilized by intramolecular coordination of sulfonyl oxygen.

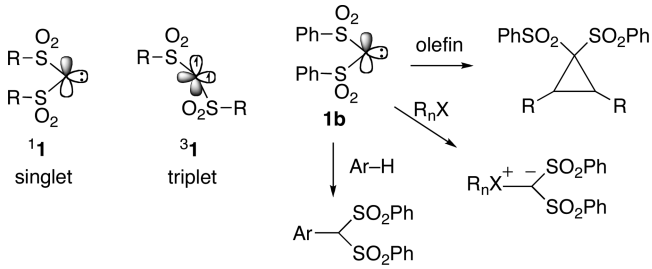
## INTRODUCTION

Since the first report on the generation of carbene in 1903 by Buchner and Feldmann,[1] alkyl-, aryl-, acyl-, and heteroatom-substituted carbenes have been widely used in synthetic organic chemistry as versatile one-carbon sources.[2,3] In contrast, the chemical properties of highly electron-deficient disulfonylcarbenes with aryl or perfluoroalkyl substituents have been essentially ignored, probably because of the lack of suitable preparation methods and precursors. There have been only a few studies on the reactivity of disulfonylcarbenes **1** (or their metal carbenoids), which were generated by either photochemical or transition metal-catalyzed decomposition of aryl-$\lambda^3$-iodonium ylides or diazo compounds.[4] Bis(phenylsulfonyl)carbene **1b** (R = Ph) undergoes a variety of typical carbene reactions, such as cyclopropanation of electron-rich olefins,[5] electrophilic attack on noncharged tertiary N, P, As, and S nucleophiles to give onium ylides,[6] and C−H insertion reaction into electron-rich aromatics (Scheme 1).[7]

Most disulfonylcarbenes and metal carbenoids are converted into thiosulfonate **4** (e.g., R = Ph), probably via unimolecular decomposition of **1** through a facile [1,2]oxygen-shift from sulfur to carbon with formation of dithiocarbonate *S,S,S*′-trioxide **3** (Scheme 2).[4a,8,9] This unique [1,2]oxygen shift has been applied synthetically by Shibata and co-workers;[10] in situ-generated benzoyl(trifluoromethylsulfonyl)carbene **5** and/or its copper carbenoid spontaneously degraded to afford thioperoxoate **7**, which serves as a good electrophilic trifluoromethylthiolating agent for enamines, allylsilanes, and pyrroles. A similar type of oxygen atom migration of a nitro group has been well established for singlet nitrocarbene **6**, affording nitrosoformaldehyde **8**.[11]

From the theoretical viewpoint, Sander and co-workers reported that, because of the unusually large electron affinity (EA) and high ionization potential (IP), extremely high electrophilicity of the disulfonylcarbene **1a** (R = H) is expected

**Scheme 1. Chemical Properties of Disulfonylcarbenes 1**

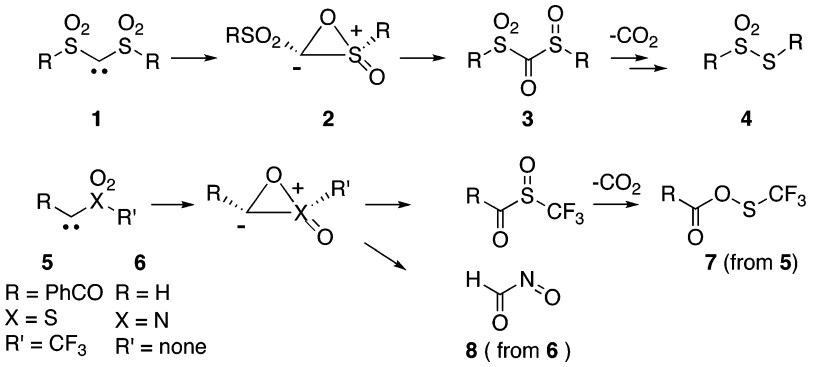



**Received:** January 22, 2016
**Published:** March 24, 2016




DOI: 10.1021/acs.joc.6b00142
J. Org. Chem. 2016, 81, 3188−3198

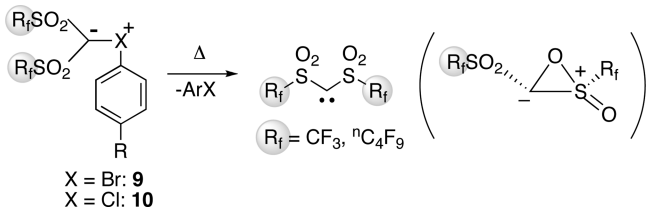
**Scheme 2. Properties of Disulfonylcarbenes 1**




both in the singlet and triplet states, and it is a long-standing issue which state is dominant (Scheme 1).[8]

Recently, we reported that bis(triflyl)bromonium ylide **9a** (R = $CF_3$) undergoes thermal intermolecular transylidation to halobenzenes (ArX: X = I, Br, and Cl), yielding halonium ylides, and we proposed that generation of active bis(triflyl)-carbene **1c** (R = $CF_3$) was involved (Scheme 3).[12] Here, we

**Scheme 3. Unimolecular Decomposition of Halonium Ylides 9 and 10**

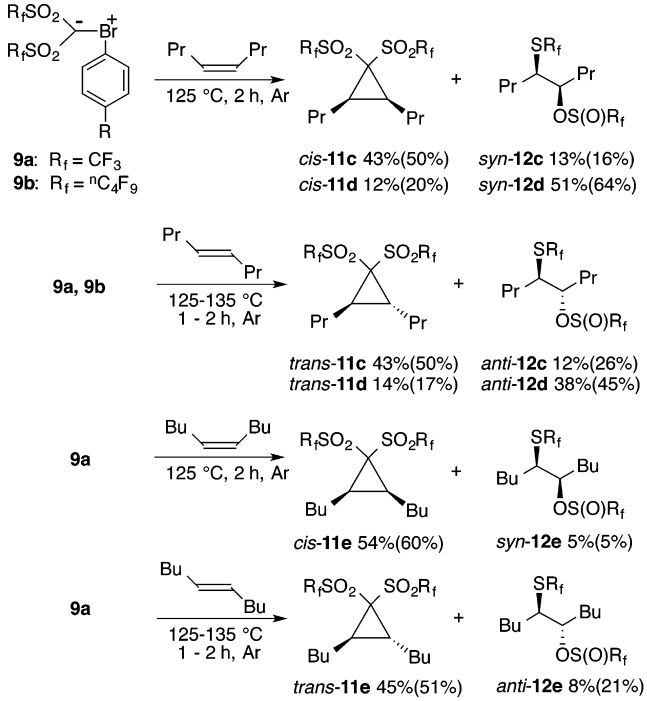



report a chemical, kinetic, and theoretical examination of the thermal generation of highly electron-deficient bis-(perfluoroalkanesulfonyl)carbenes from bis(perfluoroalkane-sulfonyl)halonium ylides **9** and **10**, and we discuss their spin multiplicity.

## RESULTS AND DISCUSSION

Thermal solvolysis of bromonium ylide **9a** in monosubstituted terminal alkenes as solvents afforded cyclopropane **11** and an 1,2-*S*,*O*-addition products **12** with high chemoselectivity (Scheme 4). Ylide **9a** is sparingly soluble in these olefins at room temperature, but rapidly dissolves on heating at around 100 °C to give a pale yellow solution. Thermal solvolysis of ylide **9a** at 125 °C for 2 h in 1-octene and 1-decene (0.2 M) afforded *geminal* bis(triflyl)cyclopropanes **11a** and **11b**, respectively, with high selectivity (>97%) in good yield, along with formation of a trace amount (1−2%) of 1,2-*S*,*O*-addition products **12a** and **12b** (see also Scheme 5). It is noteworthy that no allylic C−H insertion products at all were observed under these reaction conditions, suggesting the absence of the triplet state of carbene **1c** ($^3$**1c**).

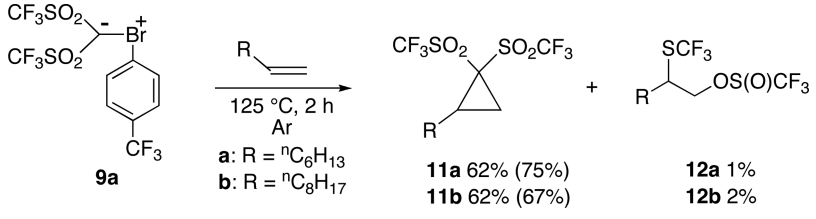
**Scheme 5. Thermal Solvolysis of Bromonium Ylides 9 in *cis*- and *trans*-Olefins**




Isolated yields ($^1$H NMR yields).

Rates of thermal decomposition of bromonium ylide **9a** were measured spectrophotometrically in perfluorodecalin as a solvent at temperatures in the range of 92−108 °C in the presence and absence of 1-octene by monitoring the decrease

**Scheme 4. Reaction of Bromonium Ylide 9a with Terminal Alkenes**






DOI: 10.1021/acs.joc.6b00142
J. Org. Chem. 2016, 81, 3188−3198

of absorbance at 275 nm (Figure S1). The pseudo-first-order rate constant $k_{obs}$ was obtained for each run, and the values for at least triplicate runs were averaged (Table 1). Remarkably,

**Table 1. Observed Rate Constants ($10^4 k_{obs}/s^{-1}$) for Thermal Decomposition of Bromonium Ylide 9 in Perfluorodecalin**[a]

| | | temp (°C) | | | | | |
|---|---|---|---|---|---|---|---|
| entry | 1-octene $10^3$ M | 92 | 100 | 104 | 108 | $\Delta H^{\ddagger}$/kcal mol$^{-1}$ | $\Delta S^{\ddagger}$/cal mol$^{-1}$ K$^{-1}$ |
| 1 | 0.0 | 0.829 | 2.54 | 4.06 | 6.91 | 35.7 | 20.3 |
| 2 | 0.66 | | | | 6.57 | | |
| 3 | 3.3 | | | | 6.74 | | |
| 4 | 6.6 | | | | 6.64 | | |
| 5 | 13 | | | | 6.73 | | |
| 6[b] | 0.0 | | | | 0.618 | | |
| 7[b] | 0.0 | | | | 0.336 | | |
| 8[b] | 0.0 | | | | 1.67 | | |
| 9[c,d] | 0.0 | 68.5 | 144 | | | 29.6 | 12.0 |

[a]Initial concentration of ylide **9**, $6.6 \times 10^{-4}$ M. [b]Thermal decomposition of bromonium ylides **9c** (R = H, $R_f$ = $CF_3$, entry 6), **9d** (R = Me, $R_f$ = $CF_3$, entry 7), and **9e** (R = Cl, $R_f$ = $CF_3$, entry 8). [c]Chloronium ylide **10a** was used instead of **9a**. [d]Rate constants measured 84 and 76 °C are shown in Figure S2.

zero-order dependency on the thermal decomposition rate constant at 108 °C was established for the substrate 1-octene, indicating a reaction process in which the rate-limiting step precedes the interaction of ylide **9a** with the terminal olefin (Figure 1).[12a] The large positive activation entropy (20.3 cal

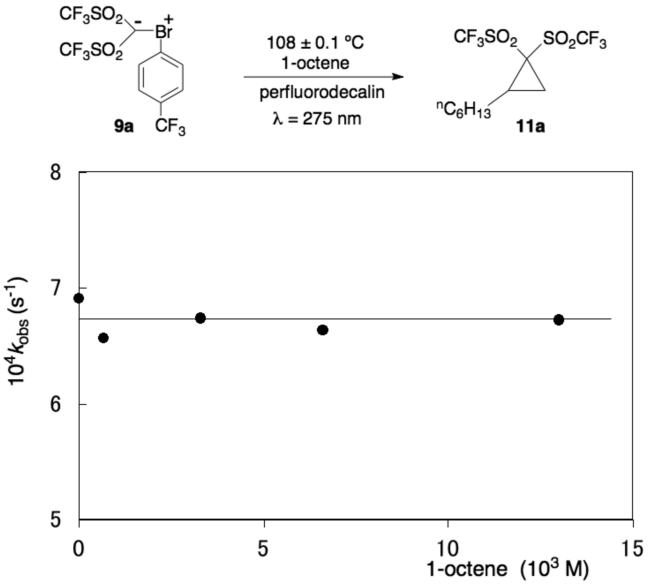


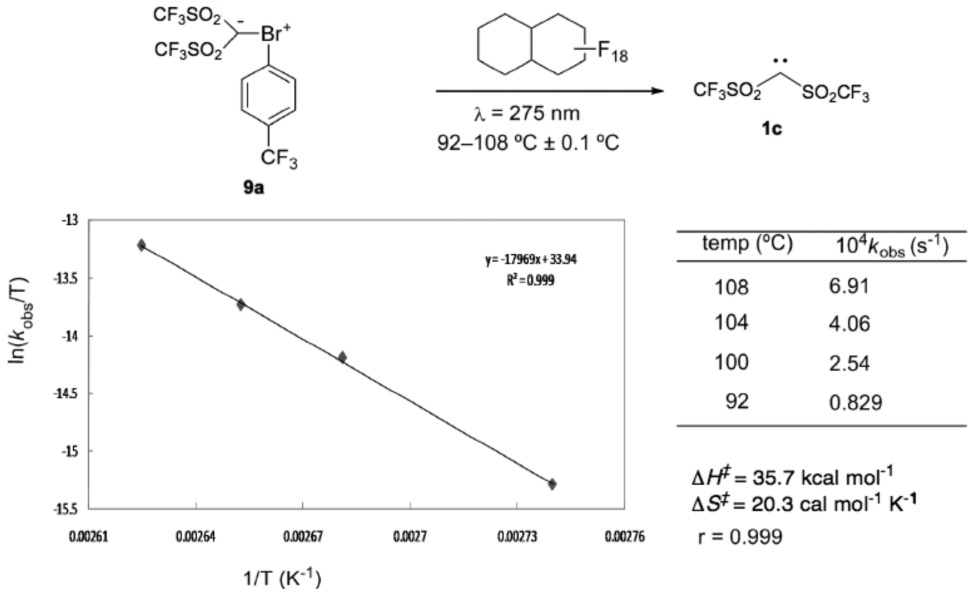

**Figure 1.** Observed rate constants ($10^4$ $k_{obs}/s^{-1}$) for thermal decomposition of bromonium ylide **9a** at 108 ± 0.1 °C in the presence and absence of 1-octene in perfluorodecalin as a solvent. Initial concentration of ylide **9a**, $6.6 \times 10^{-4}$ M.

mol$^{-1}$ K$^{-1}$) for thermal decomposition of ylide **9a** is in good agreement with the view that the cyclopropanation of 1-octene proceeds via unimolecular rate-limiting generation of free bis(trifyl)carbene **1c** (Figure 2). Entries 6–8 illustrate the electronic effects of *para*-substituents of bromonium ylides **9** on the rate of thermal decomposition at 108 °C. The thermolysis rate of phenylbromonium ylide **9c** was decreased to about one-tenth of that of *p*-(trifluoromethyl)phenylbromonium ylide **9a** (Table 1, entry 6), probably because of the decreased nucleofugality of the unsubstituted phenyl-$\lambda^3$-bromanyl group.[13] Introduction of *p*-methyl group **9d** further slowed down the thermal decomposition, whereas the electron-withdrawing *p*-chloro group in **9e** enhanced the rate of carbene generation (entries 7 and 8). The Hammett plot showed an excellent correlation of the relative rate factors with $\sigma_p$ constants and gave a reasonable reaction constant, $\rho$ = 1.9 ($r$ = 1.0) (Figure 3).[14] It should be noted that about 60–80 times greater thermolysis rates were observed for chlorine(III) analogue *p*-$CF_3C_6H_4Cl^+-C^-Tf_2$ **10a** (Table 1, entry 9) (Figure S2), while iodine analogue *p*-$CF_3C_6H_4I^+-C^-Tf_2$ did not decompose at all even at 108 °C, probably reflecting differences in leaving-group ability among $\lambda^3$-chloranyl, -bromanyl, and -iodanyl groups.[15,16]

To gain further mechanistic insight, thermal solvolysis of bromonium ylide **9a** in internal olefins with stereochemical information was carried out (Scheme 5). The solvolysis in *cis*-4-octene at 125 °C stereospecifically afforded *cis*-1,1-bis(trifyl)-cyclopropane **11c** as a major product in 43% yield. Careful $^1$H NMR analysis of the crude reaction mixture failed to detect formation of the stereoisomeric *trans*-**11c**. On the other hand, under similar conditions, the stereoisomeric *trans*-**11c** was selectively produced in 43% yield in the thermal reaction in *trans*-**4**-octene. These exclusive stereospecificities with retention of olefin geometry were also observed in the thermolysis of bis(nonafluorobutanesulfonyl)bromonium ylide **9b** in *cis*- and *trans*-4-octene, although the yields of the products **11d** were decreased to around one-third (12–14%) compared to those of **11c**, probably because of the increased steric demand of the active carbene species. Comparable results were obtained from the thermal cyclopropanation of *cis*- and *trans*-5-decene, yielding cyclopropanes *cis*- and *trans*-**11e**, respectively. It should be noted that yields and perfect stereoselectivity of these products were not affected by the presence of radical scavengers: thus, no formation of stereoisomeric *trans*-**11c** was observed in thermolysis of **9a** in *cis*-4-octene under air or in the presence of 9,10-dihydroanthracene (Scheme S1). These stereochemical evidence strongly support the idea that the reactive carbene intermediates have singlet spin multiplicity during the thermal decomposition of **9** in simple olefins, and the cyclopropanation reaction is sufficiently faster than intersystem crossing to the carbene triplet state.[2b,17]

Remarkably, stereoselective *trans*-1,2-*S*,*O*-addition reactions of perfluoroalkylthio $R_fS$ and perfluoroalkylsulfinyloxy $R_fS(O)O$ groups to a double bond were also observed, along with the stereospecific cyclopropanations: bromonium ylide **9a** stereoselectively afforded *syn*-$\beta$-thiosulfinate ester **12c** in 13% yield in the reaction with *cis*-4-octene, whereas *anti*-**12c** was obtained in 12% yield when the *trans* olefin was employed. Unimolecular decomposition of bis(trifyl)carbene **1c** to *S*-trifluoromethyl thiosulfonate $CF_3SO_2SCF_3$ **4**, as shown in Scheme 2, followed by electrophilic *anti*-addition to the double bond of the olefins can reasonably explain the stereoselective formation of these thiosulfinates **12**.[18,19] Competition between cyclopropanation and 1,2-*S*,*O*-addition was also observed in the reaction with cyclic olefins such as cycloheptene, cyclooctene, cyclooctadiene (Scheme 6), while cyclohexene afforded only a low yield of *anti*-1,2-*S*,*O*-addition product (14%, not shown) with no formation of the corresponding cyclopropane, probably because of its unstable nature under the conditions used.[7a,20–22] In fact,


DOI: 10.1021/acs.joc.6b00142
J. Org. Chem. 2016, 81, 3188–3198




| temp (°C) | $10^4 k_{obs}$ ($s^{-1}$) |
|---|---|
| 108 | 6.91 |
| 104 | 4.06 |
| 100 | 2.54 |
| 92 | 0.829 |

$\Delta H^{\ddagger}$ = 35.7 kcal $mol^{-1}$
$\Delta S^{\ddagger}$ = 20.3 cal $mol^{-1}$ $K^{-1}$
r = 0.999

**Figure 2.** Activation parameter for thermal decomposition of **9a** in perfluorodecalin.

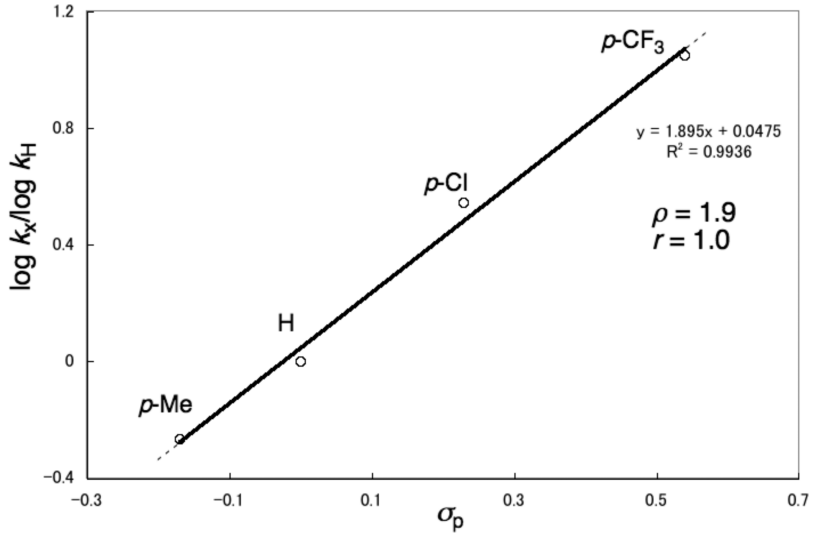
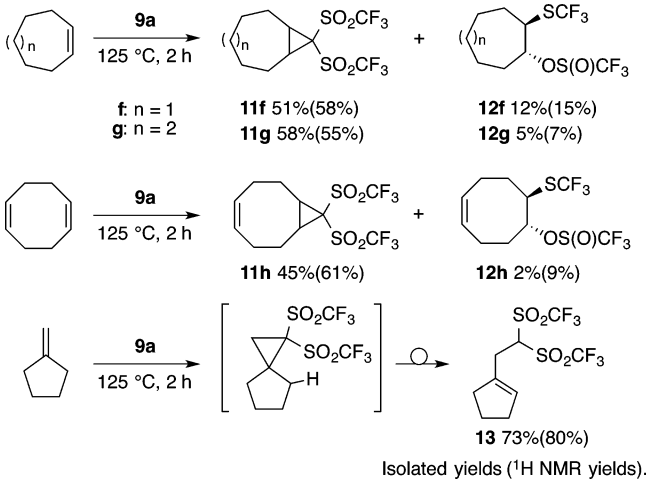



**Figure 3.** Hammett plot of log $k_X$/log $k_H$ vs $\sigma_p$ constants in perfluorodecalin.

**Scheme 6. Thermal Solvolysis of Bromonium Ylides 9a in Cyclic Olefins**

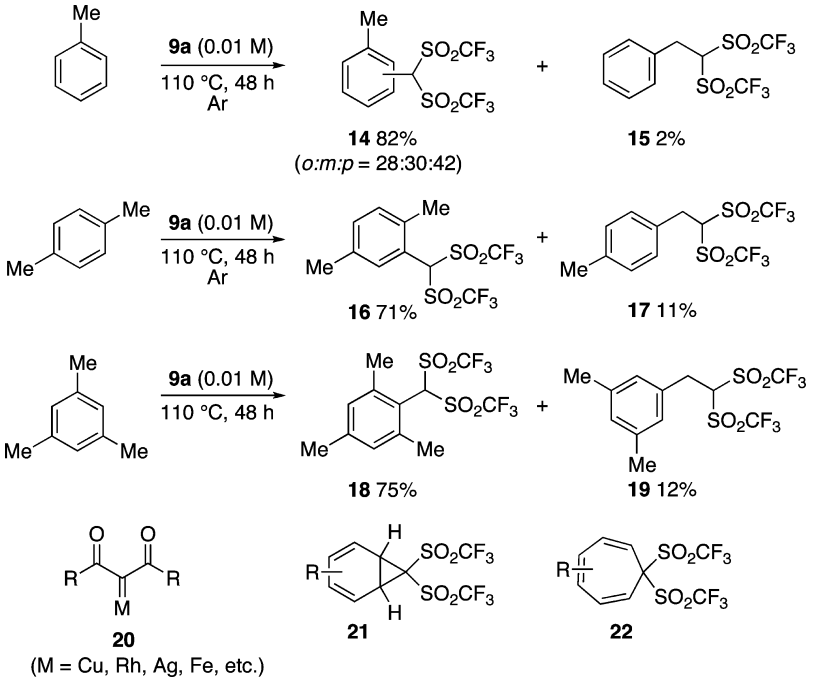



thermolysis of ylide **9a** in methylenecyclopentane selectively produced homoallyl disulfone **13** (73%), probably through ring-opening of the initially formed labile intermediary spirocyclopropane.

Further evidence for singlet nature of bis(triflyl)carbene **1c** was obtained by examination of the thermolysis in simple arenes (Scheme 7). Thermal decomposition of bromonium ylide **9a** in toluene at 110 °C afforded a regioisomeric mixture of Ar $sp^2$ C−H insertion products **14**, accompanied by only a small amount of benzylic $sp^3$ C−H insertion product **15** (2%). Similarly, thermolysis in *p*-xylene and mesitylene having a benzylic C−H bond selectively gave Ar $sp^2$ C−H insertion products **16** and **18**. These isomeric distributions are quite different from those observed for metal-carbenoids **20**, which showed much lower aromatic C−H/benzylic C−H bond selectivities.[23] The unusually high $sp^2$ C−H selectivities are probably due to the greater $\pi$-philicity of singlet carbene **1c**. Thus, electrophilic attack of **1c** on the aromatic $\pi$ system, leading to formation of transient intermediates: norcaradiene


DOI: 10.1021/acs.joc.6b00142
J. Org. Chem. 2016, 81, 3188−3198

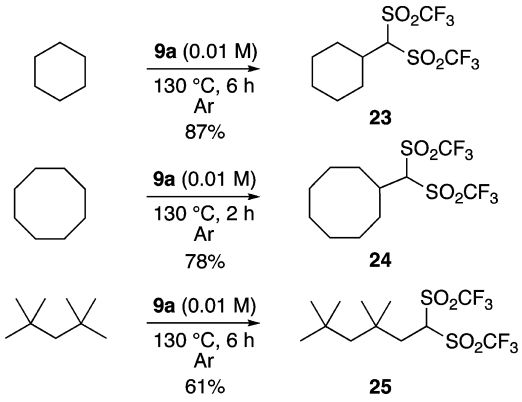
**Scheme 7. Thermal Solvolysis of Bromonium Ylide 9a in Aromatic Hydrocarbons**




**21** and its equilibrium isomer cycloheptatriene **22**, would constitute a major reaction pathway of the Ar C−H insertion process (Scheme 7).[24]

In marked contrast, solvolysis of bromonium ylide **9a** in unactivated hydrocarbons afforded C−H insertion products **23**−**25** in good to high yields, suggesting remarkably high electrophilicity of singlet bis(triflyl)carbene **1c** toward even $\pi$-lacking nucleophiles (Scheme 8). These C−H insertion

**Scheme 8. Thermal Solvolysis of Bromonium Ylide 9a in Unactivated Hydrocarbons**




products: alkyl- and arylbis(triflyl)methane have potential synthetic value, because they can serve as strong Br$\phi$nsted acid catalysts for various organic transformations.[22b] Further studies on the C−H insertions are in progress.

Finally, we performed theoretical calculations on the thermal decomposition of phenylbromonium ylide **9c** at the MP2/6-311G(d) level.[25] These calculations indicate that the generation of intramolecularly stabilized bis(triflyl)carbene **1c** is plausible (Figure 4). The unimolecular decomposition proceeds as one of the sulfonyl oxygen lone pairs approaches the low-lying C−Br $\sigma^*$ orbital (**26** (**TS**)), giving metastable species **27** (**MS**) with an activation energy of 33.8 kcal mol$^{-1}$. Interestingly, metastable species **27** (**MS**) is still stabilized by the bromine atom of PhBr. Finally, **27** (**MS**) ejects PhBr and generates the carbene $^1$**1c** with an energy gain of only 13.2 kcal mol$^{-1}$; the resulting $^1$**1c** would serve as the superelectrophilic carbene active species for cyclopropanation of olefins and sp$^2$-selective C−H insertion of arenes. It should be noted that the triplet state of carbene $^3$**1c** is energetically less favorable than the singlet $^1$**1c** by at least 6.8 kcal mol$^{-1}$, which is consistent with the experimental observation of perfect stereospecificity (see also Table S1−S4, and Figure S3).[26]

In conclusion, thermal decomposition of bromonium ylides in olefins, arenes, and alkanes appears to be an efficient source of highly electron-deficient singlet bis(perfluoroalkanesulfonyl)-carbenes **1**. The first-order kinetics, large positive activation entropy for thermolysis of **9**, substituent effects, and theoretical calculations are all consistent with unimolecular rate-limiting generation of intramolecularly stabilized carbenes **1**.[27] This is probably due to the vastly enhanced nucleofugality of the aryl-$\lambda^3$-bromanyl group compared to that of the aryl-$\lambda^3$-iodanyl group.[12a,16]

## EXPERIMENTAL SECTION

**General Information.** IR spectra were recorded on a FT-IR instrument. $^1$H NMR, $^{13}$C NMR, and $^{19}$F NMR spectra were obtained on either a 300, 400, or 500 MHz spectrometer. Chemical shifts ($\delta$) are reported in parts per million (ppm) downfield from internal $Me_4Si$ or $CFCl_3$. Low mass spectra (MS) were measured on quadrupole-MS with an EI probe. High-resolution MS were measured on TOF-MS with an ESI probe. Preparative thin-layer chromatography (TLC) was carried out on precoated plates of silica gel with fluorescent indicator $F_{254}$. Melting points were determined with melting points apparatus and are uncorrected.

**Substrates.** Bromonium ylides **9a**−**e** and chloronium ylide **10a** were prepared according to a literature method.[12]

**General Procedure for Thermal Reaction of Bromonium Ylides 9a with Olefins. A Typical Example: Generation of Bis(triflyl)carbene 1c (R = $CF_3$) from Bromonium Ylide 9a in (*E*)-4-Octene (Scheme 5).** A suspension of bromonium ylide **9a** (51 mg,



DOI: 10.1021/acs.joc.6b00142
J. Org. Chem. 2016, 81, 3188−3198

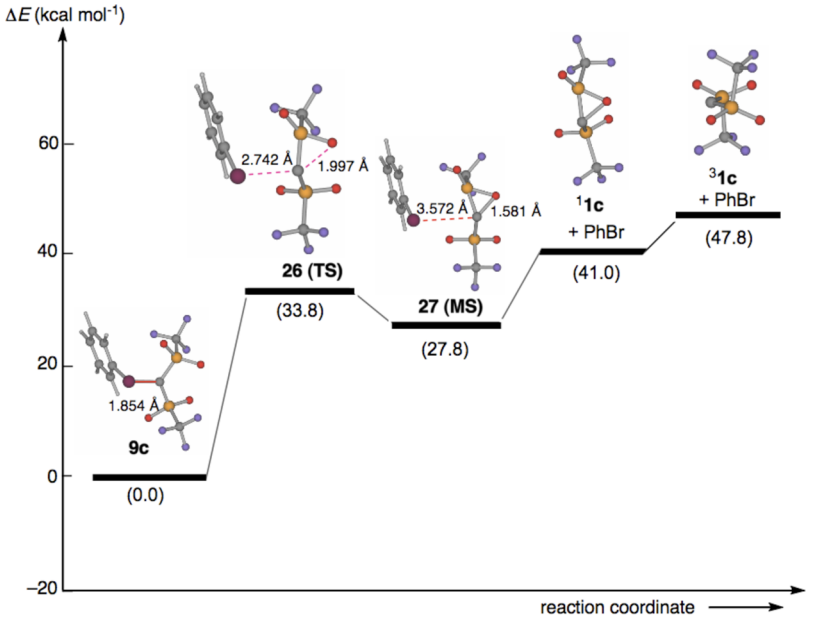



**Figure 4.** Energy profile for unimolecular decomposition of phenylbromonium ylide **9c** based on ab initio calculations optimized at the MP2/6-311G(d) (Br, S, N) and 6-31G(d, p) levels.

0.10 mmol) in (*E*)-4-octene (0.5 mL) was heated rapidly to 135 °C under argon and the resulting clear colorless solution was stirred for 1 h. After cooling, the yields of products were determined by $^1$H NMR (1,1,2,2-tetrachloroethane as an internal standard). The reaction mixture was purified by column chromatography (hexane:dichloromethane = 1:9) to yield cyclopropane *trans*-**11c** (17 mg, 43%) ($R_f$ = 0.5) and *β*-thiosulfinate ester *anti*-**12c** (4.2 mg, 12%) ($R_f$ = 0.4).

*trans-2,3-Dipropyl-1,1-bis(trifluoromethanesulfonyl)-cyclopropane trans-(**11c**).* Purification by preparative TLC (pentane−dichloromethane 9:1); a colorless oil (15 mg); IR (neat) $\nu$ = 2968, 2939, 2881, 1469, 1392, 1205, 1107, 974, 914, 665, 627 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 2.75−2.64 (m, 2H), 1.98−1.85 (m, 2H), 1.82−1.68 (m, 2H), 1.51 (sext, $J$ = 7.3 Hz, 4H), 1.01 (t, $J$ = 7.3 Hz, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ = 119.5 (q, $^1J_{CF}$ = 330.1 Hz), 62.7, 40.3, 28.8, 22.4, 13.7; $^{19}$F NMR (376 MHz, $CDCl_3$) $\delta$ −70.3 (s, 6F); MS (EI) $m/z$ (relative intensity) 347 (12%, [$(M - Pr)^+$]), 335 (7), 123 (11), 81 (100), 67 (52), 56 (82), 55 (61); HRMS (ESI, positive) $m/z$ calcd for $C_{11}H_{16}F_6NaO_4S_2$ [$(M + Na)^+$] 413.0292, found 413.0303.

*(1R*,2S*)-1-Propyl-2-(trifluoromethylthio)pentyl Trifluoromethanesulfinate anti-(**12c**) (A 1:1 Mixture of Diastereoisomers).* Purification by preparative TLC (pentane−dichloromethane 9:1); a colorless oil (5 mg); IR (neat) $\nu$ = 2966, 2939, 2879, 1468, 1385, 1201, 1120, 962, 864, 789, 756, 580 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 4.67−4.59 (m, 1H for both isomers), 3.30 (dt, $J$ = 10.3, 3.0 Hz, 1H for both isomers), 1.94−1.22 (m, 8H for both isomers), 0.97 (t, $J$ = 7.2 Hz, 6H), 0.96 (t, $J$ = 7.2 Hz, 3H), and 0.96 (t, $J$ = 7.2 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ = 130.7 (q, $^1J_{CF}$ = 307.0 Hz for both isomers), 122.7 (q, $^1J_{CF}$ = 335.7 Hz for both isomers), 87.2 and 87.0, 49.6, and 49.5 (q, $^3J_{CF}$ = 1.3 Hz each), 35.0 and 34.7, 31.2 and 30.1, 20.0 (for both isomers), 18.8 and 18.6, 13.6 and 13.4; $^{19}$F NMR (376 MHz, $CDCl_3$) $\delta$ = −40.27 and −40.32 (s, 3F each), −79.46 and −80.22 (s, 3F each); MS (EI) $m/z$ (relative intensity) 213 (18%, [$(M - CF_3SO_2)^+$]), 157 (10), 115 (16), 111 (14), 69 (100), 55 (84); HRMS (ESI, positive) $m/z$ calcd for $C_{10}H_{16}F_6NaO_2S_2$ [$(M + Na)^+$] 369.0394, found 369.0389. Elemental analysis (%), calculated for $C_{10}H_{16}F_6O_2S_2 \cdot 1/2H_2O$: C 33.80, H 4.82. Found: C 33.74, H 4.46. The structure of *anti*-**12c** was determined by the comparison of spectral data with those of an authentic sample, prepared from *trans*-4-octene according to the reported procedure (Scheme S2).[21]

*2-Hexyl-1,1-bis(trifluoromethanesulfonyl)cyclopropane (**11a**).* Purification by preparative TLC (pentane−dichloromethane 9:1); a colorless oil (19 mg); IR (neat) $\nu$ = 2960, 2933, 2862, 1468, 1439, 1392, 1211, 1111, 931, 852, 800, 752, 661, 611 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 2.70 (dq, $J$ = 5.8, 10.1 Hz, 1H), 2.41 (dd, $J$ = 10.1, 6.6 Hz, 1H), 2.29 (dd, $J$ = 10.1, 6.6 Hz, 1H), 2.05−1.95 (m, 1H), 1.89−1.78 (m, 1H), 1.58−1.22 (m, 8H), 0.90 (t, $J$ = 6.5 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ = 119.7 (q, $^1J_{CF}$ = 327.6 Hz), 119.4 (q, $^1J_{CF}$ = 327.6 Hz), 56.6, 34.6, 31.4, 29.0, 28.7, 26.3, 22.50, 22.46, 13.9; $^{19}$F NMR (376 MHz, $CDCl_3$) $\delta$ = −70.4 (s, 3F), −71.0 (s, 3F); MS (EI) $m/z$ (relative intensity) 293 (5%), 123 (25), 96 (23), 93 (23), 83 (48), 81 (79), 70 (90), 69 (100), 56 (96), 55 (96); HRMS (ESI, positive) $m/z$ calcd for $C_{12}H_{20}F_6NaO_5S_2$ [$(M + MeOH + Na)^+$] 445.0575, found 445.0554.

*2-(Trifluoromethylthio)octyl Trifluoromethanesulfinate (**12a**) (A 1:1 Mixture of Diastereoisomers).* Purification by preparative TLC (pentane−dichloromethane 9:1); a colorless oil (12 mg); IR (neat) $\nu$ = 2960, 2933, 2862, 1462, 1381, 1207, 1161, 1128, 951, 924, 777, 758, 607 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 4.57 (dd, $J$ = 10.3, 4.9 Hz, 1H) and 4.43 (dd, $J$ = 10.3, 7.0 Hz, 1H), 4.32 (dd, $J$ = 10.3, 4.2 Hz, 1H) and 4.16 (dd, $J$ = 10.3, 7.0 Hz, 1H), 3.44−3.33 (m, 1H for both isomers), 1.90−1.78 (m, 1H for both isomers), 1.66−1.48 (m, 2H for both isomers), 1.47−1.23 (m, 7H for both isomers), 0.89 (t, $J$ = 6.8 Hz, 3H for both isomers); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ = 130.5 (q, $^1J_{CF}$ = 304.7 Hz for both isomers), 122.8 (q, $^1J_{CF}$ = 336.3 Hz for both isomers), 69.2 and 69.0, 44.7 and 44.5, 31.4 (both isomers), 30.9 and 30.8, 28.6 (both isomers), 26.1 (both isomers), 22.5 (both isomers), 13.9 (both isomers); $^{19}$F NMR (376 MHz, $CDCl_3$) $\delta$ = −40.0 and −40.1 (s, 3F each), −78.56 and −78.58 (s, 3F each); MS (EI) $m/z$ (relative intensity) 213 (16%, [$(M - CF_3SO_2)^+$]), 129 (5), 115 (7), 111 (6), 69 (100), 57 (16), 55 (52); HRMS (ESI, positive) $m/z$ calcd for $C_{10}H_{16}F_6NaO_2S_2$ [$(M + Na)^+$] 369.0394, found 369.0414. Elemental analysis (%), calculated for $C_{10}H_{16}F_6O_2S_2 \cdot 1/2H_2O$: C 33.80, H 4.82. Found: C 33.65, H 4.44. The structure of **12a** was determined by the comparison of spectral data with those of an authentic sample, prepared from 1-octene according to the reported procedure (Scheme S2).[21]

*2-Octyl-1,1-bis(trifluoromethanesulfonyl)cyclopropane (**11b**).* Purification by preparative TLC (pentane−dichloromethane 9:1); a pale yellow oil (14 mg); IR (neat) $\nu$ = 2929, 2860, 1468, 1439, 1392, 1209, 1113, 856, 798, 752, 661, 611 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 2.70 (dq, $J$ = 5.6, 10.0 Hz, 1H), 2.41 (dd, $J$ = 10.0, 6.5 Hz, 1H), 2.29 (dd, $J$ = 10.0, 6.5 Hz, 1H), 2.05−1.94 (m, 1H), 1.89−1.77 (m, 1H), 1.58−1.22 (m, 12H), 0.89 (t, $J$ = 6.8 Hz, 3H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ = 119.7 (q, $^1J_{CF}$ = 327.6 Hz), 119.4 (q, $^1J_{CF}$ =



DOI: 10.1021/acs.joc.6b00142
J. Org. Chem. 2016, 81, 3188−3198

327.7 Hz), 56.6 (sept, $^3J_{CF}$ = 2.8 Hz), 34.6, 31.7, 29.2, 29.1, 29.03, 29.0, 26.3, 22.6, 22.5, 14.0; $^{19}$F NMR (376 MHz, $CDCl_3$) $\delta$ = −70.4 (s, 3F), −71.0 (s, 3F); MS (EI) *m*/*z* (relative intensity) 418 (<1%, [$M^+$]), 293 (5), 124 (12), 109 (17), 97 (26), 95 (30), 83 (33), 70 (81), 69 (88), 56 (100), 55 (74); HRMS (ESI, positive) *m*/*z* calcd for $C_{13}H_{20}F_6NaO_4S_2$ [(M + Na)$^+$] 441.0605, found 441.0610. Elemental analysis (%), calculated for $C_{13}H_{20}F_6O_4S_2$: C 37.32, H 4.82. Found: C 37.62, H 4.75.

*2-(Trifluoromethylthio)decyl Trifluoromethanesulfinate (**12b**) (A 1:1 Mixture of Diastereoisomers).* Purification by preparative TLC (pentane−dichloromethane 9:1); a colorless oil (18 mg); IR (neat) $\nu$ = 2929, 2858, 1466, 1379, 1209, 1161, 1128, 953, 922, 777, 758, 688, 607 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 4.57 (dd, *J* = 10.4, 4.7 Hz, 1H) and 4.43 (dd, *J* = 10.4, 7.1 Hz, 1H), 4.32 (dd, *J* = 10.4, 4.7 Hz, 1H) and 4.16 (dd, *J* = 10.4, 6.6 Hz, 1H), 3.45−3.30 (m, 1H for both isomers), 1.90−1.78 (m, 1 H for both isomers), 1.66−1.18 (m, 13 H for both isomers), 0.89 (t, *J* = 6.7 Hz, 3H for both isomers); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ = 130.5 (q, $^1J_{CF}$ = 305.1 Hz for both isomers), 122.9 (q, $^1J_{CF}$ = 337.0 Hz for both isomers), 69.2 and 69.0, 44.7 and 44.5, 31.8 (both isomers), 30.9 and 30.8, 29.2 (both isomers), 29.1 (both isomers), 29.0 (both isomers), 26.2 (both isomers), 22.6 (both isomers), 14.0 (both isomers); $^{19}$F NMR (376 MHz, $CDCl_3$) $\delta$ = −40.02 and −40.05 (s, 3F each), −78.55 and −78.57 (s, 3F each); MS (EI) *m*/*z* (relative intensity) 241 (44%, [($M$ − $CF_3SO_2$)$^+$]), 115 (12), 97 (39), 83 (77), 69 (79), 55 (100). Elemental analysis (%), calculated for $C_{12}H_{20}F_6O_2S_2$: C 38.50, H 5.38. Found: C 38.50, H 5.12.

*cis-2,3-Dipropyl-1,1-bis(trifluoromethanesulfonyl)cyclopropane cis-(**11c**).* Purification by preparative TLC (hexane−dichloromethane 9:1); a colorless oil (22 mg); IR (neat) $\nu$ = 3057, 2966, 2933, 2877, 1469, 1390, 1266, 1209, 1111, 741 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 2.78−2.69 (m, 2H), 2.00−1.84 (m, 4H), 1.63−1.44 (m, 4H), 1.02 (t, *J* = 7.3 Hz, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ = 119.8 (q, $^1J_{CF}$ = 330.1 Hz), 119.4 (q, $^1J_{CF}$ = 330.3 Hz), 59.7, 37.6, 24.5, 22.3, 13.9; $^{19}$F NMR (376 MHz, $CDCl_3$) $\delta$ = −69.56 (s, 3F), −70.71 (s, 3F); MS (EI) *m*/*z* (relative intensity) 390 (<1%, [$M^+$]), 347 (8), 335 (6), 123 (9), 81 (100), 67 (50), 56 (31), 55 (36); HRMS (ESI, positive) *m*/*z* calcd for $C_{11}H_{16}F_6NaO_4S_2$ [(M + Na)$^+$] 413.0292, found 413.0307.

*(1R*,2R*)-1-Propyl-2-(trifluoromethylthio)pentyl Trifluoromethanesulfinate syn-(**12c**).* Purification by preparative TLC (hexane−dichloromethane 9:1); a colorless oil (15 mg); IR (neat) $\nu$ = 2968, 2879, 1468, 1385, 1205, 1124, 920, 858, 791, 756, 698, 584 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 4.68−4.59 (m, 1H for both isomers), 3.32 (ddd, *J* = 9.7, 4.6, 3.2 Hz, 1H) and 3.25 (ddd, *J* = 9.7, 4.6, 3.2 Hz, 1H), 1.94−1.30 (m, 8H for both isomers), 0.98 (t, *J* = 7.5 Hz, 6H) and 0.96 (t, *J* = 7.5 Hz, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ = 130.70 and 130.66 (q, $^1J_{CF}$ = 306.4 Hz each), 122.6 (q, $^1J_{CF}$ = 335.5 Hz for both isomers), 85.5 and 85.2, 48.7 (for both isomers), 33.0 and 32.9, 32.5 and 32.3, 20.1 and 20.0, 18.8 (for both isomers), 13.5 and 13.3; $^{19}$F NMR (376 MHz, $CDCl_3$) $\delta$ = −40.40 and −40.44 (s, 3F each), −80.07 and −80.09 (s, 3F each); MS (EI) *m*/*z* (relative intensity) 213 (16%, [($M$ − $CF_3SO_2$)$^+$]), 157 (9), 115 (17), 111 (14), 71 (15), 69 (100), 55(98); HRMS (ESI, positive) *m*/*z* calcd for $C_{10}H_{16}F_6NaO_2S_2$ [(M + Na)$^+$] 369.0394, found 369.0386. Elemental analysis (%), calculated for $C_{10}H_{16}F_6O_2S_2{\cdot}1/2H_2O$: C 33.80, H 4.82. Found: C 33.32, H 4.44; 4.46. The structure of *syn*-**12c** was determined by the comparison of spectral data with those of an authentic sample, prepared from *cis*-4-octene according to the reported procedure (Scheme S2).[21]

*cis-2,3-Dipropyl-1,1-bis(nonafluorobutanesulfonyl)cyclopropane cis-(**11d**).* Purification by preparative TLC (hexane−dichloromethane 9:1); a colorless oil (7 mg); IR (neat) $\nu$ = 2970, 2943, 2881, 1469, 1394, 1350, 1238, 1144, 1117, 1020, 1005, 943, 868, 779, 731, 698, 621 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 2.83−2.67 (m, 2H), 2.0−1.88 (m, 4H), 1.65−1.46 (m, 4H), 1.02 (t, *J* = 7.5 Hz, 6H); $^{13}$C NMR (125 MHz, $CDCl_3$)[28] $\delta$ = 62.5, 24.6, 22.3, 13.8; $^{19}$F NMR (376 MHz, $CDCl_3$) $\delta$ = −81.17 (t, *J* = 9.7 Hz, 3F), −81.18 (t, *J* = 9.7 Hz, 3F), −102.1 (t, *J* = 13.9 Hz, 2F), −103.4 (br s, 2F), −121.7 (s, 2F), −121.8 (s, 2F), −125.9 (s, 4F); MS (EI) *m*/*z* (relative intensity) 241 (15%), 171 (6), 139 (6), 115 (5), 97 (26), 83 (65), 69 (100), 55 (58); HRMS (ESI, positive) *m*/*z* calcd for $C_{17}H_{16}F_{18}NaO_4S_2$ [(M + Na)$^+$] 713.0100, found 713.0101.

*(1R*,2R*)-1-Propyl-2-(nonafluorobutylthio)pentyl Nonafluorobutanesulfinate syn-(**12d**) (A 1:1 Mixture of Diastereoisomers).* Purification by preparative TLC (hexane−dichloromethane 9:1); a colorless oil (9 mg); IR (neat) $\nu$ = 2968, 2933, 2881, 1468, 1350, 1240, 1138, 1097, 1001, 920, 862, 796, 746, 731, 692 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 4.63−4.55 (m, 1H for both isomers), 3.49 (ddd, *J* = 9.3, 5.1, 2.5 Hz, 1H) and 3.40 (ddd, *J* = 10.2, 4.3, 3.0 Hz), 1.99−1.29 (m, 8H for both isomers), 0.98 (t, *J* = 7.3 Hz, 6H) and 0.95 (t, *J* = 7.3 Hz, 6H); $^{13}$C NMR (125 MHz, $CDCl_3$)[28] $\delta$ = 86.1 and 85.4, 47.5 and 47.4, 33.0 and 32.7, 32.6 and 31.9, 20.7 (for both isomers), 18.8 and 18.7, 13.51 and 13.47, 13.33 and 13.27; $^{19}$F NMR (376 MHz, $CDCl_3$) $\delta$ = −81.3 (t, *J* = 9.3 Hz, 3F for both isomers), −81.5 (t, *J* = 9.3 Hz, 3F for both isomers), −84.6 and −86.0 (AB type, *J* = 234.9 Hz, each 1F. Both signals appear as triplet, *J* = 12.7 Hz), −85.0 and −86.4 (AB type, *J* = 234.9 Hz, each 1F. Both signals appear as triplet, *J* = 12.7 Hz), −119.8 and −120.9 (AB type, *J* = 250.1 Hz, each 1F. Both signals appear as triplet, *J* = 12.4 Hz), −120.3 (t, *J* = 12.4 Hz, 1F) and −120.4 (t, *J* = 12.4 Hz, 1F), −120.9 (m, 2F for both isomers), −122.4 (m, 2F for both isomers), −125.9 (m, 2F for both isomers), −126.6 (m, 2F for both isomers); MS (EI) *m*/*z* (relative intensity) 363 (10%, [($M$ − $C_4F_9SO_2$)$^+$]), 307 (8), 265 (7), 111 (17), 69 (100), 55 (63); HRMS (ESI, positive) *m*/*z* calcd for $C_{16}H_{16}F_{18}NaO_2S_2$ [(M + Na)$^+$] 669.0202, found 669.0211. Elemental analysis (%), calculated for $C_{16}H_{16}F_{18}O_2S_2$: C 29.73, H 2.49. Found: C 29.86, H 2.75.

*trans-2,3-Dipropyl-1,1-bis(nonafluorobutanesulfonyl)-cyclopropane trans-(**11d**).* Purification by preparative TLC (hexane−dichloromethane 9:1); a colorless oil (8 mg); IR (neat) $\nu$ = 2970, 2883, 1469, 1394, 1352, 1213, 1144, 1117, 1020, 912, 866, 727, 698, 617 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 2.79−2.67 (m, 2H), 2.02−1.66 (m, 4H), 1.51 (sext, *J* = 7.4 Hz, 4H), 1.01 (t, *J* = 7.4 Hz, 6H); $^{13}$C NMR (75 MHz, $CDCl_3$):[28] $\delta$ = 67−63 (br), 29.0, 22.4, 13.7; $^{19}$F NMR (376 MHz, $CDCl_3$) $\delta$ = −81.2 (t, *J* = 9.5 Hz, 6F), −102.6 (br m, 2F), −104.3 (d, *J* = 249.2 Hz, 2F), −121.6 (m, 4F), −125.9 (m, 4F); MS (EI) *m*/*z* (relative intensity) 395 (19%), 123 (19), 87 (100), 81 (97), 69 (43), 67 (44), 55 (52); HRMS (ESI, negative) *m*/*z* calcd for $C_{17}H_{15}F_{18}O_4S_2$ [(M − H)$^-$] 689.0124, found 689.0103.

*(1R*,2S*)-1-Propyl-2-(nonafluorobutylthio)pentyl Nonafluorobutanesulfinate anti-(**12d**) (A 1:1 Mixture of Diastereoisomers).* Purification by preparative TLC (hexane−dichloromethane 9:1); a colorless oil (7 mg); IR (neat) $\nu$ = 2968, 2881, 1468, 1352, 1236, 1138, 1001, 962, 864, 796, 746, 731, 692 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 4.68−4.61 (m, 1H for both isomers), 3.48 (dt, *J* = 7.9, 2.8 Hz, 1H) and 3.45 (dt, *J* = 7.9, 2.6 Hz, 1H), 1.94−1.29 (m, 8H for both isomers), 1.01−0.94 (6H for both isomers); $^{13}$C NMR (75 MHz, $CDCl_3$):[28] $\delta$ = 87.9 and 87.7, 48.2 (for both isomers), 35.4 and 34.9, 31.4 and 30.1, 20.1 and 20.0, 18.8 and 18.6, 13.61 and 13.58, 13.44 and 13.40; $^{19}$F NMR (376 MHz, $CDCl_3$) $\delta$ = −81.3 (t, *J* = 8.6 Hz, 3F for both isomers), −81.5 (t, *J* = 8.6 Hz, 3F for both isomers), −85.3 and −86.2 (AB type, *J* = 235.9 Hz, each 1F. Both signals appear as triplet, *J* = 11.5 Hz), −85.6 and −86.2 (AB type, *J* = 235.9 Hz, each 1F. Both signals appear as triplet, *J* = 11.5 Hz), −118.2 and −121.2 (AB type, *J* = 248.6 Hz, each 1F. Both signals appear as triplet, *J* = 13.2 Hz), −119.3 and −121.4 (AB type, *J* = 248.6 Hz, each 1F. Both signals appear as triplet, *J* = 13.2 Hz), −120.9 (m, 1F for both isomers), −121.1 (m, 1F for both isomers), −122.4 (m, 2F for both isomers), −125.9 (m, 2F for both isomers), −126.6 (m, 2F for both isomers); MS (EI) *m*/*z* (relative intensity) 363 (12%, [($M$ − $C_4F_9SO_2$)$^+$]), 307 (4), 265 (6), 111 (19), 69 (100), 55 (67); HRMS (ESI, positive) *m*/*z* calcd for $C_{16}H_{16}F_{18}NaO_2S_2$ [(M + Na)$^+$] 669.0202, found 669.0182. Elemental analysis (%), calculated for $C_{16}H_{16}F_{18}O_2S_2$: C 29.73, H 2.49. Found: C 29.97, H 2.78.

*cis-2,3-Dibutyl-1,1-bis(trifluoromethanesulfonyl)cyclopropane cis-(**11e**).* Purification by preparative TLC (hexane−dichloromethane 9:1); a colorless oil (11 mg); IR (neat) $\nu$ = 2964, 2935, 2877, 1469, 1392, 1203, 1109, 955, 856, 660, 636, 617 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 2.77−2.67 (m, 2H), 2.01−1.86 (m, 4H), 1.61−1.30 (m, 8H), 0.95 (t, *J* = 7.4 Hz, 6H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ = 119.6 (q, $^1J_{CF}$ = 272.5 Hz), 59.7, 37.8, 31.0, 22.4, 22.1, 13.8; $^{19}$F NMR (376



DOI: 10.1021/acs.joc.6b00142
J. Org. Chem. 2016, 81, 3188−3198

MHz, $CDCl_3$) $\delta$ = −69.5 (s, 3F), −70.7 (s, 3F); MS (EI) $m/z$ (relative intensity) 241 (15%), 171 (6), 139 (6), 115 (5), 97 (26), 83 (65), 69 (100), 55 (58); HRMS (ESI, positive) $m/z$ calcd for $C_{13}H_{20}F_6NaO_4S_2$ $[(M + Na)^+]$ 441.0605, found 441.0606.

*(1R*,2R*)-1-Butyl-2-(trifluoromethylthio)hexyl Trifluoromethanesulfinate syn-(**12e**) (A 1:1 Mixture of Diastereoisomers).* Purification by preparative TLC (hexane−dichloromethane 9:1); a colorless oil (8 mg); IR (neat) $\nu$ = 2962, 2937, 2875, 1468, 1383, 1350, 1205, 1159, 1120, 943, 922, 868, 827, 758, 698 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ = 4.60−4.54 (m, 1H for both isomers), 3.30 (ddd, $J$ = 9.5, 5.2, 2.6 Hz, 1H) and 3.23 (ddd, $J$ = 9.5, 4.8, 3.3 Hz, 1H), 1.96−1.74 (m, 3H for both isomers), 1.64−1.24 (m, 9H for both isomers), 0.934 (t, $J$ = 7.1 Hz, 6H) and 0.929 (t, $J$ = 7.1 Hz, 6H); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ = 130.6 (q, $^1J_{CF}$ = 304.5 Hz for both isomers), 122.6 (q, $^1J_{CF}$ = 334.0 Hz for both isomers), 85.6 and 85.4, 49.03 and 48.97, 30.7 (for both isomers), 30.20 and 30.07, 28.9 (for both isomers), 27.5 and 27.4, 22.1 (for both isomers), 22.0 and 21.97, 13.7 (for both isomers); $^{19}F$ NMR (376 MHz, $CDCl_3$) $\delta$ = −40.37 (s, 3F) and −40.42 (s, 3F), −80.03 (s, 3F) and −80.05 (s, 3F); MS (EI) $m/z$ (relative intensity) 241 (25%, $[(M - CF_3SO_2)^+]$), 171 (5), 129 (5), 115 (9), 97 (33), 83 (85), 69 (100), 55(78); HRMS (ESI, positive) $m/z$ calcd for $C_{12}H_{20}F_6NaO_2S_2$ $[(M + Na)^+]$ 397.0707, found 397.0701. Elemental analysis (%), calculated for $C_{12}H_{20}F_6O_2S_2$: C 38.49, H 5.38. Found: C 38.19, H, 5.24. The structure of *syn*-**12e** was determined by the comparison of spectral data with those of an authentic sample, prepared from *cis*-5-decene according to the reported procedure (Scheme S2).[21]

*trans-2,3-Dibutyl-1,1-bis(trifluoromethanesulfonyl)cyclopropane trans-(**11e**).* Purification by preparative TLC (hexane−dichloromethane 9:1); a colorless oil (16 mg); IR (neat) $\nu$ = 2962, 2933, 2877, 1468, 1390, 1203, 1109, 941, 785, 748, 665, 627 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ = 2.73−2.64 (m, 2H), 2.01−1.89 (m, 2H), 1.85−1.69 (m, 2H), 1.53−1.33 (m, 8H), 0.94 (t, $J$ = 7.3 Hz, 6H); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ = 119.5 (q, $^1J_{CF}$ = 330.1 Hz), 62.6, 40.6, 31.0, 26.5, 22.3, 13.8; $^{19}F$ NMR (376 MHz, $CDCl_3$) $\delta$ = −70.4 (s, 6F); MS (EI) $m/z$ (relative intensity) 241 (20%), 171 (7), 139 (5), 115 (7), 97 (38), 83 (84), 69 (100), 57 (33), 55 (81); HRMS (ESI, positive) $m/z$ calcd for $C_{13}H_{20}F_6NaO_4S_2$ $[(M + Na)^+]$ 441.0605, found 441.0581. Elemental analysis (%), calculated for $C_{13}H_{20}F_6O_4S_2$: C 37.32, H 4.82. Found: C 37.31, H 4.79.

*(1R*,2S*)-1-Butyl-2-(trifluoromethylthio)hexyl Trifluoromethanesulfinate anti-(**12e**) (A 1:1 Mixture of Diastereoisomers).* Purification by preparative TLC (hexane−dichloromethane 9:1); a colorless oil (12 mg); IR (neat) $\nu$ = 2962, 2935, 2875, 1468, 1383, 1201, 1120, 976, 881, 820, 758, 661 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ = 4.66−4.57 (m, 1H for both isomers), 3.27 (dt, $J$ = 10.2, 3.1 Hz, 1H for both isomers), 1.93−1.22 (m, 12H for both isomers), 0.934 and 0.930 (t, $J$ = 7.3 Hz, 3H each, both isomers); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ = 130.7 (q, $^1J_{CF}$ = 306.3 Hz for both isomers), 122.73 (q, $^1J_{CF}$ = 335.0 Hz) and 122.70 (q, $^1J_{CF}$ = 333.8 Hz), 87.4 and 87.2, 49.8 (for both isomers), 32.7 and 32.4, 28.94 and 28.92, 27.8 and 27.3, 27.5 (for both isomers), 13.8 (for both isomers); $^{19}F$ NMR (376 MHz, $CDCl_3$) $\delta$ = −40.2 and −40.3 (s, 3F each), −79.5 and −80.2 (s, 3F each); MS (EI) $m/z$ (relative intensity) 241 (15%, $[(M - CF_3SO_2)^+]$), 171 (6), 129 (3), 115 (5), 97 (36), 83 (77), 69 (100), 55 (70); HRMS (ESI, positive) $m/z$ calcd for $C_{12}H_{20}F_6NaO_2S_2$ $[(M + Na)^+]$ 397.0707, found 397.0708. The structure of *anti*-**12e** was determined by the comparison of spectral data with those of an authentic sample, prepared from *trans*-5-decene according to the reported procedure (Scheme S2).[21]

*8,8-Bis(trifluoromethanesulfonyl)bicyclo[5.1.0]octane (**11f**).* Purification by preparative TLC (hexane−dichloromethane 9:1); a colorless oil (10 mg); IR (neat) $\nu$ = 2929, 2858, 1471, 1392, 1375, 1201, 1157, 1105, 972, 916, 866, 837, 800, 750, 660, 634 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ = 2.86−2.74 (m, 2H), 2.36−2.11 (m, 4H), 2.07−1.91 (m, 3H), 1.46−1.28 (m, 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ = 119.7 (q, $^1J_{CF}$ = 330.1 Hz), 119.3 (q, $^1J_{CF}$ = 330.1 Hz), 61.4 (sept, $^3J_{CF}$ = 2.6 Hz), 37.3, 31.2, 27.8, 22.7; $^{19}F$ NMR (376 MHz, $CDCl_3$) $\delta$ = −69.4 (s, 3F), −71.3 (s, 3F); MS (EI) $m/z$ (relative intensity) 241 (4%, $[(M - CF_3SO_2)^+]$), 171 (22), 107 (41), 91 (48), 79 (100), 69 (74), 55 (30); HRMS (ESI, positive) $m/z$ calcd for $C_{10}H_{12}F_6NaO_4S_2$ $[(M + Na)^+]$ 396.9979, found 396.9972.

*trans-2-(Trifluoromethylthio)cycloheptyl Trifluoromethanesulfinate (**12f**) (A 1:1 Mixture of Diastereoisomers).* Purification by preparative TLC (hexane−dichloromethane 9:1); a colorless oil (14 mg); IR (neat) $\nu$ = 2939, 2866, 1460, 1201, 1124, 1011, 980, 960, 910, 885, 849, 822, 804, 758 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ = 4.79 (dt, $J$ = 3.1, 5.8 Hz, 1H) and 4.67 (dt, $J$ = 3.1, 6.5 Hz, 1H), 3.65 (ddd, $J$ = 7.8, 5.8, 3.1 Hz, 1H) and 3.48 (ddd, $J$ = 8.6, 6.5, 3.1 Hz, 1H), 2.32−1.42 (m, 10H for both isomers); $^{13}C$ NMR (100 MHz, $CDCl_3$) $\delta$ = 130.5 (q, $^1J_{CF}$ = 305.2 Hz for both isomers), 122.6 (q, $^1J_{CF}$ = 334.0 Hz for both isomers), 85.8 and 85.1, 50.7 and 49.7, 33.0 and 31.9, 31.1 and 29.9, 27.8 and 27.4, 25.2 and, 24.4, 21.4 and 20.7; $^{19}F$ NMR (376 MHz, $CDCl_3$) $\delta$ = −40.2 (s, 3F) and −40.3 (s, 3F), −80.0 (s, 3F) and −80.5 (s, 3F); MS (EI) $m/z$ (relative intensity) 197 (12%, $[(M - CF_3SO_2)^+]$), 95 (100), 67 (33), 55 (18); HRMS (ESI, positive) $m/z$ calcd for $C_9H_{12}F_6NaO_2S_2$ $[(M + Na)^+]$ 353.0081, found 353.0081. Elemental analysis (%), calculated for $C_9H_{12}F6O_2S_2$: C 32.73, H 3.66. Found: C 32.45, H 3.70. The structure of **12f** was determined by the comparison of spectral data with those of an authentic sample, prepared from cycloheptene according to the reported procedure (Scheme S2).[21]

*9,9-Bis(trifluoromethanesulfonyl)bicyclo[6.1.0]nonane (**11g**).* Purification by preparative TLC (hexane−dichloromethane 9:1); colorless needles (recrystallized from pentane); mp 55−56 °C (6 mg); IR (KBr) $\nu$ = 2922, 2864, 1475, 1446, 1394, 1369, 1209, 1111, 1005, 976, 939, 856, 796, 750, 660, 634, 580 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ = 2.70−2.60 (m, 2H), 2.22−2.05 (m, 4H), 1.90−1.77 (m, 2H), 1.65−1.42 (m, 6H); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ = 119.8 (q, $^1J_{CF}$ = 330.7 Hz), 119.3 (q, $^1J_{CF}$ = 330.1 Hz), 59.5, 37.7, 28.3, 25.6, 20.6; $^{19}F$ NMR (376 MHz, $CDCl_3$) $\delta$ = −68.7 (s, 3F), −70.5 (s, 3F); MS (EI) $m/z$ (relative intensity) 388 (<1%, $[M^+]$), 319 (5), 255 (4, $[(M - CF_3SO_2)^+]$), 185 (12), 121 (57), 93 (68), 79 (100), 67 (46), 55 (77); HRMS (ESI, positive) $m/z$ calcd for $C_{11}H_{14}F_6NaO_4S_2$ $[(M + Na)^+]$ 411.0135, found 411.0135.

*trans-2-(Trifluoromethylthio)cyclooctyl Trifluoromethanesulfinate (**12g**) (A 1:1 Mixture of Diastereoisomers).* Purification by preparative TLC (hexane−dichloromethane 9:1); a colorless oil (9 mg); IR (neat) $\nu$ = 2931, 2864, 1469, 1448, 1201, 1119, 1026, 899, 839, 791, 758 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ = 4.58 (dt, $J$ = 8.8, 4.3 Hz, 1H) and 4.52 (ddd, $J$ = 9.2, 6.5, 2.3 Hz, 1H), 3.60 (ddd, $J$ = 8.8, 7.3, 2.1 Hz, 1H) and 3.52 (ddd, $J$ = 9.2, 7.2, 2.3 Hz, 1H), 2.36−2.22 (m, 1H for both isomers), 2.20−1.20 (m, 11H for both isomers); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ = 130.6 (q, $^1J_{CF}$ = 307.0 Hz), 122.7 (q, $^1J_{CF}$ = 336.3 Hz) and 117.3 (q, $^1J_{CF}$ = 336.9 Hz), 85.0 (both isomers), 50.3 and 49.6, 32.2 and 30.9, 30.1 and 29.7, 25.6 (both isomers), 25.4, 25.2 (both isomers), 25.1, 24.4 and 23.5; $^{19}F$ NMR (376 MHz, $CDCl_3$) $\delta$ = −40.1 (s, 3F) and −40.3 (s, 3F), −79.8 (s, 3F) and −80.5 (s, 3F); MS (EI) $m/z$ (relative intensity) 279 (12%, $[M - SO_2H]^+$), 167 (35), 149 (100), 112 (11), 83 (14), 71 (23), 70 (30), 57 (32), 55 (29); HRMS (ESI, positive) $m/z$ calcd for $C_{10}H_{14}F_6NaO_2S_2$ $[(M + Na)^+]$ 367.0237, found 367.0233. The structure of **12g** was determined by the comparison of spectral data with those of an authentic sample, prepared from cyclooctene according to the reported procedure (Scheme S2).[21]

*9,9-Bis(trifluoromethanesulfonyl)bicyclo[6.1.0]non-4-ene (**11h**):*[12] Purification by preparative TLC (hexane−dichloromethane 9:1); a colorless solid (12 mg); IR (KBr) $\nu$ = 3018, 2966, 2933, 2902, 1657, 1493, 1450, 1392, 1365, 1201, 1136, 1115, 960, 877, 860, 710, 650, 613 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ = 5.71−5.61 (m, 2H), 2.82−2.54 (m, 6 H), 2.28−2.11 (m, 4H); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ = 128.9, 119.4 (q, $^1J_{CF}$ = 330.3 Hz), 119.3 (q, $^1J_{CF}$ = 330.9 Hz), 59.2, 36.5, 26.3, 26.0; MS (EI) $m/z$ (relative intensity) 386 (8%, $[M^+]$), 183 (6), 119 (45), 91 (100), 81 (84), 67 (82), 54 (31).

*trans-8-(Trifluoromethylthio)cyclooct-4-enyl Trifluoromethanesulfinate (**12h**) (A 1:1 Mixture of Diastereoisomers).* Purification by preparative TLC (hexane−dichloromethane 9:1); a colorless oil (8 mg); IR (neat) $\nu$ = 3026, 2943, 1655, 1487, 1471, 1435, 1203, 1119, 1016, 987, 937, 887, 804, 756, 735, 696, 663 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ = 5.81−5.65 (m, 2 H for both isomers), 4.90 (ddd, $J$



DOI: 10.1021/acs.joc.6b00142
J. Org. Chem. 2016, 81, 3188−3198

= 8.4, 5.6, 2.7 Hz, 1H) and 4.84−4.73 (m, 1H), 3.80 (dt, $J$ = 8.4, 5.6 Hz, 1H) and 3.70 (dt, $J$ = 4.3, 8.0 Hz, 1H), 2.63−2.01 (m, 8 H for both isomers); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ = 130.5 (q, $^1J_{CF}$ = 305.7 Hz for both isomers), 131.2 and 130.9, 130.1 and 128.9, 122.8 (q, $^1J_{CF}$ = 335.6 Hz for both isomers), 82.8 and 82.6, 47.0 and 45.7, 34.2, 33.1, 33.0, 32.9, 23.9 and 23.5, 22.0 and 21.0; $^{19}$F NMR (376 MHz, $CDCl_3$) $\delta$ = −41.7 (s, 3F) and −42.4 (s, 3F), −79.5 (s, 3F) and −80.2 (s, 3F); MS (EI) $m/z$ (relative intensity) 273 (57%, [$(M - CF_3)^+$]), 209 (10), 139 (29), 107 (67), 91 (34), 79 (100), 67 (47), 53 (26). Elemental analysis (%), calculated for $C_{10}H_{12}F_6O_2S_2 \cdot 1/2H_2O$: C 34.19, H 3.73. Found: C 34.30, H 3.58. The structure of **12h** was determined by the comparison of spectral data with those of an authentic sample, prepared from cyclooctadiene according to the reported procedure (Scheme S2).[21]

*1-[2,2-Bis(trifluoromethanesulfonyl)ethyl]cyclopent-1-ene (**13**).* Purification by acid base extraction with 1 N NaOH aq. and 1 N HCl; a pale yellow oil (11 mg); IR (neat) $\nu$ = 3064, 2941, 2854, 1433, 1394, 1211, 1113, 779, 698 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 5.71 (s, 1H), 4.95 (t, $J$ = 5.7 Hz, 1H), 3.28 (d, $J$ = 5.7 Hz, 2H), 2.42−2.35 (m, 2H), 2.35−2.28 (m, 2H), 1.96 (quint, $J$ = 7.2 Hz, 2H); $^{13}$C NMR (100 MHz, $CDCl_3$) $\delta$ = 134.7, 131.4, 119.3 (q, $^1J_{CF}$ = 330.1 Hz), 76.4, 34.3, 32.6, 26.4, 23.2; $^{19}$F NMR (376 MHz, $CDCl_3$) $\delta$ = −73.3 (s, 6F); MS (EI) $m/z$ (relative intensity) 360 (7%, [$M^+$]), 226 (23), 157 (90), 93 (75), 91 (100), 79 (49), 77 (84), 67 (39), 53 (16); HRMS (ESI, negative) $m/z$ calcd for $C_9H_9F_6O_4S_2$ [$(M - H)^-$] 358.9846, found 358.9855. Elemental analysis (%), calculated for $C_9H_{10}F_6O_4S_2$: C 30.00, H 2.80. Found: C 29.96, H, 2.84.

**General Procedure for Billard *anti*-1,2-*S*,*O*-Addition to Olefins. A Typical Example: Synthesis of Authentic Sample of *β*-Trifluoromethylthiosulfinate Ester 12.**[21] To a stirred solution of *N*-(trifluoromethylthio)aniline (292 mg, 1.5 mmol) in dichloromethane (3.0 mL) was added *trans*-4-octene (237 mL, 1.5 mmol) and trifluoroacetic acid (281 mL, 3.8 mmol) under argon and the mixture was stirred at 50 °C for 24 h. After cooling, the solvent was removed under an aspiratory vacuum and then neutralized with excess sodium carbonate in MeOH for 5 min. The mixture was poured into 5% aqueous HCl and extracted with diethyl ether four times. The combined organic phases were dried over magnesium sulfate, filtered, and evaporated an aspiratory vacuum to give an oil, which was purified by column chromatography (dichloromethane−hexane 3:2) ($R_f$ = 0.3) to give alcohol *syn*-**28** (177 mg, 51%) as a pale yellow oil: IR (neat) $\nu$ = 3377, 2962, 2877, 1466, 1383, 1120, 1018, 928, 845, 756 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 3.83−3.73 (m, 1H), 3.08 (ddd, $J$ = 8.7, 5.4, 3.4 Hz, 1H), 1.89−1.30 (m, 8H), 0.96 (t, $J$ = 7.4 Hz, 3H), 0.95 (t, $J$ = 7.4 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ = 131.4 (q, $^1J_{CF}$ = 305.6 Hz), 73.1, 52.5, 36.5, 35.2, 20.2, 19.1, 13.9, 13.7; $^{19}$F NMR (376 MHz, $CDCl_3$) $\delta$ = −39.7 (s, 3F); MS (EI) $m/z$ (relative intensity) 207 (10%), 159 (9), 73 (80), 69 (20), 55 (100); HRMS (ESI, positive) $m/z$ calcd for $C_{10}H_{21}F_3NaO_2S$ [$(M + Na + MeOH)^+$] 285.1112, found 285.1121.

*(1R*,2S*)-1-Propyl-2-(trifluoromethylthio)-1-pentanol anti-(**28**).* Purification by column chromatography (dichloromethane−hexane 3:2); pale yellow oil (155 mg); IR (neat) $\nu$ = 3377, 2962, 2875, 1468, 1383, 1298, 1217, 1124, 1030, 849, 756 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 3.92−3.80 (m, 1H), 3.23 (dt, $J$ = 9.9, 3.4 Hz, 1H), 1,98 (br s, 1H, OH), 1.74−1.30 (m, 8H), 0.953 (t, $J$ = 7.3 Hz, 3H), 0.95 (t, $J$ = 7.3 Hz, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ = 131.2 (q, $^1J_{CF}$ = 305.8 Hz), 73.7, 53.0, 35.7, 31.7, 20.4, 19.4, 13.9, 13.7; $^{19}$F NMR (376 MHz, $CDCl_3$) $\delta$ = −39.8 (s, 3F); MS (EI) $m/z$ (relative intensity) 207 (2%), 159 (4), 73 (58), 69 (8), 55 (100); HRMS (ESI, positive) $m/z$ calcd for $C_{10}H_{21}F_3NaO_2S$ [$(M + Na + MeOH)^+$] 285.1112, found 285.1102.

**Synthesis of *syn*- and *anti*-*β*-Thiosulfinate Esters 12c by Triflination of Alcohols 28. A Typical Example: Synthesis of *syn*-12c.**[22] Sodium trifluoromethanesulfinate $CF_3SO_2Na$ (83 mg, 0.53 mmol) and mesitylenesulfonyl chloride (109 mg, 0.50 mmol) were dissolved in MeCN (0.66 mL) at room temperature. After being stirred for 1 h, the mixture was cooled to 0 °C and a solution of *syn*-**28** (76 mg, 0.33 mmol) and pyridine (39 mg, 0.50 mmol) in MeCN (0.16 mL) was added dropwise. This mixture was allowed to warm to room temperature and stirred for 12 h. The reaction mixture was diluted with $Et_2O$, and then washed with water and a saturated aqueous NaCl solution. The organic phase was dried over $MgSO_4$ and evaporated in vacuo to give an oil, which was purified by column chromatography (hexane/dichloromethane 9:1) ($R_f$ = 0.4) to afford ester *syn*-**12c** (68 mg, 59%) as a 1:3 mixture of diastereoisomers.

The alcohol *anti*-**28** was converted into corresponding tosylate **29** by using tosyl chloride in a typical tosylation conditions (Scheme S2).

*(1R*,2S*)-1-Propyl-2-(trifluoromethylthio)-1-pentyl tosylate anti-(**29**).*[21] A colorless oil; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 7.81 (d, $J$ = 8.2 Hz, 2H), 7.35 (d, $J$ = 8.2 Hz, 2H), 4.06 (dt, $J$ = 8.4, 3.0 Hz, 1H), 3.36−3.29 (m, 1H), 2.45 (s, 3H), 1.85−1.72 (m, 1H), 1.69−1.30 (m, 6H), 1.29−1.12 (m, 1H), 0.91 (t, $J$ = 7.3 Hz, 3H), 0.87 (t, $J$ = 7.3 Hz, 3H); $^{19}$F NMR (376 Hz, $CDCl_3$) $\delta$ = −40.15 (s, 3F). $^1$H/$^{19}$F NMR chemical shifts of compound **29** were in good agreement with Billard's reported data.

In a similar manner, triflination of alcohol *anti*-**28** produced ester *anti*-**12c** (73%) as a 1:1 mixture of diastereoisomers. Authentic samples of **12a**, **12b**, *syn*-**12c**, *trans*-**12f**, *trans*-**12g**, and *trans*-**12h** were also prepared from olefins via Billard *anti*-1,2-*S*,*O*-addition and triflination sequence (Scheme S2).

**General Procedure for Thermal Decomposition of Bromonium Ylide 1a in Aliphatic and Aromatic Hydrocarbons. A Typical Example: Reaction with *p*-Xylene (Scheme 7).** A suspension of bromonium ylide **1a** (41 mg, 0.082 mmol) in *p*-xylene (8.2 mL) was heated in a sealed tube to 110 °C under argon and the resulting clear colorless solution was stirred for 48 h. After cooling, the yields of products were determined by $^1$H NMR (1,1,2,2-tetrachloroethane as an internal standard). The reaction mixture was purified by preparative TLC (ethyl acetate:hexane = 1:1) to yield pale yellow oil contaminated with impurities. The oil was dissolved in dichloromethane and extracted with NaOH aqueous solution (1 M) two times, the resulting aqueous phase was washed with dichloromethane several times. After neutralization with HCl aqueous solution (1 M), the aqueous phase was extracted with dichloromethane four times. The dichloromethane phase was filtered and evaporated under an aspiratory vacuum to give a 87:13 mixture of 2,5-dimethylphenylbis-(trifluoromethanesulfonyl)methane (**16**) and 2-(4-methylphenyl)-1,1-bis(trifluoromethanesulfonyl)ethane (**17**)[29] (25.8 mg, 82%) as a colorless oil. Authentic samples of *o*-**14**, *m*-**14**, *p*-**14**, and **16** were prepared according to the Yamamoto's method[22b] and compounds **17** and **19** were prepared according to the Yanai's method.[22c]

*2,5-Dimethylphenylbis(trifluoromethanesulfonyl)methane (**16**).* Purified by preparative TLC (ethyl acetate:hexane:AcOH = 100:100:1); a colorless oil (14 mg); IR (neat) $\nu$ = 2958, 1698, 1457, 1391, 1210, 1111, 897, 784, 749, 703, 589, 490, 452 cm$^{-1}$; $^1$H NMR (400 MHz, $CD_2Cl_2$) $\delta$ = 7.79 (s, 1H), 7.36 (d, $J$ = 7.7 Hz, 2H), 7.29 (d, $J$ = 7.7 Hz, 2H), 6.35 (s, 1H), 2.40 (s, 3H), 2.35 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ = 137.7, 136.2, 133.9, 131.8, 131.4, 119.4 (q, $^1J_{CF}$ = 330.1 Hz), 76.3, 21.0, 18.6; HRMS (ESI, negative) $m/z$ calcd for $C_{11}H_9F_6O_4S_2$ [$(M - H)^-$] 382.9846, found 382.9830.

*1-[2,2-Bis(trifluoromethanesulfonyl)ethyl]-4-methylbenzene (**17**).* Purified by preparative TLC (ethyl acetate:hexane:AcOH = 100:100:1); a colorless oil (12 mg); IR (neat) $\nu$ = 2929, 1389, 1206, 1106, 687, 635, 586 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 7.4−7.1 (m, 4H), 5.03 (t, $J$ = 6.1 Hz, 1H), 3.76 (d, $J$ = 6.1 Hz, 2 H), 2.35 (s, 3H); $^{13}$C NMR (125 MHz, $CDCl_3$) $\delta$ = 138.5, 130.0, 128.9, 119.3 (q, $^1J_{CF}$ = 327.5 Hz), 80.0, 30.2, 21.1; $^{19}$F NMR (376 MHz, $CDCl_3$) $\delta$ = −72.6 (s, 6F); HRMS (ESI, negative) $m/z$ calcd for $C_{11}H_9F_6O_4S_2$ [$(M - H)^-$] 382.9846, found 382.9823.

*2-Methylphenylbis(trifluoromethanesulfonyl)methane o-(**14**).* Purified by preparative TLC (ethyl acetate:hexane = 1:1); a colorless oil (18 mg); IR (neat) $\nu$ = 2959, 1605, 1493, 1379, 1226, 1189, 1107, 1058, 763, 458 cm$^{-1}$; $^1$H NMR (400 MHz, $CDCl_3$) $\delta$ = 8.02 (d, $J$ = 7.7 Hz, 1H), 7.52 (t, $J$ = 7.7 Hz, 1H), 7.43 (t, $J$ = 7.7 Hz, 1H), 7.37 (d, $J$ = 7.7 Hz, 1H), 6.32 (s, 1H), 2.40 (s, 3H); $^{13}$C NMR (75 MHz, $CDCl_3$) $\delta$ = 139.4, 132.9, 131.9, 131.2, 127.7, 117.6, 119.4 (q, $^1J_{CF}$ = 330.2 Hz), 76.2, 19.1; $^{19}$F NMR (376 MHz, $CDCl_3$) $\delta$ = −73.4 (s, 6F); HRMS (ESI, negative) $m/z$ calcd for $C_{10}H_7F_6O_4S_2$ [$(M - H)^-$] 368.9690, found 368.9671.



DOI: 10.1021/acs.joc.6b00142
J. Org. Chem. 2016, 81, 3188−3198

*3-Methylphenylbis(trifluoromethanesulfonyl)methane m-(**14**).* Purified by preparative TLC (ethyl acetate:hexane = 1:1); a colorless oil (13 mg); IR (neat) $\nu$ = 2948, 1605, 1490, 1386, 1215, 1105, 888, 779, 734, 696, 592, 456 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ = 7.45 (br s, 4H), 5.87 (s, 1H), 2.44 (s, 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ = 140.3, 133.8, 132.1, 129.8, 129.0, 119.7, 119.4 (q, $^1J_{CF}$ = 330.7 Hz), 80.8, 21.4; HRMS (ESI, negative) $m/z$ calcd for $C_{10}H_7F_6O_4S_2$ [$(M - H)^-$] 368.9690, found 382.9676.

*4-Methylphenylbis(trifluoromethanesulfonyl)methane p-(**14**).*[29] Purified by preparative TLC (ethyl acetate:hexane = 1:1); a colorless oil (12 mg); IR (neat) $\nu$ = 2933, 1610, 1512, 1391, 1380, 1218, 1187, 1113, 1093, 838, 644, 510, 454 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ = 7.45 (br s, 2H), 7.36 (d, $J$ = 8.1 Hz, 2H), 5.89 (s, 1H), 2.45 (s, 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ = 143.9, 131.7, 130.8, 119.4 (q, $^1J_{CF}$ = 330.7 Hz), 116.0, 80.7, 21.6; $^{19}F$ NMR (376 MHz, $CDCl_3$) $\delta$ = −72.4 (s, 6F).

*2,4,6-Trimethylphenylbis(trifluoromethanesulfonyl)methane (**18**).*[22b] Purified by preparative TLC (ethyl acetate:hexane = 1:1); a colorless oil (12 mg); IR (neat) $\nu$ = 2929, 1609, 1459, 1381, 1301, 1184, 1113, 855, 787, 668, 623, 581 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ = 7.08 (s, 1H), 7.00 (s, 1H), 6.48 (s, 1H), 2.61 (s, 3H), 2.35 (s, 3H), 2.32 (s, 3H); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ = 142.7, 142.3, 139.7, 132.2, 130.5, 119.5 (q, $^1J_{CF}$ = 330.1 Hz), 77.8, 22.3, 21.1, 20.2.

*1-[2,2-Bis(trifluoromethanesulfonyl)ethyl]-3,5-dimethylbenzene (**19**).* Purified by preparative TLC (ethyl acetate:hexane = 1:1); a colorless oil (13 mg); IR (neat) $\nu$ = 2926, 2856, 1608, 1393, 1336, 1212, 1113, 1038, 850, 768, 689, 581 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ = 6.96 (s, 1H), 6.89 (s, 2H), 5.05 (t, $J$ = 6.2 Hz, 1H), 3.72 (d, $J$ = 6.2 Hz, 2 H), 2.31 (s, 6H); $^{13}C$ NMR (125 MHz, $CDCl_3$) $\delta$ = 139.1, 133.0, 130.2, 126.7, 119.4 (q, $^1J_{CF}$ = 328.8 Hz), 80.2, 30.4, 21.2; HRMS (ESI, negative) $m/z$ calcd for $C_{12}H_{11}F_6O_4S_2$ [$(M - H)^-$] 397.0000, found 397.0008.

*Cyclohexylbis(trifluoromethanesulfonyl)methane (**23**).* Purification by base acid extraction with 1 N NaOH aq. and 1 N HCl; a colorless oil (12 mg); IR (neat) $\nu$ = 2935, 2862, 1454, 1392, 1209, 1113, 1055, 897, 796, 773, 714, 663, 617, 586, 573, 544, 501 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ = 4.77 (br s, 1H), 2.54 (br t, $J$ = 11.8 Hz, 1H), 2.12−1.81 (m, 6H), 1.74 (d, $J$ = 10.1 Hz, 1H), 1.39−1.16 (m, 6H); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ = 119.3 (q, $^1J_{CF}$ = 330.9 Hz), 80.6 (br s), 40.8, 29.5, 26.8, 25.0; HRMS (ESI, negative) $m/z$ calcd for $C_9H_{11}F_6O_4S_2$ [$(M - H)^-$] 361.0003, found 361.0008.

*Cyclooctylbis(trifluoromethanesulfonyl)methane (**24**).* Purification by acid base extraction with 1 N NaOH aq. and 1 N HCl; a colorless oil (11 mg); IR (neat) $\nu$ = 2927, 2860, 1417, 1450, 1392, 1211, 1113, 777, 704, 658, 609 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ = 4.79 (d, $J$ = 1.5 Hz, 1H), 2.86 (br t, $J$ = 9.1 Hz, 1H), 2.16−1.91 (m, 4H), 1.91−1.75 (m,2H), 1.75−1.51 (m, 7H), 1.51−1.36 (m, 1H); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ = 119.2 (q, $^1J_{CF}$ = 330.7 Hz), 82.1 (br s), 39.1, 31.1, 26.6, 25.9, 25.5; HRMS (ESI, negative) $m/z$ calcd for $C_{11}H_{15}F_6O_4S_2$ [$(M - H)^-$] 389.0316, found 389.0316.

*1,1-Bis(trifluoromethanesulfonyl)-3,3,5,5-tetramethylhexane (**25**).* Purification by base acid extraction with 1 N NaOH aq. and 1 N HCl; a colorless oil (8 mg); IR (neat) $\nu$ = 2957, 2904, 1475, 1393, 1210, 1111, 890, 791, 709, 586, 544, 501, 436 $cm^{-1}$; $^1H$ NMR (400 MHz, $CDCl_3$) $\delta$ = 4.79 (t, $J$ = 4.1 Hz, 1H), 2.47 (d, $J$ = 4.1 Hz, 2 H), 1.37 (s, 2H), 1.06 (s, 6H), 1.03 (s, 9H); $^{13}C$ NMR (75 MHz, $CDCl_3$) $\delta$ = 120.5 (q, $^1J_{CF}$ = 329.7 Hz), 78.9, 55.5, 37.7, 36.8, 32.9, 32.3, 27.2; HRMS (ESI, negative) $m/z$ calcd for $C_{12}H_{19}F_6O_4S_2$ [$(M - H)^-$] 405.0634, found 405.0632.

**Kinetic Measurements (Table 1, Figure 1−3, Figure S1 and S2).** Rates for thermal decomposition of bromonium ylide **9** and chloronium ylide **10a** were measured by monitoring the decrease in absorbance at 275 nm at different temperatures in the range of 92−108 °C on UV−vis spectrophotometer (Figure S1). The reaction temperature was controlled by a temperature controller and accurate to within ±0.1 °C. A stock solution of bromonium ylide **9** was prepared by weighting and dissolving in dichloromethane (0.04 M) at room temperature and stored in a refrigerator at −20 °C. To perfluorodecalin (3.0 mL) in a quartz cuvette inserted in a cell compartment of the spectrophotometer and equilibrated at the reaction temperature was added 20−50 mL of the stock solution of bromonium ylide **9** or chloronium ylide **10a** from a microsyringe. The absorbance change was fed to a computer through an interface and processed by a pseudo-first-order kinetics program. The reaction followed pseudo-first-order kinetics for at least 4 half-lives and the pseudo-first-order rate constants $k_{obs}$ were calculated. The values for triplicate runs were averaged.

## ■ ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.joc.6b00142.

UV spectra (Figure S1), Eyring plot (Figure S2), radical trapping experiments (Scheme S1), synthesis of authentic samples (Scheme S2), calculation results (Figure S3 and Table S1−S4). $^1H/^{13}C$ NMR spectra of products. (PDF)

## ■ AUTHOR INFORMATION


### Corresponding Authors

*E-mail: kmiya@mol.f.u-tokyo.ac.jp.
*E-mail: nakanishi@sys.wakayama-u.ac.jp.
*E-mail: uchiyama@mol.f.u-tokyo.ac.jp.


### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This work was supported by a Grant-in-Aid for Scientific Research (B, 23390006) and (C, 25460016) (JSPS). We thank Central Glass Co., Ltd. (Japan) for a generous gift of $BrF_3$.

## ■ REFERENCES


(1) Buchner, E.; Feldmann, L. *Ber. Dtsch. Chem. Ges.* **1903**, *36*, 3509.

(2) Reviews: (a) Hine, J. *Divalent Carbon*; Ronald Press: New York, 1964. (b) Kirmse, W. *Carbene Chemistry*; Academic Press: New York, 1971. (c) Platz, M. S.; Moss, R. A.; Jones, M. *Reviews of Reactive Intermediate Chemistry*; Wiley: Hoboken, NJ, 2007. (d) Moss, R. A. *Acc. Chem. Res.* **1989**, *22*, 15.

(3) For seminal work on the reactions of electrophilic carbenes, see: (a) Webster, O. W. *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 210. (b) Sheppard, W. A.; Webster, O. W. *J. Am. Chem. Soc.* **1973**, *95*, 2675. (c) Janulism, E. P., Jr.; Arduengo, A. J., III *J. Am. Chem. Soc.* **1983**, *105*, 3563. (d) Frey, H. M.; Stevens, D. R. *J. Chem. Soc.* **1965**, 3101.

(4) (a) Hadjiarapoglou, L.; Spyroudis, S.; Varvoglis, A. *J. Am. Chem. Soc.* **1985**, *107*, 7178. (b) Zhu, S.-Z.; Chen, Q.-Y. *J. Chem. Soc., Chem. Commun.* **1990**, 1459. (c) Diekmann, J. *J. Org. Chem.* **1965**, *30*, 2272. (d) Ortica, F.; Pohlers, G.; Coenjarts, C.; Bejan, E. V.; Cameron, J. F.; Zampini, A.; Haigh, M.; Scaiano, J. C. *Org. Lett.* **2000**, *2*, 3591. (e) Ochiai, M.; Okada, T.; Tada, N.; Yoshimura, A. *Org. Lett.* **2008**, *10*, 1425.

(5) (a) Hatjiarapoglou, L.; Varvoglis, A.; Alcock, N. W.; Pike, G. A. *J. Chem. Soc., Perkin Trans. 1* **1988**, 2839. (b) Adam, W.; Gogonas, E. P.; Hadjiarapoglou, L. P. *Synlett* **2003**, 1165.

(6) Hadjiarapoglou, L.; Varvoglis, A. *Synthesis* **1988**, *1988*, 913.

(7) (a) Hatjiarapoglou, L.; Varvoglis, A. *J. Heterocycl. Chem.* **1988**, *25*, 1599. (b) Batsila, C.; Gogonas, E. P.; Kostakis, G.; Hadjiarapoglou, L. P. *Org. Lett.* **2003**, *5*, 1511.

(8) (a) Sander, W.; Strehl, A.; Winkler, M. *Eur. J. Org. Chem.* **2001**, *2001*, 3771. (b) Bucher, G.; Strehl, A.; Sander, W. *Eur. J. Org. Chem.* **2003**, *2003*, 2153. (c) Sander, W.; Kotting, C.; Hubert, R. *J. Phys. Org. Chem.* **2000**, *13*, 561.

(9) Loss of $CO_2$ from dithiocarbonate **3b** would give rise to thiosulfonate **4b** selectively. Both atoms of oxygen of $CO_2$ probably originate from the same sulfonyl group of **1b** (ref 4a).




DOI: 10.1021/acs.joc.6b00142
*J. Org. Chem.* 2016, 81, 3188−3198

(10) (a) Yang, Y.-D.; Azuma, A.; Tokunaga, E.; Yamasaki, M.; Shiro, M.; Shibata, N. *J. Am. Chem. Soc.* **2013**, *135*, 8782. (b) Arimori, S.; Takada, M.; Shibata, N. *Org. Lett.* **2015**, *17*, 1063. (c) Huang, Z.; Yang, Y.-D.; Tokunaga, E.; Shibata, N. *Org. Lett.* **2015**, *17*, 1094.
(11) (a) Bolton, E. E.; Schaefer, H. F., III *J. Am. Chem. Soc.* **1993**, *115*, 6207. (b) O'Bannon, P. E.; Dailey, W. P. *Tetrahedron Lett.* **1988**, *29*, 5719. (c) O'Bannon, P. E.; Dailey, W. P. *Tetrahedron Lett.* **1988**, *29*, 987.
(12) (a) Ochiai, M.; Tada, N.; Okada, T.; Sota, A.; Miyamoto, K. *J. Am. Chem. Soc.* **2008**, *130*, 2118. (b) Ochiai, M.; Tada, N.; Murai, K.; Goto, S.; Shiro, M. *J. Am. Chem. Soc.* **2006**, *128*, 9608. (c) Ochiai, M.; Tada, N.; Miyamoto, K.; Shiro, M. *Heteroat. Chem.* **2011**, *22*, 325.
(13) Comparable values of 8−23 times were obtained from the reported relative rate constants as substituent effects of the *p*-$CF_3$ group in the solvolysis of 1-cyclohexenyl(aryl) (tetrafluoroborato)-$\lambda^3$-iodanes. See: (a) Okuyama, T.; Takino, T.; Sueda, T.; Ochiai, M. *J. Am. Chem. Soc.* **1995**, *117*, 3360. (b) Ochiai, M.; Suefuji, T.; Miyamoto, K.; Shiro, M. *Org. Lett.* **2005**, *7*, 2893. For solvolysis of 1-cyclopentenyl(aryl) (tetrafluoroborato)-$\lambda^3$-bromanes, see: (c) Miyamoto, K.; Shiro, M.; Ochiai, M. *Angew. Chem., Int. Ed.* **2009**, *48*, 8931.
(14) Hansch, C.; Leo, A.; Taft, R. W. *Chem. Rev.* **1991**, *91*, 165.
(15) No cyclopropanation or 1,2-*S*,*O*-addition reaction was observed in attempted thermal decomposition of iodonium ylide in an olefin solvent under these conditions, and the iodonium ylide was recovered unchanged.
(16) For a preliminary study on relative leaving group abilities between $\lambda^3$-iodanyl group and $\lambda^3$-bromanyl group, see: Miyamoto, K. *Yakugaku Zasshi* **2014**, *134*, 1287.
(17) The high degree of stereospecificity in thermal decomposition of iodonium ylide $PhI^+-C^-(CO_2Et)_2$ in (*Z*)- and (*E*)-3-heptene, yielding *cis*- and *trans*-bis(ethoxycarbonyl) cyclopropane respectively, suggests cyclopropanation by a singlet carbene. See: Camacho, M. B.; Clark, A. E.; Liebrecht, T. A.; DeLuca, J. P. *J. Am. Chem. Soc.* **2000**, *122*, 5210.
(18) Formation of *S*-trifluoromethyl thiosulfonate $CF_3SO_2SCF_3$ **4a** (ref 19) in 41% yield was detected by $^{19}F$ NMR in solid-state thermolysis (175 °C, 10 min) of bromonium ylide **9a** in the absence of olefin, although the reproducibility of the yield was poor.
(19) De Marco, R. A.; Shreeve, J. M. *Inorg. Chem.* **1973**, *12*, 1896.
(20) The structures of sulfinate esters **12c** were confirmed by direct comparison with authentic samples prepared independently. Billard *anti*-1,2-oxy-trifluoromethylthiolation of olefins by using *N*-(trifluoromethanethio)aniline in the presence of $CF_3CO_2H$, followed by alkaline hydrolysis, afforded *syn*- and *anti*-*β*-hydroxysulfide **28** stereoselectively (ref 21). Triflination of these alcohols **28** with unstable $CF_3SOCl$, generated in situ from sodium trifluoromethanesulfinate and mesitylsulfonyl chloride, provided triflinates **12c** in good yields (ref 22).
(21) Ferry, A.; Billard, T.; Langlois, B. R.; Bacque, E. *Angew. Chem., Int. Ed.* **2009**, *48*, 8551.
(22) (a) Hendrickson, J. B.; Skipper, P. L. *Tetrahedron* **1976**, *32*, 1627. (b) Hasegawa, A.; Ishikawa, T.; Ishihara, K.; Yamamoto, H. *Bull. Chem. Soc. Jpn.* **2005**, *78*, 1401. (c) Yanai, H.; Egawa, S.; Taguchi, T. *Tetrahedron Lett.* **2013**, *54*, 2160.
(23) (a) Mbuvi, H. M.; Woo, L. K. *Organometallics* **2008**, *27*, 637. (b) Davies, H. M. L.; Jin, Q.; Ren, P.; Kovalevsky, A. Y. *J. Org. Chem.* **2002**, *67*, 4165. (c) Ledon, H.; Linstrumelle, G.; Julia, S. *Bull. Chim. Soc. Fr.* **1973**, *6*, 2065.
(24) McNamara, O. A.; Maguire, A. R. *Tetrahedron* **2011**, *67*, 9.
(25) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Montgomery, J. A.; Vreven, T.; Kudin, K. N.; Burant, J. C.; Millam, J. M.; Iyengar, S. S.; Tomasi, J.; Barone, V.; Mennucci, B.; Cossi, M.; Scalmani, G.; Rega, N.; Petersson, G. A.; Nakatsuji, H.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Klene, M.; Li, X.; Knox, J. E.; Hratchian, H. P.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Ayala, P. Y.; Morokuma, K.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Zakrzewski, V. G.; Dapprich, S.; Daniels, A. D.; Strain, M. C.; Farkas, O.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Ortiz, J. V.; Cui, Q.; Baboul, A. G.; Clifford, S.; Cioslowski, J.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Challacombe, M.; Gill, P. M. W.; Johnson, B.; Chen, W.; Wong, M. W.; Gonzalez, C.; Pople, J. A. *Gaussian 03*, Revision D.02; Gaussian, Inc.: Wallingford, CT, 2004.
(26) A smaller triplet/singlet gap (∼2 kcal) has been estimated for parent disulfonylcarbene **1a** (ref 8a).
(27) For intramolecular thermal cyclopropanation of alkenes with phenyliodonium ylides under metal-free conditions, see: (a) Moriarty, R. M.; Tyagi, S.; Kinch, M. *Tetrahedron* **2010**, *66*, 5801. (b) Moriarty, R. M.; Prakash, O.; Vaid, R. K.; Zhao, L. *J. Am. Chem. Soc.* **1989**, *111*, 6443. (c) Gallos, J. K.; Koftis, T. V.; Massen, Z. S.; Dellios, C. C.; Mourtzinos, I. T.; Coutouli-Argyropoulou, E.; Koumbis, A. E. *Tetrahedron* **2002**, *58*, 8043. See also ref 17.
(28) Chemical shifts of carbon atoms attached to fluorine atoms were not determined.
(29) Zhu, S.-Z.; Xu, B.; Zhang, J. *Synthesis* **1994**, *1994*, 261−263.


DOI: 10.1021/acs.joc.6b00142
*J. Org. Chem.* 2016, 81, 3188−3198