J. Am. Chem. Soc. **1996,** *118,* 10141−10149

Evidence for Reversible Ylide Formation: Equilibrium between Free Alkylidenecarbenes and Ethereal Solvent−Alkylidenecarbene Complexes (Oxonium Ylides)

Takuya Sueda, Takema Nagaoka, Satoru Goto, and Masahito Ochiai*

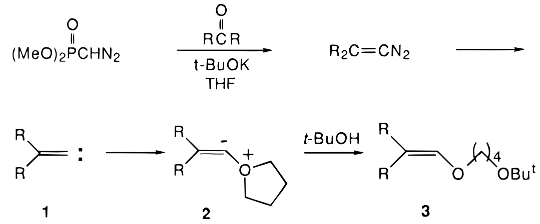
Contribution from the Faculty of Pharmaceutical Sciences, University of Tokushima,
1-78 Shomachi, Tokushima 770, Japan

Received May 28, 1996[⊗]

Abstract: The free alkylidenecarbene, 2-butyl-1-hexenylidene **1** (R = Bu), generated by triethylamine-induced α-elimination of 2-butyl-1-hexenyliodonium tetrafluoroborate **7** in tetrahydrofuran undergoes regioselective 1,5-C-H insertions, 1,2-shifts of the butyl group, and electrophilic attack on the tertiary amine followed by protonation to give the cyclopentene **8**, the alkyne **9**, and the vinylammonium salt **10**, respectively. In addition to these free carbene-derived products, the reaction affords the three-component coupling product, the vinyl ether **11**, produced through nucleophilic attack of tetrahydrofuran on **1** (R = Bu) generating the oxonium ylide **2** (R = Bu), followed by protonation with subsequent ring-opening of the resulting cyclic oxonium salt **15** (R = Bu) by nucleophilic attack of triethylamine. Reactions were observed to be temperature dependent, as reflected in variations in the product profiles: decreasing the reaction temperature tended to decrease the yields of free alkylidenecarbene-derived products, i.e., cyclopentenes, alkynes, and vinylammonium salts, and to increase those of the vinyloxonium ylide-derived products, vinyl ethers. This temperature dependence is explained in terms of reversible oxonium ylide formation. No evidence was observed to suggest the existence of an equilibrium between the free alkylidenecarbene and the sulfonium ylide in the reaction in tetrahydrothiophene. These results are consistent with quantum calculations using the MOPAC 93 program.

Although no stable and isolable oxonium ylide has been reported in the literature[1,2] and no spectroscopic data are available to establish the intermediacy of oxonium ylides in the reaction of carbenes or carbenoids with ethers, they have been postulated as intermediates to explain the products observed on either transition metal-catalyzed, thermal, or photochemical reaction of diazocompounds.[3]

Alkylidenecarbenes possess a singlet ground state and are electrophilic in nature.[4] When they are generated in ethereal solvents, the transient formation of the solvent−alkylidenecarbene complex, i.e., oxonium ylide, has also been proposed; in 1980, Gilbert and Weerasooriya reported that the generation of 1-diazoethene by *t*-BuOK-promoted reaction of dimethyl diazomethylphosphonate with acetone in tetrahydrofuran (THF) gave the enol ether **3** (R = Me) in 15% yield, via the formation of THF−alkylidenecarbene complex **2** (R = Me) followed by the ring-opening with *t*-BuOH.[5] Base-induced α-elimination of 2-methylpropenyl triflate in THF similarly produced the oxonium ylide-derived enol ethers, along with the formation of the alkylidenecarbene-derived enol ether.[6,7]



On the other hand, detailed measurements by Gilbert and Giamalva of the ρ value for the cycloaddition of 2-methyl-1-propenylidene **1** (R = Me) derived from 1-diazoethene to substituted styrenes as a function of solvent molecules such as THF and Et_2O showed evidence against the intervention of an ethereal solvent−alkylidenecarbene complex. Their results indicated that the carbene is free of encumbrance with the solvent molecules, at least in the sense that the latter are functioning as Lewis bases and that bulk properties of the solvent, not complexation, are responsible for the observed variation in ρ values as a function of solvent.[8]

[⊗] Abstract published in *Advance ACS Abstracts,* October 1, 1996.

(1) For reviews of carbene-derived oxonium ylides, see: (a) Padwa, A.; Hornbuckle, S. F. *Chem. Rev.* **1991**, *91*, 263. (b) Padwa, A.; Krumpe, K. E. *Tetrahedron* **1992**, *48*, 5385. (c) Jones, M.; Moss, R. A. *Carbenes*; Wiley-Interscience: New York, 1973.

(2) For stable carbene-derived sulfonium ylides, see: Ando, W. *Acc. Chem. Res.* **1977**, *10*, 179.

(3) (a) Nozaki, H.; Takaya, H.; Noyori, R. *Tetrahedron Lett.* **1965**, 2563. (b) Nozaki, H.; Takaya, H.; Moriuti, S.; Noyori, R. *Tetrahedron* **1968**, *24*, 3655. (c) Ando, W.; Kondo, S.; Nakayama, K.; Ichibori, K.; Kohoda, H.; Yamato, H.; Imai, I.; Nakaido, S.; Migita, T. *J. Am. Chem. Soc.* **1972**, *94*, 3870. (d) Iwamura, H.; Imahashi, Y.; Kushida, K. *Tetrahedron Lett.* **1975**, 1401. (e) Kirmse, W.; Chiem, P. V. *Tetrahedron Lett.* **1985**, *26*, 197. (f) Pirrung, M. C.; Werner, J. A. *J. Am. Chem. Soc.* **1986**, *108*, 6060. (g) Roskamp, E. J.; Johnson, C. R. *J. Am. Chem. Soc.* **1986**, *108*, 6062. (h) Shields, C. J.; Schuster, G. B. *Tetrahedron Lett.* **1987**, *28*, 853. (i) Doyle, M. P.; Bagheri, V.; Harn, N. K. *Tetrahedron Lett.* **1988**, *29*, 5119. (j) Kirmse, W.; Kund, K. *J. Am. Chem. Soc.* **1989**, *111*, 1465. (k) Kido, F.; Sinha, S. C.; Abiko, T.; Yoshikoshi, A. *Tetrahedron Lett.* **1989**, *30*, 1575. (l) Eberlein, T. H.; West, F. G.; Tester, R. W. *J. Org. Chem.* **1992**, *57*, 3479. (m) West, F. G.; Eberlein, T. H.; Tester, R. W. *J. Chem. Soc., Perkin Trans. 1* **1993**, 2857.

(4) (a) Stang, P. J. *Chem. Rev.* **1978**, *78*, 383. (b) Stang, P. J. *Acc. Chem. Res.* **1982**, *15*, 348.

(5) (a) Gilbert, J. C.; Weerasooriya, U. *Tetrahedron Lett.* **1980**, *21*, 2041. (b) Gilbert, J. C.; Weerasooriya, U. *J. Org. Chem.* **1983**, *48*, 448. (c) Newman, M. S.; Beard, C. D. *J. Am. Chem. Soc.* **1970**, *92*, 7564.

(6) (a) Oku, A.; Harada, T.; Hattori, K.; Nozaki, Y.; Yamaura, Y. *J. Org. Chem.* **1988**, *53*, 3089. (b) Oku, A.; Harada, T.; Nozaki, Y.; Yamaura, Y. *J. Am. Chem. Soc.* **1985**, *107*, 2189. (c) Ohira, S.; Noda, I.; Mizobata, T.; Yamato, M. *Tetrahedron Lett.* **1995**, *36*, 3375.

(7) Formation of three-component coupling products consisting of a carbene [phenylcarbene and ethoxycarbonylcarbene], THF, and an alcohol has been reported. See: Oku, A.; Kimura, K.; Ohwaki, S. *Acta Chem. Scand.* **1993**, *47*, 391.

(8) Gilbert, J. C.; Giamalva, D. H. *J. Org. Chem.* **1992**, *57*, 4185.

S0002-7863(96)01797-0 CCC: $12.00 © 1996 American Chemical Society

Table 1. Effects of Reaction Temperature on Reaction of Vinyliodonium Salt **7** with Triethylamine in THF

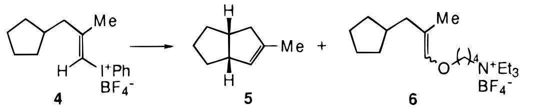
entry	Et_3N (equiv)	conditions	product, % yield[a]					ratio	
			8	**9**	**10**	**11**	total[b]	(**8** + **9** + **10**):**11**[c]	**8**:**9**[d]
1	1.2	60 °C (10 h)	74	14	<1	2	90	98:2	84:16
2	1.2	40 °C (10 h)	75	11	<1	9	95	90:10	87:13
3	1.2	20 °C (10 h)	75	8	1	15	99	85:15	90:10
4	1.2	0 °C (10 h)	71	3	1	23	98	77:23	96:4
5	1.2	−20 °C (2 days), 0 °C (10 h)	48	2	1	27	78	65:35	97:3
6	1.2	−40 °C (2 days), 0 °C (10 h)	44	2	1	40	87	54:46	95:5
7	1.2	−60 °C (2 days), 0 °C (10 h)	44	3	3	42	92	54:46	94:6
8	2.0	40 °C (10 h)	75	11	1	11	98	89:11	87:13
9	2.0	20 °C (10 h)	71	7	2	15	95	84:16	91:9
10	2.0	0 °C (10 h)	71	2	2	22	97	78:22	97:3
11	2.0	−20 °C (2 days), 0 °C (10 h)	54	1	2	27	84	68:32	97:3
12	2.0	−40 °C (2 days), 0 °C (10 h)	34	1	2	53	90	42:58	97:3
13	2.0	−60 °C (2 days), 0 °C (10 h)	41	2	4	45	92	51:49	95:5

[a] Yields of **8** and **9** were determined by GC. Yields of **10** and **11** were determined by ^1H NMR. [b] Total yields of **8**, **9**, **10**, and **11**. [c] Ratios of the free alkylidenecarbene-derived products (**8** + **9** + **10**) versus the vinyloxonium ylide-derived product **11**. [d] Ratios of 1,5-C−H insertions versus 1,2-shifts.

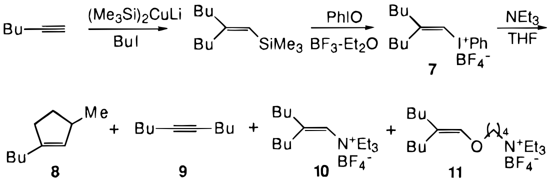
These results on the reactions of alkylidenecarbenes can be explained, we believe, in terms of a rapid equilibrium between free alkylidenecarbenes **1** and vinyloxonium ylides **2** in which free alkylidenecarbenes **1** are responsible for cycloaddition to styrenes. In the present paper we show that the ratio of the free alkylidenecarbene-derived and the oxonium ylide-derived products is temperature dependent, which strongly suggests reversible oxonium ylide formation.

Results and Discussion

Recently we reported that base treatment of alkenyl(phenyl)iodonium tetrafluoroborates leads to reductive α-elimination of iodobenzene under mild conditions to generate alkylidenecarbenes, because of the very high leaving group ability of the phenyliodonio groups.[9,10] The findings of complete stereoconvergence for intramolecular 1,5-carbon−hydrogen insertions of the resulting alkylidenecarbenes[9a] and a small ρ value of −0.56 obtained by a Hammett study for the cycloaddition of 2-methyl-1-propenylidene **1** (R = Me) derived from an alkenyliodonium salt to ring-substituted styrenes[11,12] suggest that the reactive intermediate involved is a free carbene and not a carbenoid.



Reaction of the alkenyliodonium salt **4** with triethylamine or *t*-BuOK in THF at room temperature has been shown to result in the selective formation of bicyclo[3.3.0]octene **5** in 80−84% yields, through regioselective 1,5-carbon−hydrogen insertions of the alkylidenecarbene formed by α-elimination.[9a] Surprisingly, however, when the reaction using triethylamine as a base was carried out under the same conditions, except for the reaction temperature of −78 °C, the triethylammonium vinyl ether **6** was obtained as the major product (43% yield) in addition to the formation of **5** (39%). The structure of **6** was determined by spectroscopy using two-dimensional (2D) NMR techniques, i.e., $^1H,^1H$-COSY, $^{13}C,^1H$-COSY, and nuclear Overhauser enhancement spectroscopy (NOESY), and fast atom bombardment (FAB) mass spectrometry. The vinyl ether **6** that is a 7:3 mixture of *E*- and *Z*-isomers was found to be a coupling product consisting of three components: alkenyliodonium salt **4**, THF, and triethylamine.



To uncover the effects of reaction temperature on the formation of the three-component coupling products as well as to gain some insight into the nature of alkylidenecarbenes in THF, we synthesized simple β,β-dibutylvinyliodonium tetrafluoroborate **7**, bearing the same alkyl substituent at the β-carbon atom, from 1-hexyne by the reaction with lithium bis(trimethylsilyl)cuprate and butyl iodide,[15] and subsequently allowed the resulting vinylsilane to react with iodosylbenzene in the presence of BF_3-Et_2O.[16] The results on the temperature dependence of the reaction of **7** with triethylamine in THF are summarized in Table 1. When the reaction with 1.2 equiv of triethylamine was carried out at 60 °C for 10 h in nitrogen, analysis by gas chromatography (GC) showed the formation of two major products, the cyclopentene **8** (74%) and the rearranged alkyne **9** (14%). ^1H NMR also detected the presence of the vinylammonium salt **10** (<1%) and the triethylammonium vinyl ether **11** (2%) (Table 1, entry 1). Table 1 clearly shows that the yields of both the 1,5-C−H insertion product **8** and of the rearranged product **9** decrease with a decrease in the reaction temperature while that of the three-component coupling product **11** increases. For instance, by starting at −60 °C for 2 days and then gradually raising the temperature to 0 °C, 44% of **8**, 3% of **9**, 3% of **10**, and 42% of **11** were produced.[17] A similar temperature dependence was observed in the reaction using 2 equiv of triethylamine (Table 1, entries 8−13).

Because the yields of the vinylammonium salt **10** were very low, it was difficult to measure the effects of temperature on

---

[9] (a) Ochiai, M.; Takaoka, Y.; Nagao, Y. *J. Am. Chem. Soc.* **1988**, *110*, 6565. (b) Ochiai, M.; Kunishima, M.; Tani, S.; Nagao, Y. *J. Am. Chem. Soc.* **1991**, *113*, 3135.

[10] For a very high leaving group ability of phenyliodonio groups, see: Okuyama, T.; Takino, T.; Sueda, T.; Ochiai, M. *J. Am. Chem. Soc.* **1995**, *117*, 3360.

[11] Ochiai, M.; Sueda, T.; Uemura, K.; Masaki, Y. *J. Org. Chem.* **1995**, *60*, 2624.

[12] Stang and Mangum reported that the free alkylidenecarbene is mildly electrophilic in nature and shows a relatively small negative ρ value,[13] whereas the carbenoid shows a very large degree of electrophilicity and a large negative ρ value.[14]

[13] Stang, P. J.; Mangum, M. G. *J. Am. Chem. Soc.* **1975**, *97*, 6478.

[14] (a) Newman, M. S.; Patrick, T. B. *J. Am. Chem. Soc.* **1969**, *91*, 6461. (b) Patrick, T. B.; Haynie, E. C.; Probst, W. J. *J. Org. Chem.* **1972**, *37*, 1553.

[15] (a) Fleming, I.; Newton, T. W. *J. Chem. Soc., Perkin Trans. 1* **1984**, 1805. (b) Fleming, I.; Newton, T. W.; Roessler, F. *J. Chem. Soc., Perkin Trans. 1* **1981**, 2527.

[16] (a) Ochiai, M.; Sumi, K.; Takaoka, Y.; Kunishima, M.; Nagao, Y.; Shiro, M.; Fujita, E. *Tetrahedron* **1988**, *44*, 4095. (b) Hinkle, R. J.; Poulter, G. T.; Stang, P. J. *J. Am. Chem. Soc.* **1993**, *115*, 11626.

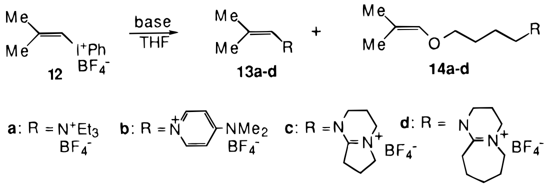
[17] The reaction at −60 °C was found to be very slow, since, even after 2 days at the temperature, 70% of **7** was recovered unchanged.

Table 2. Effects of Temperature on Reaction of Vinyliodonium Salt **12** with Amines in THF

entry	base (equiv)	conditions T/°C (*t*/h)	product	% yield[a,b]	ratio[a] **13:14**
1	Et_3N (1.2)	25 (17)	**13a**, **14a**	62	35:65
2	Et_3N (1.2)	−20 (5), 25 (12)	**13a**, **14a**	55	22:78
3	Et_3N (1.2)	−78 (5), 25 (10)	**13a**, **14a**	63	14:86
4	Et_3N (2)	25 (17)	**13a**, **14a**	60	45:55
5	Et_3N (2)	−20 (5), 25 (12)	**13a**, **14a**	62	29:71
6	Et_3N (2)	−78 (5), 25 (10)	**13a**, **14a**	63	19:81
7	DMAP (1.2)	25 (24)	**13b**, **14b**	76	55:45
8	DMAP (1.2)	−20 (5), 25 (19)	**13b**, **14b**	68	12:88
9	DMAP (1.2)	−78 (5), 5 (19)	**13b**, **14b**	73	10:90
10	DMAP (2)	25 (24)	**13b**, **14b**	87	55:45
11	DMAP (2)	−20 (5), 25 (19)	**13b**, **14b**	58	43:57
12	DMAP (2)	−78 (5), 25 (19)	**13b**, **14b**	89	39:61
13	DBN (1.2)	25 (24)	**13c**, **14c**	85	47:53
14	DBN (1.2)	−78 (5), 25 (48)	**13c**, **14c**	76	5:95
15	DBU (1.2)	25 (24)	**13d**, **14d**	52	31:69
16	DBU (1.2)	−78 (5), 25 (48)	**13d**, **14d**	87	3:97

[a] Yields and ratios were determined by ^1H NMR. [b] Total yields of **13** and **14**.

the formation of the vinylammonium salt. 2-Methyl-1-propenyliodonium tetrafluoroborate **12**[11] was the substrate of choice to investigate this temperature effect because 2-methyl-1-propenylidene **1** (R = Me) generated from **12** does not undergo the intramolecular 1,5-C−H insertions yielding cyclopentenes, one of the most facile reactions of alkylidenecarbenes, and thus the reaction may lead to increased yields both of the vinylammonium salts and of the vinyl ethers. In fact, exposure of the vinyliodonium salt **12** to 1.2 equiv of triethylamine in THF at 25 °C resulted in the formation of a large amount of the vinylammonium salt **13a** (22%) and, in addition, the vinyl ether **14a** (40%) was obtained as a major product. In this reaction, yields of the rearranged alkyne, 2-butyne, were not determined. As a base, 4-(dimethylamino)pyridine (DMAP), 1,5-diazabicyclo-[4.3.0]non-5-ene (DBN), and 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU) were also used; the results are summarized in Table 2.



As shown in Table 2, formation of the vinylammonium salt **13a** exhibited a temperature dependence similar to that of the 1,5-C−H insertion product **8** and the rearranged product **9**; decreasing temperature trends to decrease the yield of **13a** while increasing that of the three-component coupling product **14a**, as observed in the reaction of **7**. This tendency was further confirmed in the reaction with DMAP, which yielded a mixture of **13b** and **14b**. Concentration of a base also affects the ratios of the vinylammonium salts **13** to the vinyl ethers **14**; thus, increasing the concentration of a base by using **2** equiv of triethylamine of DMAP increased the relative amounts of **13a,b**. (Compare entries 1−3 with 4−6, and entries 7−9 with 10−12 of Table 2.) Note that DBN and DBU, known as nonnucleophilic strong bases,[18] can act both as nucleophiles and as bases in this reaction. Here, they afforded a mixture of **13c,d** and **14c,d**—notably, the reaction at −78 °C gave the vinyl ethers **14c,d** with more than 95% selectivity. At 25 °C, again, these bicyclic imidines afforded a large amount of the vinylammonium salts **13c,d**. The structure of **13** and **14** was determined by 2D NMR and NOESY.

Triethylamine-induced reductive α-elimination of iodobenzene from the alkenyliodonium salt **7** generates the alkylidenecarbene **1** (R = Bu), which undergoes regioselective 1,5-C−H insertions yielding the cyclopentene **8**[19] as well as 1,2-shift of the Bu group to the carbenic center to give the alkyne **9**.[20] The electrophilic nature of alkylidenecarbenes[4] makes the nucleophilic attack of the tertiary amine possible, which produces the triethylammonium ylide **16** (R = Bu).[21] The follow-up protonation with ammonium tetrafluoroborate produced *in situ* affords the vinylammonium salt **10**.[22] On the other hand, nucleophilic attack of nonbonding electrons of THF oxygen on **1** produces the vinyloxonium ylide **2** (R = Bu). After protonation with the ammonium tetrafluoroborate, ring-opening of the resulting cyclic oxonium salt **15** (R = Bu) by the nucleophilic attack of triethylamine gives the three-component coupling product, the vinyl ether **11**.[23]

As an alternative process leading to the formation of the vinylammonium salts, we may consider nucleophilic substitutions of the alkenyliodonium salts **7** and **12** and the cyclic alkenyloxonium salt **15** with amines at the vinylic carbon atoms. This process, however, does not seem to occur perhaps because (1) S_N1 type reactions of these onium salts involving the intermediacy of primary vinyl cations will not be important (there are no known primary vinyl cations probably because of their low thermodynamic stability)[24] and (2) there has been no well established direct S_N2 displacement at a vinylic carbon atom, which has been calculated to be more difficult energetically than displacement at an sp^3 carbon atom.[25,26]

---

(18) (a) Hermecz, I. *Adv. Heterocycl. Chem.* **1987**, *42*, 83. (b) Cowley, A. H. *Acc. Chem. Res.* **1984**, *17*, 386. (c) Oedidiger, H.; Moller, F.; Eiter, K. *Synthesis* **1972**, 591. (d) Reed, R.; Reau, R.; Dahan, F.; Bertrand, G. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 399. (e) McCoy, L. L.; Mal, D. *J. Org. Chem.* **1981**, *46*, 1016. (f) Alder, R. W.; Sessions, R. B. *Tetrahedron Lett.* **1982**, *23*, 1121. (g) Schwesinger, R.; Willaredt, J.; Schlemper, H.; Keller, M.; Schmitt, D.; Fritz, H. *Chem. Ber.* **1994**, *127*, 2435.

(19) For intramolecular 1,5-C−H insertion of alkylidenecarbenes, see: (a) Walsh, R. A.; Bottini, A. T. *J. Org. Chem.* **1970**, *35*, 1086. (b) Baumann, M.; Kobrich, G. *Tetrahedron Lett.* **1974**, 1207. (c) Karpf, M.; Dreiding, A. S. *Helv. Chim. Acta* **1979**, *62*, 852. (d) Gilbert, J. C.; Giamalva, D. H.; Weerasooriya, U. *J. Org. Chem.* **1983**, *48*, 5251. (e) Gilbert, J. C.; Blackburn, B. K. *Tetrahedron Lett.* **1984**, *25*, 4067. (f) Gilbert, J. C.; Giamalva, D. H.; Baze, M. E. *J. Org. Chem.* **1985**, *50*, 2557. (g) Gilbert, J. C.; Blackburn, B. K. *J. Org. Chem.* **1986**, *51*, 3656. (h) Gilbert, J. C.; Blackburn, B. K. *J. Org. Chem.* **1986**, *51*, 4087. (i) Baird, M. S.; Baxter, A. G. W.; Hoorfar, A.; Jefferies, I. *J. Chem. Soc., Perkin Trans. 1* **1991**, 2575. (j) Ohira, S.; Okai, K.; Moritani, T. *J. Chem. Soc., Chem. Commun.* **1992**, 721. (k) Kunishima, M.; Hioki, K.; Tani, S.; Kato, A. *Tetrahedron Lett.* **1994**, *35*, 7253. (l) Kim, S.; Cho, C. M. *Tetrahedron Lett.* **1994**, *35*, 8405. (m) Williamson, B. L.; Tykwinski, R. R.; Stang, P. J. *J. Am. Chem. Soc.* **1994**, *116*, 93. (n) Tykwinski, R. R.; Stang, P. J.; Persky, N. E. *Tetrahedron Lett.* **1994**, *35*, 23. (o) Schildknegt, K.; Bohnstedt, A. C.; Feldman, K. S.; Sambandam, A. *J. Am. Chem. Soc.* **1995**, *117*, 7544.

(20) For 1,2-shift of alkylidenecarbenes, see: (a) Bothner-By, A. A. *J. Am. Chem. Soc.* **1955**, *77*, 3293. (b) Wolinsky, J. *J. Org. Chem.* **1961**, *26*, 704. (c) Erickson, K. L.; Wolinsky, J. *J. Am. Chem. Soc.* **1965**, *87*, 1142. (d) Newman, M. S.; Gromelski, S. J. *J. Org. Chem.* **1972**, *37*, 3220. (e) Kobrich, G.; Merkel, D.; Thiem, K.-W. *Chem. Ber.* **1972**, *105*, 1683. (f) Wolinsky, J.; Clark, G. W.; Thorstenson, P. C. *J. Org. Chem.* **1976**, *41*, 745. (g) Kowalski, C. J.; Fields, K. W. *J. Am. Chem. Soc.* **1982**, *104*, 321. (h) Gilbert, J. C.; Weerasooriya, U. *J. Org. Chem.* **1982**, *47*, 1837. (i) McDougall, J. J. W.; Schlegel, H. B.; Francisco, J. S. *J. Am. Chem. Soc.* **1989**, *111*, 4622. (j) Walsh, R; Untiedt, S.; Stohlmeier, M.; Meijere, A. *Chem. Ber.* **1989**, *122*, 637. (k) Ochiai, M.; Ito, T.; Takaoka, Y.; Masaki, Y.; Kunishima, M.; Tani, S.; Nagao, Y. *J. Chem. Soc., Chem. Commun.* **1990**, 118. (l) Kunishima, M.; Hioki, K.; Ohara, T.; Tani, S. *J. Chem. Soc., Chem. Commun.* **1992**, 219. (m) Fischer, D. R.; Williamson, B. L.; Stang, P. J. *Synlett* **1992**, 535.

(21) For generation of carbene-derived ammonium ylides, see ref 1a.

(22) Generation of alkylidenecarbenes in the presence of secondary amines and alcohols has been reported to produce enamines and enols, respectively.[5] See, also: (a) Gilbert, J. C.; Weerasooriya, U.; Wiechman, B.; Ho, L. *Tetrahedron Lett.* **1980**, *21*, 5003. (b) Ohira, S. *Synth. Commun.* **1989**, *19*, 561. (c) Miwa, K.; Aoyama, T.; Shioiri, T. *Synlett* **1994**, 109.

(23) Generation of 2-methyl-1-propenylidene **1** (R = Me) in THF in the presence of alcohols has been reported to result in formation of the similar three-component coupling products albeit in low yield (11−15%), via the intermediacy of the oxonium ylide **2** (R = Me).[5,6]

(24) Stang, P. J.; Rappoport, Z.; Hanack, M.; Subramanian, L. R. *Vinyl Cations*; Academic Press, New York, 1979.

Scheme 1

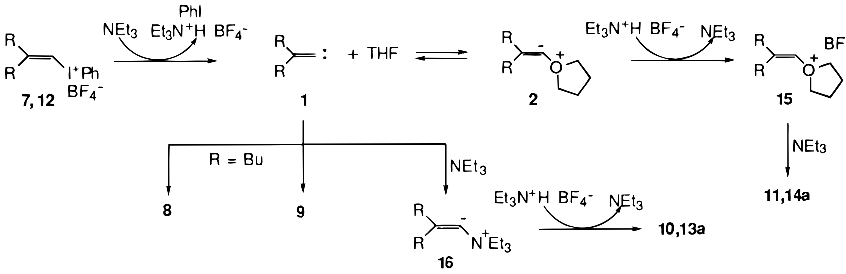


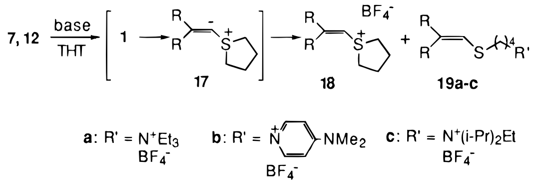
Table 3. Reaction of Vinyliodonium Salt **12** with Amines in THT[a]

entry	base (equiv)	conditions	product[b]	% yield[c]	**18:19**
1	Et_3N (1.2)	25 °C (24 h)	**18**, **19a**	100	75:25
2	DMAP (1.2)	25 °C (24 h)	**18**, **19b**	94	60:40
3	$(i\text{-}Pr)_2NEt$ (1.2)	25 °C (3 h)	**18**, **19c**	100	100:0

[a] Yields and ratios were determined by ^{1}H NMR. [b] R of **18** and **19** = Me. [c] Total yields of **18** and **19**.

The temperature dependence of the product profiles described above (that decreasing temperature has a tendency to decrease the yield of the free alkylidenecarbene-derived products, i.e., cyclopentenes, alkynes, and vinylammonium salts and increase that of the vinyloxonium ylide-derived products, vinyl ethers) might be attributed to a rapid equilibrium between the free alkylidenecarbene **1** and the oxonium ylide **2**.[27,28] Based on the assumption that the process leading to the formation of the oxonium ylide **2** from the alkylidenecarbene **1** and THF is associated with a decrease in entropy,[29] decreasing the reaction temperature can reasonably be expected to yield a higher concentration of the oxonium ylide **2**, which, in turn, increases the relative amount of the three-component coupling products, as was indeed observed. The reaction pathways of Scheme 1 suggest that the concentration of amines has some influence on the yield of vinylammonium salts and vinyl ethers; the yield of vinylammonium salts will depend upon the concentration of amines used and will increase with the higher concentrations of amines, as shown in Table 2.

The fact that neither **13c** nor **14c** was detected by exposure of the vinylammonium salt **13a** to DBN at room temperature in THF, and that **13a** was recovered unchanged, clearly implies that regeneration of the alkylidenecarbene **1** (R = Me) from **13a** does not proceed to any appreciable extent under these reaction conditions. Similarly, **13a** was recovered in the reaction with triethylamine in THF. No deuterium incorporation of α-vinylic proton of **13a** was observed in the reaction with butyllithium, phenyllithium, or lithium diisopropylamide, followed by quenching with D_2O. Furthermore, the possibility for regeneration of the oxonium ylide **2** (R = Me) from the vinyl ether **14a** under these conditions was also ruled out because no reaction of **14a** with DBN and triethylamine in THF was observed.



In marked contrast to the cyclic oxonium ylide **2**, it seems reasonable to assume that the corresponding cyclic sulfonium ylide **17**[30,31] would not establish an equilibrium with the free alkylidenecarbene **1**, given that no evidence for formation of the alkylidenecarbene-derived products was obtained when the reaction was carried out in tetrahydrothiophene (THT) instead of THF as a solvent. Thus, reaction of **7** with triethylamine in THT at 25 °C for 10 h afforded only sulfonium ylide-derived products, the sulfonium salt **18** (R = Bu; 87%) and the three-component coupling product **19a** (R = Bu; 7%). Careful GC and ^{1}H NMR analyses of the crude reaction mixture showed no evidence of formation of the alkylidenecarbene-derived products **8**, **9**, and **10**. These results indicate that relatively rapid intramolecular 1,5-C−H insertions of alkylidenecarbenes yielding cyclopentenes[32] cannot compete with nucleophilic attack of the sulfur atom of THT on the electron-deficient carbenic center. Similar results were obtained in the reaction of **12** with triethylamine in THT at 25 °C, which produced, quantitatively, a 75:25 mixture of **18** (R = Me) and **19a** (R = Me). Use of the more sterically demanding diisopropylethylamine resulted in selective formation of the sulfonium salt **18** (R = Me) (Table 3).

The mechanism involving the intermediacy of the alkylidenecarbene **1** and the sulfonium ylide **17** will predict deuterium incorporation at the α-vinylic position of **18**, if the reaction in THT is carried out in the presence of relatively acidic deuterium atoms. In the presence of methanol-d_4, the reaction of the vinyliodonium salt **7** with diisopropylethylamine in THT resulted in 61% deuterium incorporation at the α-vinylic position of **18** (R = Bu) in an 88% yield, as expected. Since no evidence for deuterium exchange of the α-vinylic hydrogen of **18** (R = Bu) was observed under our reaction conditions, we interpret these results to mean that neither an S_N1 and S_N2 mechanism nor an addition−elimination mechanism for this onium transfer reaction of **7**—both of which predict retention of the α-vinylic hydrogen atom of **7**—is involved.

Furthermore, the involvement of free alkylidenecarbenes was firmly established by the stereochemical outcome of this onium

---

(25) (a) Kelsey, D. R.; Bergman, R. G. *J. Am. Chem. Soc.* **1971**, *93*, 1953. (b) Bunnett, J. F.; Zahler, R. E. *Chem. Rev.* **1951**, *49*, 273. (c) Bunnett, J. F. *Quart Rev.* **1958**, *12*, 1. (d) Glukhovtsev, M. N.; Pross, A.; Radom, L. *J. Am. Chem. Soc.* **1994**, *116*, 5961. (e) Lucchini, V.; Modena, G.; Pasquato, L. *J. Am. Chem. Soc.* **1995**, *117*, 2297.

(26) Reaction of 1-decenyl(phenyl)iodonium salt with triethylamine affords 1-decyne exclusively and no formation of vinylammonium salts is detected.[9a]

(27) Equilibrium between Rh-carbenoids and oxonium ylides has been proposed for intramolecular C−H insertion of carbenoids.[3m]

(28) The equilibrium constant of the reaction of (biphenyl-4-yl)-chlorocarbene with THF yielding oxonium ylide has been determined by Naito and Oku to be 0.5 M^{-1} at 293 K in 2,2,4-trimethylpentane. See: Naito, I.; Oku, A.; Otani, N.; Fujiwara, Y.; Tanimoto, Y. *J. Chem. Soc., Perkin Trans. 2* **1996**, 725. Kinetic studies for oxonium ylide formation from carboalkoxycarbenes by the reaction with ethers have been reported. See: (a) Toscano, J. P.; Platz, M. S.; Nikolaev, V.; Popic, V. *J. Am. Chem. Soc.* **1994**, *116*, 8146. (b) Wang, J.-L.; Toscano, J. P.; Platz, M. S.; Nikolaev, V.; Popik, V. *J. Am. Chem. Soc.* **1995**, *117*, 5477.

(29) (a) Lucht, B. L.; Collum, D. B. *J. Am. Chem. Soc.* **1995**, *117*, 9863. (b) Strong, J.; Tuttle, T. R., Jr. *J. Phys. Chem.* **1973**, *77*, 533.

(30) 1,2-Shifts of α-phenylsulfenyl groups of alkylidenecarbenes yielding alkynyl sulfides were proposed to involve generation of sulfonium ylides produced by nucleophilic attack of lone pair electrons on the sulfur atoms to the electron-deficient carbenic center.[9b] See, also: (a) Delavarenne, S. Y.; Viehe, H. G. *Chem. Ber.* **1970**, *103*, 1209. (b) Viehe, H. G.; Delavarenne, S. Y. *Chem. Ber.* **1970**, *103*, 1216.

(31) For sulfonium ylides, see: Trost, B. M.; Melvin, L. S. *Sulfur Ylides*; Academic Press: New York, 1975.

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

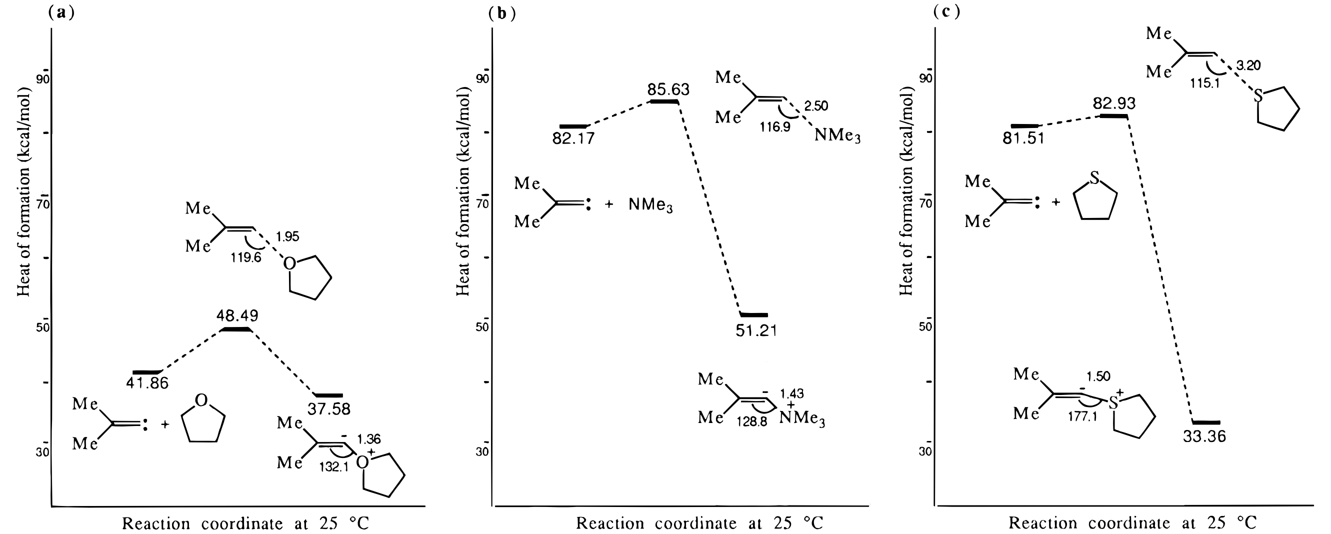
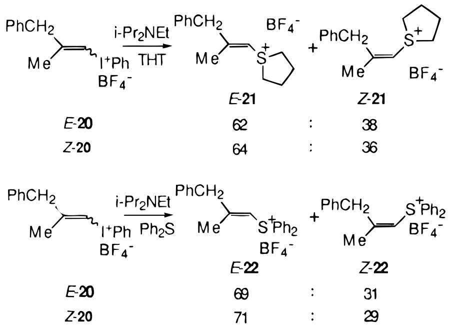
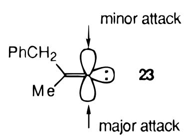


Figure 1. Reaction coordinates for onium ylide formation with selected geometrical parameters: (a) reaction of **1** (R = Me) with THF; (b) reaction of **1** (R = Me) with trimethylamine: and (c) reaction of **1** (R = Me) with THT. Bond distances in Å; angles in deg.

transfer reaction; i.e., treatment of the *E*-vinyliodonium salt **20** with diisopropylethylamine in THT afforded a mixture of stereoisomers of the vinylsulfonium salt **21** with *E*-isomer as a major product, and the ratio of *E*- and *Z*-isomers was determined by ^{1}H NMR analysis to be 62:38. The *E*-sulfonium salt **21** was also obtained as a major product (*E*:*Z* = 64:36) in the reaction of the *Z*-vinyliodonium salt **20**. Similar stereoconvergence with *E*-isomer **22** as a major product was observed in the reaction with diphenyl sulfide. Since reactions of alkylidenecarbenoids with nucleophiles have been shown to proceed in favor of inversion of configuration,[33] the high degree of stereoconvergence of the olefin geometry in this onium transfer reaction that we observed strongly indicates intermediacy of the free alkylidenecarbene **23**. This stereoselectivity is most likely a consequence of the steric differences between the two α-substituents of the alkylidenecarbene **23**.





The variation in behavior of THF and THT toward the alkylidenecarbenes is probably attributable to the difference in nucleophilicities of the oxygen and sulfur atoms and in the inherent stability of their onium ylides.[3c,i] Computational simulations of the reaction path between the free alkylidenecarbene **1** (R = Me) and the corresponding onium ylides were carried out with the quantum calculations using the MOPAC 93 program.[34] THF, trimethylamine, and THT were used as model nucleophiles for our calculations. Energy calculations, performed with the PM3 Hamiltonian, are summarized in Figure 1.

For the oxonium ylide **2** (R = Me: the reaction coordinate, 1.36 Å), the amount of polarization, i.e., the partial charges of the alkylidenecarbene and THF portions, were estimated as the au values of −0.359 and +0.359. These polarization values were found to be less than half of those of the trimethylammonium and the sulfonium ylides (±0.774 and ±0.755, respectively), implying that the trimethylammonium and the sulfonium ylides **17** (R = Me) were more efficiently stabilized than the oxonium ylide **2** (R = Me). The relatively small intrinsic barrier of formation (6.63 kcal/mol) and dissociation (10.91 kcal/mol) of the oxonium ylide **2** (R = Me) probably suggests that the free alkylidenecarbene **1** (R = Me) and the cyclic oxonium ylide **2** (R = Me) is in equilibrium in THF. This does not seem to hold for the ammonium ylides, given that 2-methylpropenyl(trimethyl)ammonium ylide shows a large dissociation barrier of 34.42 kcal/mol. Similarly, a large energy barrier of 49.57 kcal/mol is obtained for dissociation of the sulfonium ylide **17** (R = Me). These values are in good agreement with the experimental results and are consistent with the reaction pathway discussed above.

As shown in Table 1, the ratios of intramolecular 1,5-C−H insertions versus 1,2-shifts of the alkyl group in the reaction of **7** in THF vary with reaction temperature to a small but discernible extent, and the relative amount of the insertion product **8** increases with a decrease in reaction temperature. We attribute these findings to the difference in entropy of their transition states; that is, 1,5-C−H insertions of **1** (R = Bu) may require a more conformationally limited transition state than that for 1,2-shifts of the alkyl group.

Conclusion

Reactions of alkylidenecarbenes generated by amine-induced α-elimination of vinyliodonium salts in tetrahydrofuran were observed to be temperature dependent: decreasing the reaction temperature tended to decrease the yields of free alkylidenecarbene-derived products and to increase those of the vinyloxonium

---

(33) (a) Duraisamy, M.; Walborsky, H. M. *J. Am. Chem. Soc.* **1984**, *106*, 5035. (b) Rachon, J.; Goedken, V.; Walborsky, H. M. *J. Am. Chem. Soc.* **1986**, *108*, 7435. (c) Oku, A.; Yamaura, Y.; Harada, T. *J. Org. Chem.* **1986**, *51*, 3730. (d) Topolski, M.; Duraisamy, M.; Rachon, J.; Gawronski, J.; Gawronska, K.; Goedken, V.; Walborsky, H. M. *J. Org. Chem.* **1993**, *58*, 546. (e) Oku, A. *J. Synth. Org. Chem., Jpn.* **1995**, *53*, 2.

(34) Stewart, J. J. P. *J. Comput. Chem.* **1989**, *10*, 209.

(35) Tanaka, K.; Shiraishi, S.; Nakai, T.; Ishikawa, N. *Tetrahedron Lett.* **1978**, *34*, 3103.

ylide-derived products. Although all attempts to detect directly the intermediacy of the vinyloxonium ylide were fruitless, this temperature dependence strongly suggests reversible oxonium ylide formation. In marked contrast, no evidence was observed to suggest the existence of an equilibrium between the free alkylidenecarbene and the vinylsulfonium ylide.

Experimental Section

General Information. IR spectra were recorded on JASCO IRA-1 and Perkin Elmer 1720 FT-IR spectrometers. ^{1}H and ^{13}C NMR were recorded in $CDCl_3$ on a JEOL JNM-FX 200 or JNM-GX 400 spectrometer. Chemical shifts were reported in parts per million (ppm) downfield from internal Me_4Si. Mass spectra (MS) were obtained on a JEOL JMS-DX300 spectrometer. Analytical gas chromatography (GC) was conducted on a Shimadzu GC-14A gas chromatograph with 10% or 20% Silicone GE SF-96 on a Chromosorb W-AWDMCS column (3 m) and on a Shimadzu GC-15A gas chromatograph with an 0.25 mm × 50 m FFS ULBON HR-20M capillary column. Preparative GC was performed on a Shimadzu GC-14A gas chromatograph with 10% or 20% Silicone GE SF-96 on a Chromosorb W-AWDMCS column. 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. Melting points were determined with a Yanaco micro melting points apparatus and are uncorrected.

Dichloromethane was dried over CaH_2 and distilled. BF_3-Et_2O was distilled from CaH_2 under nitrogen. THF was distilled from sodium benzophenone ketyl under nitrogen.

Substrates. Phenyl(2-methyl-1-propenyl)iodonium tetrafluoroborate (**12**) was prepared by silicon-iodonium exchange reaction of 2-methyl-1-(trimethylsilyl)prop-1-ene with iodosylbenzene.[11]

Synthesis of (*E*)-Phenyl(3-cyclopentyl-2-methyl-1-propenyl)iodonium Tetrafluoroborate (4). (*E*)-3-Cyclopentyl-2-methyl-1-(trimethylsilyl)prop-1-ene was prepared stereoselectively from 3-cyclopentyl-1-propyne by the reaction with lithium bis(trimethylsilyl)cuprate and methyl iodide in 54% yield according to the procedure developed by Fleming.[15] To a stirred suspension of iodosylbenzene (3.84 g, 17.5 mmol) and the vinylsilane (2.14 g, 10.9 mmol) in dichloromethane (50 mL) was added dropwise BF_3-Et_2O (2.48 g, 17.5 mmol) at 0 °C in nitrogen, and the mixture was stirred for 0.3 h at 0 °C. After the addition of a saturated aqueous solution of sodium tetrafluoroborate (23 g, 0.21 mol), the mixture was stirred for 15 min. Extraction with dichloromethane, filtration, and then concentration under aspirator vacuum gave an oil, which was washed several times with hexane by decantation at −78 °C. Further purification by decantation using diethyl ether at −78 °C gave the iodonium salt **4** (3.7 g, 82%) as colorless needles: mp 69−71 °C (recrystallized from dichloromethane−diethyl ether−hexane); IR (KBr) 3080, 2950, 2860, 1608, 1568, 1473, 1443, 1380, 1260, 1200−1000, 995, 745, 683 cm^{-1}; ^{1}H NMR δ 7.91 (d, J = 8.1 Hz, 2 H), 7.64 (t, J = 7.5 Hz, 1 H), 7.50 (dd, J = 8.1, 7.5 Hz, 2 H), 6.67 (s, 1 H), 2.49 (d, J = 7.4 Hz, 2 H), 2.20 (s, 3 H), 2.06 (septet, J = 7.4 Hz, 1 H), 1.78−1.50 (m, 6 H), 1.13−1.04 (m, 2 H); FAB MS *m/z* 327 [(M − BF_4)$^+$]. Anal. Calcd for $C_{14}H_{20}BF_4I$: C, 43.51; H, 4.87. Found: C, 43.15; H, 4.82.

Synthesis of Phenyl(2-butyl-1-hexenyl)iodonium Tetrafluoroborate (7). 2-Butyl-1-(trimethylsilyl)hex-1-ene was prepared from 1-hexyne by the reaction with lithium bis(trimethylsilyl)cuprate and 1-iodobutane in 64% yield.[15] To a stirred suspension of iodosylbenzene (3.65 g, 16.6 mmol) and the vinylsilane (2.2 g, 10 mmol) in dichloromethane (50 mL) was added dropwise BF_3-Et_2O (2.35 g, 16.6 mmol) at 0 °C in nitrogen, and the mixture was stirred for 0.25 h at 0 °C. After the addition of a saturated aqueous solution of sodium tetrafluoroborate (23 g, 0.21 mol), the mixture was stirred for 15 min. Extraction with dichloromethane, filtration, and then concentration under aspirator vacuum gave an oil, which was washed several times with hexane by decantation at −78 °C. Recrystallization from dichloromethane−diethyl ether gave the iodonium salt **7** (3.8 g, 86%) as colorless plates: mp 77−78 °C; IR (KBr) 3032, 2959, 2871, 1605, 1565, 1472, 1441, 1267, 1060 (br), 991, 739, 680, 649, 534 cm^{-1}; ^{1}H NMR δ 7.95 (d, J = 8.0 Hz, 2 H), 7.61 (t, J = 7.4 Hz, 1 H), 7.47 (dd, J = 8.0, 7.4 Hz, 2 H), 6.71 (s, 1 H), 2.54−2.33 (m, 4 H), 1.59−1.15 (m, 8 H), 0.99−0.76 (m, 6 H); FAB MS *m/z* 343 [(M − BF_4)$^+$]; HRFAB MS Calcd for $C_{16}H_{24}I$[(M − BF_4)$^+$] 343.0923. Found 343.0915. Anal. Calcd for $C_{16}H_{24}BF_4I$: C, 44.68; H, 5.62. Found: C, 44.28, H, 5.50.

Synthesis of (*E*)-Phenyl(2-methyl-3-phenyl-1-propenyl)iodonium Tetrafluoroborate (*E*)-(20). (*E*)-2-Methyl-3-phenyl-1-(trimethylsilyl)prop-1-ene was prepared stereoselectively from 3-phenyl-1-propyne by the reaction with lithium bis(trimethylsilyl)cuprate and methyl iodide in 72% yield according to the procedure developed by Fleming.[15] To a stirred suspension of iodosylbenzene (1.58 g, 7.20 mmol) and the vinylsilane (917 mg, 4.50 mmol) in dichloromethane (50 mL) was added dropwise BF_3-Et_2O (1.02 g, 7.20 mmol) at 0 °C in nitrogen and the mixture was stirred for 0.25 h at 0 °C. After the addition of a saturated aqueous solution of sodium tetrafluoroborate (9.9 g, 90 mmol), the mixture was stirred for 15 min. Extraction with dichloromethane, filtration, and then concentration under aspirator vacuum gave an oil, which was washed several times with hexane by decantation at −78 °C. Recrystallization from dichloromethane−diethyl ether gave the iodonium salt (***E***)-**20** (774 mg, 48%) as colorless prisms: mp 104−105 °C; IR (KBr) 3073, 1598, 1495, 1472, 1453, 1443, 1260, 1058 (br), 745, 704, 682 cm^{-1}; ^{1}H NMR δ 7.89 (d, J = 8.1 Hz, 2 H), 7.59 (t, J = 7.4 Hz, 1 H), 7.45 (dd, J = 8.1, 7.4 Hz, 2 H), 7.35−7.05 (m, 5 H), 6.80 (s, 1 H), 3.75 (s, 2 H), 2.11 (s, 3 H); FAB MS *m/z* 335 [(M − BF_4)$^+$]; HRFAB MS Calcd for $C_{16}H_{16}I$ [(M − BF_4)$^+$] 335.0297. Found 335.0319. Anal. Calcd for $C_{16}H_{16}BF_4I$: C, 45.54; H, 3.82. Found: C, 45.24; H, 3.83.

Synthesis of (*Z*)-Phenyl(2-methyl-3-phenyl-1-propenyl)iodonium Tetrafluoroborate (*Z*)-(20). (*Z*)-2-Methyl-3-phenyl-1-(trimethylsilyl)prop-1-ene was prepared stereoselectively from propyne by the reaction with lithium bis(trimethylsilyl)cuprate and benzyl bromide in 68% yield according to the procedure developed by Fleming.[15] To a stirred suspension of iodosylbenzene (3.57 g, 16.2 mmol) and the vinylsilane (2.07 g, 10.1 mmol) in dichloromethane (30 mL) was added dropwise BF_3-Et_2O (2.23 g, 16.2 mmol) at 0 °C in nitrogen, and the mixture was stirred for 0.5 h at 0 °C. After the addition of a saturated aqueous solution of sodium tetrafluoroborate (22.2 g, 203 mmol), the mixture was stirred for 15 min. Extraction with dichloromethane, filtration, and then concentration under aspirator vacuum gave an oil, which was washed several times with hexane by decantation at −78 °C. Recrystallization from dichloromethane−diethyl ether gave the iodonium salt (***Z***)-**20** (3.0 g, 70%) as colorless prisms: mp 91−92 °C; IR (KBr) 3092, 1596, 1495, 1471, 1445, 1261, 1050 (br), 752, 705, 651, 521 cm^{-1}; ^{1}H NMR δ 7.89 (d, J = 8.0 Hz, 2 H), 7.57 (t, J = 7.4 Hz, 1 H), 7.41 (dd, J = 8.0, 7.4 Hz, 2 H), 7.30−7.15 (m, 3 H), 7.07−6.93 (m, 2 H), 6.86 (s, 1 H), 3.80 (s, 2 H), 2.06 (s, 3 H); FAB MS *m/z* 335 [(M − BF_4)$^+$]; HRFAB MS Calcd for $C_{16}H_{16}I$ [(M − BF_4)$^+$] 335.0297. Found 335.0320. Anal. Calcd for $C_{16}H_{16}BF_4I$: C, 45.54; H, 3.82. Found: C, 45.32; H, 3.89.

Reaction of (*E*)-Phenyl(3-cyclopentyl-2-methyl-1-propenyl)iodonium Tetrafluoroborate (4) with Triethylamine. To a solution of the iodonium salt **4** (41 mg, 0.10 mmol) in 1 mL of THF was added triethylamine (12 mg, 0.12 mmol) at −78 °C under nitrogen, and the mixture was stirred for 5 h. The reaction mixture was gradually warmed to 0 °C over 4 h and stirred for another 10 h at the temperature. After addition of 1 mL of water and 2 mL of dichloromethane to the mixture, analytical GC using a column of 20% Silicone GE SF-96 (3 m, 100 °C) with nonane as an internal standard showed the formation of the bicyclo[3.3.0]octene **5** in 39% yield. Extraction with dichloromethane, filtration, and then concentration under aspirator vacuum gave an oil, which was washed several times with pentane by decantation to give the triethylammonium vinyl ether **6**, contaminated with a small amount of impurity (ca. 4%). ^{1}H NMR spectra with nitrobenzene as an internal standard showed formation of **6** in 43% yield. A pure sample of **6** (*E*:*Z* = 7:3) was obtained by preparative TLC (dichloromethane−methanol 9:1). (*E*)- and (*Z*)-**6**: pale yellow oil; IR (film) 2920, 2840, 1705, 1670, 1460, 1390, 1160, 1130−930, 790 cm^{-1}; ^{1}H NMR δ 5.80 (br s, C=C**H**, *Z*-isomer), 5.78 (br s, C=C**H**, *E*-isomer), 3.74 (t, J = 5.6 Hz, OC**H$_2$**, *E*-isomer), 3.70 (t, J = 5.7 Hz, OC**H$_2$**, *Z*-isomer), 3.31 (q, J = 7.1 Hz, N(C**H$_2$**CH$_3$)$_3$, *E*-isomer), 3.31 (q, J = 7.1 Hz, N(C**H$_2$**CH$_3$)$_3$, Z-isomer), 3.26−3.18 (m, 2 H), 2.02 (d, J = 7.7 Hz, CC**H$_2$**, *Z*-isomer), 1.94 (septet, J = 7.7 Hz, 1 H, C**H**CH$_2$), 1.85−1.45 (m, NC**H$_2$**CH$_2$, 8 H), 1.82 (d, J = 7.7 Hz, CC**H$_2$**, *E*-isomer), 1.56 (br s, CC**H$_3$**, *E*-isomer), 1.52 (br s, CC**H$_3$**, *Z*-isomer), 1.33 (t, J = 7.1 Hz, 9 H, (CH$_2$**CH$_3$**)$_3$), 1.2−1.0 (m, 2 H); FAB MS *m/z* 296 [(M − BF_4)$^+$].

HRFAB MS Calcd for $C_{19}H_{38}ON$ $[(M - BF_4)^+]$ 296.2953. Found 296.2959. ^{1}H NMR signals of (*E*)- and (*Z*)-**6** were assigned by ^{1}H,^{1}H- and ^{13}C,^{1}H-COSY spectra. The stereochemistry of (*E*)-**6** was established by the observation of a nuclear Overhauser effect (NOE) enhancement between the vinylic proton and the allylic methylene protons. The stereochemistry of (*Z*)-**6** was established by the observation of an NOE enhancement between the vinylic proton and the allylic methyl group. A pure sample of **5** was obtained by preparative GC using a column of 20% Silicone GE SF-96 (3 m, 70 °C) in a separate experiment. **5**: colorless oil; IR (film) 2930, 2855, 1598, 1443, 1373 cm^{-1}; ^{1}H NMR δ 5.06 (m, 1 H), 3.09 (m, 1 H), 2.90−2.30 (m, 2 H), 2.10−1.20 (7 H), 1.67 (m, 3 H); MS *m/z* (relative intensity) 122 (59, M^+), 107 (22), 94 (78), 93 (100), 91 (25), 80 (33), 79 (47), 77 (23), 67 (11); HRMS Calcd for $C_9H_{14}(M^+)$ 122.1096. Found 122.1096.

General Procedure for the Reaction of Phenyl(2-butyl-1-hexenyl)iodonium Tetrafluoroborate (7) with Triethylamine in THF. To a solution of the iodonium salt **7** (43 mg, 0.10 mmol) in 1 mL of THF was added triethylamine (12 mg, 0.12 mmol) under nitrogen. The mixture was stirred under the conditions described in Table 1. After addition of 1 mL of water and 2 mL of dichloromethane, the reaction mixture was analyzed by GC using a column of 15% FFAP (3 m, 70 °C) with undecane as an internal standard, which showed the formation of 1-butyl-3-methylcyclopentene (**8**) and 5-decyne (**9**). The yields of **8** and **9** are reported in Table 1. Extraction with dichloromethane, filtration, and then concentration under aspirator vacuum gave an oil, which was washed several times with pentane by decantation to give a mixture of the vinylammonium salt **10** and the triethylammonium vinyl ether **11**. The yields of **10** and **11** were determined by ^{1}H NMR analyses of the mixture with nitrobenzene as an internal standard and are reported in Table 1. Pure samples of the cyclopentene **8** and the alkyne **9** were obtained by preparative GC using a column of 15% FFAP (3 m, 70 °C) in a separate experiment. **8**:[19d] colorless oil; IR ($CHCl_3$) 2950, 2920, 2850, 1600, 1455, 910 cm^{-1}; ^{1}H NMR δ 5.25−5.16 (m, 1 H), 2.80−2.59 (m, 1 H), 2.30−1.90 (m, 5 H), 1.50−1.16 (m, 5 H), 0.98 (d, *J* = 6.8 Hz, 3 H), 0.90 (t, *J* = 6.8 Hz, 3 H); MS *m/z* (relative intensity) 138 (33, M^+), 123 (30), 81 (100), 67 (76), 55 (34). **9**:[35] colorless oil; IR ($CHCl_3$) 2950, 2915, 2850, 1660, 1600, 1457, 1370, 910 cm^{-1}; ^{1}H NMR δ 2.20−2.07 (m, 4 H), 1.59−1.23 (m, 8 H), 0.90 (t, *J* = 6.9 Hz, 6 H); ^{13}C NMR δ 140.16, 119.34, 70.22, 56.91, 53.13, 31.10, 30.45, 29.98, 26.67, 26.23, 22.75, 22.44, 18.78, 13.98, 7.53; MS *m/z* (relative intensity) 138 (17, M^+), 123 (14), 81 (100), 67 (73), 54 (13). A pure sample of the triethylammonium vinyl ether **11** was obtained by preparative TLC (dichloromethane−methanol 9:1). **11**: pale yellow powder; IR (KBr) 2957, 2946, 2889, 2863, 1674, 1467, 1100 (br), 798 cm^{-1}; ^{1}H NMR δ 5.78 (s, 1 H), 3.72 (t, *J* = 5.3 Hz, 2 H), 3.39−3.11 (m, 8 H), 2.01 (t, *J* = 7.1 Hz, 2 H), 1.85 (t, *J* = 7.4 Hz, 2 H), 1.79−1.48 (m, 4 H), 1.43−1.15 (m, 17 H), 0.89 (t, *J* = 6.6 Hz, 6 H); FAB MS *m/z* 312 $[(M - BF_4)^+]$; HRFAB MS Calcd for $C_{20}H_{42}NO$ $[(M - BF_4)^+]$ 312.3266. Found 312.3289.

To obtain a pure sample of the vinylammonium salt **10**, reaction of the iodonium salt **7** (215 mg, 0.50 mmol) with triethylamine (1.0 g, 10 mmol) was carried out in dichloromethane (5 mL) at 25 °C for 9 h under nitrogen. Preparative TLC (dichloromethane−methanol 9:1) gave **10** (3 mg, 2%) as a pale yellow oil: IR (film) 2925, 1450, 1380, 1060 (br) cm^{-1}; ^{1}H NMR δ 5.39 (br s, 1 H), 3.59 (q, *J* = 7.2 Hz, 6 H), 2.39−2.11 (m, 4 H), 1.80−1.18 (m, 17 H), 1.06−0.79 (m, 6 H); FAB MS *m/z* 240 $[(M - BF_4)^+]$; HRFAB MS Calcd for $C_{16}H_{34}N$ $[(M - BF_4)^+]$ 240.2691. Found 240.2706.

General Procedure for the Reaction of Phenyl(2-methyl-1-propenyl)iodonium Tetrafluoroborate (12) with Base in THF. To a solution of the iodonium salt **12** (35 mg, 0.10 mmol) in 1 mL of THF was added a base (0.12 or 2.0 mmol) under nitrogen. The mixture was stirred under the conditions described in Table 2. The organic solvent was evaporated off in vacuo to give an oil, which was washed several times with hexane by decantation to give a mixture of the vinylammonium salt **13** and the vinyl ether **14**. The yields of **13** and **14** were determined by ^{1}H NMR analyses of the mixture with dichloromethane as an internal standard and are reported in Table 2. Pure samples of the vinylammonium salt **13** and the vinyl ether **14** were obtained by preparative TLC (dichloromethane−methanol 8:2).

13a: colorless plates: mp 250−254 °C (recrystallized from dichloromethane−diethyl ether−hexane); IR (KBr) 2990, 1461, 1403, 1070 (br), 792, 522 cm^{-1}; ^{1}H NMR δ 5.54 (br s, 1 H), 3.56 (q, *J* = 7.6 Hz, 6 H), 1.99 (s, 3 H), 1.92 (s, 3 H), 1.34 (t, *J* = 7.6 Hz, 9 H); MS *m/z* (relative intensity) 156 [7, $(M - BF_4)^+$], 127 (41), 112 (100), 98 (21), 56(81); FAB MS *m/z* 156 $[(M - BF_4)^+]$; HRMS Calcd for $C_{10}H_{22}N$ $[(M - BF_4)^+]$ 156.1753. Found 156.1762. Anal. Calcd for $C_{10}H_{22}BF_4N$: C, 49.41; H, 9.12; N, 5.76. Found: C, 49.26; H, 9.11; N, 5.59.

14a: oil; IR (film) 2905, 1685, 1480, 1400, 1090 (br), 795 cm^{-1}; ^{1}H NMR δ 5.78 (br s, 1 H), 3.79−3.61 (m, 2 H), 3.38−3.10 (8 H), 1.88−1.47 (10 H), 1.33 (t, *J* = 6.6 Hz, 9 H); ^{13}C NMR δ 139.72, 110.84, 70.09, 56.67, 52.95, 26.12, 19.45, 18.51, 15.07, 7.37; MS *m/z* (relative intensity) 228 [5, $(M - BF_4)^+$], 128 (9), 101 (9), 86 (100), 72 (20), 55 (19); FAB MS *m/z* 228 $[(M - BF_4)^+]$; HRMS Calcd for $C_{14}H_{30}NO$ $[(M - BF_4)^+]$ 228.2326. Found 228.2333.

13b: colorless crystals; mp 97−98 °C (recrystallized from dichloromethane−diethyl ether−hexane); IR (Nujol) 2900, 1635, 1560, 1435, 1390, 1180, 1030 (br), 820 cm^{-1}; ^{1}H NMR δ 7.84 (d, *J* = 7.8 Hz, 2 H), 6.98 (d, *J* = 7.8 Hz, 2 H), 6.64 (br s, 1 H), 3.29 (s, 6 H), 1.91 (d, *J* = 1.5 Hz, 3 H), 1.70 (d, *J* = 1.2 Hz, 3 H); FAB MS *m/z* 177 $[(M - BF_4)^+]$; HRMS Calcd for $C_{11}H_{17}N_2$ $[(M - BF_4)^+]$ 177.1391. Found 177.1379.

14b: yellow oil; IR (film) 3080, 2920, 2870, 1690, 1655, 1575, 1440, 1405, 1170, 1060 (br), 830 cm^{-1}; ^{1}H NMR δ 8.07 (d, *J* = 7.8 Hz, 2 H), 6.90 (d, *J* = 7.8 Hz, 2 H), 5.76 (br s, 1 H), 4.20 (t, *J* = 7.8 Hz, 2 H), 3.68 (t, *J* = 6.0 Hz, 2 H), 3.24 (s, 6 H), 2.11−1.83 (m, 2 H), 1.72−1.37 (m, 2 H), 1.57 (d, *J* = 0.7 Hz, 3 H), 1.52 (d, *J* = 1.0 Hz, 3 H); ^{13}C NMR δ 156.37, 141.89, 139.84, 110.76, 108.17, 70.68, 57.96, 40.17, 27.92, 26.04, 19.46, 15.10; FAB MS *m/z* 249 $[(M - BF_4)^+]$; HRMS Calcd for $C_{15}H_{25}N_2O$ $[(M - BF_4)^+]$ 249.1967. Found 249.1970.

13c: orange oil; IR (film) 2950, 1660, 1525, 1440, 1380, 1310, 1060 (br), 810 cm^{-1}; ^{1}H NMR δ 6.03 (br s, 1 H), 3.85 (t, *J* = 7.6 Hz, 2 H), 3.57−3.39 (m, 4 H), 2.86 (t, *J* = 7.9 Hz, 2 H), 2.30−2.05 (m, 4 H), 1.76 (d, *J* = 1.2 Hz, 3 H), 1.72 (d, *J* = 1.2 Hz, 3 H); ^{13}C NMR δ 165.71, 139.02, 123.13, 54.71, 46.89, 42.28, 31.11, 21.64, 19.04, 18.02, 17.57; MS *m/z* (relative intensity) 179 [100, $(M - BF_4)^+$], 177 (90), 163 (62), 149 (61), 135 (55), 109 (65), 55 (83); HRMS Calcd for $C_{11}H_{19}N_2$ $[(M - BF_4)^+]$ 179.1549. Found 179.1550.

14c: orange oil; IR (film) 2915, 1665, 1440, 1310, 1060 (br), 1055 cm^{-1}; ^{1}H NMR δ 5.77 (sept, *J* = 1.5 Hz, 1 H), 3.78 (t, *J* = 7.3 Hz, 2 H), 3.69 (t, *J* = 6.1 Hz, 2 H), 3.54−3.35 (m, 6 H), 3.02 (t, *J* = 7.9 Hz, 2 H), 2.32−2.07 (m, 4 H), 1.88−1.48 (m, 4 H), 1.59 (br s, 3 H), 1.54 (br s, 3 H); ^{13}C NMR δ 164.69, 139.84, 110.84, 70.73, 54.31, 53.04, 44.26, 42.25, 30.37, 26.51, 24.20, 19.47, 18.91, 18.12, 15.05; FAB MS *m/z* 251 $[(M - BF_4)^+]$; HRFAB MS Calcd for $C_{15}H_{27}N_2O$ $[(M - BF_4)^+]$ 251.2123. Found 251.2092.

13d: orange oil; IR (film) 2920, 2850, 1620, 1510, 1445, 1320, 1200, 1060 (br), 820 cm^{-1}; ^{1}H NMR δ 6.05 (br s, 1 H), 3.74−3.60 (m, 4 H), 3.51 (t, *J* = 5.9 Hz, 2 H), 2.90−2.77 (m, 2 H), 2.26−2.11 (m, 2 H), 1.94−1.54 (m, 6 H), 1.79 (d, *J* = 1.2 Hz, 3 H), 1.69 (d, *J* = 1.2 Hz, 3 H); ^{13}C NMR δ 167.28, 138.99, 124.10, 55.61, 49.15, 47.69, 29.85, 28.83, 25.97, 22.83, 21.59, 19.78, 17.57; FAB MS *m/z* 207 $[(M - BF_4)^+]$; HRFAB MS Calcd for $C_{13}H_{23}N_2$ $[(M - BF_4)^+]$ 207.1861. Found 207.1871.

14d: orange oil; IR (film) 2970, 2900, 1700, 1623, 1540, 1450, 1340, 1170, 1060 (br) cm^{-1}; ^{1}H NMR δ 5.78 (m, 1 H), 3.80−3.46 (m, 10 H), 2.91−2.75 (m, 2 H), 2.22−2.04 (m, 2 H), 1.90−1.40 (m, 10 H), 1.58 (br s, 3 H), 1.53 (br s, 3 H); ^{13}C NMR δ 166.62, 139.87, 110.72, 70.71, 55.26, 53.78, 49.12, 47.02, 28.65, 28.30, 26.44, 25.99, 25.41, 22.99, 20.03, 19.47, 15.05; FAB MS *m/z* 279 $[(M - BF_4)^+]$; HRMS Calcd for $C_{17}H_{31}N_2O$ $[(M - BF_4)^+]$ 279.2436. Found 279.2407.

Reaction of (2-Methyl-1-propenyl)triethylammonium Tetrafluoroborate (13a) with DBN in THF. Vinylammonium salt **13a** (19 mg, 0.08 mmol) was treated with DBN (10 mg, 0.08 mmol) and iodobenzene (16 mg, 0.08 mmol) in 1.5 mL of THF at room temperature for 2 days under nitrogen. Extraction with dichloromethane and decantation with hexane recovered the vinylammonium salt **13a** (16 mg, 87%). Formation of the vinylammonium salt **13c** and the vinyl ether **14c** was not detected by ^{1}H NMR analyses of the crude reaction mixture.

Reaction of (2-Methyl-1-propenyl)triethylammonium Tetrafluoroborate (13a) with Triethylamine in THF. Vinylammonium salt **13a** (38 mg, 0.16 mmol) was treated with triethylamine (16 mg, 0.16 mmol) and iodobenzene (33 mg, 0.16 mmol) in 3 mL of THF at room temperature for 2 days under nitrogen. Extraction with dichloromethane and decantation with hexane recovered the vinylammonium salt **13a**

(35 mg, 93%). Formation of the vinyl ether **14a** was not detected by ^{1}H NMR analyses of the crude reaction mixture.

Reaction of 2-Methyl-1-propenyl Ether 14a with DBN in THF. Vinyl ether **14a** (8.1 mg, 0.026 mmol) was treated with DBN (3.7 mg, 0.03 mmol) in 0.3 mL of THF at room temperature for 2 days under nitrogen. Extraction with dichloromethane and decantation with hexane recovered the vinyl ether **14a** (6.5 mg, 80%). Formation of the vinylammonium salt **13c** and the vinyl ether **14c** was not detected by ^{1}H NMR analyses of the crude reaction mixture.

Reaction of 2-Methyl-1-propenyl Ether 14a with Triethylamine in THF. Vinyl ether **14a** (10 mg, 0.03 mmol) was treated with triethylamine (3 mg, 0.03 mmol) and iodobenzene (6 mg, 0.03 mmol) in 0.3 mL of THF at room temperature for 2 days under nitrogen. Extraction with dichloromethane and decantation with hexane recovered the vinyl ether **14a** (9.7 mg, 95%). Formation of the vinylammonium salt **13a** was not detected by ^{1}H NMR analyses of the crude reaction mixture.

Reaction of Phenyl(2-butyl-1-hexenyl)iodonium Tetrafluoroborate (7) with Triethylamine in THT. To a solution of the iodonium salt **7** (43 mg, 0.10 mmol) in 1 mL of THT was added triethylamine (12 mg, 0.12 mmol) at room temperature under nitrogen and the mixture was stirred for 10 h. After addition of 1 mL of water and 2 mL of dichloromethane, the reaction mixture was analyzed by GC using a column of 15% FFAP (3 m, 70 °C). Formation of 1-butyl-3-methylcyclopentene (**8**) and 5-decyne (**9**) was not detected. Extraction with dichloromethane, filtration, and then concentration under aspirator vacuum gave an oil, which was washed several times with hexane by decantation to give a mixture of the vinylsulfonium salt **18** (R = Bu; 87%) and the triethylammonium vinyl sulfide **19a** (R = Bu; 7%). The yields of **18** and **19a** were determined by ^{1}H NMR analyses. A pure sample of **18** was obtained by preparative TLC (dichloromethane−methanol 9:1). **18** (R = Bu): pale yellow oil; IR (film) 2950, 2860, 1610, 1460, 1380, 1280, 1060 (br), 880 cm^{-1}; ^{1}H NMR δ 6.00 (s, 1 H), 3.93−3.70 (m, 2 H), 3.41−3.20 (m, 2 H), 2.66−2.20 (m, 8 H), 1.57−1.20 (m, 8 H), 0.95 (t, J = 6.7 Hz, 3 H), 0.92 (t, J = 6.7 Hz, 3 H); FAB MS *m/z* 227 [(M − BF$_4$)$^+$]; HRFAB MS Calcd for $C_{14}H_{27}S$ [(M − BF$_4$)$^+$] 227.1833. Found 227.1844. A pure sample of **19a** (R = Bu) was obtained by the reaction of **18** (R = Bu) with triethylamine in dichloromethane at 50 °C for 3 days. **19a** (R = Bu): colorless crystals; mp 99−101 °C (recrystallized from dichloromethane−hexane); IR (KBr) 2965, 2928, 2872, 2851, 1621, 1461, 1397, 1301, 1060 (br), 803, 535, 523 cm^{-1}; ^{1}H NMR δ 5.55 (s, 1 H), 3.30 (q, J = 7.2 Hz, 6 H), 3.23−3.10 (m, 2 H), 2.70 (t, J = 6.1 Hz, 2 H), 2.18−1.96 (m, 4 H), 1.85−1.63 (m, 4 H), 1.45−1.20 (m, 17 H), 0.97−0.84 (m, 6 H); FAB MS *m/z* 328 [(M − BF$_4$)$^+$]; HRFAB MS Calcd for $C_{20}H_{42}NS$ [(M − BF$_4$)$^+$] 328.3038. Found 328.3054. Anal. Calcd for $C_{20}H_{42}BF_4NS\cdot 1/2\ H_2O$: C, 56.59; H, 10.21; N, 3.30. Found: C, 56.96; H, 10.15; N, 3.20.

Reaction of Phenyl(2-butyl-1-hexenyl)iodonium Tetrafluoroborate (7) with Diisopropylethylamine in THT and Methanol-*d*$_4$. Iodonium salt **7** (43 mg, 0.10 mmol) was treated with diisopropylethylamine (16 mg, 0.12 mmol) in 0.5 mL of THT and 1.5 mL of methanol-*d*$_4$ at room temperature for 0.5 h under nitrogen. The reaction gave the vinylsulfonium salt **18** (R = Bu; 88%), in which 61% deuterium incorporation at the α-vinylic position was observed by ^{1}H NMR.

No deuterium incorporation at the α-vinylic position of **18** (R = Bu) was observed in the reaction with diisopropylethylamine in THT and methanol-*d*$_4$ (1:3) at room temperature for 0.5 h under nitrogen.

General Procedure for the Reaction of Phenyl(2-methyl-1-propenyl)iodonium Tetrafluoroborate (12) with Base in THT. To a solution of the iodonium salt **12** (35 mg, 0.10 mmol) in 1 mL of THT was added a base (0.12 mmol) under nitrogen. The mixture was stirred under the conditions described in Table 3. The organic solvent was evaporated off in vacuo to give an oil, which was washed several times with hexane by decantation to give the vinylsulfonium salt **18** (R = Me) and the vinyl sulfide **19** (R = Me). The yields of **18** and **19** (R = Me) were determined by ^{1}H NMR analyses of the mixture with dichloromethane as an internal standard and are reported in Table 3. Pure samples of **18** and **19** (R = Me) were obtained by preparative TLC (dichloromethane−methanol 85:15).

18 (R = Me): colorless crystal; mp 59−62 °C (recrystallized from dichloromethane−ethyl acetate); IR (KBr) 2944, 1630, 1441, 1306, 1060 (br), 540, 523 cm^{-1}; ^{1}H NMR δ 6.03 (s, 1 H), 3.88−3.67 (m, 2 H), 3.44−3.23 (m, 2 H), 2.61−2.23 (m, 4 H), 2.14 (s, 3 H), 2.05 (s, 3 H); ^{13}C NMR δ 160.83, 109.53, 47.38, 28.72, 25.95, 21.21; FAB MS *m/z* 143 [(M − BF$_4$)$^+$]; HRFAB MS Calcd for $C_8H_{15}S$ [(M − BF$_4$)$^+$] 143.0894. Found 143.0896. Anal. Calcd for $C_8H_{15}BF_4S$: C, 41.76; H, 6.57. Found: C, 41.93; H, 6.45.

19a (R = Me): pale yellow oil; IR: (film) 2900, 1625, 1480, 1450, 1395, 1370, 1280, 1170, 1060 (br), 855, 800 cm^{-1}; ^{1}H NMR δ 5.57 (s, 1 H), 3.31 (q, J = 7.3 Hz, 6 H), 3.24−3.11 (m, 2 H), 2.69 (t, J = 6.4 Hz, 2 H), 1.90−1.56 (m, 4 H), 1.78 (s, 3 H), 1.73 (s, 3 H), 1.34 (t, J = 7.0 Hz, 9 H); FAB MS *m/z* 244 [(M − BF$_4$)$^+$]; HRFAB MS Calcd for $C_{14}H_{30}NS$ [(M − BF$_4$)$^+$] 244.2099. Found 244.2101.

19b (R = Me): pale yellow oil; IR (film) 2910, 1715, 1650, 1570, 1440, 1405, 1280, 1235, 1180, 1060 (br), 830 cm^{-1}; ^{1}H NMR δ 8.06 (d, J = 7.7 Hz, 2 H), 6.89 (d, J = 7.7 Hz, 2 H), 5.56 (s, 1 H), 4.18 (t, J = 7.3 Hz, 2 H), 3.24 (s, 6 H), 2.63 (t, J = 6.8 Hz, 2 H), 2.11−1.49 (m, 4 H), 1.76 (s, 3 H), 1.71 (s, 3 H); ^{13}C NMR δ 156.38, 141.89, 135.11, 117.33, 108.20, 57.86, 40.22, 33.10, 29.67, 26.37, 25.22, 19.66; FAB MS *m/z* 265 [(M − BF$_4$)$^+$]; HRFAB MS Calcd for $C_{15}H_{25}N_2S$ [(M − BF$_4$)$^+$] 265.1738. Found 265.1767.

Reaction of (*E*)-Phenyl(2-methyl-3-phenyl-1-propenyl)iodonium Tetrafluoroborate (*E*)-(20) with Diisopropylethylamine in THT. To a solution of the iodonium salt (*E*)-**20** (42 mg, 0.10 mmol) in 3 mL of THT was added diisopropylethylamine (16 mg, 0.12 mmol) at room temperature under nitrogen, and the mixture was stirred for 3 h. After addition of 1 mL of water, extraction with dichloromethane, filtration, and then concentration under aspirator vacuum gave an oil, which was washed several times with hexane by decantation to give a mixture of stereoisomers of the vinylsulfonium salt **21** (19.3 mg, 63%). The *E:Z* ratio of **21** was determined to be 62:38 by ^{1}H NMR analyses. (*E*)- and (*Z*)-**21**: IR (film) 3043, 3013, 2943, 2913, 1623, 1594, 1493, 1448, 1428, 1378, 1288, 1060 (br), 743, 703 cm^{-1}; ^{1}H NMR δ 7.43−7.05 (m, 5 H), 6.18 (s, C=C**H**, Z-isomer), 6.09 (s, C=C**H**, *E*-isomer), 3.95−3.68 (m, 2 H), 3.79 (s, PhC**H$_2$**, Z-isomer), 3.57 (s, PhC**H$_2$**, *E*-isomer), 3.45−3.22 (m, 2 H), 2.63−2.21 (m, 4 H), 2.04 (s, **Me**, *E*-isomer), 1.99 (s, **Me**, *Z*-isomer); FAB MS *m/z* 219 [(M − BF$_4$)$^+$]; HRFAB MS Calcd for $C_{14}H_{19}S$ [(M − BF$_4$)$^+$] 219.1207. Found 219.1214. The stereochemistry of (*E*)-**21** was established by the observation of an NOE enhancement between the vinylic and benzylic protons. The stereochemistry of (*Z*)-**21** was established by the observation of an NOE enhancement between the vinylic proton and the methyl group.

Reaction of (*Z*)-Phenyl(2-methyl-3-phenyl-1-propenyl)iodonium Tetrafluoroborate (*Z*)-(20) with Diisopropylethylamine in THT. Iodonium salt (*Z*)-**20** (42 mg, 0.10 mmol) was treated with diisopropylethylamine (16 mg, 0.12 mmol) in 3 mL of THT at room temperature for 3 h under nitrogen. Extraction with dichloromethane and decantation with hexane gave a mixture of (*E*)- and (*Z*)-**21** (17.3 mg, 56%) in a ratio 64:36.

Reaction of (*E*)-Phenyl(2-methyl-3-phenyl-1-propenyl)iodonium Tetrafluoroborate (*E*)-(20) with Diisopropylethylamine and Diphenyl Sulfide. To a solution of the iodonium salt (*E*)-**20** (42 mg, 0.10 mmol) and diphenyl sulfide (22 mg, 0.12 mmol) in 1 mL of dichloromethane was added diisopropylethylamine (16 mg, 0.12 mmol) at room temperature under nitrogen, and the mixture was stirred for 0.5 h. After addition of 1 mL of water, extraction with dichloromethane, filtration, and then concentration under aspirator vacuum gave an oil, which was washed several times with hexane by decantation to give a mixture of stereoisomers of the vinylsulfonium salt **22** (20.3 mg, 50%). The *E:Z* ratio of **22** was determined to be 69:31 by ^{1}H NMR analyses. A pure sample of (*E*)- and (*Z*)-**22** was obtained by fractional recrystallization from dichloromethane−diethyl ether−hexane. (*E*)-**22**: colorless plates; mp 195−197 °C; IR (KBr) 3060, 1620, 1479, 1445, 1387, 1055 (br), 757, 742, 710, 681, 469 cm^{-1}; ^{1}H NMR (CD_3CN) δ 7.85−7.63 (m, 10 H), 7.45−7.20 (m, 5 H), 6.62 (s, 1 H), 3.76 (s, 2 H), 2.16 (s, 3 H); FAB MS *m/z* 317 [(M − BF$_4$)$^+$]; HRFAB MS Calcd for $C_{22}H_{21}S$ [(M − BF$_4$)$^+$] 317.1364. Found 317.1357. Anal. Calcd for $C_{22}H_{21}BF_4S$: C, 65.36; H, 5.24. Found: C, 64.94; H, 5.22. The stereochemistry of (*E*)-**22** was established by the observation of an NOE enhancement between the vinylic and benzylic protons. (*Z*)-**22**: colorless solid; IR (KBr) 3060, 1620, 1600, 1580, 1479, 1445, 1387, 1289, 1073, 757, 742, 710, 681 cm^{-1}; ^{1}H NMR δ 7.94−7.78 (m, 4 H), 7.77−7.58 (m, 6 H), 7.36−7.18 (m, 3 H), 7.13−7.00 (m, 3 H), 3.95 (s, 2 H), 2.25 (d, J = 0.9 Hz, 3 H); FAB MS *m/z* 317 [(M − BF$_4$)$^+$]; HRFAB MS Calcd for $C_{22}H_{21}S$ [(M − BF$_4$)$^+$] 317.1364. Found

317.1350. The stereochemistry of (*Z*)-**22** was established by the observation of an NOE enhancement between the vinylic proton and the methyl group.

Reaction of (*Z*)-Phenyl(2-methyl-3-phenyl-1-propenyl)iodonium Tetrafluoroborate (*Z*)-(20) with Diisopropylethylamine and Diphenyl Sulfide. Iodonium salt (*Z*)-**20** (42 mg, 0.10 mmol) was treated with diisopropylethylamine (16 mg, 0.12 mmol) and diphenyl sulfide (22 mg, 0.12 mmol) in 1 mL of dichloromethane at room temperature for 0.5 h under nitrogen. Extraction with dichloromethane and decantation with hexane gave a mixture of (*E*)- and (*Z*)-**22** (22.1 mg, 55%) in a ratio 71:29.

MNDO Calculations. MNDO calculations were carried out using the MOPAC 93 program.[34] THF, trimethylamine, and THT were used as model nucleophiles for the calculations. Energy calculations were performed with the PM3 Hamiltonian, and the stable and transient structures were initially built with the general parameters of bond lengths, bond angles, and dihedral angles, and refined with the eigenvector following (EF) optimization method. Their reaction coordinates were defined by the distance (Å) of the atomic centers between carbene and the heteroatoms of THF, trimethylamine, and THT.

JA961797Q