Regioselective Allylation of Ketenes Promoted by SmI_2

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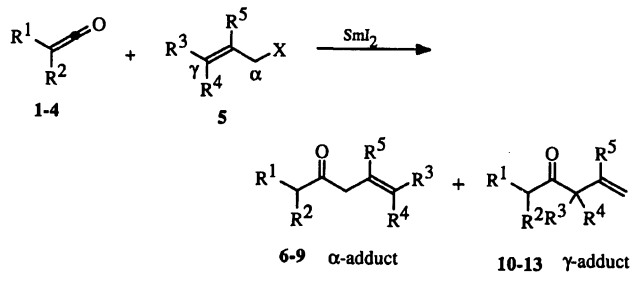
Ketenes react with various allylic halides mediated by 2 equiv samarium(II) diiodide (SmI_2) to the ketenes to afford allylated ketones in good yields. In the reaction with γ-substituted allylic halides, the regioselectivity is influenced by the olefinic geometry of allylic halides. By using γ-substituted (*E*)-allylic halides, the allylation proceeds on the less hindered site (α-position) of allylic groups predominantly and the tendency was enhanced by the addition of HMPA.

In the course of our investigation on the SmI_2 mediated reactions,[1,2] ketenes were found to react with allyl iodide to afford the adducts as the forms of samarium enolate, protonation of which with chiral proton sources afforded the optically active allylated ketones with good enantioselectivity.[3]

Allylation of carbonyl compounds is one of the useful tools in organic synthesis. Although the allylation reactions to aldehydes and ketones have been investigated extensively,[4] there are few reports on allylation of ketenes,[5] and, to our knowledge, no reports on that with γ-substituted allylating agents. Using γ-substituted allylic halides, it would be considered that allylation of ketenes would give two regioisomers, α-adduct **6**—**9** and γ-adduct **10**—**13** (Eq. 1). Furthermore the isomerization of olefinic double bonds (*E* to *Z* geometries and/or β,γ-unsaturated ketones **6**—**9** to α,β-unsaturated isomer **6′**—**9′**) sometimes occurred. It is necessary to control the regio- and stereoselectivities to enhance the synthetic usefulness of the allylation of ketenes.

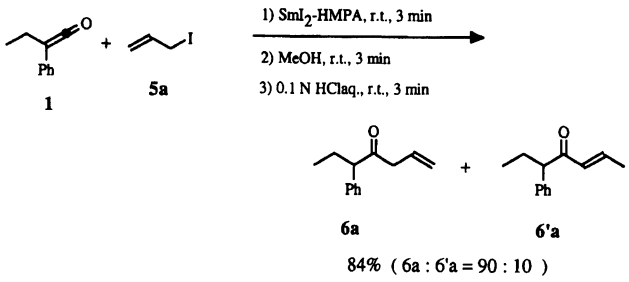


(1)

In this paper are reported the scope and limitation of the SmI_2 mediated allylation of ketenes particularly using γ-substituted allylic halides and the regio- and stereoselectivities of the allylation.

Results and Discussion

First, the reaction between ethylphenylketene (**1**) and allyl iodide (**5a**) was examined under various reaction conditions. Optimum conditions were as follows: Under an argon atmosphere a 0.1 mol dm^{-3} THF solution of SmI_2 was added to the solution of **1** and **5a** at room temperature. After this was stirred for 3 min, the reaction was quenched with methanol, then with 0.1 mol dm^{-3} hydrochloric acid. After the usual work-up, the corresponding product was obtained in 75% yield with the ratio of β,γ-unsaturated ketone **6a**:α,β-unsaturated one **6′a**=ca. 90:10 (Eq. 2). By the addition of 1 mol equiv HMPA to SmI_2, the yield was increased to 84% (**6a**:**6′a**=ca. 90:10). When the reaction was quenched directly with 0.1 mol dm^{-3} hydrochloric acid, the generated samarium enolate reacted with oxygen in air to give a by-product, 3-hydroperoxy-3-phenyl-6-hepten-4-one, in 22% yield, and the total yield of the adduct **6a** and **6′a** was decreased to 54%. By the addition of methanol, the oxidation of the samarium enolate didn't occur, and the adducts **6a** and **6′a** were obtained in good yield.



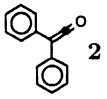
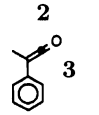
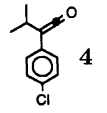
(2)

Furthermore, investigating the reaction of ethylphenylketene (**1**) with several allylating agents under similar conditions, allyl bromide was found also to be an effective allylating agent. The yield slightly decreased to 73%, but the formation of α,β-unsaturated ketone **6′a** was not detected in the products by the 200 MHz ^{1}H NMR spectrum. Though allyl chloride and allyl *p*-toluenesulfonate are useful reagents for the SmI_2 mediated allylation of aldehydes,[6] for the allylation of the ketene **1** the yield was decreased to 17% with allyl *p*-toluenesulfonate, and the product was not isolated with allyl chloride. Organic tin compounds, such as allyltriphenyltin and trialkyltin hydride, have a powerful reactivity for radical species,[7] and the SmI_2-mediated reaction with tributyltin hydride as hydrogen donor to the ketyl radical has been reported.[8] If the radical species was generated from the ketene and SmI_2 in this reaction, it was considered to react with allyltriphenyltin. However, use of allyltriphenyltin afforded none of the adduct.

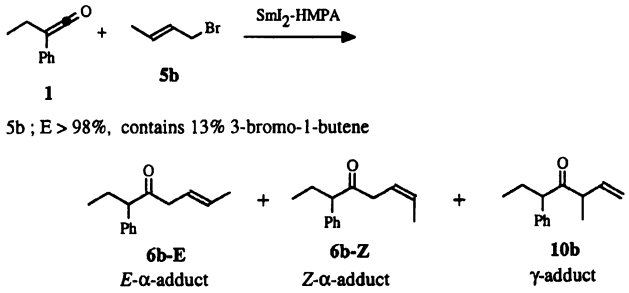
Based on these results, the generality of this allylation reaction was examined using several ketenes and substituted allylic halides. The results are shown in Table 1. Except for the use of γ,γ-disubstituted allylic halide, 1-bromo-3-methyl-2-butene (**5d**) (Entries 4 and 10), the reactions proceeded smoothly to afford the adducts **6**—**9** in moderate to good yields, and benzyl bromide (**5f**) also reacted with ketenes to give the product **6f**,**7f** in good yield (Entries 6 and 12). In these reactions, β,γ-unsaturated ketones were obtained exclusively, and the isomerized α,β-unsaturated ketones were not detected in 200 MHz ^{1}H NMR spectra. Although it has been reported that HMPA accelerates the reactions mediated by SmI_2,[9] in some cases of this system, the yields were decreased by the addition of HMPA.

It is noticed that 1-bromo-2-butene (**5b**) and 3-bromo-1-phenyl-1-propene (**5e**) react smoothly with ethylphenylketene (**1**) and diphenylketene (**2**) to give the α-adducts **6**,**7** with high selectivity (Entries 2,5,8, and 11).[10,11] In the detailed analysis of the products of the reaction between the bromide **5b** and the ketene **1**, the ratio of the α-adducts **6b-*E***, **6b-*Z*** and the γ-adduct **10b** was found to be 84 : 5 : 11 by 400 MHz NMR spectra (Eq. 3). The reactions of 1-bromo-2-butene (**5b**) with various ketenes were also carried out, and the results are shown in Table 2. Except for diphenylketene (**2**) (Entry 4), α-selectivity was increased by the addition of HMPA, and in the reaction of ethylphenylketene (**1**) and 4-chlorophenylisopropylketene (**4**), the yield was also increased (Entries 2 and 3). However the reaction of diphenylketene (**2**) showed the opposite tendency upon the addition of HMPA (Entry 4). The reaction of the ketene **1** with another γ-substituted allylic bromide, 3-bromo-1-phenyl-1-propene (**5e**), gave only the (*E*)-α-adduct in 44% yield by the addition of HMPA (Entry 5).

Table 1. The reaction of Ketenes **1**—**4** with Substituted Allylic Halides **5**

Entry	Ketene	Allyl halide	Product[a]	Yield/%[a] HMPA[b]	Yield/%[a] —[c]
1	 **1**	 **5a**	**6a**[d]	84	70
2	**1**	 **5b**	**6b**	70	ca.30
3	**1**	 **5c**	**6c**	59	66
4	**1**	 **5d**	**6d**	ca.16	Trace
5	**1**	 **5e**	**6e**	46	Trace
6	**1**	$PhCH_2Br$ **5f**	**6f**	62	Trace
7	 **2**	**5a**	**7a**[d]	85	90
8	**2**	**5b**	**7b**	49	85
9	**2**	**5c**	**7c**	49	76
10	**2**	**5d**	**7d**	ca.29	Trace
11	**2**	**5e**	**7e**	72	35
12	**2**	**5f**	**7f**	56	78
13	 **3**	**5a**	**8a**[d]	56	62
14	 **4**	**5a**	**9a**[d]	77	73

a) Isolated yield. Each product was satisfactory by 200 MHz ^{1}H NMR spectrum. b) Addition of HMPA (1 mol equiv to SmI_2). c) No addition of HMPA. d) About 10% of the product was isomerized to α,β-unsaturated ketone.



(3)

To compare the regio- and stereoselectivities of this system with those of butenyllithium or butenylmagnesium bromide, the reagents were reacted with ethylphenylketene (**1**). Butenylmagnesium bromide was generated from 1-bromo-2-butene and magnesium metal.[12] Butenyllithium was prepared from phenyllithium and 2-butenyltriphenyltin ($E:Z=1:1$) formed by the reaction of butenyl Grignard reagent with chlorotriphenyltin.[13] The geometry of Grignard and lithium reagents was considered to be equilibrated completely in the reaction conditions.[14] Reactions with the ketene **1** were carried out in THF at 0 °C, and the results are presented in Table 3. Butenylmagnesium bromide gave only the γ-adduct and butenyllithium α- and γ-adducts in the ratio of 65 : 35; the α-adduct had only (*Z*)-olefinic geometry. On the other hand, Kagan and co-workers have reported that SmI_2 promoted reactions of γ-substituted bromide **5b** or **5e** with octanal to afford a mixture of α- and γ-adducts ($\alpha:\gamma$=ca. 65 : 35).[14] In marked contract to these reactions, the SmI_2 mediated allylation of the ketenes had higher α-selectivity.[16]

To investigate further the regioselectivity of the allylation of the ketene, ethylphenylketene was reacted with 3-bromo-1-butene (**5b′**) of the diasteroisomer of 1-bromo-2-butene (**5b**). As shown in Eq. 4, the γ-adduct was obtained preferentially in 68% yield with the ratio of (*E*)-γ-adduct **5b-*E***: (*Z*)-γ-one **5b-*Z***: α-one **4b**=87 : 6 : 7. In this case, γ-products were the same as α-ones when 1-bromo-2-butene (**5b**) was used. This suggests that in

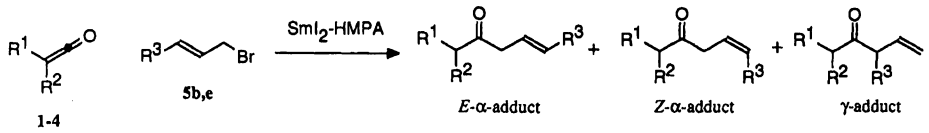


Table 2. The Reactions of Ketenes **1**—**4** with 1-Bromo-2-butene (**5b**) and 3-Bromo-1-phenyl-1-pentene (**5e**)

Entry	R^1	R^2	$R^{3d)}$	Yield/%[a)]	$\alpha-E$	:	$\alpha-Z$	:	γ[b)]
1	Me	Ph **3**	Me **5b**	56	75	:	0	:	25
				48[c)]	84	:	6	:	10
2	Et	Ph **1**	Me **5b**	29	72	:	—	:	28
				78[c)]	84	:	5	:	11
3	*i*-Pr	*p*-Cl–C_6H_4 **4**	Me **5b**	39	60	:	18	:	22
				61[c)]	77	:	11	:	12
4	Ph	Ph **2**	Me **5b**	81	91	:	5	:	4
				49[c)]	78	:	13	:	9
5	Et	Ph **1**	Ph **5e**	4	—	:	—	:	>98
				44[c)]	>98	:	—	:	—

a) Isolated yield. b) The ratio was measured by ^{1}H NMR spectra. The γ-adducts were obtained with the ratio of *dl*:*meso*=ca. 1:1. c) The reaction was carried out by the addition of HMPA (1 mol equiv to SmI_2). d) **2b**: E>98%. Contains 13% 3-bromo-1-butene. **2e** ; E>98%. One isomer.

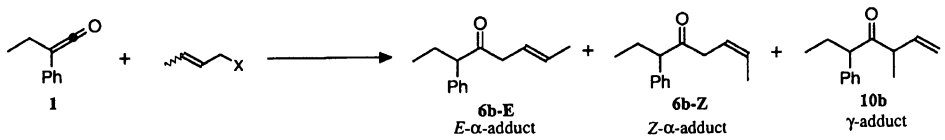
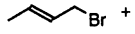
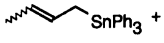
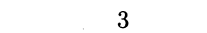
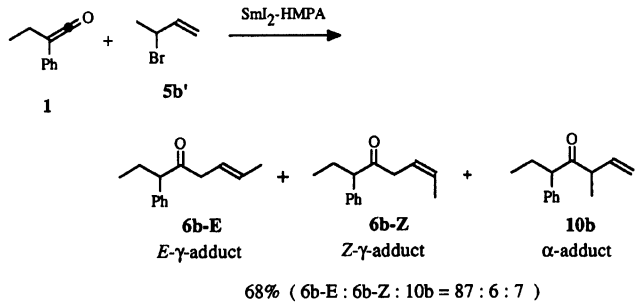


Table 3. The Reaction of Ethylphenylketene (**1**) with Butenyl Metal Reagents[a)]

Entry	Reagent	Yield/%[b)]	**6b**–E	:	**6b**–Z	:	**10b**[c)]
1		62	—	:	—	:	>98
2		53	—	:	65	:	35
3	 [d)]	78	84	:	5	:	11

a) In Entries 1 and 2, the reactions were carried out at 0 °C. b) Isolated yield. c) The ratio was measured by ^{1}H NMR spectra. The γ-adducts were obtained with the ratio of *dl*:*meso*=ca. 1:1. d) E>98%. Contains 13% 3-bromo-1-butene.

this allylation the addition to the ketene proceeded via the same intermediates produced by the reaction of the allylic bromides with SmI_2 and then occurs at the less hindered site (α-position) of allylic halides.



(4)

Next, we examined the relationship between the ratio of the α-adduct **6** and the γ-adduct **10**, and the double-bond geometry of allylic bromides. Table 4 summarizes the results obtained for the reaction of ethylphenylketene with almost stereochemically pure allylic bromides. The ratio of each isomer was measured by 400 MHz ^{1}H NMR spectra. The reaction with (*E*)-allylic bromide, (*E*)-1-bromo-2-hexene (**5g**) (E>98%, contains 11% of 3-bromo-1-hexene), gave the adducts in the ratio of (*E*)-α-adduct **6g-*E***:(*Z*)-α-one **6g-*Z***:γ-one **10g**=75:8:17 (Entry 1). By the addition of HMPA, the yield increased and (*E*)-α-product **6g-*E*** was obtained exclusively (Entry 2). The reaction with (*E*)-1-bromo-2-methyl-2-butene (**5h**) (E>98%, contains 14% of 3-bromo-2-methyl-1-butene) had a similar tendency, and by the addition of HMPA the products were obtained in the ratio of **6h-*E***:**10h**=92:8, and the product **6h-*Z*** was not detected (Entry 6). In contrast, the reaction with (*Z*)-allylic bromide, (*Z*)-1-bromo-2-hexene (**6g′**) (Z>98%, contains 6% of 3-bromo-1-hexene), gave the

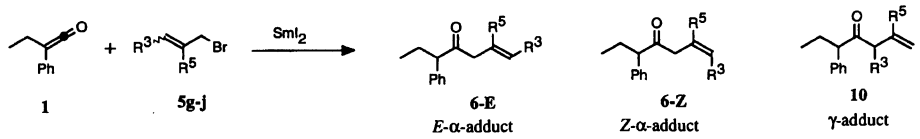
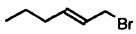
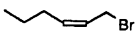
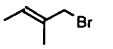
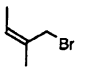


Table 4. The reaction of Ethylphenylketene (**1**) with Diastereomerically Pure Allylic Bromide **5g,h**

Entry	Allylic Bromide		Additive	Yield/%[a]	**6**–*E*	:	**6**–*Z*	:	**10**[b]
1		**5g**[c]	None	18 (50)	75	:	8	:	17
2			HMPA[g]	54 (80)	>98	:	—	:	—
3		**5g′**[d]	None	26 (41)	26	:	11	:	63
4			HMPA[g]	51 (77)	63	:	13	:	24
5		**5h**[e]	None	24 (38)	81	:	—	:	19
6			HMPA[g]	53 (72)	92	:	—	:	8
7		**5h′**[f]	None	26 (40)	35	:	—	:	65
8			HMPA[g]	47 (70)	56	:	12	:	32

a) Isolated yield. The yield in the parentheses was given by the measurement of ^{1}H NMR spectra of the crude product. b) The ratio was measured by ^{1}H NMR spectra. The γ-adducts were obtained with the ratio of *dl*: *meso*=ca. 1:1. c) *E*>98%. Contains 11% 3-bromo-1-hexene. d) *Z*>98% Contains 6% 3-bromo-1-hexene. e) *E*>98% Contains 14% 3-bromo-2-methyl-1-butene. f) *Z*:*E*=81:19. Contains 19% 3-bromo-2-methyl-1-butene. g) Addition of HMPA (1 mol equiv to SmI_2).

γ-product **10g** mainly, and the double-bond geometry of the product **6g** was mainly (*E*)-form (the ratio of **6g-*E***:**6g-*Z***:**10g**=26:11:63) (Entry 3). However, by the addition of HMPA, the reaction showed the opposite tendency to afford the α-adduct and the γ-adduct in the ratio of 76:24 (**6g**:**10g**), and the ratio of **6g-*E*** to **6g-*Z*** increased in 63:13 (Entry 4). The reaction with (*Z*)-1-bromo-2-methyl-2-butene (**5h**) (*Z*:*E*=81:19, contains 19% of 3-bromo-2-methyl-1-butene) had a similar tendency, in the ratio of **6h-*E***:**6h-*Z***:**10h**=35:0:65 without HMPA, and 56:12:32 with HMPA. The above results show that the olefinic geometry was concerned with the ratio of α- and γ-adducts. The reaction with (*E*)-allylic bromides gave the α-adducts predominantly, but using (*Z*)-allylic bromides the regio- and stereoselectivity were decreased and the γ-adducts were obtained in preference to the α-ones. Since in either case, the double-bond geometry of the adducts **6** was mainly (*E*)-form, the isomerization of the double-bond geometry from (*Z*)-form to (*E*)-form occured in the intermediates produced by the reaction of the allylic bromides with SmI_2. By the addition of HMPA, the isomerization to (*E*)-form was accelerated, the ratio of (*E*)-α-adducts were increased,and the reaction with (*Z*)-allylic bromides also gave the α-adducts as main product.

In conclusion, the SmI_2-mediated allylation of ketenes with various substituted allylic halides gives the corresponding allylated ketones which are formed by the reaction at the less hindered sites of the allylic halides. The addition of HMPA enhanced the (*E*)-α-selectivity. The regio- and stereoselectivity in this reaction has a different tendency from the reactivity of allylic lithium or allylic magnesium reagents.

Experimental

General. The ^{1}H NMR spectra were recorded with JEOL EX-200 and JEOL α-400 spectrometers, using tetramethylsilane as an internal standard. The IR spectra were taken on a Perkin–Elmer 1720-X spectrometer. Tetrahydrofuran was freshly distilled from sodium diphenyl ketyl. Each ketene was prepared by the reaction of the corresponding acid chloride with triethylamine in THF, and was purified by distillation.[17] HMPA, allyl iodide, benzyl bromide, and cinnamyl bromide of commercial grade were distilled. Other bromides were prepared according to the literature.[18] Products were purified by preparative TLC on silica gel (Wakogel B-5F). The regio- and stereoselectivity of allylation was measured by 400 MHz ^{1}H NMR spectrum of the products mixture.

5-Phenyl-1-hepten-4-one (6a); A 8.0 ml THF solution of SmI_2 (0.1 mol dm^{-3}, 0.8 mmol) was added to a 8.0 ml THF solution of ethylphenylketene (46.5 mg, 0.318 mmol), allyl iodide (84.7 mg, 0.504 mmol), and HMPA (141.6 mg, 0.790 mmol) with vigorous stirring at room temperature under an argon atmosphere. After this was stirred for 3 min, methanol (1 ml) was added to the solution and the mixture was stirred for 3 min. The solution was treated with 0.1 mol dm^{-3} hydrochloric acid, and organic materials were extracted with ether. The combined extracts were successively washed with a brine, 4% $Na_2S_2O_3$aq, and a brine, and were dried over anhydrous Na_2SO_4. After evaporation of the solvent, the crude product was purified by preparative

TLC (hexane : diethyl ether=10 : 1) to afford the product as colorless oil (50.4 mg, 84%). 200 MHz ^{1}H NMR ($CDCl_3$) δ=0.82 (3H, t, J=7 Hz), 1.60—1.82 (1H, m), 1.96—2.18 (1H, m), 3.10—3.15 (2H, m), 3.58 (1H, t, J=7 Hz), 4.94—5.16 (2H, m), 5.72—5.93 (1H, m), 7.14—7.38 (5H, m). IR (neat) 3028, 2965, 1714, 1637, 993, 920, 757, and 701 cm^{-1}. Found: C, 83.08; H, 8.75%; HRMS m/z 188.1172. Calcd for $C_{13}H_{16}O$: C, 82.94; H, 8.57%; M, 188.1202.

3-Phenyl-6-octen-4-one (6b); 200 MHz ^{1}H NMR ($CDCl_3$) δ=0.82 (3H, t, J=8 Hz), 1.64—1.66 (3H, m), 1.60—1.82 (1H, m), 1.96—2.16 (1H, m), 3.02—3.04 (2H, m), 3.57 (1H, t, J=8 Hz), 5.38—5.46 (2H, m), 7.10—7.26 (5H, m). IR (neat) 3029, 2934, 1714, 967, 759, and 702 cm^{-1}. HRMS Found: m/z 202.1367. Calcd for $C_{14}H_{18}O$: M, 202.1358.

2-Methyl-5-phenyl-1-hepten-4-one (6c); 200 MHz ^{1}H NMR ($CDCl_3$) δ=0.82 (3H, t, J=7 Hz), 1.62 (3H, s), 1.60—1.82 (1H, m), 1.90—2.16 (1H, m), 2.95—3.16 (2H, m), 3.66 (1H, t, J=8 Hz), 4.72—4.75 (1H, m), 4.89—4.92 (1H, m), 7.10—7.26 (5H, m). IR (neat) 3029, 2966, 1714, 1650, 895, 757, and 701 cm^{-1}. HRMS Found: m/z 202.1375. Calcd for $C_{14}H_{18}O$: M, 202.1358.

2-Methyl-6-phenyl-2-octen-5-one (6d); 200 MHz ^{1}H NMR ($CDCl_3$) δ=0.81 (3H, t, J=7 Hz), 1.47 (3H, s), 1.70 (3H, s), 1.40—1.75 (1H, m), 1.90—2.18 (1H, m), 3.04 (2H, d, J=7 Hz), 3.56 (1H, t, J=7 Hz), 5.12—5.27 (1H, m), 7.00—7.40 (5H, m). IR (neat) 3028, 2966, 1714, 758, and 701 cm^{-1}. HRMS Found: m/z 216.1499. Calcd for $C_{15}H_{20}O$: M, 216.1515.

1,5-Diphenyl-1-hepten-4-one (6e); 200 MHz ^{1}H NMR ($CDCl_3$) δ=0.84 (3H, t, J=7 Hz), 1.62—1.85 (1H, m), 1.96—2.20 (1H, m), 3.26 (2H, d, J=6 Hz), 3.63 (1H, t, J=7 Hz), 6.10—6.40 (2H, m), 7.10—7.40 (10H, m). IR (neat) 3027, 2965, 1714, 966, 751, and 700 cm^{-1}. HRMS Found: m/z 264.1501. Calcd for $C_{19}H_{20}O$: M, 264.1515.

1,3-Diphenyl-2-pentanone (6f); 200 MHz ^{1}H NMR ($CDCl_3$) δ=0.72 (3H, t, J=7 Hz), 1.60—1.80 (1H, m), 1.92—2.16 (1H, m), 3.60 (2H, s), 3.60 (1H, t, J=7 Hz), 6.98—7.38 (10H, m). IR (neat) 3029, 2965, 1713, 1494, 1455, 758, 738, and 700 cm^{-1}. HRMS Found: m/z 238.1370. Calcd for $C_{17}H_{18}O$: M, 238.1358.

1,1-Diphenyl-4-penten-2-one (7a); 200 MHz ^{1}H NMR ($CDCl_3$) δ=3.26—3.32 (2H, m), 5.02—5.30 (2H, m), 5.18 (1H, s), 5.80—6.02 (1H, m), 7.10—7.38 (10H, m). IR (neat) 3028, 1719, 1635, 993, 922, 745, and 702 cm^{-1}. HRMS Found: m/z 236.1209. Calcd for $C_{17}H_{16}O$: M, 236.1202.

1,1-Diphenyl-4-hexen-2-one (7b); 200 MHz ^{1}H NMR ($CDCl_3$) δ=1.62—1.70 (3H, m), 3.16—3.23 (2H, m), 5.18 (1H, s), 5.40—5.56 (2H, m), 7.15—7.36 (10H, m). IR (neat) 3028, 2917, 1719, 967, 747, and 701 cm^{-1}. HRMS Found: m/z 250.1337. Calcd for $C_{18}H_{18}O$: M, 250.1358.

1,1-Diphenyl-4-methyl-4-penten-2-one (7c); 200 MHz ^{1}H NMR ($CDCl_3$) δ=1.71 (3H, s), 3.20 (2H, s), 4.79 (1H, s), 4.96 (1H, s), 5.27 (1H, s), 7.10—7.40 (10H, m). IR (neat) 3029, 2973, 1718, 1649, 897, 744, 732, and 701 cm^{-1}. HRMS Found: m/z 250.1343. Calcd for $C_{18}H_{18}O$: M, 250.1358.

1,1-Diphenyl-5-methyl-4-hexen-2-one (7d); 200 MHz ^{1}H NMR ($CDCl_3$) δ=1.55 (3H, s), 1.78 (3H, s), 3.24 (2H, d, J=7.2 Hz), 5.20 (1H, t, J=7.2 Hz), 7.00—7.88 (10H, m).

1,1,5-Triphenyl-4-penten-2-one (7e); 200 MHz ^{1}H NMR ($CDCl_3$) δ=3.42 (2H, d, J=7 Hz), 5.22 (1H, s), 6.25—6.44 (2H, m), 7.00—7.50 (15H, m). IR (neat) 3027, 2924, 1719, 967, 746, and 701 cm^{-1}. HRMS Found: m/z 312.1505. Calcd for $C_{23}H_{20}O$: M, 312.1515.

1,1,3-Triphenyl-2-propanone (7f); 200 MHz ^{1}H NMR ($CDCl_3$) δ=3.67 (2H, s), 5.20 (1H, s), 7.00—7.38 (15H, m). IR (neat) 3028, 2923, 1718, 1495, 1454, 763, 743, and 702 cm^{-1}. HRMS Found: m/z 286.1358. Calcd for $C_{21}H_{18}O$: M, 286.1358.

2-Phenyl-5-hexen-3-one (8a); 200 MHz ^{1}H NMR ($CDCl_3$) δ=1.39 (3H, d, J=7 Hz), 3.08—3.14 (2H, m), 3.81 (1H, q, J=7 Hz), 4.93—5.19 (2H, m), 5.72—5.94 (1H, m), 7.05—7.40 (5H, m). IR (neat) 3028, 2979, 1717, 1641, 994, 921, 763, and 702 cm^{-1}. HRMS Found: m/z 174.1010. Calcd for $C_{12}H_{14}O$: M, 174.1045.

3-(4-Chlorophenyl)-2-methyl-6-hepten-4-one (9a); 200 MHz ^{1}H NMR ($CDCl_3$) δ=0.66 (3H, d, J=7 Hz), 0.96 (3H, d, J=7 Hz), 2.20—2.48 (1H, m), 3.10—3.18 (2H, m), 3.35 (1H, d, J=12 Hz), 4.98—5.18 (2H, m), 5.68—5.91 (1H, m), 7.10—7.32 (4H, m). IR (neat) 2961, 1715, 1635, 993, and 923 cm^{-1}. HRMS Found: m/z 236.0897. Calcd for $C_{14}H_{17}ClO$: M, 236.0969.

The diastereometic ratio was calculated by the integrations of the signals of the olefinic protons in 400 MHz ^{1}H NMR spectrum of the products mixture. The 400 MHz ^{1}H NMR spectrum of each product obtained by the reaction of ethylphenylketene with 1-bromo-2-butene was described as follows;

(*E*)-3-Phenyl-6-octen-4-one (6b-*E*); 400 MHz ^{1}H NMR ($CDCl_3$) δ=0.81 (3H, t, J=7.5 Hz), 1.60—1.75 (4H, m), 1.98—2.10 (1H, m), 3.02—3.05 (2H, m), 3.58 (1H, t, J=7.5 Hz), 5.41—5.44 (2H, m), 7.18—7.34 (5H, m).

(*Z*)-3-Phenyl-6-octen-4-one (6b-*Z*); 400 MHz ^{1}H NMR ($CDCl_3$) δ=0.82 (3H, t, J=7.4 Hz), 1.47—1.50 (3H, m), 1.60—1.75 (1H, m), 2.00—2.12 (1H, m), 3.08—3.13 (2H, m), 3.58 (1H, t, J=7.4 Hz), 5.41—5.52 (1H, m), 5.57—5.66 (1H, m), 7.20—7.40 (5H, m). The coupling constant between the signals of δ=5.41—5.52 and one of δ=5.57—5.66 was J=10.4 Hz (lit,[19] J=11 Hz).

3-Methyl-5-phenyl-1-hepten-4-one (10b) (*dl*: *meso*-1 : 1); 400 MHz ^{1}H NMR ($CDCl_3$) δ=0.78 (1.5 H, t, J=7.4 Hz), 0.83 (1.5 H, t, J=7.5 Hz), 1.01 (1.5H, d, J=6.8 Hz), 1.14 (1.5H, d, J=7.1 Hz), 1.60—1.77 (1H, m), 1.90—2.10 (1H, m), 3.20—3.30 (1H, m), 3.72 (0.5H, t, J=7.3 Hz), 3.76 (0.5H, t, J=7.4 Hz), 4.88—5.19 (2H, m), 5.64—5.76 (1H, m), 7.10—7.40 (5H, m), IR (neat) 1713, 1634, 743, and 700 cm^{-1}.

400 MHz ^{1}H NMR spectrum of the products mixture (α-E : α-Z : γ=84 : 5 : 11) obtained by the reaction of ethylphenylketene with 1-bromo-2-butene was described as follows; 400 MHz ^{1}H NMR ($CDCl_3$) δ=0.81 (3H, t, J=7.3 Hz), 1.11 (0.15H, d, J=6.9 Hz), 1.14 (0.15H, d, J=7.0 Hz), 1.44—1.54 (0.15H, m), 1.60—1.85 (3.5H, m), 1.98—2.15 (1H, m), 3.00—3.05 (1.7H, m), 3.06—3.13 (0.1H, m), 3.20—3.29 (0.1H, m), 3.57 (0.9H, t, J=7.4 Hz), 3.70—3.78 (0.1H, m), 4.89—4.99 (0.1H, m), 5.12—5.19 (0.1H, m), 5.37—5.52 (1.8H, m), 5.57—5.64 (0.05H, m), 5.64—5.76 (0.1H, m), 7.00—7.40 (5H, m). In this data, the signals of δ=5.37—5.52, 5.57—5.64, and 4.89—4.99, 5.12—5.19, 5.64—5.76 were assigned to the olefinic protons of **6b-*E***, **6b-*Z***, and **10b**, respectively.

The diastereomeric ratio of the products **7**—**9b** and **11**—**13b** was calculated by the method used for the prod-

ucts **6b** and **10b**. 400 MHz ^{1}H NMR spectra of main products were described as follows:

(*E*)-1,1-Diphenyl-4-hexen-2-one (7b-*E*); The signals of the olefinic protons of **7b-*E***, **7b-*Z***, and **11b** were observed at δ=5.44—5.61, 5.63—5.72, and 4.87—4.90, 5.12—5.16, 5.74—5.84, respectively.

(*E*)-2-Phenyl-5-hepten-3-one (8b-*E*); 400 MHz ^{1}H NMR ($CDCl_3$) δ=1.38 (3H, d, J=7 Hz), 1.62—1.66 (3H, m), 3.00—3.06 (2H, m), 3.81 (1H, q, J=7 Hz), 5.39—5.46 (2H, m), 7.18—7.38 (5H, m), IR (neat) 3028, 2976, 1716, 967, 963, and 701 cm^{-1}. HRMS Found: m/z 188.1241. Calcd for $C_{13}H_{16}O$: M, 188.1202. The signals of the olefinic protons of **8b-*E***, **8b-*Z***, and **12b** were observed at δ=5.30—5.54, 5.54—5.64, and 4.87—5.00, 5.11—5.16, 5.30—5.54, respectively.

(*E*)-3-(4-Chlorophenyl)-2-methyl-6-octen-4-one (9b-*E*); 400 MHz ^{1}H NMR ($CDCl_3$) δ=0.65 (3H, d, J=7 Hz), 0.95 (3H, d, J=6 Hz), 1.65—1.67 (2H, m), 2.30—2.40 (1H, m), 3.04—3.06 (2H, m), 3.34 (1H, d, J=10 Hz), 5.36—5.52 (2H, m), 7.15—7.20 (2H, m), 7.24—7.32 (2H, m). IR (neat) 3029, 2962, 1714, and 966 cm^{-1}. HRMS Found: m/z 250.1188. Calcd for $C_{15}H_{18}ClO$: M, 250.1123. The signals of the olenfinic protons of **9b-*E***, **9b-*Z***, and **13b** were observed at δ=5.36—5.52, 5.10—5.40, and 4.98—5.04, 5.16—5.23, 5.56—5.73, respectively.

(*E*)-3-Phenyl-6-decen-4-one (6g-*E*); 400 MHz ^{1}H NMR ($CDCl_3$) δ=0.81 (3H, t, J=7 Hz), 0.86 (3H, t, J=7 Hz), 1.30—1.40 (2H, m), 1.64—1.75 (1H, m), 1.93—2.00 (2H, m), 2.00—2.10 (1H, m), 3.02—3.05 (2H, m), 3.59 (1H, t, J=7 Hz), 5.40—5.43 (2H, m), 7.18—7.34 (5H, m). IR (neat) 3028, 2962, 1714, 969, 758, and 701 cm^{-1}. HRMS Found: m/z 230.1585. Calcd for $C_{16}H_{22}O$: M, 230.1671. The signals of δ=3.02—3.05 and 5.40—5.43 in (*E*)-product were observed at δ=3.09—3.12 and 5.44—5.56 in (*Z*)-product. Two kinds of γ-adducts (**10g** and **10g′**) were obtained with the ratio of 1 : 1, but which were not identified as *dl* or *meso*.

γ-Adduct 10g; 400 MHz ^{1}H NMR ($CDCl_3$) δ=0.66 (3H, t, J=7.3 Hz), 0.78 (3H, t, J=7.3 Hz), 0.95—1.00 (2H, m), 1.20—1.38 (2H, m), 1.62—1.72 (1H, m), 1.96—2.06 (1H, m), 3.10—3.17 (1H, m), 3.70 (1H, t, J=7.3 Hz), 5.13—5.19 (2H, m), 5.55—5.64; (1H, m), 7.16—7.35 (5H, m).

γ-Adduct 10g′; 400 MHz ^{1}H NMR ($CDCl_3$) δ=0.84 (6H, q, J=7.6 Hz), 1.10—1.40 (2H, m), 1.50—1.75 (3H, m), 1.95—2.10 (1H, m), 3.10—3.18 (1H, m), 3.64 (1H, t, J=7.3 Hz), 4.76—4.82 (1H, m), 4.92—4.96 (1H, m), 5.56—5.66 (1H, m), 7.18—7.40 (5H, m).

(*E*)-3-Methyl-6-phenyl-2-octen-5-one (6h-*E*); 400 MHz ^{1}H NMR ($CDCl_3$) δ=0.81 (3H, t, J=7 Hz), 1.48 (3H, brm), 1.57—1.61 (3H, m), 1.63—1.74 (1H, m), 1.98—2.09 (1H, m), 2.94—3.05 (2H, m), 3.64 (1H, t, J=7 Hz), 5.21—5.28 (1H, m), 7.18—7.38 (5H, m), IR (neat) 3062, 3028, 2965, 1712, 759, and 701 cm^{-1}. HRMS Found: m/z 216.1523. Calcd for $C_{15}H_{20}O$: M, 216.1515. The signals of δ=2.94—3.05, 5.21—5.28 in (*E*)-product were observed at δ=3.00—3.20 and 5.37—5.44 in (*Z*)-product. Two kinds of γ-adducts (**10h** and **10h′**) were obtained with the ratio of 1 : 1, but which were not identified as *dl* or *meso*.

γ-Adduct 10h; 400 MHz ^{1}H NMR ($CDCl_3$) δ=0.77 (3H, t, J=7.3 Hz), 1.02 (3H, d, J=6.9 Hz), 1.61—1.72 (3H, m), 1.95—2.05 (1H, m), 3.25 (1H, q, J=6.8 Hz), 3.78 (1H, t, J=7.5 Hz), 4.86 (1H, brm), 4.94 (1H, brm), 7.15—7.35 (5H, m).

γ-Adduct 10h′; 400 MHz ^{1}H NMR ($CDCl_3$) δ=0.82, (3H, t, J=7.3 Hz), 1.15 (3H, d, J=7.1 Hz), 1.35 (3H, brs), 1.65—1.80 (1H, m), 1.95—2.10 (1H, m), 3.30(1H, q, J=7.1 Hz), 3.77 (1H, t, J=7.6 Hz), 4.79 (1H, brm), 4.83—4.85 (1H, m), 7.15—7.30 (5H, m).

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References

1) S. Takeuchi, N. Miyoshi, K. Hirata, H. Hayashida, and Y. Ohgo, *Bull. Chem. Soc. Jpn.*, **65**, 2001 (1992). For the SmI_2 mediated reactions, see Ref. 2.

2) H. B. Kagan and J. L. Namy, *Tetrahedron*, **42**, 6573 (1977); J. A. Soderquist, *Aldrichimica Acta*, **24**, 15 (1991); G. A. Molander, *Chem. Rev.*, **92**, 29 (1992).

3) S. Takeuchi, N. Miyoshi, and Y. Ohgo, *Chem. Lett.*, **1992**, 551.

4) For reviews of stereoselective allylation, see: R. W. Hoffmann, *Angew. Chem., Int. Ed. Engl.*, **21**, 555 (1982); See also Refs. 9, 10, and 11.

5) F. Naef and R. Docorzant, *Tetrahedron*, **42**, 3245 (1986); C. Fehr and J. Galindo, *J. Am. Chem. Soc.*, **110**, 6909 (1988).

6) P. Girard, J. L. Namy, and H. B. Kagan, *J. Am. Chem. Soc.*, **102**, 2693 (1980).

7) M. Kosugi and T. Migita, *J. Synth. Org. Chem., Jpn.*, **38**, 1142 (1980).

8) J. Inanaga, J. Katsuki, O. Ujikawa, and M. Yamaguchi, *Tetrahedron Lett.*, **37**, 4921 (1991).

9) J. Inanaga, M. Ishikawa, and M. Yamaguchi, *Chem. Lett.*, **1987**, 1485.

10) a) Y. Yamamoto and K. Maruyama, *J. Org. Chem.*, **48**, 1564 (1983); b) Y. Yamamoto, N. Maeda, and K. Maruyama, *J. Chem. Soc., Chem. Commun.*, **1983**, 742; c) M. Clarembeau and A. Krief, *Tetrahedron Lett.*, **25**, 3629 (1984); d) S. Araki and Y. Butsugan, *J. Organomet. Chem.*, **333**, 329 (1987); e) S. Araki and Y. Butsugan, *Chem. Lett.*, **1988**, 457; f) J. Iqbal and S. P. Joseph, *Tetrahedron Lett.*, **30**, 2421 (1989); g) S. R. Wilson, M. S. Hague, and R. N. Misra, *J. Org. Chem.*, **47**, 747 (1982); h) A. Yanagisawa, S. Habaue, and H. Yamamoto, *J. Org. Chem.*, **54**, 5198 (1989); i) M. Suzuki, Y. Morita, and R. Noyori, *J. Org. Chem.*, **55**, 441 (1990); j) B. -S. Guo, W. Doubleday, and T. Cohen, *J. Am. Chem. Soc.*, **109**, 4710 (1987).

11) Recently, highly α-selective and stereospecific allylation of carbonyl compounds using allylbariums has reported by H. Yamamoto, see: A. Yanagisawa, S. Habaue, and H. Yamamoto, *J. Am. Chem. Soc.*, **113**, 8955 (1991), and references therein for α-allylation.

12) R. A. Benkeser, *Synthesis*, **1971**, 347.

13) J. Gilman and J. Eisch, *J. Org. Chem.*, **20**, 763 (1955); D. Seyferth and M. A. Weiner, *J. Org. Chem.*, **26**, 4797 (1961).

14) A. Yanagisawa, S. Habaue, and H. Yamamoto, *J. Am. Chem. Soc.*, **113**, 5893 (1991).

15) J. Souppe, J. L. Namy, and H. B. Kagan, *Tetrahedron Lett.*, **23**, 3497 (1982).
16) We have found that HMPA affected the regio- and disastereoselectivities of the SmI_2-mediated allylation of carbonyl compounds such as aldehydes. Details will be published elsewhere.
17) W. T. Brady, *Synthesis*, **1971**, 415.
18) V. J. Davisson, A. B. Woodside, T. R. Neal, K. E. Stremler, M. Muehlbacher, and C. D. Poulter, *J. Org. Chem.*, **51**, 4768 (1986).
19) A. J. A. van der Weerdt and H. Cerfontain, *J. Chem. Soc., Perkin Trans. 2*, **1980**, 592.