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Reactions of 1,1-Dihaloalkenes with Triorganozincates: A Novel Method for the Preparation of Alkenylzinc Species Associated with Carbon–Carbon Bond Formation

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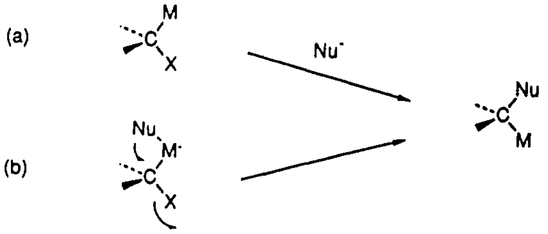
Lithium trialkylzincates react with 1,1-dibromoalkenes **1** and 1-bromo-1-chloroalkenes **2** at −85 °C in THF to give 1-bromoalkenes **5** and 1-chloroalkenes **7**, respectively, upon hydrolysis. The intermediate (1-haloalkenyl)zincates **4** and **6** are stable at low temperature but, when allowed to warm to 0 °C, they undergo a 1,2-alkyl migration reaction to afford alkenylzinc species **10**. A variety of alkylation products **11** are obtained by the hydrolysis of **10**. In the presence of (Ph$_3$P)$_2$Pd (5 mol%), alkenylzinc species **10** react smoothly with organic halides (AcCl, EtOCOCl, CH$_2$=CH-(Me)Br, PhBr) to yield the corresponding coupling products **13–16**.

Introduction

α-Haloorganometallic compounds (so-called carbenoids) are versatile reagents that possess ambiphilic reactivity.[1] Although many useful reactions utilizing carbenoids as equivalents of α-halo carbanions (XCH$_2^-$)[2] have been developed, the synthetic potentiality of carbenoids as equivalents of α-metalated carbocations (MCH$_2^+$) has not been fully elucidated.[3]

As depicted in Scheme Ia, substitution reactions of carbenoids with carbon nucleophiles can be utilized for generating homologated organometallics. Recently, Walborsky and co-workers elegantly demonstrated that (1-bromoalkenyl)lithiums undergo nucleophilic substitution with ^{t}BuLi with partial inversion of stereochemistry at the carbenoid carbon.[4] Unfortunately, however, the practical use of the reaction for generation of alkenyllithiums is restricted by several competing side reactions as well as the thermal instability of the lithium carbenoid.[5] Substitution of an ate-type carbenoid bearing a nucleophilic ligand at the negatively charged metal atom can proceed effectively in an intramolecular manner (Scheme Ib). Indeed, tetracoordinate borate salts bearing a leaving group α to the boron atom are known to undergo an intramolecular displacement or a 1,2-migration to afford homologated organoboron compounds.[6] Although such 1,2-migration reactions are well-known as one of the most fundamental carbon–carbon bond-forming reactions of organoboron compounds, little attention has been focused on the 1,2-migration reactions of ate-type carbenoids involving main group metals other than boron.[7]

Scheme I



Organozinc compounds that can undergo efficient and highly selective carbon–carbon bond formation are becoming increasingly important as intermediates in synthetic organic chemistry.[8,9] Due to their versatility, considerable effort has been devoted, especially in recent years, to the preparation of organozinc compounds.[8e,10] The present study was undertaken to develop a new method for the preparation of alkenylzinc compounds by means of the 1,2-migration reactions of zincate carbenoids (Scheme II). The investigation was also devoted to developing a method for generating the hitherto unknown

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(8) (a) Negishi, E.; Okukado, N.; King, A. O.; Van Horn, D. E.; Spiegel, B. I. *J. Am. Chem. Soc.* **1978**, *100*, 2254. (b) Sato, T.; Naruse, K.; Enokiya, M.; Fujisawa, T. *Chem. Lett.* **1981**, 1135. (c) Negishi, E.; Miller, J. A. *J. Am. Chem. Soc.* **1983**, *105*, 6761. (d) Hayashi, T.; Konishi, M.; Kobori, Y.; Kumada, M.; Higuchi, T.; Hirotsu, K. *J. Am. Chem. Soc.* **1984**, *106*, 158. (e) Tamaru, Y.; Ochiai, H.; Nakamura, T.; Tsubaki, K.; Yoshida, Z. *Tetrahedron Lett.* **1985**, *26*, 5559.

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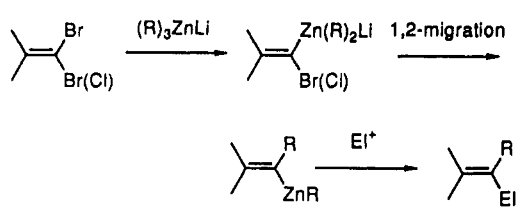
(10) (a) Nakamura, E.; Sekiya, K.; Kuwajima, I. *Tetrahedron Lett.* **1987**, *28*, 337. (b) Yeh, M. C. P.; Knochel, P. *Tetrahedron Lett.* **1988**, *29*, 2395. (c) AchyuthaRao, S.; Knochel, P. *J. Org. Chem.* **1991**, *56*, 4591. (d) Rao, C. J.; Knochel, P. *J. Org. Chem.* **1991**, *56*, 4593. (e) Srebnik, M. *Tetrahedron Lett.* **1991**, *22*, 2449. (f) Rozema, M. J.; Sidduri, A.; Knochel, P. *J. Org. Chem.* **1992**, *1992*, 1956. (g) Waas, J. R.; Sidduri, A.; Knochel, P. *Tetrahedron Lett.* **1992**, *33*, 3717.

0022-3263/93/1958-4897$04.00/0

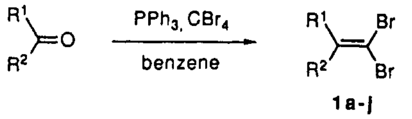
Scheme II



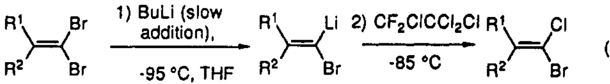
zincate carbenoids by means of bromine/zinc exchange reactions of 1,1-dihaloalkenes.[11]

Results and Discussion

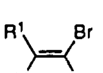
Preparation of 1,1-Dihaloalkenes. Dibromoalkenes **1a-j** were prepared by Wittig reaction[12] of the corresponding carbonyl compounds (eq 1). Bromochloroalkenes **2a-d** were prepared by chlorination of (1-bromoalkenyl)lithiums **3**, generated stereoselectively from the corresponding dibromoalkenes under thermodynamic conditions (eq 2). Thus, slow addition of BuLi to THF solutions of the dibromoalkenes at −95 °C followed by chlorination of the resulting carbenoids gave **2a-d** of high geometrical purities. The method is based on the recent finding by Braun[13] and by our group[14] that, in the presence of the starting dibromoalkene, (1-bromoalkenyl)lithium **3** undergoes a rapid geometrical isomerization by a mechanism involving Br/Li exchange with **1**. During slow addition of BuLi, a rapid equilibrium is established between isomeric (bromoalkenyl)lithiums to give stereoselectively **3**, the thermodynamically favorable isomer.



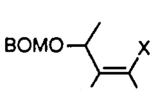
1a-j (1)



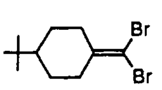
1f,h,i,j 3 2a-d (2)



1a-e

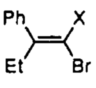


1f; X = Br
2a; X = Cl
(E:Z = >40:1)
(BOM = PhCH2OCH2-)

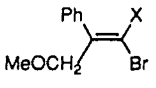


1g

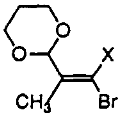
a; R1 = PhCH(CH3)-
b; R1 = cHex
c; R1 = Ph
d; R1 = PhCH2CH2-
e; R1 = PhCH2OCH2CH2-



1h; X = Br
2b; X = Cl
(E:Z = 5.2:1)



1i; X = Br
2c; X = Cl
(Z:E = 10:1)



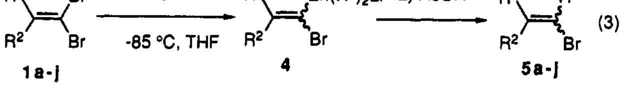
1j; X = Br
2d; X = Cl
(E:Z = 10:1)

Table I. Preparation of Haloalkenes 5 and 7 by the Reactions of 1,1-Dihaloalkenes 1a-l and 2a-d with Triorganozincates[a]

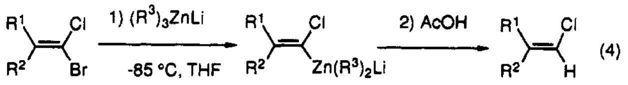
entry	substrate	$(R^3)_3ZnLi$	reaction time (h)	products	yield[b] (%)	ratio[c] (E/Z)
1	**1a**	$(Bu)_3ZnLi$	0.1	**5a**	61 (35)	2.2:1
2			3	**5a**	82	2.6:1
3			24	**5a**	74	3.5:1
				11a	10	33:1
4[d]			24	**5a**	47 (40)	3.8:1
				11a	5	3.9:1
5[e]			3	**5a**	61 (31)	2.6:1
				9a	4	–
6		$(Bu)_3ZnMgCl$	3	**5a**	68 (9)	7.8:1
				9a	23	–
7		$(^sBu)_3ZnLi$	0.1	**5a**	86 (5)	1:1.1
8		$(^tBu)_3ZnLi$	3	**5a**	7 (91)	1:1.1
9		$(Bu)_2(^tBu)ZnLi$	1	**5a**	30 (41)	1.9:1
10	**1a**	$(^tBu)_2(Bu)ZnLi$	14	**5a**	30 (35)	7.5:1
				11a	3	>20:1
				11c	12	>20:1
11[f]	**1b**	$(Bu)_3ZnLi$	3	**5b**	33	2.4:1
12	**1c**	$(Bu)_3ZnLi$	0.1	**5c**	98	3.4:1
13			3	**5c**	97	3.6:1
14	**1d**	$(Bu)_3ZnLi$	3	**5d**	66	1.1:1
15[f]	**1e**	$(Bu)_3ZnLi$	3	**5e**	83[g]	1:1
16	**1f**	$(Bu)_3ZnLi$	0.1	**5f**	93 (9)	1:1.2
17		$(^sBu)_3ZnLi$	0.1	**5f**	99	1:2.4
18		$(^tBu)_3ZnLi$	0.1	**5f**	19 (83)	1:1.3
19[f]	**1g**	$(Bu)_3ZnLi$	13	**5g**	54 (46)	–
20	**1h**	$(Bu)_3ZnLi$	0.1	**5h**	30 (67)	1:4.1
21			1	**5h**	73 (28)	4.4:1
22	**1i**	$(Bu)_3ZnLi$	0.1	**5i**	83	20:1
23[d]			24	**5i**	53 (47)	18:1
24		$(^sBu)_3ZnLi$	0.1	**5i**	86 (16)	18:1
25		$(^tBu)_3ZnLi$	0.1	**5i**	29 (68)	11:1
26	**1j**	$(Bu)_3ZnLi$	0.1	**5j**	96	21:1
27[d]			24	**5j**	63 (33)	16:1
28	**2a**	$(Bu)_3ZnLi$	17	**7a**	92[g]	>40:1
29	**2c**	$(Bu)_3ZnLi$	0.5	**7c**	91[g] (5)	45:1
30	**2d**[h]	$(Bu)_3ZnLi$	3	**7d**	67[g] (19)	1:>40

[a] Unless otherwise noted, reactions were performed at −85 °C in THF with 1.25 equiv of trialkylzincates. [b] GC yield unless otherwise noted. The yield of recovered starting material is shown in parentheses. [c] The ratio was determined by capillary GC analysis. [d] 0.5 Equivalents of the trialkylzincate was employed. [e] The reaction was performed in THF-HMPA (2:1). [f] 2.0 Equivalents of the trialkylzincate were employed. [g] Isolated yield. [h] Pure E isomer was used.

Generation of (1-Haloalkenyl)zincates by Br/Zn Exchange Reactions with Trialkylzincates. Lithium triorganozincates ($(R^3)_3ZnLi$) were prepared by the reaction of $ZnCl_2$ with 3 equiv of the appropriate organolithium at 0 °C in THF.[15] Treatment of dihaloalkenes **1** and **2** with $(R^3)_3ZnLi$ (1.25 equiv) in THF at −85 °C, followed by hydrolysis of intermediate (1-haloalkenyl)zincates **4** and **6** at low temperature, yielded bromoalkenes **5** and chloroalkenes, **7**, respectively (eqs 3 and 4, Table I).



1a-j 4 5a-j (3)



2a,c,d 6 7a,c,d (4)

The reactivity of the 1,1-dibromoalkenes varied with their structures. In general, the exchange reactions of the monosubstituted dibromoalkenes (R^2 = H) with $(Bu)_3ZnLi$ were completed within 3 h at −85 °C, but a longer

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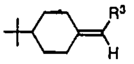
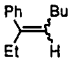
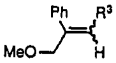
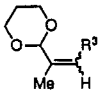
[11] For a preliminary report, see: Harada, T.; Hara, D.; Hattori, K.; Oku, A. *Tetrahedron Lett.* **1988**, *29*, 3821.

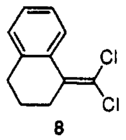
[12] (a) Corey, E. J.; Fuchs, P. L. *Tetrahedron Lett.* **1972**, 3769. (b) Posner, G. H.; Loomis, G. L.; Swya, H. S. *Tetrahedron Lett.* **1975**, 1372. (c) Hessig, R.; Seebach, D.; Siegel, H. *Chem. Ber.* **1984**, *117*, 1877.

Table II. Alkylation Reactions of 1,1-Dihaloalkenes 1 and 2 with Triorganozincates[a]

entry	substrate	reagent	time[b] (h)	products	yield[c] (%)	ratio[d] (*E*/*Z*)
1	**1a**	$(Bu)_3ZnLi$	3	$Ph(Me)CHCH{=}CHR^3$ **11a**; R^3 = Bu	(61)	1:1.8
2[e]			0	**11a**	83	1:2.3
3		$(Bu)_3ZnMgCl$	3	**11a**	(15)	1:1.7
				9a	(82)	–
4		$(^sBu)_3ZnLi$	3	**11b**; R^3 = ^{s}Bu	(83)	1.2:1
5		$(^tBu)_3ZnLi$	1	**11c**; R^3 = ^{t}Bu	(42)	9.2:1
				9a	(48)	–
6		$(Bu)_2(^tBu)ZnLi$	1	**11a**	(32)	1:1.2
				11c	(20)	8.3:1
				9a	(7)	–
7		$(^tBu)_2(Bu)ZnLi$	2	**11a**	(12)	1:1.5
				11c	(35)	9.7:1
				9a	(25)	–
8[e]	**1b**	$(Bu)_3ZnLi$	0	c-HexCH=CHBu **11d**	86	1:2.9
9	**1c**	$(Bu)_3ZnLi$	3	PhCH=CHBu **11e**	(24)	1:4.1
				5c	(52)	>20:1
				9c	(29)	–
10	**1d**	$(Bu)_3ZnLi$	2	$Ph(CH_2)_2CH{=}CHBu$ **11f**	63	1.0:1
11[e]			0	**11f**	(72)	1.0:1
12[e]	**1e**	$(Bu)_3ZnLi$	2	$BnO(CH_2)_2CH{=}CHBu$ **11g**	82	1.0:1
13	**1f**	$(Bu)_3ZnLi$	0	BOMOCH(Me)CH=CHBu **11h**	62	4.0:1
14[f]			–	**11h**	67	1:>40
15	**2a**	$(Bu)_3ZnLi$	0	**11h**	82	>40:1
16[e]	**1g**	$(Bu)_3ZnLi$	0.5	 **11i**; R^3 = Bu	(70)	–
17		$(^tBu)_3ZnLi$	3	**11j**; R^3 = ^{t}Bu	(60)	–
18[e]	**1h**	$(Bu)_3ZnLi$	0	 11k	92	1.8:1
				11k		
19	**2b**	$(Bu)_3ZnLi$	0	**11k**	83	1.8:1
20	**1i**	$(Bu)_3ZnLi$	0	 **11l**; R^3 = Bu	96	1:1.3
21		$(Me)_3ZnLi$	0	**11m**; R^3 = Me	90	1:1.3
22		$(^sBu)_3ZnLi$	0	**11n**; R^3 = ^{s}Bu	95	1:1.2
23		$(^tBu)_3ZnLi$	0	**11o**; R^3 = ^{t}Bu	84	1:1.5
24[e]	**1j**	$(Bu)_3ZnLi$	0.5	 **11p**; R^3 = Bu	71	1:2.9
25		$(^sBu)_3ZnLi$	0	**11q**; R^3 = ^{s}Bu	61	1:1.2
26		$(^tBu)_3ZnLi$	0	**11r**; R^3 = ^{t}Bu	76	6.4:1
27	**2d**	$(Bu)_3ZnLi$	0	**11p**	82	>20:1
28		$(^sBu)_3ZnLi$	0	**11q**	83	4.0:1
29		$(^tBu)_3ZnLi$	0	**11r**	75	1:1.4

[a] Unless otherwise noted, reactions were performed in THF at temperatures from −85 °C to 0 °C with 1.25 equiv of $(R^3)_3ZnLi$. [b] After being stirred at −85 °C for the time indicated, the reaction mixture was allowed to warm to 0 °C or rt over a period of 1.5–2.5 h. [c] Isolated yield. GC yield is shown in parentheses. [d] The ratio was determined by capillary GC analysis. [e] 2.0 Equvalents of zincate were employed. [f] The intermediate (1-bromoalkenyl)zincate was prepared by the reaction of the corresponding (1-bromoalkenyl)lithium and $(Bu)_2Zn$.

time was required for the disubstituted dibromoalkenes. Dibromoalkenes bearing electron-withdrawing groups such as phenyl and alkoxymethyl were reactive. Thus, **1c** and **1f** reacted faster than other monosubstituted dibromoalkenes (entries 12 and 16). Moreover, disubstituted dibromoalkenes **1i** and **1j** were highly reactive, and the exchange reactions were completed within 5 min (entries 22 and 26). Bromochloroalkenes **2** exhibited reactivities comparable with those of the dibromoalkenes. The exchange reactions took place exclusively at the bromine atom to give chloroalkenes **7** (entries 28–30). Dichloroalkene **8** did not react with $(Bu)_3ZnLi$ even at rt.



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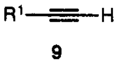

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(14) Harada, T.; Katsuhira, T.; Oku, A. *J. Org. Chem.* **1992**, *57*, 5806.

(15) Isobe, M.; Kondo, S.; Nagasawa, N.; Goto, T. *Chem. Lett.* **1977**, 679.

The exchange reaction could be carried out with various triorganozincates. The reactivities of the lithium zincates decreased roughly in the order (R^3=) ^{n}Bu ≃ ^{s}Bu > ^{t}Bu > Me ≫ Ph. No reaction proceeded with $(Me)_3ZnLi$ at −85 °C, but, at higher temperatures, the exchange reaction took place with a simultaneous 1,2-migration of the resulting (1-haloalkenyl)zincate (*vide infra*). No reaction was observed with $(Ph)_3ZnLi$ even at rt. Reactions of dibromoalkenes with 0.5 equiv of $(Bu)_3ZnLi$ did not give more than 50% yield of bromoalkenes **5** (entries 4 and 23), a result that shows that intermediate (1-bromoalkenyl)zincate **4** cannot undergo a further exchange reaction with **1**. One exception was the reaction of highly reactive **1j** for 24 h (entry 27), which gave **5j** in 63% yield. (Chloromagnesium)zincate $(Bu)_3ZnMgCl$, generated by the reaction of $ZnCl_2$ with 3 equiv of BuMgCl, also underwent the exchange reaction with **1a** (entry 6). The resulting (bromoalkenyl)zincate was less stable than the lithium zincate, and the formation of byproduct alkyne **9a** (R^1 = $PhCH(CH_3)$)was observed.

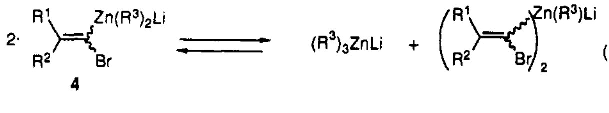
Recently, we have demonstrated that (1-haloalkenyl)zincates are configurationally stable at −85 °C and that, therefore, the stereoselectivity in the Br/Zn exchange reaction is determined kinetically.[14] In general, the exchange reaction took place preferentially at the more hindered bromine atom of **1**.[14] Although the level of selectivity was moderate in the reactions of the monosubstituted dibromoalkenes, disubstituted dibromoalkenes **1i,j**, in which the chelation effect of the alkoxy substituents may play some additional role,[16] exhibited high stereoselectivities (entries 22–27).

(1-Haloalkenyl)lithiums of structure $R^1CH{=}C(X)Li$ (**3**; R^2 = H) are known to undergo a facile Fritsh–Butenberg–Wiechel rearrangement to alkyne **9** even at low temperatures (> −100 °C).[5] In contrast, lithium (1-haloalkenyl)zincates **4** (R^2 = H) are stable at −85 °C for at least 3 h. Upon standing for a longer period, they undergo slow 1,2-alkyl migration reactions rather than rearrange to the alkynes. Thus, the reaction of **1a** and $(Bu)_3ZnLi$ for 24 h afforded **5a** in 74% yield with a small amount of 2-phenyl-3-octene (**11a**) (entry 3). Alkyne **9a** (R^1 = PhCH(Me)) was formed as a byproduct in the reaction of **1a** when HMPA was used as a cosolvent (entry 5) and when $(Bu)_3ZnMgCl$ was employed (entry 6).

The reactivity of triorganozincates toward 1,1-dibromoalkenes deserves comparison with that of organocuprates. Posner et al. reported the dimethylation reactions of disubstituted dibromoalkenes with $(Me)_2CuLi$.[12b] For comparison, we carried out the reaction of monosubstituted dibromoalkene **1a** with $(Bu)_2CuLi$ in THF at −85 °C. The reaction gave rearranged alkyne **9a** (76%), but neither bromoalkene **3a** nor the dibutylated product was obtained.

There have been a few physical studies of triorganyl zincate species.[17] Recently, the X-ray structure of the related zincate species $[Et_2Zn(t\text{-}BuO)_2ZnEt_2]_2^{-}2K^+$ was reported,[18] but no X-ray crystallographic data are available for triorganozincate species. Their solution structures and properties are even less clear. The present study provides some information on this issue.

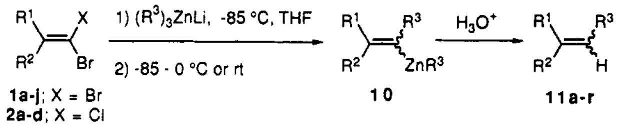
The stability of lithium (1-haloalkenyl)zincate **4** (R^2 = H) at −85 °C indicates that it cannot dissociate reversibly into the dialkylzinc and (1-haloalkenyl)lithium, which, if formed, would rearrange to alkyne **9**. Such a dissociation may explain the formation of alkyne **9a** as a byproduct in the reaction with HMPA as a cosolvent and in the reaction with the chloromagnesium zincate. The absence of the alkyne also shows that the Br/Zn exchange reaction with lithium trialkylzincate does not proceed through a stepwise mechanism involving Br/Li exchange by the alkyllithium liberated from the zincate and subsequent recombination of the resulting (1-haloalkenyl)lithium with dialkylzinc. When 0.5 equiv of $(Bu)_3ZnLi$ was used, the yields of bromoalkenes did not exceed 50%. If intermediate (1-haloalkenyl)zincate **4** disproportionated as shown in eq 5,



(5)

the yield would be more than 50%. Accordingly, the less than 50% yield excludes the possibility of the disproportionation of triorganyl zincates.

Alkylation Reactions of 1,1-Dihaloalkenes with Trialkylzincates. On warming, (1-haloalkenyl)zincates **4** and **6** underwent a 1,2-alkyl migration to generate alkenylzinc species **10** (eq 6). Thus, treating dihaloalkenes **1** and **2** with $(R^3)_3ZnLi$ (1.25 equiv) at −85 °C and then slowly warming up the resulting (1-haloalkenyl)zincates to 0 °C or rt gave alkylation products **11** after hydrolysis. A wide range of the alkylation reactions of 1,1-dihaloalkenes are summarized in Table II.



(6)

A variety of alkyl groups can be introduced via the corresponding zincates. Even the introduction of the sterically demanding *tert*-butyl group proceeded effectively in the reaction with disubstituted dihaloalkenes (entries 17, 23, 26, and 29). In the reaction of monosubstituted dibromoalkene **1a** with $({}^tBu)_3ZnLi$, a considerable amount of alkyne **9a** was obtained as a byproduct (entry 5). Although the Br/Zn exchange reaction with $(Me)_3ZnLi$ did not take place at −85 °C, methylation of **1i** proceeded when the reaction mixture was warmed from −85 °C to rt (entry 21). As anticipated from the result observed in the reaction at −85 °C, the reaction with $(Bu)_3ZnMgCl$ afforded alkyne **9a** as the major product (entry 3).

It is well known that 1,2-alkyl migrations of (1-haloalkenyl)boronates[6,19] and -alanates[7a,b] proceed with inversion of configuration at the carbon bearing the halogen. A similar stereochemical outcome was observed in the alkylation reactions of the monosubstituted dihaloalkenes (**1** and **2** (R^2 = H)) (Scheme III, path a). Thus, when a 2.6:1 mixture of (*E*)- and (*Z*)-**4a**, generated by the reaction of **1a** with $(Bu)_3ZnLi$ at −85 °C, was allowed to warm to 0 °C, a 1.8:1 mixture of (*Z*)- and (*E*)-**11a** was

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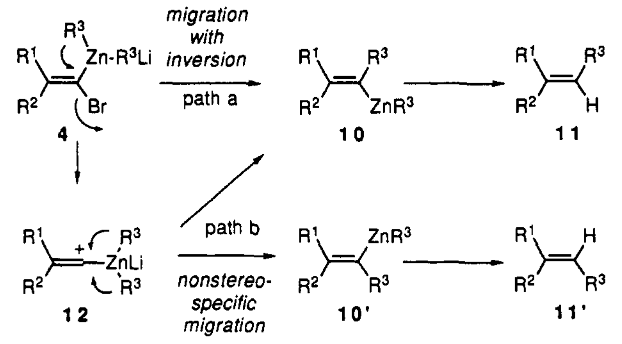
(16) Meyers, A. I.; Spohn, R. F. *J. Org. Chem.* **1985**, *50*, 4872.

(17) (a) Seitz, L. M.; Brown, T. L. *J. Am. Chem. Soc.* **1966**, *88*, 4140. (b) Toppet, S.; Slinckx, G.; Smets, G. *J. Organomet. Chem.* **1967**, *9*, 205. (c) Weiss, E.; R., W. *Chem. Ber.* **1968**, *101*, 35. (d) Weiss, E.; Plass, H. *J. Organomet. Chem.* **1968**, *14*, 21. (e) Seitz, L. M.; Little, B. F. *J. Organomet. Chem.* **1969**, *18*, 227.

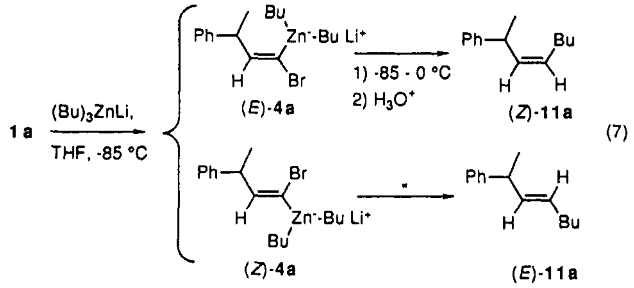
(18) Fabicon, R. M.; Prvez, M.; H. G. Rickey, J. *J. Am. Chem. Soc.* **1991**, *113*, 1412.

(19) (a) Matteson, D. S.; Mah, R. W. H. *J. Am. Chem. Soc.* **1963**, *85*, 2599. (b) Pasto, D. J.; Miesel, J. L. *J. Am. Chem. Soc.* **1963**, *85*, 2118. (c) Brown, H. C.; Basavaiah, D.; Kulkarni, S. U.; Lee, H. D.; Negishi, E.; Katz, J.-J. *J. Org. Chem.* **1986**, *51*, 5270.

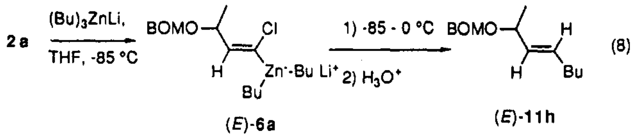
Scheme III



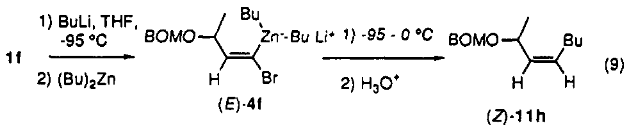
obtained (eq 7, entry 1). The reaction of bromochloroalkene **2a** of *E* configuration with $(Bu)_3ZnLi$ afforded the stereoselective alkylation product (*E*)-**11h** via carbenoid (*E*)-**6a** (eq 8, entry 15). Treating (1-bromoalkenyl)lithium **3f**[20] (which was generated stereoselectively by slow addition of BuLi (*vide supra*)) with $(Bu)_2Zn$ at −95 °C and then warming up the resulting (1-bromoalkenyl)zincate (*E*)-**4f** to rt yielded stereoselectively (*Z*)-**11h** (eq 9, entry 14).



(7)



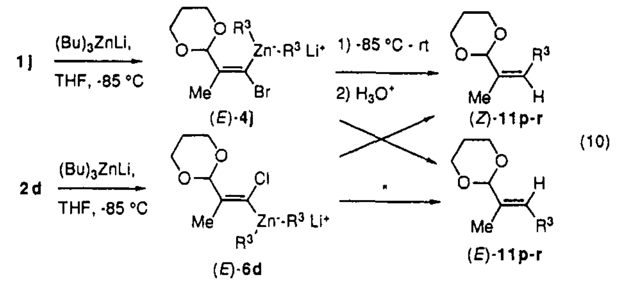
(8)



(9)

The steric interaction between the migrating group (R^3) and the neighboring substituent (R^1 or R^2) is also an important factor in the stereochemistry. Treatment of **1a** with $(Bu)_3ZnLi$ at −85 °C for 24 h (compared to 3 h for Table I, entry 2) gave **5a** (E/Z = 3.5:1) together with a small amount of alkylation product **11a** (E/Z = 33:1) (Table I, entry 3). The selective formation of the *E*-alkylation product and the increase in the E/Z ratio of **5a** (Table I, entry 3 vs entry 2) indicate that (bromoalkenyl)zincate (*Z*)-**4a** undergoes the alkyl migration more readily than (*E*)-**4a**. The migration of the alkyl group of (*E*)-**4a** may be hampered by a repulsive interaction between the butyl ($=R^3$) and the 1-phenylethyl ($=R^1$) group (see eq 7).

When the migration of the alkyl group causes severe steric repulsion between the alkyl group and the substituent located *cis* to the zincate group, the alkyl migration becomes nonstereospecific. In spite of the fact that the intermediate (bromoalkenyl)zincate was formed with a high *E*-selectivity in the reaction of **1j** with $(Bu)_3ZnLi$, alkylation product **11p** was obtained with moderate *Z*-selectivity (eq 10, entry 24). Moreover, the alkylation of **1j** with $(^sBu)_3ZnLi$ was nonselective (entry 25), and the selectivity was reversed in the reaction of **1j** with $(^tBu)_3ZnLi$ (entry 26). In contrast, 1,2-butyl migration from (1-chloroalkenyl)zincate (*E*)-**6d** (R^3 = Bu), generated from (*E*)-**2d**, proceeded with a complete inversion at the carbenoid carbon to give (*E*)-**11p**; but the migration of the more sterically demanding *sec*-butyl and *tert*-butyl groups were less stereoselective (entries 27–29).



(10)

The timing of carbon–halogen bond breaking and carbon–carbon bond formation probably plays an important role in determining the stereochemical outcome of the 1,2-alkyl migrations of zincate carbenoids (Scheme III). Without any unfavorable steric interactions, the stereoelectronically favored alkyl migration with inversion may take place synchronously with the breaking of the carbon–halogen bond. When the migration becomes sterically less feasible, the bond breaking may precede the migration, and, in the extreme case, the alkyl migration may proceed nonstereospecifically in a stepwise manner via intermediate **12** (Scheme III).

The use of unsymmetrical zincates $(R^3)_2(R^4)ZnLi$[21] as alkylating reagents was briefly examined. Both $(Bu)_2(^tBu)ZnLi$ and $(^tBu)_2(Bu)ZnLi$ underwent Br/Zn exchange slowly at −85 °C (Table I, entries 9 and 10). Their reactivities were roughly in between those of $(Bu)_3ZnLi$ and $(^tBu)_3ZnLi$. When similar reactions were performed at temperatures between −85 and 0 °C, alkylation products **11a** and **11c** were formed without appreciable selectivity (Table II, entries 6 and 7). While the observed ratios of **11a** and **11c** are probably the result of the differing reactivity of the butyl and *tert*-butyl groups in the Br/Zn exchange and 1,2-alkyl migration, it can at least be deduced that the first Br/Zn exchange occurs nonselectively with the liberation of both BuBr and ^{t}BuBr.

Palladium(0)-Catalyzed Coupling Reactions of Alkenylzinc Species Generated by the Reactions of Dihaloalkenes and Trialkylzincates. One of the most characteristic features of the alkylation reactions of dihaloalkenes with trialkylzincates is that alkenylzinc species are formed in the reaction mixture before aqueous workup, and further reactions of the alkenylzincs with electrophiles are possible under palladium(0) catalysis (eq 11).[8] The synthetic potential of the formation of two carbon–carbon bonds with dihaloalkenes is exemplified by the results shown in Table III.

Treatment of the alkenylzinc species **10**, generated by the reaction of dibromoalkenes **1** and $(Bu)_3ZnLi$, with

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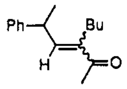
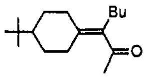
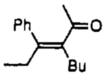
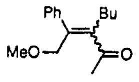
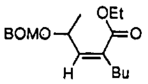
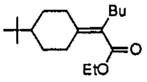
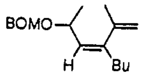
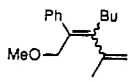
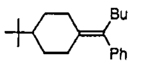
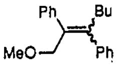
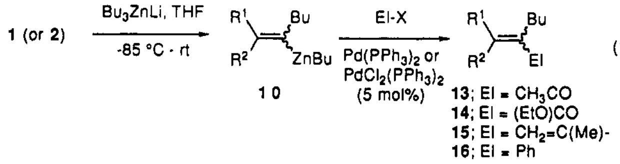
(20) (1-Haloalkenyl)lithium **3** (R^2 = H) is generally unstable at −95 °C, but **3f** was found to be relatively stable at this temperature.

(21) Tückmantel, W.; Ohshima, K.; Nozaki, H. *Chem. Ber.* 1986, 1581.

Table III. Palladium(0)-Catalyzed Coupling Reactions of Alkenylzinc Species Generated by the Reactions of 1,1-Dihaloalkenes and $(Bu)_3ZnLi$[a]

entry	substrate	electrophile (equiv)	catalyst	product	yield[b] (%)	ratio[c] (E/Z)
1	**1a**	AcCl (3.8)	$Pd(PPh_3)_2$	 **13a**	56	2.2:1
2[d]	**1g**	AcCl (6.0)	$Pd(PPh_3)_2$	 **13b**	43	-
3	**1h**	AcCl (3.8)	$PdCl_2(PPh_3)_2$	 **13c**	63	1:3.6
4	**1i**	AcCl (3.8)	$PdCl_2(PPh_3)_2$	 **13d**	72	1.6:1
5	**2a**	EtOCOCl (4.0)	$Pd(PPh_3)_2$	 **14a**	56	1:>40
6[d]	**1g**	EtOCOCl (6.0)	$Pd(PPh_3)_2$	 **14b**	62	-
7	**2a**	$CH_2{=}C(CH_3)Br$ (4.0)	$PdCl_2(PPh_3)_2$	 **15a**	52	1:>40
8	**1i**	$CH_2{=}C(CH_3)Br$ (4.0)	$PdCl_2(PPh_3)_2$	 **15b**	77	1:1.1
9[d]	**1g**	PhBr (6.0)	$Pd(PPh_3)_2$	 **16a**	33[e]	-
10	**1a**	PhBr (4.0)	$PdCl_2(PPh_3)_2$	 **16b**	73	1.1:1[f]

[a] Unless otherwise noted, 1.25 equiv of $(Bu)_3ZnLi$ was used. The coupling reactions were performed at rt for 10–15 h with 5 mol% of the catalyst. $Pd(PPh_3)_2$ was prepared by the reaction of $PdCl_2(PPh_3)_2$ with DIBALH in THF. [b] Isolated yield unless otherwise noted. [c] Unless otherwise noted, the ratio was determined by capillary GC analysis. [d] 2.0 Equivalents of $(Bu)^3ZnLi$ were used. [e] GC yield. [f] The ratio was determined by ^1H-NMR analysis.



(11)

acetyl chloride in the presence of $Pd(PPh_3)_2$ (prepared in situ by the reaction of $PdCl_2(PPh_3)_2$ with DIBALH) or $PdCl_2(PPh_3)_2$ (5 mol%), gave enones **13a-d** (entries 1–4). Under similar conditions, the reaction of **10** with ethyl chloroformate afforded enones **14a,b** (entries 5 and 6). Alkenylzinc species **10** also underwent the Pd(0)-catalyzed coupling reaction with 2-bromopropene and bromobenzene to yield dienes **15a** and **15b** (entries 7 and 8) and styrene derivatives **16a** and **16b** (entries 9 and 10), respectively. In these reactions, it was necessary to use an excess of the electrophile because the butyl group in **10** also undergoes a coupling reaction. The butyl adduct byproducts are volatile and readily removable (see Experimental Section).

The Pd(0)-catalyzed coupling reaction of alkenylzinc species **10** proceeded with retention of configuration. The E/Z ratio of the products reflects that of the alkenylzinc intermediate. The reaction of bromochloroalkene **2a** with $(Bu)_3ZnLi$ stereoselectively produced the corresponding E-alkenylzinc intermediate, and the coupling reaction of the E-alkenylzinc with ethyl chloroformate and 2-bromopropene yielded Z-enone **14a** and Z-diene **15a**, respectively, with high stereoselectivity (entries 5 and 7).

Determination of the Stereochemistry of the Products. The double bond stereochemistry of disubstituted alkenes **5a-f**, **7a**, and **11a-h** was determined on the basis of an analysis of coupling constants between olefinic protons. NOESY spectral measurements were used in determining the stereochemistry of trisubstituted alkenes **5h-j**, **7c,d**, and **11k-o** and tetrasubstituted alkenes **13c,d**,

15b, and **16b**. The stereochemical assignment of bromochloroalkenes **2a-d** was based on the assumption that chlorination of the lithium carbenoid proceeded with retention of configuration at the carbenoid carbon.

Conclusion

We have demonstrated that 1,1-dihaloalkenes undergo facile Br/Zn exchange reactions with trialkylzincates to give (1-haloalkenyl)zincates **4**. (1-Haloalkenyl)zincates thus generated are stable at low temperatures and afford 1-haloalkenes by hydrolysis. Upon warming to rt, they undergo 1,2-alkyl migration reaction to yield alkylation products **11**. Intermediate alkenylzinc species **10** was found to be a versatile reagent in palladium-catalyzed coupling reactions with organyl halides. 1,1-Dihaloalkenes can be readily prepared from ketones or aldehydes and are frequently utilized as precursors of alkynes by means of their reactions with alkyllithium. We believe that these reactions with trialkylzincates expand the utility of 1,1-dihaloalkenes in organic synthesis.

Experimental Section

Unless otherwise noted, ^{1}H- and ^{13}C-NMR spectra were recorded in $CDCl_3$ at 300 MHz and 75.6 MHz, respectively. Microanalyses were performed by the Microanalysis Center of Kyoto University. GC analyses were performed with 20-m PEG-20M and 30-m OV-1 capillary columns. Wakogel C-300 was used for flash chromatography. Unless otherwise specified, all organic extracts were dried over Na_2SO_4. THF was distilled from sodium benzophenone ketyl. CH_2Cl_2 and DMF were distilled from CaH_2. Commercial anhyd $ZnCl_2$ was dried in vacuo at 100 °C for 10 h over P_2O_5. All the reactions were performed under a nitrogen atmosphere. Reactions at −85 °C were performed with a Neslab Cryo Cool immersion cooler.

Preparation of 1,1-Dibromoalkenes 1a-j. Dibromoalkenes **1a-j** were prepared by the reaction of the corresponding carbonyl compounds with PPH_3–CBr_4.[12] Reaction conditions and isolated yields are as follows: **1a** (CH_2Cl_2, 0 °C, 1 h, 73%), **1b**[22] (CH_2Cl_2, reflux, 16 h, 98%), **1c**[23] (CH_2Cl_2, 0 °C, 1 h, 84%), **1d** (CH_2Cl_2, 0 °C – rt, 87%), **1e** (CH_2Cl_2, 0 °C, 1 h, 77%), **1f** (benzene, rt – 85 °C, 79%), **1g**[22] (benzene, reflux, 18 h, 96%), **1h** (toluene, reflux, 15 h, 52%), **1i** (benzene, reflux, 12 h, 71%), and **1j** (benzene, reflux, 14 h, 49%). Spectral data for new compounds are as follows.

1,1-Dibromo-3-phenyl-1-butene (1a): ^{1}H-NMR δ 1.41 (3H, d, J = 7.0 Hz), 3.78 (1H, qd, J = 7.0 and 9.5 Hz), 6.52 (1H, d, J = 9.5 Hz), 7.23–7.37 (5H, m); IR (liquid film) 1600 (m), 1490 (s), 1450 (s), 1015 (m), 815 (s), 755 (s), 695 cm^{-1} (s); MS, m/z (rel inten) 292, 290, 288 (M$^+$, 3, 6, 3), 277, 275, 273 (2, 5, 2), 211, 209 (19, 19), 195, 193 (21, 21), 130 (56), 129 (100); HRMS calcd for $C_{10}H_{10}{}^{79}Br_2$ 287.9149, found 287.9125; calcd for $C_{10}H_{10}{}^{79}Br^{81}Br$ 289.9129, found 289.9115; calcd for $C_{10}H_{10}{}^{81}Br_2$ 291.9109, found 291.9137. Anal. Calcd for $C_{10}H_{10}Br_2$: C, 41.42; H, 3.48. Found C, 41.69; H, 3.44.

1,1-Dibromo-4-phenyl-1-butene (1d): ^{1}H-NMR δ 2.41 (2H, dt, J = 7.2, 7.7 Hz), 2.73 (2H, t, J = 7.7 Hz), 6.41 (1H, t, J = 7.2 Hz), 7.17–7.33 (5H, m); ^{13}C-NMR δ 140.5, 137.6, 128.5, 128.3, 126.2, 89.5, 34.6, 33.8; IR (liquid film) 1600 (s), 1495 (s), 1450 (s), 1080 (s), 805 (s), 795 (s), 745 (s), 695 cm^{-1} (s); MS m/z (rel inten) 211, 209 (M$^+$ – Br, 9, 9), 129 (4), 128 (6), 91 (100). Anal. Calcd for $C_{10}H_{10}Br_2$: C, 41.42; H, 3.48. Found: C, 41.72; H, 3.43.

1,1-Dibromo-4-(phenylmethoxy)-1-butene (1e): ^{1}H-NMR (60 MHz, $CDCl_3$) δ 2.40 (2H, q, J = 6.8 Hz), 3.53 (2H, t, J = 6.8 Hz), 4.52 (2H, s), 6.50 (1H, t, J = 6.8 Hz), 7.33 (5H, br s).

1,1-Dibromo-3-[(phenylmethoxy)methoxy]-1-butene (1f): ^{1}H-NMR δ 1.28 (3H, d, J = 6.5 Hz), 4.51 (1H, qd, J = 6.5, 8.2 Hz), 4.59 (1H, d, J = 11.8 Hz), 4.65 (1H, d, J = 11.8 Hz), 4.73 (1H, d, J = 7.0 Hz), 4.78 (1H, d, J = 7.0 Hz), 6.42 (1H, d, J = 8.2 Hz), 7.27–7.37 (5H, m); IR (liquid film) 1610 (s), 1455 (s), 1370 (s), 1175 (s), 1135 (s), 1110 (s), 1080 (s), 1035 (s), 1030 (s), 780 (s), 735 (s), 700 cm^{-1} (s); MS, m/z (rel inten) 245, 243, 241 (M$^+$ – OCH_2Ph, 1, 2, 1), 215, 213, 211 (7, 13, 7), 164, 162 (7, 7), 107 (13), 91 (100). Anal. Calcd for $C_{12}H_{14}O_2Br_2$: C, 41.17; H, 4.03; Br, 45.65. Found: C, 41.06; H, 4.00; Br, 45.57.

1,1-Dibromo-2-phenyl-1-butene (1h): ^{1}H-NMR δ 0.98 (3H, t, J = 7.5 Hz), 2.60 (2H, q, J = 7.5 Hz), 7.17 (2H, m), 7.32–7.41 (3H, m); ^{13}C-NMR δ 148.8, 140.8, 128.3, 127.8, 127.6, 87.5, 32.7, 11.4; IR (liquid film) 1595 (m), 1490 (s), 1455 (s), 1440 (s), 815 (s) 795 (s), 755 (s), 695 cm^{-1} (s); MS, m/z (rel inten) 292, 290, 288 (M$^+$, 15, 30, 15), 195, 193 (8, 8), 182, 180 (5, 5), 130 (59), 129 (100), 115 (43); HRMS calcd for $C_{10}H_{10}{}^{79}Br_2$ 287.9149, found 287.9156; calcd for $C_{10}H_{10}{}^{79}Br^{81}Br$ 289.9129, found 289.9143; calcd for $C_{10}H_{10}{}^{81}Br_2$ 291.9109, found 291.9126. Anal. Calcd for $C_{10}H_{10}Br_2$: C, 41.42; H, 3.48; Br, 55.11. Found C, 41.52; H, 3.49; Br, 55.22.

1,1-Dibromo-3-methoxy-2-phenyl-1-propene (1i): bp 106 °C/0.06 mmHg; ^{1}H-NMR δ 3.34 (3H, s), 4.37 (2H, s), 7.26 (2H, m), 7.34–7.42 (3H, m); ^{13}C-NMR δ 143.7, 139.3, 128.3, 128.0, 127.9, 93.1, 75.3, 58.1; IR (liquid film) 2815 (s), 1595 (m), 1490 (s), 1440 (s), 1185 (s), 1095 (s), 820 (s), 810 (s), 750 (s), 695 cm^{-1} (s); MS, m/z (rel inten) 308, 306, 304 (M$^+$, 9, 18, 9), 227, 225 (94, 94), 195, 193 (76, 76), 182, 180 (71, 71), 146 (61), 115 (100); HRMS calcd for $C_{10}H_{10}O^{79}Br_2$ 303.9098, found 303.9123; calcd for $C_{10}H_{10}O^{79}Br^{81}Br$ 305.9078, found 305.9104; calcd for $C_{10}H_{10}O^{81}Br_2$ 307.9058; found 307.9042. Anal. Calcd for $C_{10}H_{10}Br_2$: C, 39.25; H, 3.29; Br, 52.23. Found: C, 39.13; H, 3.23; Br, 52.05.

2-(1,1-Dibromo-1-propen-2-yl)-1,3-dioxane (1j): mp 85–87 °C (recrystallized from hexane); ^{1}H-NMR δ 1.37 (1H, ttd, J = 1.4, 2.5, 13.5 Hz), 1.90 (3H, s), 2.13 (1H, ttd, J = 5.1, 12.5, 13.5 Hz), 3.88 (2H, m), 4.15 (2H, m), 5.43 (1H, s); IR (KBr disk) 1640 (m), 1605 (m), 1380 (s), 1240 (s), 1100 (s), 990 (s), 920 (s), 815 cm^{-1} (s); MS, m/z (rel inten) 288, 286, 284 (M$^+$, 3,6,3), 273, 271, 269 (12, 25, 12), 230, 228, 226 (7, 14, 7), 229, 227, 225 (7, 14, 7), 207, 205 (29, 29), 149, 147 (34, 34), 87 (100); HRMS calcd for $C_7H_{10}O_2{}^{79}Br_2$ 283.9047, found 283.9040; calcd for $C_7H_{10}O_2{}^{79}Br^{81}Br$ 285.9027, found 285.9061; calcd for $C_7H_{10}O_2{}^{81}Br_2$ 287.9007, found 287.8993. Anal. Calcd for $C_7H_{10}O_2Br_2$: C, 29.40; H, 3.52; Br, 55.89. Found: C, 29.46; H, 3.47; Br, 55.66.

Stereoselective Preparation of Bromochloroalkenes 2a-d. The preparation of (*E*)-1-bromo-1-chloro-3-[(phenylmethoxy)methoxy]-1-butene (**2a**) is given as a representative example. To a solution of **1f** (1.416 g, 4.04 mmol) in THF (12 mL) at −95 °C was slowly added BuLi (1.62 M in hexane) (2.74 mL, 4.45 mmol) by syringe-pump over a 30-min period, and the mixture was allowed to warm to −85 °C. To the resulting mixture of the lithium carbenoid at −85 °C was added CF_2ClCCl_2F (0.96 mL, 8.08 mmol). The mixture was stirred at −85 °C for 1 h before the reaction was quenched with 10% AcOH in THF. The mixture was poured into brine and was extracted twice with ether. The combined organic layers were dried and concentrated in vacuo. Kugelrohr distillation of the residue gave 505.6 mg (41%) of **2a** (E/Z > 40:1) and 648 mg of a 3:1 mixture of **2a** and 3-[(phenylmethoxy)methoxy]butyne (**9f**) (**2a** (43%) and **9f** (15%)). **2a**: bp 120 °C/0.05 mmHg (Kugelrohr); ^{1}H-NMR δ 1.29 (3H, d, J = 6.5 Hz), 4.59 (1H, d, J = 11.9 Hz), 4.61 (1H, qd, J = 6.5, 8.4 Hz), 4.65 (1H, d, J = 11.9 Hz), 4.73 (1H, d, J = 7.0 Hz), 4.78 (1H, d, J = 7.0 Hz), 6.12 (1H, d, J = 8.4 Hz), 7.25–7.39 (5H, m); IR (liquid film) 1715 (s), 1695 (s), 1615 (s), 1590 (s), 1425 (s), 1365 (s), 1170 (s), 1130 (s), 1100 (s), 1070 (s), 1030 (s), 1020 (s), 800 (s), 730 (s), 690 cm^{-1} (s); MS, m/z (rel inten) 199 (M$^+$ – OCH_2Ph, 4), 171 (18), 169 (57), 167 (42), 107 (33), 91 (100). Anal. Calcd for $C_{12}H_{14}O_2BrCl$: C, 47.16; H, 4.62; Br, 26.15; Cl, 11.60. Found: C, 47.33; H, 4.65; Br, 26.25; Cl, 11.65. **9f**: ^{1}H-NMR δ 1.46 (3H, d, J = 6.7 Hz), 2.41 (1H, d, J = 2.0 Hz), 4.51 (1H, dq, J = 2.0 and 6.7 Hz), 4.59 (1H, d, J = 11.8 Hz), 4.67 (1H, d, J = 11.8 Hz), 4.78 (1H, d, J = 7.0 Hz), 5.02 (1H, d, J = 7.0 Hz), 7.25–7.39 (5H, m); IR (liquid film) 3285 (s), 2110 (m), 1175 (s), 1105 (s), 1085 (s), 1040 (s), 1025 (s), 735 (s), 695 cm^{-1} (s). Anal. Calcd for $C_{12}H_{14}O_2$: C, 75.76; H, 7.42. Found: C, 75.91; H, 7.39.

Bromochloroalkenes **2b** (E/Z = 5.2:1), **2c** (E/Z = 1:10), and **2d** (E/Z = 10:1) were obtained in 88, 94, and 94% yield, respectively, by a procedure similar to that described above.

(*E*)- and (*Z*)-1-Bromo-1-chloro-2-phenyl-1-butene (2b): a 5.2:1 mixture of the *E* and *Z* isomers; ^{1}H-NMR δ 0.965 (3H for

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(23) Bestmann, H. J.; Li, K. *Chem. Ber.* **1982**, *115*, 828.

the *E* isomer, t, *J* = 7.5 Hz), 0.973 (3H for the *Z* isomer, t, *J* = 7.5 Hz), 2.59 (2H for the *E* isomer, q, *J* = 7.5 Hz), 2.60 (2H for the *Z* isomer, q, *J* = 7.5 Hz), 7.16–7.40 (5H, m); ^{13}C-NMR δ 145.6 (*Z*), 145.2 (*E*), 140.6 (*Z*), 139.1 (*E*), 128.3, 128.05 (*Z*), 127.97 (*E*), 127.7, 103.4 (*E*), 103.0 (*Z*), 32.4 (*E*), 30.1 (*Z*), 11.48 (*E*), 11.45 (*Z*); IR (liquid film) 1600 (s), 1490 (s), 1460 (s), 1440 (s), 860 (s), 810 (s), 760 (s), 750 (s), 700 cm^{-1} (s); MS, *m/z* (rel inten) 246, 244 (M^+, 29, 23), 165 (3), 129 (100), 115 (29); HRMS calcd for $C_{10}H_{10}{}^{35}Cl^{79}Br$ 243.9655, found 243.9661; calcd for $C_{10}H_{10}{}^{35}Cl^{81}Br$ 245.9635, found 245.9615. Anal. Calcd for $C_{10}H_{10}ClBr$: C, 48.91; H, 4.10; Cl, 14.44; Br, 32.54. Found: C, 48.91; H, 4.10; Cl, 14.38; Br, 32.41.

(*Z*)-1-Bromo-1-chloro-3-methoxy-2-phenyl-1-propene (2c): ^1H-NMR δ 3.34 (3H, s), 4.39 (2H, s), 7.28–7.42 (5H, m); ^{13}C-NMR δ 140.1, 137.6, 128.4, 128.13, 128.08, 108.8, 75.6, 58.2; IR (liquid film) 1605 (s), 1595 (s), 1490 (s), 1445 (s), 1190 (s), 1105 (s), 860 (s), 755 (s), 700 cm^{-1} (s); MS, *m/z* (rel inten) 262, 260 (M^+, 8, 8), 227, 225 (8, 8), 181 (75), 149 (86), 115 (57), 45 (100); HRMS calcd for $C_{10}H_{10}O^{79}Br^{35}Cl$ 259.9604, found 259.9613; calcd for $C_{10}H_{10}O^{81}Br^{35}Cl$ 261.9584, found 261.9586. Anal. Calcd for $C_{10}H_{10}OBrCl$: C, 45.92; H, 3.85; Br, 30.55; Cl, 13.55. Found C, 45.90; H, 3.97; Br, 30.28; Cl, 13.43.

(*E*)-2-(1-Bromo-1-chloro-1-propen-2-yl)-1,3-dioxane (2d): mp 71.5–72.0 °C (recrystallized from hexane); ^1H-NMR δ 1.37 (1H, ttd, *J* = 1.4, 2.5, 13.5 Hz), 1.91 (3H, s), 2.13 (1H, ttd, *J* = 5.1, 12.6, 13.5 Hz), 3.87 (2H, m), 4.15 (2H, m), 5.49 (1H, s); IR (KBr disk) 1620 (s), 1390 (s), 1375 (s), 1240 (s), 1150 (s), 1095 (s), 1010 (s), 985 (s), 935 (s), 915 (s), 885 (s), 850 cm^{-1} (s); MS, *m/z* (rel inten) 242, 240 (M^+, 6, 6), 227 (33), 225 (24), 207, 205 (4, 4), 161 (32), 103 (64), 87 (100); HRMS calcd for $C_7H_{10}O_2{}^{79}Br^{35}Cl$ 239.9553, found 239.9534; calcd for $C_7H_{10}O_2{}^{81}Br^{35}Cl$ 241.9533, found 241.9530. Anal. Calcd for $C_7H_{10}O_2BrCl$: C, 34.78; H, 4.14; Br, 33.09; Cl, 14.68. Found: C, 34.81; H, 4.24; Br, 33.02; Cl, 14.65.

Preparation of Bromoalkenes 5 and Chloroalkenes 7 by the Reactions of 1,1-Dihaloalkenes with Trialkylzincate. The reaction of dibromoalkene **1a** with $(Bu)_3ZnLi$ (Table I, entry 2) is given as a representative example. To a solution of $ZnCl_2$ (82.7 mg, 0.606 mmol) in THF (2 mL) was added BuLi (1.62 M in hexane, 1.12 mL, 1.82 mmol) at 0 °C. After being stirred for 15 min, the mixture was cooled at −85 °C. To the cooled mixture was slowly added a THF (1.2 mL) solution of **1a** (142.2 mg, 0.490 mmol), and the mixture was stirred for 3 h at the same temperature. The reaction was quenched with 10% AcOH in THF. The mixture was poured into aqueous 1 N HCl and was extracted twice with ether. The combined organic layers were washed with aqueous $NaHCO_3$ and dried. Analysis of the mixture by GC (OV-17) using an internal standard method showed the formation of (*E*)- and (*Z*)-1-bromo-3-phenyl-1-butene (**5a**) (2.6:1) in 82% yield. (*E*)-**5a**: ^1H-NMR δ 1.38 (3H, t, *J* = 7.1 Hz), 3.50 (1H, d quint, *J* = 1.3, 7.1 Hz), 6.06 (1H, dd, *J* = 1.3, 13.6 Hz), 6.37 (1H, dd, *J* = 7.1, 13.6 Hz), 7.19–7.35 (5H, m); IR (liquid film) 1615 (s), 1490 (s), 1450 (s), 940 (s), 760 (s), 700 cm^{-1} (s); MS (a mixture of the *E* and *Z* isomers), *m/z* (rel inten) 212, 210 (M^+, 2, 2), 131 (100), 116 (27), 115 (47), 91 (27); HRMS (a mixture of the *E* and *Z* isomers) calcd for $C_{10}H_{11}{}^{79}Br$ 210.0044, found 210.0044; calcd for $C_{10}H_{11}{}^{8}1Br$ 212.0024, found 211.9997. Anal. A mixture of the *E* and *Z* isomers calcd for $C_{10}H_{11}Br$: C, 56.90; H, 5.25. Found: C, 57.18; H, 5.33. (*Z*)-**5a**: ^1H-NMR δ 1.39 (3H, d, *J* = 7.0 Hz), 4.03 (1H, qd, *J* = 7.1, 8.1 Hz), 6.20 (2H, m), 7.18–7.34 (5H, m); IR (liquid film) 1620 (s), 1495 (s), 1450 (s), 760 (s), 750 (s), 715 (s), 700 (s), 665 cm^{-1} (s).

Bromoalkenes **5b-j** and chloroalkenes **7a,c,d** were obtained by a procedure similar to that described above. Spectral data of new compounds are as follows.[24–26]

(*E*)- and (*Z*)-1-Bromo-4-(phenylmethoxy)-1-butene (5e): a mixture of the isomers; ^1H-NMR (200 MHz) δ 2.27–2.59 (2H, m), 3.53 (2H, td, *J* = 6.6, 10.6 Hz), 4.52 (2H, d, *J* = 3.4 Hz), 6.07–6.32 (2H, m), 7.23–7.47 (5H, m); IR (liquid film) 1620 (s), 1105 (s), 1030 (s), 940 (s), 735 (s), 700 cm^{-1} (s).

(*E*)-1-Bromo-3-[(phenylmethoxy)methoxy]-1-butene ((*E*)-5f): ^1H-NMR δ 1.27 (3H, d, *J* = 6.4 Hz), 4.24 (1*H*, br quint, *J* = ca. 7 Hz), 4.54 (1H, d, *J* = 11.7 Hz), 4.64 (1H, d, *J* = 11.7 Hz), 4.72 (1H, d, *J* = 7.0 Hz), 4.76 (1H, d, *J* = 7.0 Hz), 6.12 (1H, dd, *J* = 7.4 and 13.7 Hz), 6.30 (1H, d, *J* = 13.7 Hz), 7.25–7.38 (5H, m); ^{13}C-NMR δ 138.9, 137.7, 128.4, 127.9, 127.8, 107.8, 92.0, 72.1, 69.6, 20.9; IR (liquid film) 1620 (s), 1455 (s), 1375 (s), 1205 (s), 1170 (s), 1135 (s), 1100 (s), 1040 (s), 1025 (s), 940 (s), 735 (s), 720 (s), 700 cm^{-1} (s); MS, *m/z* (rel inten) 163, 165 ($M^+ - PhCH_2O$, 2, 2), 133, 135 (20, 20), 107 (20), 91 (100). Anal. Calcd for $C_{12}H_{15}O_2Br$: C, 53.15; H, 5.58; Br, 29.47. Found: C, 53.57; H, 5.60; Br, 29.52.

(*Z*)-1-Bromo-3-[(phenylmethoxy)methoxy]-1-butene ((*Z*)-5f): ^1H-NMR δ 1.28 (3H, d, *J* = 6.4 Hz), 4.59 (1H, d, *J* = 11.9 Hz), 4.66 (1H, d, *J* = 11.9 Hz), 4.73 (1H, d, *J* = 6.9 Hz), 4.74–4.81 (2H, m, including d (1H, *J* = 6.9 Hz) at 4.76), 6.12 (1H, br, t, *J* = 7.3 Hz), 6.27 (1H, dd, *J* = 1.0 and 7.3 Hz), 7.25–7.38 (5H, m); ^{13}C-NMR δ 137.9, 136.7, 128.4, 127.8, 127.6, 108.6, 92.5, 70.5, 69.5, 20.0; IR (liquid film) 1620 (s), 1450 (s), 1370 (s), 1285 (s), 1175 (s), 1120 (s), 1105 (s), 1090 (s), 1040 (s), 1030 (s), 735 (s), 700 cm^{-1} (s); MS, *m/z* (rel inten) 133, 135 ($M^+ - BnOCH_2O$, 8, 8), 107 (7), 91 (100). Anal. Calcd for $C_{12}H_{15}O_2Br$: C, 53.15; H, 5.58; Br, 29.47. Found: C, 53.11; H, 5.50; Br, 29.70.

(*E*)-1-Bromo-2-phenyl-1-butene ((*E*)-5h): ^1H-NMR δ 1.03 (3H, t, *J* = 7.6 Hz), 2.71 (2H, q, 7.6 Hz), 6.33 (1H, s), 7.27–7.38 (5H, m); IR (liquid film) 1595 (s), 1490 (s), 1455 (s), 1450 (s), 1435 (s), 1210 (s), 755 (s), 735 (s), 700 (s), 690 cm^{-1} (s); MS, *m/z* (rel inten) 212, 210 (M^+, 62, 62), 131 (100), 116 (49), 115 (67), 102 (41), 91 (98); HRMS calcd for $C_{10}H_{11}{}^{79}Br$ 210.0044, found 210.0046; calcd for $C_{10}H_{11}{}^{81}Br$ 212.0024; found 212.0013. Anal. Calcd for $C_{10}H_{11}Br$ (a mixture of the *E* and *Z* isomers): C, 56.90; H, 5.25. Found: C, 56.94; H, 5.34.

(*Z*)-1-Bromo-2-phenyl-1-butene ((*Z*)-5h): ^1H-NMR δ 1.01 (3H, t, *J* = 7.4 Hz), 2.46 (2H, dq, *J* = 1.4 and 7.4 Hz), 6.23 (1H, t, *J* = 1.4 Hz), 7.23–7.42 (5H, m); IR (liquid film) 1490 (s), 1455 (s), 1440 (s), 910 (s), 810 (s), 785 (s), 765 (s), 730 (s), 695 cm^{-1} (s); MS, *m/z* (rel inten) 212, 210 (M^+, 30, 30), 131 (47), 116 (25), 115 (36), 102 (22), 91 (47), 78 (100); HRMS calcd for $C_{10}H_{11}{}^{79}Br$ 210.0044, found 210.0044; calcd for $C_{10}H_{11}{}^{81}Br$ 212.0024, found 212.0011.

(*E*)-1-Bromo-3-methoxy-2-phenyl-1-propene ((*E*)-5i): ^1H-NMR δ 3.39 (3H, s), 4.18 (2H, d, *J* = 1.5 Hz), 6.57 (2H, t, *J* = 1.5 Hz), 7.34–7.45 (5H, m); IR (liquid film) 1490 (s), 1440 (s), 1190 (s), 1115 (s), 1095 (s), 830 (s), 795 (s), 780 (s), 760 (s), 695 cm^{-1} (s); MS, *m/z* (rel inten) 228, 226 (M^+, 9, 9), 147 (100), 115 (90), 102 (58); HRMS calcd for $C_{10}H_{10}O^{79}Br$ 225.9993, found 226.0002; calcd for $C_{10}H_{11}O^{81}Br$ 227.9973, found 228.0010. Anal. Calcd for $C_{10}H_{11}OBr$ (a mixture of the *E* and *Z* isomers): C, 52.89; H, 4.88; Br, 35.19. Found: C, 52.88; H, 4.69; Br, 34.97.

(*Z*)-1-Bromo-3-methoxy-2-phenyl-1-propene ((*Z*)-5i): ^1H-NMR δ 3.36 (3H, s), 4.55 (2H, d, *J* = 0.4 Hz), 6.64 (1H, t, *J* = 0.4), 7.32–7.42 (5H, m); IR (liquid film) 1605 (s), 1495 (s), 1445 (s), 1190 (s), 1100 (s), 770 (s), 715 (s), 695 cm^{-1} (s); MS, *m/z* (rel inten) 228, 226 (M^+, 9, 9), 147 (100), 115 (87), 102 (56); HRMS calcd for $C_{10}H_{11}O^{79}Br$ 225.9993, found 225.9996; calcd for $C_{10}H_{11}O^{81}Br$ 227.9973, found 227.9962.

(*E*)-2-(1-Bromo-1-propen-2-yl)-1,3-dioxane ((*E*)-5j): ^1H-NMR δ 1.38 (1H, ttd, *J* = 1.3, 2.5, 13.5 Hz), 1.84 (3H, d, *J* – 1.4 Hz), 2.13 (1H, ttd, *J* = 5.0, 12.4, 13.5 Hz), 3.84 (2H, m), 4.17 (2H, m), 4.89 (1H, s), 6.50 (1H, br quint, *J* = ca. 1.3 Hz); ^{13}C-NMR δ 139.0, 108.6, 102.1, 67.1, 25.6, 15.1; IR (liquid film) 1645 (s), 1390 (s), 1380 (s), 1240 (s), 1155 (s), 1105 (s), 1040 (s), 1005 (s), 995 (s), 855 (s), 800 (s), 720 cm^{-1} (s); MS (CI), *m/z* (rel inten) 207, 209 (MH^+, 58, 58), 191, 193 (4, 4), 151, 149 (11, 11), 135, 133 (6, 6), 127 (100), 87 (49); HRMS (CI) calcd for $C_7H_{12}O_2{}^{79}Br$ (MH^+) 207.0021, found 207.0010; calcd for $C_7H_{12}O_2{}^{81}Br$(MH^+) 209.0000, found 208.9997. Anal. Calcd for $C_7H_{11}O_2Br$: C, 40.60; H, 5.35; Br, 38.59. Found: C, 40.43; H, 5.37; Br, 38.34.

(*Z*)-1-Chloro-3-[(phenylmethoxy)methoxy]-1-butene (7a): ^1H-NMR δ 1.30 (3H, d, *J* = 6.4 Hz), 4.60 (1H, d, *J* = 11.9 Hz), 4.67 (1H, d, *J* = 11.9 Hz), 4.74 (1H, d, *J* – 6.9 Hz), 4.77 (1H, d, *J* = 6.9 Hz), 4.85 (1H, dqd, *J* = 1.1, 6.4, 8.2 Hz), 5.79 (1H, dd, *J* = 7.3, 8.2 Hz), 6.14 (1H, dd, *J* = 1.1, 7.3 Hz), 7.27–7.40 (5H, m); IR (liquid film) 1630 (s), 1455 (s), 1375 (s), 1175 (s), 1125 (s), 1105 (s), 1040 (s), 1030 (s), 740 (s), 700 cm^{-1} (s); MS, *m/z* (rel inten) 119 ($M^+ - OCH_2Ph$, 6), 107 (9), 91 (100). Anal. Calcd for $C_{12}H_{15}O_2Cl$: C, 63.58; H, 6.67; Cl, 15.64. Found: C, 63.41; H, 6.73; Cl, 15.61.

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(*E*)-1-Chloro-3-methoxy-2-phenyl-1-propene ((*E*)-7c): ^{1}H-NMR δ 3.37 (3H, s), 4.19 (2H, d, *J* = 1.4 Hz), 6.42 (1H, t, *J* = 1.4 Hz), 7.31–7.43 (5H, m); IR (liquid film) 1490 (s), 1440 (s), 1190 (s), 1120 (s), 1100 (s), 870 (s), 810 (s), 760 (s), 725 (s), 700 cm^{-1} (s); MS, *m/z* (rel inten) 182 (M$^+$, 12), 147 (100), 115 (67), 102 (37); HRMS calcd for $C_{10}H_{11}O^{35}Cl$ 182.0499, found 182.0499. Anal. Calcd for $C_{10}H_{11}OCl$ (a mixture of the *E* and *Z* isomers): C, 65.76; H, 6.07; Cl, 19.41. Found C, 65.63; H, 6.13; Cl, 19.13.

(*Z*)-1-Chloro-3-methoxy-2-phenyl-1-propene ((*Z*)-7c): ^{1}H-NMR δ 3.36 (3H, s), 4.55 (2H, d, *J* = 0.45 Hz), 6.50 (1H, brs), 7.29–7.44 (5H, m); IR (liquid film) 1600 (s), 1490 (s), 1455 (s), 1440 (s), 1190 (s), 1100 (s), 810 (s), 750 (s), 695 cm^{-1} (s); MS, *m/z* (rel inten) 182 (M$^+$, 15), 147 (100), 115 (71), 102 (41); HRMS calcd for $C_{10}H_{11}O^{35}Cl$ 182.0499, found 182.0469.

(*Z*)-2-(1-Chloro-1-propen-2-yl)-1,3-dioxane (7d): ^{1}H-NMR δ 1.35 (1H, ttd, *J* = 1.3, 2.5, 13.5 Hz), 1.79 (3H, d, *J* = 1.6 Hz), 2.12 (1H, ttd, *J* = 5.0, 12.5, 13.5 Hz), 3.88 (2H, m), 4.14 (2H, m), 5.52 (1H, s), 5.92 (1H, m); ^{13}C-NMR δ 136.0, 115.4, 98.0, 67.0, 25.7, 15.5; IR (liquid film) 16.50 (s), 1395 (s), 1235 (s), 1150 (s), 1105 (s), 1035 (s), 1015 (s), 995 (s), 930 (s), 875 cm^{-1} (s); MS (CI), *m/z* (rel inten) 163 (MH$^+$, 46), 147 (10), 127 (100), 87 (30); HRMS (CI) calcd for $C_7H_{12}O_2{}^{35}Cl$ (MH$^+$) 163.0527, found 163.0515. Anal. Calcd for $C_7H_{11}O_2Cl$: C, 51.70; H, 6.82; Cl, 21.80. Found: C, 51.71; H, 6.72; Cl, 21.67.

Reaction of 1,1-Dibromoalkene 1a with $(Bu)_2CuLi$. To a suspension of CuI (200 mg, 1.05 mmol) in THF (3.7 mL) at −85 °C was added BuLi (1.62 M in hexane) (1.30 mL, 2.1 mmol). To the resulting dark blue mixture at −85 °C was then added a THF (2.5 mL) solution of **1a** (240 mg, 0.828 mmol). After being stirred for 3 h at −85 °C, the reaction was quenched with 10% AcOH in THF. The mixture was poured into brine and was extracted twice with ether. The combined organic layers were washed with aqueous $NaHCO_3$ and dried. Analysis of the mixture by GC (OV-17) using an internal standard method showed the formation of alkyne **9a**[29] in 76% yield.

Alkylation of 1,1-Dihaloalkenes 1 and 2 with Trialkylzincates. The reaction of dibromoalkene **1a** with $(Bu)_3ZnLi$ (Table II, entry 2) is given as a representative example. To a solution of $ZnCl_2$ (243 mg, 1.78 mmol) in THF (6 mL) at 0 °C was added BuLi (1.62 M in hexane, 3.16 mL, 5.12 mmol). After being stirred for 15 min, the mixture was cooled to −85 °C. To the cooled mixture, a THF (2 mL) solution of **1a** (339 mg, 1.17 mmol) was slowly added. After being stirred for 2 h at the same temperature, the mixture was allowed to warm to 0 °C over a 2.5-h period. The reaction was quenched with 10% AcOH in THF. The mixture was poured into aqueous 1 N HCl and extracted twice with ether. (In the reaction of **1j** and **2d**, brine was used instead of aqueous HCl). The combined organic layers were washed with aqueous $NaHCO_3$ and dried. Analysis of the mixture by GC (OV-17) using an internal standard method showed the formation of (*E*)- and (*Z*)-2-phenyl-3-octene (**11a**) (1:1.9) in 61% yield. (*E*)-**11a**: ^{1}H-NMR δ 0.89 (3H, m), 1.24–1.40 (7H, m, including d (3H, *J* = 7.1 Hz) at 1.33), 2.01 (2H, br q, *J* = 6.8 Hz), 3.41 (1H, quint, *J* = 6.9 Hz), 5.45 (1H, td, *J* = 6.6 and 15 Hz), 5.59 (1H, dd, *J* = 6.6 and 15 Hz), 7.15–7.32 (5H, m); ^{13}C-NMR δ 146.6, 134.8, 129.3, 128.3, 127.1, 125.9, 42.3, 32.2, 31.7, 22.2, 21.6, 14.0; IR (liquid film) 1600 (s), 1490 (s), 1450 (s), 970 (s), 905 (s), 755 (s), 730 (s), 695 (s) cm^{-1}; MS, *m/z* (rel inten) 188 (M$^+$, 20), 173 (4), 131 (100), 118 (63), 117 (54), 105 (30), 91 (50); HRMS calcd for $C_{14}H_{20}$ 188.1566, found 188.1559. Anal. A mixture of the *E* and *Z* isomers calcd for $C_{14}H_{20}$: C, 89.29; H, 10.71. Found: C, 89.59; H, 10.67. (*Z*)-**11a**: ^{1}H-NMR δ 0.89 (3H, m), 1.25–1.40 (7H, m, including d (3H, *J* = 6.9 Hz) at 1.32), 1.97–2.22 (2H, m), 3.77 (1H, qd, *J* = 6.9, 9.3 Hz), 5.37 (1H, td, *J* = 7.1, 10.8 Hz), 5.50 (1H, tdd, *J* = 1.4, 9.3, 10.8 Hz), 7.14–7.32 (5H, m); ^{13}C-NMR δ 146.7, 134.8, 128.8, 128.3, 126.8, 125.8, 37.2, 31.9, 27.1, 22.4, 22.3, 14.0; IR (liquid film) 1605 (s), 1490 (s), 1455 (s), 1450 (s), 1020 (s), 755 (s), 730 (s), 695 (s) cm^{-1}; MS, *m/z* (rel inten) 188 (M$^+$, 24), 131 (100), 118 (62), 117 (57), 105 (35), 91 (50); HRMS calcd for $C_{14}H_{20}$ 188.1566, found 188.1556.

Alkylation products **11b–r** obtained by a procedure similar to that described above. Spectral data of new compounds are as follows.[28–30]

(*E*)-2,2-Dimethyl-5-phenyl-3-hexene ((*E*)-11c): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 1.00 (9H, s), 1.32 (3H, d, *J* = 7.0 Hz), 3.40 (1H, m), 5.50 (2H, m), 7.13–7.35 (5H, m); IR (liquid film) 2960 (s), 1600 (s), 980 (s), 760 (s), 700 (s) cm^{-1}.

(*Z*)-2,2-Dimethyl-5-phenyl-3-hexene ((*Z*)-11c): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 1.14 (9H, s), 1.32 (3H, d, *J* = 7.0 Hz), 4.02 (1H, m), 5.32 (2H, m), 7.12–7.36 (5H, m); IR (liquid film) 2960 (s), 1600 (s), 750 (s), 700 (s) cm^{-1}.

(*E*)-1-Cyclohexyl-1-hexene ((*E*)-11d): ^{1}H-NMR δ 0.87 (3H, m), 0.95–1.37 (9H, m), 1.57–1.74 (5H, m), 1.81–2.03 (3H, m), 5.33 (2H, m); ^{13}C-NMR δ 136.4, 127.7, 40.7, 33.3, 32.3, 31.9, 26.2, 26.1, 22.2, 14.0; IR (liquid film) 1465 (s), 1455 (s), 1445 (s), 965 (s) cm^{-1}; MS, *m/z* (rel inten) 166 (M$^+$, 15), 109 (53), 96 (48), 82 (32), 81 (68), 67 (100); HRMS calcd for $C_{12}H_{22}$ 166.1722, found 166.1717. Anal. A mixture of the *E* and *Z* isomers calcd for $C_{12}H_{22}$: C, 86.67; H, 13.33. Found: C, 86.48; H, 13.44.

(*Z*)-1-Cyclohexyl-1-hexene ((*Z*)-11d): ^{1}H-NMR δ 0.89 (3H, m), 0.96–1.37 (9H, m), 1.52–1.74 (5H, m), 2.02 (2H, m), 2.24 (1H, tdt, *J* = 3.7, 7.9, and 12 Hz), 5.17 (1H, dd, *J* = 7.9 and 10.9 Hz), 5.24 (1H, td, *J* = 6.7 and 10.9 Hz); ^{13}C-NMR δ 136.0, 128.0, 36.3, 33.4, 32.2, 27.1, 26.1, 26.0, 22.3, 14.0; IR (liquid film) 1655 (m), 1465 (s), 1455 (s), 1445 (s), 890 (s), 730 (s) cm^{-1}; MS, *m/z* (rel inten) 166 (M$^+$, 15), 109 (51), 96 (46), 82 (33), 81 (67), 67 (100); HRMS calcd for $C_{12}H_{22}$ 166.1722, found 166.1719.

1-Phenyl-3-octene (11f): a mixture of the *E* and *Z* isomers; ^{1}H-NMR δ 0.87 (3H, m), 1.19–1.36 (4H, m), 1.97 (2H, m), 2.32 (2H, m), 2.65 (2H, m), 5.40 (2H, m), 7.14–7.30 (5H, m); IR (liquid film) 1605 (s), 1495 (s), 1465 (s), 1455 (s), 970 (s), 745 (s), 695 (s) cm^{-1}; MS, *m/z* (rel inten) 188 (M$^+$, 6), 131 (3), 117 (5), 104 (25), 91 (100); HRMS calcd for $C_{14}H_{20}$ 188.1566, found 188.1571. Anal. Calcd for $C_{14}H_{20}$: C, 89.29; H, 10.71. Found: C, 89.01; H, 10.65.

1-(Phenylmethoxy)-3-octene (11g): a mixture of the *E* and *Z* isomers; ^{1}H-NMR (60 MHz, $CDCl_3$) δ 0.73–1.07 (3H, m), 1.08–1.53 (4H, m), 1.80–2.60 (4H, m), 3.48 (2H, t, *J* = 7.0 Hz), 4.52 (2H, s), 5.47 (2H, m), 7.33 (5H, br s); IR (liquid film) 1500 (s), 1360 (s), 1205 (s), 1105 (s), 1030 (s), 970 (s), 910 (s), 735 (s), 700 (s) cm^{-1}; MS, *m/z* (rel inten) 218 (M$^+$, 2), 161 (5), 107 (10), 91 (100); HRMS calcd for $C_{15}H_{22}O$ 218.1672, found 218.1670.

(*E*)-2-[(Phenylmethoxy)methoxy]-3-octene ((*E*)-11h): ^{1}H-NMR δ 0.88 (3H, m), 1.22–1.40 (7H, m, including d at 1.25 (3H, *J* = 6.4 Hz)), 2.02 (2H, br q, *J* = ca. 7 Hz), 4.20 (1H, br quint, *J* = ca. 7 Hz), 4.54 (1H, d, *J* = 11.8 Hz), 4.67 (1H, d, *J* = 11.8 Hz), 4.70 (1H, d, *J* = 6.9 Hz), 4.79 (1H, d, *J* = 6.9 Hz), 5.33 (1H, tdd, *J* = 1.4, 7.8, and 15.4 Hz), 5.63 (1H, dtd, *J* = 0.4, 6.7, 15.4 Hz), 7.25–7.38 (5H, m); IR (liquid film) 1180 (s), 1105 (s), 1090 (s), 1040 (s), 1030 (s), 970 (s), 735 (s), 700 (s) cm^{-1}. Anal. Calcd for $C_{16}H_{24}O_2$: C, 77.38; H, 9.74. Found: C, 77.25; H, 9.93.

(*Z*)-2-[(Phenylmethoxy)methoxy]-3-octene ((*Z*)-11h): ^{1}H-NMR δ 0.88 (3H, m), 1.18–1.41 (7H, m, including d at 1.23 (3H, *J* = 6.4 Hz)), 2.08 (2H, m), 4.55 (1H, d, *J* = 11.9 Hz), 4.62 (1H, dqd, *J* = 0.8, 6.4, and 9.2 Hz), 4.68 (1H, d, *J* = 11.9 Hz), 4.69 (1H, d, *J* = 6.9 Hz), 4.76 (1H, d, *J* = 6.9 Hz), 5.28 (1H, tdd, *J* = 1.5, 9.2, 11.0 Hz), 5.54 (1H, dtd, *J* = 0.8, 7.5, 11.0 Hz), 7.25–7.38 (5H, m); IR (liquid film) 1650 (m), 1175 (s), 1100 (s), 1080 (s), 1035 (s), 1025 (s), 730 (s), 695 (s) cm^{-1}. Anal. Calcd for $C_{16}H_{24}O_2$: C, 77.38; H, 9.74. Found: C, 77.20; H, 9.97.

1-*tert*-Butyl-4-(1-pentylidene)cyclohexane (11i): bp 100–105 °C/0.25 mmHg; ^{1}H-NMR (200 MHz, $CDCl_3$) δ 0.83 (9H, s), 0.84 (3H, m), 1.11–12.08 (15H, m), 5.37 (1H, m); IR (liquid film) 1670 (w), 1475 (s), 1465 (s), 1460 (s), 1440 (s), 1390 (s), 1365 (s), 1240 (s), 925 (s), 845 (s) cm^{-1}; MS, *m/z* (rel inten) 208 (M$^+$, 18), 193 (6), 165 (8), 123 (12), 109 (46), 95 (75), 81 (64), 67 (52), 57 (100); HRMS calcd for $C_{15}H_{28}$ 208.2192, found 208.2194. Anal. Calcd for $C_{15}H_{28}$: C, 86.46; H, 13.54. Found C, 86.19; H, 13.26.

1-*tert*-Butyl-4-(neopentylidene)cyclohexane (11j): ^{1}H-NMR δ 0.83–1.22 (21H, m, including s (9H) at 0.83 and another s (9H) at 1.08), 1.69 (1H, m), 1.81 (2H, m), 1.95 (1H, m), 2.09 (1H, br qd, *J* = ca. 3, 13 Hz), 2.86 (1H, br qd, *J* = ca. 3, 13.5 Hz), 5.11 (1H, br s); ^{13}C-NMR δ 139.3, 131.7, 48.3, 38.6, 32.4, 31.6, 29.7, 28.4, 27.6: IR (liquid film) 16.55 (m), 1475 (s), 1465 (s), 1455 (s),

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1440 (s), 1390 (s), 1365 (s), 1240 (s), 995 (s), 840 cm^{-1} (s); MS, *m/z* (rel inten) 208 (M$^+$, 8), 193 (12), 151 (3), 137 (11), 123 (15), 109 (23), 95 (28), 81 (20), 69 (34), 57 (100); HRMS calcd for $C_{15}H_{28}$ 208.2192, found 208.2198.

(*E*)-1-Methoxy-2-phenyl-2-heptene ((*E*)-11l): ^{1}H-NMR δ 0.83 (3H, t, *J* = 7.1 Hz), 1.20–1.40 (4H, m), 2.04 (2H, br q, *J* = 7.4 Hz), 3.33 (3H, s), 4.12 (2H, br d, *J* = 0.8 Hz), 5.73 (1H, tt, *J* = 0.8 and 7.4 Hz), 7.20–7.37 (5H, m); IR (liquid film) 1500 (m), 1490 (s), 1465 (s), 1455 (s), 1445 (s), 1440 (s), 1190 (s), 1110 (s), 1100 (s), 850 (m), 765 (s), 700 cm^{-1} (s); MS, *m/z* (rel inten) 204 (M$^+$, 6), 172 (37), 147 (66), 143 (50) 129 (100), 115 (46), 91 (54), 84 (64); HRMS calcd for $C_{14}H_{20}O$ 204.1414, found 204.1519. Anal. A mixture of the *E* and *Z* isomers calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.00; H, 10.03.

(*Z*)-1-Methoxy-2-phenyl-2-heptene ((*Z*)-11l): ^{1}H-NMR δ 0.94 (3H, t, *J* = 7.2 Hz), 1.33–1.52 (4H, m), 2.31 (2H, br q, *J* = 7.3 Hz), 3.35 (3H, s), 4.36 (2H, s), 5.99 (1H, t, *J* = 7.5 Hz), 7.21–7.35 (3H, m), 7.41–7.45 (2H, m); IR (liquid film) 1595 (m), 1490 (s), 1465 (s), 1455 (s), 1450 (s), 1190 (s), 1095 (s), 950 (s), 755 (s), 695 (s) cm^{-1}; MS, *m/z* (rel inten) 204 (M$^+$, 1), 172 (52), 147 (32), 143 (56), 129 (100), 115 (36), 91 (42); HRMS calcd for $C_{14}H_{20}O$ 204.1515, found 204.1513.

(*E*)-1-Methoxy-2-phenyl-2-butene ((*E*)-11m): ^{1}H-NMR δ 1.67 (3H, td, *J* = 1.1, 6.9 Hz), 3.33 (3H, s), 4.12 (2H, quint, *J* = 1.1 Hz), 5.85 (1H, tq, *J* = 1.1, 6.9 Hz), 7.22–7.39 (5H, m); IR (liquid film) 1595 (m), 1120 (s), 1105 (s), 1090 (s), 910 (s), 830 (s), 760 (s), 695 cm^{-1} (s); MS, *m/z* (rel inten) 162 (M$^+$, 32), 161 (11), 147 (57), 130 (100), 115 (93), 91 (90); HRMS calcd for $C_{11}H_{14}O$ 162.1045, found 162.1032.

(*Z*)-1-Methoxy-2-phenyl-2-butene ((*Z*)-11m): ^{1}H-NMR δ 1.91 (3H, d, *J* = 7.1 Hz), 3.36 (3H, s), 4.37 (2H, s), 6.08 (1H, q, *J* = 7.1 Hz), 7.16–7.35 (3H, m), 7.40–7.45 (2H, m); IR (liquid film) 1600 (m), 1490 (s), 1190 (s), 1095 (s), 950 (s), 840 (m), 755 (s), 695 cm^{-1} (s); MS, *m/z* (rel inten) 162 (M$^+$, 16), 161 (9), 147 (39), 130 (100), 115 (75), 91 (62); HRMS calcd for $C_{11}H_{14}O$ 162.1045, found 162.1058.

(*E*)-1-Methoxy-4-methyl-2-phenyl-2-hexene ((*E*)-11n): ^{1}H-NMR δ 0.78 (3H, t, *J* = 7.4 Hz), 0.93 (3H, d, *J* = 6.7 Hz), 1.19–1.34 (2H, m), 2.15 (1H, m), 3.33 (3H, s), 4.09 (2H, d, *J* = 0.92 Hz), 5.46 (1H, br d, *J* = 10.3 Hz), 7.16–7.36 (5H, m); ^{13}C-NMR δ 139.5, 136.8, 136.1, 128.5, 128.1, 126.7, 77.9, 57.6, 34.3, 30.1, 20.9, 11.9; IR (liquid film) 1600 (m), 1490 (s), 1455 (s), 1375 (s), 1190 (s), 1105 (s), 875 (s), 765 (s), 700 (s) cm^{-1}; MS, *m/z* (rel inten) 204 (M$^+$, 0.5), 172 (6), 157 (40), 143 (58), 128 (36), 87 (100); HRMS calcd for $C_{14}H_{20}O$ 204.1515, found 204.1525. Anal. A mixture of the *E* and *Z* isomers calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.32; H, 9.93.

(*Z*)-1-Methoxy-4-methyl-2-phenyl-2-hexene ((*Z*)-11n): ^{1}H-NMR δ 0.90 (3H, t, *J* = 7.4 Hz), 1.05 (3H, d, *J* = 6.6 Hz), 1.27–1.52 (2H, m), 2.56 (1H, m), 3.32 (3H, s), 4.33 (1H, d, *J* = 11.4 Hz), 4.38 (1H, d, *J* = 11.4 Hz), 5.72 (1H, d, *J* = 10.0 Hz), 7.19–7.34 (3H, m), 7.41–7.45 (2H, m); ^{13}C-NMR δ 141.7, 140.1, 134.8, 128.2, 126.8, 126.2, 69.3, 57.7, 34.6, 30.4, 21.0, 12.0; IR (liquid film) 1595 (m), 1490 (s), 1455 (s), 1185 (s), 1095 (s), 950 (s), 755 (s), 695 cm^{-1} (s); MS, *m/z* (rel inten) 204 (M$^+$, 1), 172 (29), 157 (83), 143 (98), 128 (59), 87 (100). HRMS calcd for $C_{14}H_{20}O$ 204.1515, found 204.1498.

(*E*)-1-Methoxy-4,4-dimethyl-2-phenyl-2-pentene ((*E*)-11o): ^{1}H-NMR δ 0.88 (9H, s), 3.32 (3H, s), 3.94 (2H, d, *J* = 1.2 Hz), 5.67 (1H, t, *J* = 1.2 Hz), 7.12–7.16 (2H, m), 7.21–7.32 (3H, m); ^{13}C-NMR δ 140.1, 139.4, 135.0, 129.2, 127.6, 126.7, 79.9, 57.7, 33.4, 31.2; IR (liquid film) 1600 (m), 1470 (s), 1455 (s), 1360 (s), 1200 (s), 1120 (s), 1105 (s) 765 (s), 700 (s) cm^{-1}; MS, *m/z* (rel inten) 204 (M$^+$, 0.2), 172 (5), 157 (39), 142 (15), 129 (28), 73 (100). Anal. A mixture of the *E* and *Z* isomers calcd for $C_{14}H_{20}O$: C, 82.30; H, 9.87. Found: C, 82.04; H, 9.88.

(*Z*)-1-Methoxy-4,4-dimethyl-2-phenyl-2-pentene ((*Z*)-11o): ^{1}H-NMR δ 1.24 (9H, s), 3.33 (3H, s), 4.42 (2H, s), 5.90 (1H, s), 7.14–7.40 (5H, m); ^{13}C-NMR δ 144.4, 143.4, 135.7, 128.1, 126.6 126.5, 69.3, 58.0, 33.3, 31.5; IR (liquid film) 1600 (m), 1490 (s), 1475 (s), 1465 (s), 1450 (s), 1365 (s), 1190 (s), 1100 (s), 955 (s), 750 (s), 695 (s) cm^{-1}; MS, *m/z* (rel inten) 204 (M$^+$, 2), 172 (3), 157 (35), 142 (13), 129 (23), 73 (100); HRMS calcd for $C_{14}H_{20}O$ 204.1515, found 204.1525.

2-(Hept-2-en-2-yl)-1,3-dioxane (11p): a mixture of the *E* and *Z* isomers; ^{1}H-NMR (200 MHz, C_6D_6) δ 0.62 (1H, m), 0.81 (3H for the *E* isomer, t, *J* = 7.2 Hz), 0.86 (3H for the *Z* isomer, t, *J* = 7.0 Hz), 1.17–1.42 (4H, m), 1.82 (1H, m), 1.90 (3H for the *E* isomer, d, *J* = 0.6 Hz), 2.00 (2H for the *E* isomer, br q, *J* = ca. 7 Hz), 2.08 (3H for the *Z* isomer, d, *J* = 1.2 Hz), 2.16 (2H for the *Z* isomer, br q, *J* = ca. 7 Hz), 3.35–3.43 (2H, m), 3.78–3.90 (2H, m), 4.77 (1H for the *E* isomer, s), 5.31 (1H for the *Z* isomer, s), 5.32 (1H for the *Z* isomer, br t, *J* = ca. 7 Hz), 5.75 (1H for the *E* isomer, br t, *J* = ca. 7 Hz); ^{13}C-NMR (*E* isomer) δ 12.32, 14.61, 23.10, 26.58, 27.81, 32.31, 67.27, 105.98, 129.22, 134.44; IR (liquid film) 1470 (s), 1400 (s), 1270 (s), 1235 (s), 1215 (s), 1150 (s), 1100 (s), 990 (s) cm^{-1}; MS (CI), *m/z* (rel inten) 185 (MH$^+$, 38), 149 (8), 127 (100); HRMS (CI) calcd for $C_{11}H_{21}O_2$(MH$^+$) 185.1542, found 185.1539.

2-(3-Methyl-hex-2-en-2-yl)-1,3-dioxane (11q): a mixture of the *E* and *Z* isomers; ^{1}H-NMR (200 MHz, C_6D_6) δ 0.58 (1H, br d, *J* = ca. 13 Hz), 0.72–0.95 (6H, m), 1.08–1.31 (2H, m), 1.63–1.89 (1H, m), 1.85 (3H for the *E* isomer, d, *J* = 1.4 Hz), 2.00 (3H for the *Z* isomer, d, *J* = 1.4 Hz), 2.13–2.52 (1H, m), 3.36 (2H, m), 3.80 (2H, m), 4.70 (1H for the *Z* isomer, s), 5.04 (1H for the *Z* isomer, br d, *J* = 9.6 Hz), 5.25 (1H for the *E* isomer, s), 5.47 (1H for the *E* isomer, br d, *J* = 9.6 Hz); IR (liquid film) 1460 (s), 1380 (s), 1235 (s), 1150 (s), 1130 (s), 1100 (s), 990 (s) 930 (s), 890 (s) cm^{-1}.

2-(3,3-Dimethylpent-2-en-2-yl)-1,3-dioxane (11r): a mixture of the *E* and *Z* isomers; ^{1}H-NMR (200 MHz, C_6D_6) δ 0.57 (1H, br d, *J* = ca. 13 Hz), 1.04 (9H for the *E* isomer, s), 1.11 (9H, for the *Z* isomer, s), 1.62–1.88 (1H, m), 1.95 (3H for the *E* isomer, d, *J* = 1.4 Hz), 2.01 (3H for the *Z* isomer, d, *J* = 1.4 Hz), 2.13–2.52 (1H, m), 3.35 (2H, dt, *J* = 2.4 and 12.3 Hz), 3.79 (2H, ddd, 1.2, 5.1, 12.3 Hz), 4.61 (1H for the *E* isomer, s), 5.36 (1H for the *Z* isomer, br s), 5.51 (1H for the *Z* isomer, s), 5.72 (1H for the *E* isomer, br s); IR (liquid film) 1460 (s), 1375 (s), 1235 (s), 1150 (s), 1105 (s), 1040 (s), 990 (s), 930 (s), 850 (s) cm^{-1}.

Palladium-Catalyzed Coupling Reactions of Alkenylzinc Species Generated by the Reactions of 1,1-Dihaloalkenes with Tributylzincate. Preparation of enone **13a** by acetylation of the alkenylzinc species generated by the reaction of **1a** and $(Bu)_3ZnLi$ is given as a representative example. To a solution of $ZnCl_2$ (137 mg, 1.01 mmol) in THF (3.5 mL) at 0 °C was added BuLi (1.62 M in hexane, 1.86 mL, 3.02 mmol). After being stirred for 15 min, the mixture was cooled to −85 °C. To the cooled solution was slowly added a THF (2 mL) solution of **1a** (232 mg, 0.80 mmol). After being stirred for 3 h at the same temperature, the mixture was allowed to warm to 0 °C over a 2-h period. Then a THF suspension of $(Ph_3P)_2Pd$ [prepared by the reaction of $(Ph_3P)_2PdCl_2$ (57.3 mg, 0.082 mmol) and DIBALH (1.5 M in toluene, 0.11 mL, 0.16 mmol) in THF 5.7 mL] and acetyl chloride (0.21 mL, 3.02 mmol) were successively added. After being stirred at rt for 21 h, the mixture was poured into aq 1 N HCl and was extracted twice with ether. The combined organic layers were washed with aq $NaHCO_3$, dried over Na_2SO_4, and concentrated in vacuo. After removal of volatile byproducts by Kugelrohr distillation (80 °C/20 mmHg), the residue was purified by flash chromatography (3% EtOAc in hexane) to give 102.4 mg (56%) of a 2.2:1 mixture of (*E*)- and (*Z*)-3-butyl-5-phenylhex-3-en-2-one (**13a**). (*E*)-**13a**: ^{1}H-NMR (200 MHz) δ 0.89 (3H, br t, *J* = 6.4 Hz), 1.20–1.38 (4H, m), 1.42 (3H, d, *J* = 6.8 Hz), 2.28 (3H, s), 2.35 (2H, br t, *J* = 7.6 Hz), 3.86 (1H, qd, *J* = 7.0 and 9.8 Hz), 6.62 (1H, d, *J* = 9.8 Hz), 7.16–7.43 (5H, m); IR (liquid film) 1670 (s), 760 (s), 700 cm^{-1} (s); MS, *m/z* (rel inten) 230 (M$^+$, 62), 187 (90), 143 (34), 131 (90), 105 (100); HRMS calcd for $C_{16}H_{22}O$ 230.1672, found 230.1688. (*Z*)-**13a**: ^{1}H-NMR (200 MHz) δ 0.88 (3H, br t, *J* = 6.8 Hz), 1.12–1.47 (7H, m, including d (3H, *J* = 7.0) at 1.34) 2.18–2.30 (5H, m, including s (3H) at 2.24), 3.91 (1H, qd, *J* = 6.6 and 10.2), 5.6 (1H, brd, *J* = 10.2), 7.09–7.40 (5H, m); IR (liquid film) 1690 (s), 760 (s), 700 (s) cm^{-1}; MS, *m/z* (rel inten) 230 (M$^+$, 73), 187 (93), 143 (45), 131 (100); HRMS calcd for $C_{16}H_{22}O$ 230.1672, found 230.1688.

3-(4-*tert*-Butylcyclohexylidene)-2-heptanone (13b): ^{1}H-NMR (200 MHz) δ 0.80 (9H, s), 0.86 (3H, t, *J* = 7.0), 0.94–1.83 (11H, m), 2.05 (3H, s), 2.19 (2H, t, *J* = 7.2), 2.51 (1H, br d, *J* = 13.1), 2.76 (1H, br d, *J* = 13.1); IR (liquid film) 1685 (s), 1360 (s), 1350 (s) cm^{-1}; MS, *m/z* (rel inten) 250 (M$^+$, 100), 235 (60), 207 (20), 193 (30), 151 (50); HRMS calcd for $C_{17}H_{30}O$ 250.2298, found 250.2299.

(*E*)-3-Butyl-4-phenylhex-3-en-2-one ((*E*)-13c): ^{1}H-NMR δ 0.75 (3H, t, *J* = 7.1 Hz), 0.89 (3H, t, *J* = 7.4 Hz), 1.09–1.29 (4H, m), 2.06 (2H, br dd, *J* = ca. 7 and 8.5 Hz), 2.34 (2H, q, *J* = 7.4

Hz), 2.35 (3H, s), 7.08–7.38 (5H, m); ^{13}C-NMR δ 207.6, 143.1, 140.8, 139.2, 128.12, 128.08, 126.8, 31.0, 30.6, 30.5, 28.9, 22.4, 13.7, 13.0; IR (liquid film) 1690 (s), 1680 (s), 1465 (s), 1460 (s), 1445 (s), 1350 (s), 1230 (s), 1130 (s), 770 (s), 705 (s) cm^{-1}; MS *m/z* (rel inten) 230 (M$^+$, 43), 215 (10), 201 (31), 187 (15), 173 (9), 159 (7), 91 (43), 43 (100); HRMS calcd for $C_{16}H_{22}O$ 230.1671, found 230.1678. Anal. A mixture of the *E* and *Z* isomers calcd for $C_{18}H_{22}O$: C, 83.43; H, 9.63. Found: C, 83.42; H, 9.88.

(*Z*)-3-Butyl-4-phenylhex-3-en-2-one ((*Z*)-13c): ^{1}H-NMR δ 0.90 (3H, t, *J* = 7.5 Hz), 0.92 (3H, m), 1.29–1.44 (4H, m), 1.61 (3H, s), 2.41 (2H, m), 2.50 (2H, q, *J* = 7.5 Hz), 7.11–7.17 (2H, m), 7.27–7.35 (3H, m); ^{13}C-NMR δ 208.3, 145.3, 141.8, 140.9, 128.6, 128.4, 127.7, 31.4, 31.3, 30.3, 27.5, 22.8, 14.0, 12.7; IR (liquid film) 1680 (s), 1465 (s), 1460 (s), 1350 (s), 1230 (s), 1125 (s), 770 (s), 705 cm^{-1} (s); MS, *m/z* (rel inten) 230 (M$^+$, 59), 215 (14), 201 (40), 187 (19), 173 (10), 159 (9), 91 (52), 43 (100); HRMS calcd for $C_{16}H_{22}O$; 230.1671, found; 230.1676.

(*E*)-3-Butyl-5-methoxy-4-phenylpent-3-en-2-one ((*E*)-13d): bp 100–110 °C/2.0 mmHg (Kugelrohr); ^{1}H-NMR δ 0.91 (3H, m), 1.28–1.45 (4H, m), 1.66 (3H, s), 2.48 (2H, m), 3.30 (3H, s), 4.29 (2H, s), 7.18–7.34 (5H, m); ^{13}C-NMR δ 208.3, 145.7, 140.3, 137.9, 128.51, 128.45, 128.1, 72.2, 58.2, 31.2, 31.1, 30.8, 22.8, 13.9; IR (liquid film) 1685 (s), 1350 (s), 1225 (s), 1125 (s), 1090 (s), 770 (s), 705 cm^{-1} (s); MS, *m/z* (rel inten) 246 (M$^+$, 11), 203 (24), 143 (16), 129 (28), 115 (12); HRMS calcd for $C_{16}H_{22}O_2$ 246.1620, found 246.1615.

(*Z*)-3-Butyl-5-methoxy-4-phenylpent-3-en-2-one ((*Z*)-13d): bp 100–110 °C/2.0 mmHg (Kugelrohr); ^{1}H-NMR δ 0.75 (3H, t, *J* = 7.2 H), 1.10–1.32 (4H, m), 2.13 (2H, br t, *J* = ca. 8 Hz), 2.36 (3H, s), 3.24 (3H, s), 4.11 (2H, s), 7.15–7.20 (2H, m), 7.25–7.38 (3H, m); ^{13}C-NMR δ 207.2, 142.9, 139.0, 136.5, 128.3, 128.2, 127.3, 73.6, 58.2, 30.6, 30.52, 30.48, 22.4, 13.6; IR (liquid film) 1695 (s), 1355 (s), 1195 (s), 1130 (s), 1110 (s), 765 (s), 705 (s) cm^{-1}; MS, *m/s* (rel inten) 246 (M$^+$, 11), 203 (24), 143 (16), 129 (29), 115 (12), 43 (100); HRMS calcd for $C_{16}H_{22}O_2$ 246.1620, found 246.1612. Anal. Calcd for $C_{16}H_{22}O_2$: C, 78.01; H, 9.00. Found: C, 77.72; H, 9.11.

(*Z*)-Ethyl 2-Butyl-3-[(benzyloxy)methoxy]pent-2-enoate (14a): ^{1}H-NMR δ 0.88 (3H, t, *J* = 7.2 Hz), 1.23–1.43 (10H, m, including t (3H, *J* = 7.1 Hz) at 1.26 and d (3H, *J* = 6.4 Hz) at 1.28), 2.19 (1H, dtd, *J* = 0.8, 7.3, and 13.8 Hz), 2.28 (1H, td, *J* = 7.0 and 13.8 Hz), 4.17 (2H, dq, *J* = 1.1 and 7.1 Hz), 4.55 (1H, d, *J* = 11.8 Hz), 4.63 (1H, d, *J* = 11.8 Hz), 4.71 (1H, d, *J* = 6.9 Hz), 4.74 (1H, d, *J* = 6.9 Hz), 4.98 (1H, qd, *J* = 6.4, 8.3 Hz), 5.76 (1H, td, *J* = 1.1, 8.3 Hz), 7.23–7.36 (5H, m); IR (liquid film) 1710 (s), 1370 (s), 1220 (s), 1205 (s), 1175 (s), 1150 (s), 1125 (s), 1100 (s), 1035 (s), 1025 (s), 730 (s), 695 (s) cm^{-1}. Anal. Calcd for $C_{19}H_{28}O_4$: C, 71.22; H, 8.81. Found: C, 71.47; H, 9.01.

Ethyl 2-(4-*tert*-Butylcyclohexylidene)-2-hexenoate (14b): ^{1}H-NMR (200 MHz, $CDCl_3$) δ 0.83 (9H, s), 0.88 (3H, t, *J* = 7.0), 0.95–1.45 (11H, m, including t, (3H, *J* = 7.2) at 1.28, 1.70–1.98 (3H, m), 2.27 (3H, br t, *J* = 7.0), 2.66 (1H, br d, *J* = 13.7), 2.91 (1H, br d, *J* = 13.7), 4.18 (2H, q, *J* = 7.2); IR (liquid film) 1715 (s), 1110 (s), 1030 cm^{-1} (s); MS, *m/z* (rel inten) 280 (M$^+$, 100), 265 (10), 251 (5), 235 (41), 223 (16); HRMS calcd for $C_{18}H_{32}O_2$ 280.2404, found 280.2401.

(*Z*)-5-[(Benzyloxy)methoxy]-3-butyl-2-methyl-1,3-hexadiene ((*Z*)-15a): ^{1}H-NMR δ 0.88 (3H, m), 1.18–1.40 (7H, m, including d (3H, *J* = 6.4 Hz) at 1.22), 1.78 (3H, dd, *J* = 0.8, 1.4 Hz), 2.06 (2H, m), 4.52 (1H, d, *J* – 11.9 Hz), 4.55 (1H, qd, *J* = 6.4, 9.2 Hz), 4.61 (1H, m), 4.65 (1H, d, *J* = 11.9 Hz), 4.67 (1H, d, *J* = 6.8 Hz), 4.73 (1H, d, *J* = 6.8 Hz), 4.94 (1H, qd, *J* = 1.4, 2.9 Hz), 5.08 (1H, br d, *J* = 9.2 Hz), 7.25–7.38 (5H, m); IR (liquid film) 1100 (s), 1075 (s), 1030 (s), 1025 (s), 895 (s), 730 (s), 695 (s) cm^{-1}. Anal. Calcd for $C_{19}H_{28}O_2$: C, 79.12; H, 9.80. Found C, 78.96; H, 9.82.

3-Butyl-2-methyl-5-methoxy-4-phenyl-1,3-pentadiene (15b): a mixture of the *E* and *Z* isomers; ^{1}H-NMR δ 0.75 (3H for the *Z* isomer, t, *J* = 7.2 Hz), 0.94 (3H for the *E* isomer, t, *J* = 7.0 Hz), 1.15 (2H for the *Z* isomer, sext, *J* = 7.2 Hz), 1.23–1.48 (4H for the *E* isomer and 2H for the *Z* isomer, m), 1.60 (3H for the *E* isomer, s), 1.89 (3H for the *Z* isomer, s), 1.99 (2H for the *Z* isomer, br t, *J* = ca. 8 Hz), 2.37 (2H for the *E* isomer, br t, *J* = ca. 7.5 Hz), 3.22 (3H for the *Z* isomer, s), 3.31 (3H for the *E* isomer, s), 4.17 (2H for the *Z* isomer, s), 4.22 (2H for the *E* isomer, s), 4.58 (1H for the *E* isomer, br d, *J* = 1.1 Hz), 4.77 (1H for the *E* isomer, br quint, *J* = 1.6 Hz), 4.82 (1H for the *Z* isomer, br d, *J* = 2.1 Hz), 5.06 (1H for the *Z* isomer, qd, *J* = 1.4, 2.6 Hz), 7.18–7.36 (5H, m); IR (liquid film) 1630 (s), 1600 (s), 1465 (s), 1460 (s), 1445 (s), 1375 (s), 1190 (s), 1090 (s), 895 (s), 700 (s) cm^{-1}; MS, *m/z* (rel inten) 244 (M$^+$, 4), 199 (37), 187 (27), 169 (25), 155 (100), 143 (73), 129 (43), 115 (35), 91 (62); HRMS calcd for $C_{17}H_{24}O$ 244.1828, found 244.1833.

4-*tert*-Butyl-1-(1-phenylpentylidene)cyclohexane (16a): ^{1}H-NMR (200 MHz) δ 0.74–0.90 (12H, m), 0.91–1.31 (7H, m), 1.59–1.88 (2H, m), 1.89–1.98 (2H, m), 2.18–2.38 (3H, m), 2.80 (1H, br d, *J* = 13.1), 7.03–7.12 (2H, m), 7.13–7.35 (3H, m); IR (liquid film) 1390 (s), 770 (s), 700 (s) cm^{-1}; MS, *m/z/* (rel inten) 284 (M$^+$, 100), 227. (64), 171 (26), 143 (361), 129 (67) 91 (97); HRMS calcd for $C_{21}H_{32}$ 284.2506, found 284.2509.

1-Methoxy-2,3-diphenyl-2-heptene (16b): a mixture of the *E* and *Z* isomers; bp 145–150 °C/2.0 mmHg (Kugelrohr); ^{1}H-NMR δ 0.69 (3H for the *Z* isomers, t, *J* = 7.0 Hz), 0.88 (3H for the *E* isomer, m), 1.05–1.22 (4H for the *Z* isomer, m), 1.26–1.40 (4H for the *E* isomer, m), 2.25 (2H for the *Z* isomer, br t, *J* = ca. 7.5 Hz), 2.65 (2H for the *E* isomer, m), 3.12 (3H for the *Z* isomer, s), 3.37 (3H for the *E* isomer, s), 3.93 (2H for the *Z* isomer, s), 4.39 (2H for the *E* isomer, s), 6.95–7.12 (10H for the *E* isomer, m), 7.25–7.41 (10H for the *Z* isomer, m); IR (liquid film) 1600 (s), 1490 (s), 1465 (s), 1460 (s), 1445 (s), 1380 (s), 1190 (s), 1125 (s), 1090 (s), 1070 (s), 770 (s), 700 (s) cm^{-1}; MS, *m/z* (rel inten) 280 (M$^+$, 5), 248 (69), 223 (84), 205 (76), 191 (43), 115 (40), 91 (100); HRMS calcd for $C_{20}H_{24}O$ 280.1828, found 280.1831. Anal. Calcd for $C_{20}H_{24}O$: C, 85.67; H, 8.63. Found C, 85.87; H, 8.62.

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Supplementary Material Available: High-field ^{1}H-NMR spectra of **1e**, **5e**, **11c,g,m,p–r**, **13a,b**, **14b**, **15b**, and **16a** and NOESY spectra of **5h–j**, **7c,d**, **11k–o**, **13c,d**, **15b**, and **16b** (39 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.