perature, and diluted with pentane (50 mL). This pentane solution was washed with water and brine, dried ($MgSO_4$), and concentrated. The crude product was dissolved in MeOH (20 mL), and the solution was cooled to −78 °C. Ozone was bubbled through this solution at −78 °C for 40 min, and then oxygen gas was passed through the solution for 30 min at the same temperature. The reaction was quenched by the addition of dimethyl sulfide (2 mL), and warmed to room temperature, then concentrated. The resulting mixture was dissolved in ethyl acetate (50 mL), washed with water (2 × 20 mL) and brine (20 mL), dried ($MgSO_4$), and concentrated. The resulting oil was purified on a silica gel column (hexane/ethyl acetate, 3:1) to yield the known ethyl phenylglyoxylate[23] (120 mg, 67%) as a colorless oil.

Ethyl (4-Chlorophenyl)glyoxylate (Table II, entry 5).[24] The reaction of 1-chloro-4-iodobenzene (238 mg, 1 mmol) and (1-ethoxyvinyl)trimethylstannane (235 mg, 1 mmol) according to procedure G, gave the known ethyl (4-chlorophenyl)glyoxylate[24] (166 mg, 78%).

Ethyl (4-Nitrophenyl)glyoxylate (Table II, entry 6).[24] By use of procedure G, 1-iodo-4-nitrobenzene (239 mg, 1 mmol) gave the known ethyl (4-nitrophenyl)glyoxylate (51 mg, 23%).[24]

Ethyl (4-Methoxyphenyl)glyoxylate (Table II, entry 7).[24] By use of procedure G, 4-iodoanisole (234 mg, 1 mmol) gave the known ethyl (4-methoxyphenyl)glyoxylate (129 mg, 62%).[24]

Ethyl (4-Phenylphenyl)glyoxylate (Table II, entry 8). By use of procedure G, the reaction of 4-iodobiphenyl (280 mg, 1 mmol) gave ethyl (*p*-phenylphenyl)glyoxylate (183 mg, 72%) as a colorless liquid: ^1H NMR ($CDCl_3$) δ 7.7–8.1 (m, 4 H), 7.4–7.6 (m, 5 H), 4.45 (q, J = 7.2 Hz, 2 H), 1.43 (t, J = 7.2 Hz, 3 H); ^{13}C NMR ($CDCl_3$) δ 185.9, 163.8, 147.6, 139.5, 131.2, 130.6, 129.0, 128.6, 127.5, 127.3, 62.3, 14.1; IR (neat) 1735, 1683 cm^{-1}. Anal. Calcd for $C_{16}H_{14}O_3$: C, 75.57; H, 5.55. Found: C, 75.48; H, 5.57.

2-Ethoxy-1-phenyl-2-propen-1-one (Table II, entry 4)[22] was isolated from the reaction mixture of the carbonylative coupling of iodobenzene (204 mg, 1 mmol) and (α-ethoxyvinyl)trimethylstannane (235 mg, 1 mmol) as a clear liquid (118 mg, 67%) by chromatographic separation on a basic alumina column with (hexane/ethyl acetate, 3:1, with 2% Et_3N). The compound was identified by comparison of its ^1H NMR and IR spectra with those reported.[22]

2-Methyl-3-phenylquinoxaline (Table II, entry 4).[25] Crude 2-ethoxy-1-phenyl-2-propen-1-one (obtained from 204 mg of iodobenzene, 1 mmol) was dissolved in THF (10 mL) and 2 N HCl (2 mL) and stirred for 16 h at room temperature. The reaction mixture was diluted with hexane (50 mL), washed with water (2 × 10 mL) and brine (10 mL), dried ($MgSO_4$), and concentrated. The crude product of hydrolysis was treated with *o*-diaminobenzene (108 mg, 1 mmol) in benzene (10 mL) with 100 mg of activated 4-Å molecular sieves for 5 h at room temperature. Solids were removed from the reaction mixture by filtration; the filtrate was concentrated and 2-methyl-3-phenylquinoxaline[25] was purified by recrystallization from ethanol (52 mg, 24%): mp 53–55 °C.

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Registry No. $H_3C(CH_2)_3C(=CH_2)OSO_2CF_3$, 37555-23-0; $H_2C=CHBr$, 593-60-2; PhOTf, 17763-67-6; PhBr, 108-86-1; PhI, 591-50-4; $PhCoC(=CH_2)OEt$, 85616-23-5; cyclohex-1-en-1-yl triflate, 28075-50-5; 1-(1-ethoxyvinyl)cyclohexene, 118716-32-8; 1-acetylcyclohexene, 932-66-1; 4-*tert*-butylcyclohex-1-enyl triflate, 77412-96-5; 1-(1-ethoxyvinyl)-4-*tert*-butylcyclohex-1-ene, 125950-34-7; 1-acetyl-4-*tert*-butylcyclohex-1-ene, 37881-09-7; 2,2,5-trimethylcyclopent-1-enyl triflate, 91158-82-6; 1-(1-ethoxyvinyl)-2,2,5-trimethylcyclopent-1-ene, 125952-09-2; 1-acetyl-2,2,5-trimethylcyclopent-1-ene, 125952-10-5; 2-(1-ethoxyvinyl)-hex-1-ene, 125952-11-6; 2-acetylhex-1-ene, 65818-30-6; 2-ethoxy-1,3-butene, 4747-05-1; acetophenone, 98-86-2; 4-((trifluoromethyl)sulfonato)-*N*-tosylindole, 112970-71-5; 4-acetyl-*N*-tosylindole, 112970-73-7; α-ethoxystyrene, 6230-62-2; 1-bromo-4-*tert*-butylbenzene, 3972-65-4; 4-*tert*-butyl-1-(1-ethoxyvinyl)-benzene, 125952-12-7; 4-*tert*-butylphenyl methyl ketone, 943-27-1; 4-nitro-1-bromobenzene, 586-78-7; 4-nitro-1-(1-ethoxyvinyl)-benzene, 59938-04-4; 4-nitrophenyl methyl ketone, 100-19-6; 2-ethoxy-1-cyclohex-1-enylprop-2-en-1-one, 125952-13-8; 1-cyclohex-1-enylpropane-1,2-dione, 28123-53-7; 2-ethoxy-1-(2,2,5-trimethylcyclopent-1-enyl)prop-2-en-1-one, 125952-14-9; 1-(2,2,5-trimethylcyclopent-1-enyl)propane-1,2-dione, 125952-15-0; 2,3-benzocyclohept-1-en-1-yl triflate, 125952-16-1; 2-ethoxy-1-(2,3-benzocyclohept-1-enyl)prop-2-en-1-one, 125952-17-2; 1-(2,3-benzocyclohept-1-enyl)propane-1,2-dione, 125952-18-3; ethyl phenylglyoxylate, 1603-79-8; 2-methyl-3-phenylquinoxaline, 125952-19-4; 1-chloro-4-iodobenzene, 637-87-6; ethyl (4-chlorophenyl)glyoxylate, 34966-48-8; 1-iodo-4-nitrobenzene, 636-98-6; ethyl (4-nitrophenyl)glycoxylate, 70091-75-7; 4-iodoanisole, 696-62-8; ethyl (4-methoxyphenyl)glyoxylate, 40140-16-7; 4-iodobiphenyl, 1591-31-7; ethyl (4-phenylphenyl)glyoxylate, 6244-53-7; (1-ethoxyvinyl)trimethylstannane, 112713-84-5.

Stabilization and Activation of Dienolates with Germanium and Tin. Stereo- and Regioselective Aldol Reactions, Regioselective Coupling Reactions, and Regioselective Synthesis of Amino Acid Derivatives

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The reaction of lithium dienolates with tin chlorides Bu_xSnCl_{4-x} (x = 0, 1, 2, 3) produces the γ-stannylated α,β-unsaturated esters, whereas in general the same reaction with trimethylsilyl chloride gives the O-silylated dienol ethers. Quite interestingly, the reaction of certain lithium dienolates with trimethylgermanium halides produces the α-trimethylgermylated β,γ-unsaturated esters. Further synthetic applications via the γ-stannyl (Sn-masked dienolates) and α-germyl (Ge-masked dienolates) derivatives have been studied. Regio- and stereoselective aldol condensations with aldehydes are accomplished with either Lewis acid mediated or tetrabutylammonium fluoride induced reactions of Sn-masked dienolates. Arylation, acylation, and vinylation of dienolates at the γ-position are realized by the palladium-catalyzed reactions of Sn-masked dienolates. The C–C bond formation at the γ-position is achieved by the reactions of Ge-masked dienolates with variety of electrophiles. Either the α- or γ-amino acid derivatives can be prepared with very high regioselectivity by treating diethyl azodicarboxylate with (i) lithium dienolates themselves in certain cases, (ii) Sn-masked dienolates, or (iii) Ge-masked dienolates.

In order to enhance regio-, chemo-, and stereoselectivities, the stabilization–activation procedure of anionic species has frequently been used in recent synthetic organic chemistry. Some nucleophiles can be converted to derivatives of lowered reactivity which can react with weaker electrophiles, if the latter's reactivity is enhanced

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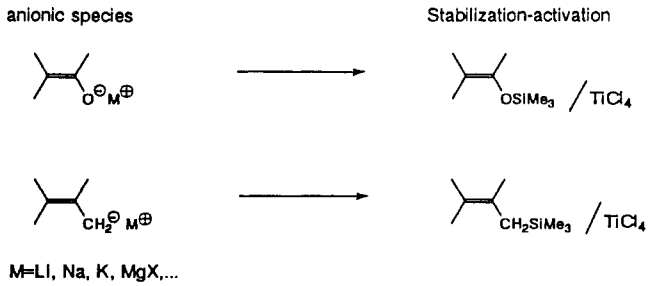
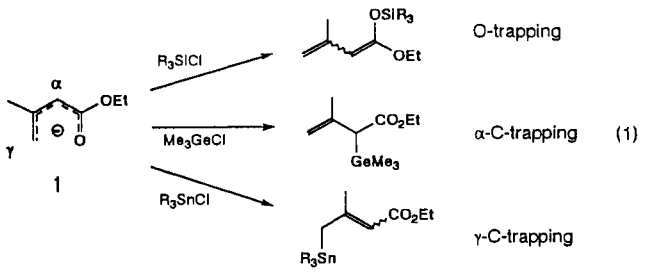
Scheme I. Stabilization-Activation Procedure



by an additive, and the regio-, chemo-, and stereoselectivity of such reactions may vary amongst different nucleophile–electrophile reactivity pairs. Two typical examples are shown in Scheme I. Alkali metal enolates are converted to the stable silyl enol ethers (stabilization), which are subsequently treated with electrophiles in the presence of Lewis acids (activation).[1] Carbanionic allylmetals are transformed to allylsilanes, which are reacted with electrophiles with the aid of Lewis acids.[2] Synthetically useful level of the selectivities is realized by using the stabilization–activation procedure.

Carbon–carbon bond formation at the γ-position of dienolates has been a long standing problem in organic chemistry. It is generally accepted that dienolates, derived from enoates, undergo selective alkylation at the α-position under kinetic control in preference to the γ-position.[3] Aldol type condensation of dienolates with aldehydes has not produced high regio- and diastereoselectivities.[4] Further, the amination reaction of lithium dienolates often produces a mixture of α- and γ-amino acid derivatives.[5] Therefore, there remain a number of problems to be solved in the dienolate chemistry.

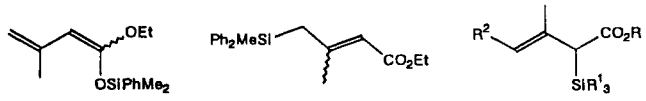
We report that use of the stabilization and activation procedure solves some of the inherent problems associated with dienolate chemistry. The stabilization of dienolates with trimethylsilyl or *tert*-butyldimethylsilyl group, which produces dienol silyl ethers (O-silylated products), followed by treatment with electrophiles in the presence of activators has been studied.[6] Carbon–carbon bond formation takes place predominantly at the γ-position if these dienol silyl ethers and aldehydes[6a,c,d] or other electrophiles[6b] are utilized. However, in certain cases low regio- and stereoselectivities are produced even by using the silyl trapping method. We have found that trapping the dienolate (**1**) with organotin halides gives γ-stannylated enoates,[7] and more interestingly α-germylated β,γ-unsaturated esters are produced by trapping with organogermanium halides[8] (eq 1). We now detail the regioselective trapping of dienolates with silicon, germanium, tin, and lead reagents and further synthetic application of these stabilized masked dienolates.



(1)

Results and Discussion

Trapping Dienolates with Group IV Elements. As mentioned above, trimethylsilyl and *tert*-butyldimethylsilyl chlorides react with **1** at the oxygen atom to give the O-silylated product.[6] We examined dimethylphenylsilyl chloride and diphenylmethylsilyl chloride in order to test whether the substituent of silyl group can exert an influence upon the regioselectivity on enolate trapping.[9] Although the former reagent gave O-silylated product (**2**), the latter reagent afforded γ-silylated product (**3**) as an E/Z mixture (E/Z = 60/40). We next examined trapping **1** and other dienolates with organotin and germanium compounds. The results are summarized in Table I.



2 **3** **20**

The lithium dienolate derived from **4** reacted with the tin chloride derivatives to give the γ-stannylated α,β-unsaturated esters **5**–**8** in high to reasonable yields (entries 1–4). On the other hand, the α-trimethylgermyl β,γ-unsaturated ester **9** was obtained in high yield upon treatment of **4** with Me_3GeCl (entry 5). Small amounts (<5%) of the γ-isomer were detected by ^1H NMR analysis of the reaction mixture. However, this did not create any trouble for further synthesis, since **9** was generally more reactive than the γ-isomer and thus the product derived from the γ-isomer was not obtained as mentioned later. Exclusive α-attack was observed with the β-disubstituted enoates **16** and **18** (entries 9 and 10). However, **14** gave exclusively

(1) Mukaiyama, T.; Narasaka, K.; Banno, K. *Chem. Lett.* **1973**, 1011.
(2) Hosomi, A.; Sakurai, H. *Tetrahedron Lett.* **1976**, 1295.
(3) (a) Albaugh-Robertson, P.; Katzenellenbogen, J. A. *J. Org. Chem.* **1983**, *48*, 5288. (b) Green, J. R.; Majewski, M.; Alo, B. I.; Snieckus, V. *Tetrahedron Lett.* **1986**, *27*, 535. (c) Cainelli, G.; Cardillo, G. *Acc. Chem. Res.* **1981**, *14*, 89. (d) Dugger, R. W.; Heathcock, C. H. *J. Org. Chem.* **1980**, *45*, 1181. (e) Kende, A. S.; Chen, J. *J. Am. Chem. Soc.* **1985**, *107*, 7184. (f) Kajikawa, A.; Morisaki, M.; Ikekawa, N. *Tetrahedron Lett.* **1975**, 4135. (g) Vedejs, E.; Gapinski, D. M. *Tetrahedron Lett.* **1981**, *22*, 4913. (h) Millard, A. A.; Rathke, M. W. *J. Am. Chem. Soc.* **1977**, *99*, 4833. (i) Chan, T. H.; Kang, G. J. *Tetrahedron Lett.* **1982**, 3011. (j) Lansbury, P. T.; Erwin, R. W. *Tetrahedron Lett.* **1978**, 2675. (k) Yashimoto, M.; Ishisa, N.; Hiraoka, T. *Tetrahedron Lett.* **1973**, 39. For other miscellaneous approaches for controlling the regiochemistry of dienolates and related systems: Blatz, P. E.; Balasubramaniyan, P.; Balasubramaniyan, V. *J. Am. Chem. Soc.* **1968**, *90*, 3282. Koppel, G. A. *Tetrahedron Lett.* **1972**, 1507. Wu, A.; Snieckus, V. *Tetrahedron Lett.* **1975**, 2057. Majewski, M.; Mpango, G. B.; Thomas, M. T.; Wu, A.; Snieckus, V. *J. Org. Chem.* **1981**, *46*, 2029. Katzenellenbogen, J. A.; Crumurine, A. L. *J. Am. Chem. Soc.* **1976**, *98*, 4925. Watanabe, S.; Suga, K.; Fujita, T.; Fujiyoshi, K. *Chem. Ind. (London)* **1972**, 80. Preffer, P. E.; Silbert, L. S.; Kinsel, E. *Tetrahedron Lett.* **1973**, 1163. Takabe, K.; Fujiwara, H.; Katagirl, T.; Tanaka, J. *Tetrahedron Lett.* **1975**, 1273. Chen, Y. L.; Mariano, P. S.; Little, G. M.; O'Brien, D.; Huesmann, P. L. *J. Org. Chem.* **1981**, *46*, 4643. Mander, L. N.; Sethi, S. P. *Tetrahedron Lett.* **1983**, *24*, 5425. Smith, A. B. III; Scarborough, R. M., Jr. *Tetrahedron Lett.* **1978**, 4193. Koreeda, M.; Chen, Y. P. L. *Tetrahedron Lett.* **1981**, *22*, 15. Lansbury, P. T.; Erwin, R. W.; Jeffrey, D. A. *J. Am. Chem. Soc.* **1980**, *102*, 1602. Pitzele, B. S.; Baran, J. S.; Steinman, D. H. *J. Org. Chem.* **1975**, *40*, 269. Stork, G.; Kraus, G. A. *J. Am. Chem. Soc.* **1976**, *98*, 2351. Donaldson, R. E.; Fuchs, P. L. *J. Org. Chem.* **1977**, *42*, 2032.
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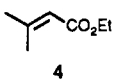
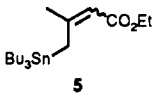
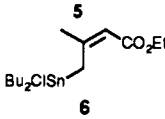
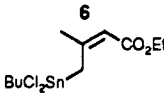
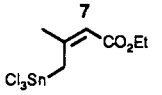
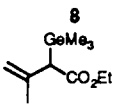
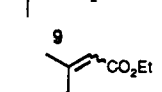
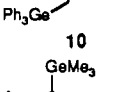
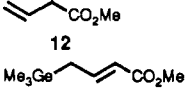
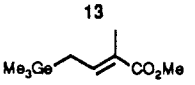
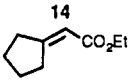
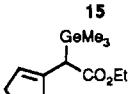
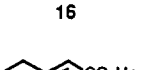
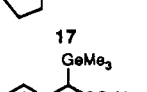
(5) Evans, D. A.; Britton, T. C.; Dorow, R. L.; Dellaria, J. F., Jr. *Tetrahedron* **1988**, *44*, 5525.
(6) (a) Kozikowski, A. P.; Jung, S. H. *J. Org. Chem.* **1986**, *51*, 3400. (b) Fleming, I.; Goldhill, J.; Paterson, I. *Tetrahedron Lett.* **1979**, *34*, 3209; **1979**, *34*, 3205. (c) Ishida, A.; Mukaiyama, T. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 2077; **1977**, *50*, 1161. (d) Hayashi, Y.; Nishizawa, M.; Sakan, T. *Chem. Lett.* **1975**, 387.
(7) Yamamoto, Y.; Hatsuya, S.; Yamada, J. *J. Chem. Soc., Chem. Commun.* **1987**, 561; **1988**, 86.
(8) Yamamoto, Y.; Hatsuya, S.; Yamada, J. *J. Chem. Soc., Chem. Commun.* **1988**, 1639; *Tetrahedron Lett.* **1989**, *30*, 3445.
(9) For the α-silylation of ester enolates with diphenylmethylsilyl chloride, see: Larson, G. L.; Fuentes, L. M. *J. Am. Chem. Soc.* **1981**, *103*, 2418.

Table I. Trapping Dienolates with Tin and Germanium Halides[a]

entry	enoate	metal halide	product	ratio E/Z	yield,[b] %
1	 **4**	Bu_3SnCl	 **5**	13/87	83
2	4	Bu_2SnCl_2	 **6**	5/>95	75
3	4	$BuSnCl_3$	 **7**	5/>95	44
4	4	$SnCl_4$	 **8**	5/>95	68
5	4	Me_3GeCl	 **9**		87[c]
6	4	Ph_3GeCl	 **10**	17/83	50[d]
7	**11**	Me_3GeBr	 **12**  **13**	**12:13** = 75:25	(100)[e]
8	**14**	Me_3GeBr	 **15**		50
9	 **16**	Me_3GeBr	 **17**		79
10	 **18**	Me_3GeCl	 **19**		79

[a] Lithium dienolates were generated by treating enoates with LDA (see Experimental Section). The product ratio was determined by ^1H NMR (90 or 270 MHz). [b] Isolated yield via Kugelrohr distillation or silica gel column chromatography, except where otherwise indicated. [c] Small amounts (<5%) of the γ-isomer were detected in the ^1H NMR spectrum. [d] The ratio of the γ/α-isomer was 88/12. [e] Crude product.

15 in moderate yield (entry 8), and **11** produced a mixture of **12** and **13** in the ratio of 75:25 (entry 7). The regioselectivity on the germylation of dienolates depends upon the substitution pattern of the double bond. Treatment of **1** with triphenylgermyl chloride gave **10** predominantly (entry 6), indicating that the regioselectivity also depends upon the substituent of germanium. It is clear that the trimethylgermylation is prone to give the α-germylated product whereas the stannylation affords the γ-stannylated product (cf. entry 1 vs 5).

The α-germylation is a reflection of kinetic control as observed in the alkylation of **1** with alkyl halides.[3] The γ-stannylation is presumably due to the thermodynamic stability of the product. The C–Ge bond is stronger than the C–Sn bond;[10] D(Ge–Et) = 237 kJ mol^{-1}, D(Sn–Et) = 193 kJ mol^{-1}.[11] The affinity of Si for oxygen is stronger than that of Ge,[10] giving the O-silylated derivative in most cases. In conclusion, the γ-metalated product is thermodynamically the most stable, and the metalation takes place essentially at the α-position except the case of trialkylsilylation. In fact, it is known that heating a certain *O*-silyl dienol ether induces the rearrangement of the silyl group to the γ-position,[3b] and we observed that the α-germylated **9** underwent rearrangement to the γ-isomer upon heating. Triphenylgermanium is directed to the γ-position presumably owing to the steric bulkiness; the *A* value of Me_3Ge is 2.07 kcal mol^{-1} whereas that of Ph_3Ge is 2.90 kcal mol^{-1}.[12]

Previously, the α-silyl β,γ-unsaturated esters **20** were prepared by a nickel-catalyzed reaction of 2-bromopropene with the lithium enolate of ethyl (trimethylsilyl)acetate,[13] or by carboxylation of the aluminium ate complexes of lithiated allylic silanes.[14] *It is not possible via the previous method to obtain such α-metalated-β,γ-unsaturated esters directly from the precursor enoates.* Further, the reactivity of **20** toward electrophiles is relatively low,

(10) Jackson, R. A. *J. Organomet. Chem.* **1979**, *166*, 17.
(11) Skinner, H. A. *Adv. Organomet. Chem.* **1964**, *2*, 49.
(12) Kitching, W.; Olszowy, H. A.; Harrey, K. *J. Org. Chem.* **1982**, *47*, 1893.
(13) (a) Albaugh-Robertson, P.; Katzenellenbogen, J. A. *Tetrahedron Lett.* **1982**, *23*, 723. (b) Morizawa, Y.; Kanemoto, S.; Oshima, K.; Nozaki, H. *Tetrahedron Lett.* **1982**, *23*, 2953. (c) Millard, A. A.; Rathke, M. W. *J. Am. Chem. Soc.*, **1977**, *99*, 4833.
(14) (a) Uno, H. *Bull. Chem. Soc. Jpn.* **1986**, *59*, 2471. (b) Naruta, Y.; Uno, H.; Maruyama, K. *Chem. Lett.* **1982**, 609. (c) Maruyama, K.; Uno, H.; Naruta, Y. *Chem. Lett.* **1983**, 1767.

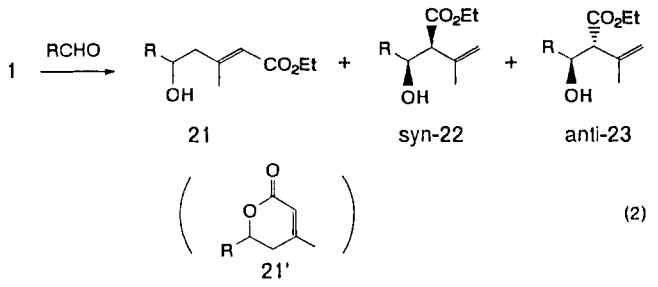
Table II. Regio- and Diastereoselective Reactions of Tin-Masked Dienolates with Aldehydes

entry	tin	aldehyde	additive	temp, °C	reaction time, h	ratio[a] 22/23	yield,[b] %
1	5	PhCHO	BF_3·OEt_2	−78	0.5	>99/1	(100)
2	5	PhCHO	$TiCl_4$	−78	0.5	61/39	(56)[c]
3	5	EtCHO	BF_3·OEt_2	−78	0.6	>99/1	34[d]
4	5	$(Et)_2CHCHO$	BF_3·OEt_2	−78	2.5	>99/1	40[d]
5	5	PhCH=CHCHO	BF_3·OEt_2	−78	6.5	84/16	69
6	5	PhCHO	Bu_4NF	−78	0.5	28/72	65
7	6	PhCHO	BF_3·OEt_2	−78	0.5	>99/1	33[d]
8	6	PhCHO	$ZnBr_2$	−78→0	3.5	>95/5	52
9	6	PhCHO	Bu_4NF	−78	0.5	>99/1	65
10	7	PhCHO	BF_3·OEt_2	−78	0.5	>99/1	30[d]
11	7	PhCHO	none	20	48	>99/1	70
12	7	PhCHO	Bu_4NF	−78	0.5	>99/1	30[d]
13	8	PhCHO	none	20	6.5	75/25	(64)[e]
14	8	PhCHO	Bu_4NF	−78	0.5	78/22	(100)

[a] Determined by ^1H NMR analysis. [b] Yield in parentheses is determined by NMR analysis of the product mixture. Others are an isolated yield. [c] The γ-adduct **21** was obtained in 44% yield. [d] The major product was the recovered aldehyde. [e] The γ-adduct was obtained in 36% yield.

compared with simple allylic silanes, presumably owing to the electron-withdrawing ester group. Accordingly, it was anticipated that the α-germylated reagent would become a useful masked dienolate since (1) it could be directly obtained from dienolates and (2) it would exhibit higher reactivity than the corresponding α-silyl derivative **20**.

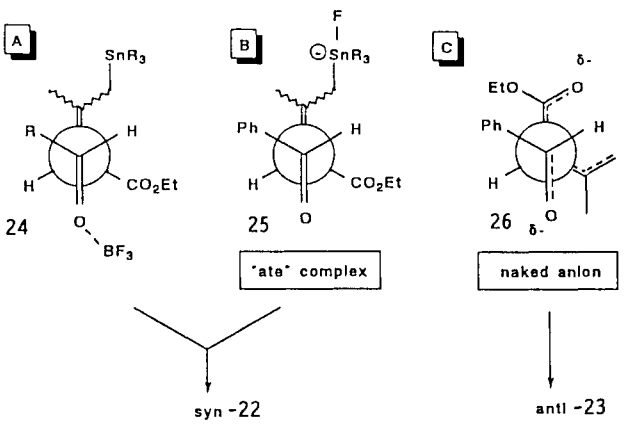
Diastereo- and Regioselective Aldol Condensation. It has been reported[3d,4] that the reaction of **1** with aldehydes at higher temperatures under thermodynamically controlled conditions leads to the γ-adduct **21**, and in turn **21′**. Regioselective formation of the γ-adducts is not a difficult task. At lower temperature under kinetic controlled conditions, α-regioselective condensation is realized. Unfortunately, however, the diastereoselectivity is low, and frequently a mixture of *syn*-**22** and *anti*-**23** is produced (eq 2).[3d,4] Therefore, a problem remained unsolved in this area is diastereoselective formation of the condensation products at the α-position.



(2)

We examined the reactions of the γ-stannylated α,β-unsaturated esters **5**–**8** with aldehydes, and the results are summarized in Table II. The BF_3- and $ZnBr_2$-mediated condensation of **5**–**7** gave the syn adduct **22** either exclusively or very predominantly (entries 1, 3–5, 7, 8, and 10). Use of $TiCl_4$ resulted in low regio- and diastereoselectivity (entry 2). Presumably, the transmetalation from tin to titanium followed by formation of the titanium enolate may take place, since the color immediately changed to deep purple by the addition of $TiCl_4$. BF_3·OEt_2 is the most efefective activator for **5**. $ZnBr_2$ is a weak activator for **5**, but suitable to **6** (cf. entry 7 vs 8). Although the F^--mediated reactions of **5** at −78 °C gave **23** (anti) predominantly (entry 6), the similar reactions of **6**, **7**, and **8** afforded **22** either exclusively or predominantly (entries 9, 12, 14). Further, **7** and **8** reacted with benzaldehyde at room temperature without assistance of Lewis acids or Bu_4NF (entries 11 and 13). The increased Lewis acidity of **7** and **8**, compared with the tributyl- and dibutyltin derivatives, presumably causes these condensation reactions without assistance of additives.

Scheme II

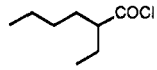
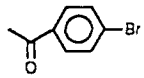
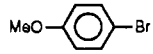
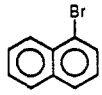
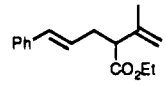


The above results on diastereoselectivity are different from the recent observations on γ-silylated α,β-unsaturated amides reported by Snieckus and co-workers.[3b] The $TiCl_4$-mediated condensation of the silylated analogue gives the corresponding anti adduct (**23**-type), whereas the F^--mediated reaction does not produce good diastereoselectivity. The reason for this difference is not clear at present.

The present diastereoselectivity can be accounted for as shown in Scheme II. The Lewis acid mediated reactions of **5**, **6**, and **7** proceed through the acyclic transition state **24**, as proposed previously in the crotyltin–aldehyde condensation,[15] to produce the syn alcohol **22** regardless of the geometry of the double bond. Without Lewis acid (entries 11 and 13), **7** and **8** again produce **22**, because the double bonds of these allylic tins possess *Z* geometry and the condensation proceeds through a six-membered chair transition state owing to the high Lewis acidity of the tin atom. The reaction of Bu_4NF and **5** may give the naked dienolate, in which the negative charge will be localized at the ester function. Therefore, the condensation proceeds through **26**, which is the most stable intermediate from both steric and electronic points of view, resulting in the predominant formation of **23**. The reactions of Bu_4NF with **6**, **7**, and **8** may produce the ate complex, owing to the strong electron-withdrawing effect of the chlorine atom. Thus, **25** must be the most stabilized transition state, leading to **22**. In conclusion, the tin masked dienolates can produce either *syn*-**22** or *anti*-**23** aldol product diastereo- and regioselectively by controlling the additive.

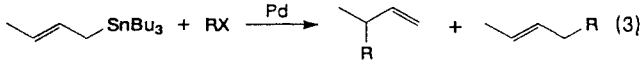
(15) Yamamoto, Y. *Acc. Chem. Res.* **1987**, *20*, 243. Yamamoto, Y.; Yatagai, H.; Naruta, Y.; Maruyama, K. *J. Am. Chem. Soc.* **1980**, *102*, 7107.

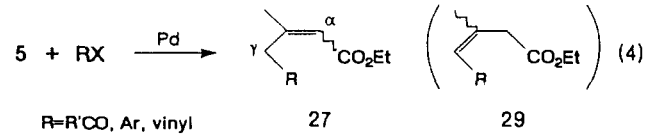
Table III. Palladium-Catalyzed Coupling of 5

entry	RX	procedure[a]	isomer ratio of 27[b] E/Z	isolated total yield of 27, %
1	PhCOCl	A	1/8	70[c]
2		A	1/5	25
3		A	1/2	25
4	PhBr	B	1/4	55[d]
5		B	1/3	60
6		C	1/1.5	30
7		C	1/10	50
8		B	1/3	20
9		B	 28	80
10		B	28	70

[a] A: 1–1.5% $PhCH_2Pd(PPh_3)_2Cl$, $CHCl_3$, reflux, 1 day. B: 5% $Pd(PPh_3)_4$, benzene, reflux, 1 day. C: 5% $Pd(OAc)_2$, 20% PPh_3, benzene, reflux, 1 day. [b] Determined by ^1H NMR analysis. [c] The isomerized β,γ-unsaturated ester was also obtained in 20% yield. [d] As a byproduct, the β,γ-unsaturated ester derivative of **27** was obtained in 5% yield.

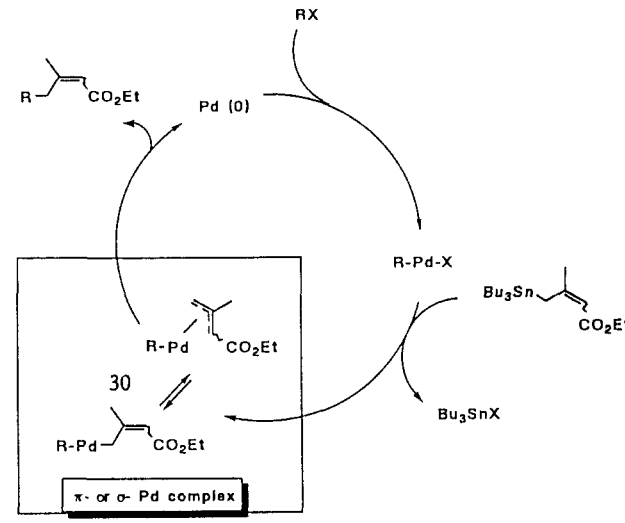
The Palladium-Catalyzed Coupling of the Tin-Masked Dienolates. Arylation and vinylation at either α- or γ-position of dienolates are not possible via ordinary ionic substitution reactions. It occurred to us that the palladium-catalyzed reaction of the tin-masked dienolates may give such arylation and vinylation products. It has been reported that the coupling of γ-substituted allylic tin compounds such as crotyltin normally proceeds through allylic transposition to give the branched isomer as the major product (eq 3).[16] It is also known that the coupling of allylic tin reagents in the presence of certain transition metals proceeds without allylic rearrangement.[17] We examined the palladium-catalyzed coupling reactions with **5** (eq 4), and the results are summarized in Table III. Interestingly, the coupling with acyl, aryl, and vinyl halides took place at the position directly bonded to tin. The couplings of **6**, **7**, and **8** were unsuccessful, presumably owing to formation of the Lewis acid Bu_xSnCl_{4-x} (x = 0, 1, 2).





Aryl halides (entries 4–7), vinyl bromide (entry 8), and acyl halides (entries 1–3) produced **27** in good to allowable yields. The aromatic acid halide and aryl halides substituted with an electron-withdrawing group gave good yields (cf. entry 5 vs 6). In entries 1 and 4, the β,γ-unsaturated ester derivatives **29** were produced as byproducts. The coupling of aliphatic acid halides and vinyl halide produced low yields (entries 2, 3, 8). It is now clear that the coupling of **5** proceeds without allylic rearrangement. On the other hand, cinnamyl acetate and bromide gave 1,5-diene **28** in good yield (entries 9 and 10). These couplings took place with allylic transposition. A similar observation is made in the palladium-catalyzed coupling of cinnamyl acetate with crotyltin.[16c]

Scheme III

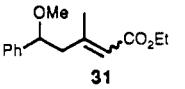
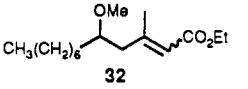
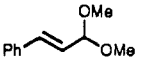
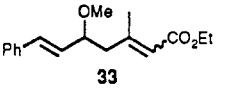
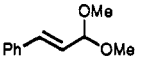
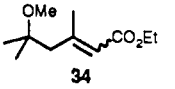
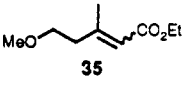
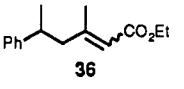
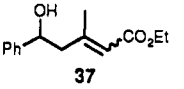
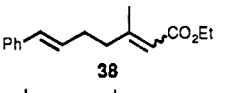
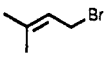
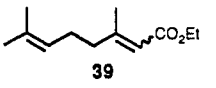


The present regioselective carbon–carbon bond formation can be accounted for by a π-allyl mechanism instead of the direct attack mechanism[16b,c] of allylic tins (Scheme III). Transmetalation of the initially formed Pd^{II} species R–Pd–X presumably gives the intermediate **30** (π- or σ-Pd complex), which undergoes reductive elimination to pro-

(16) (a) Labadie, J. W.; Tueting, D.; Stille, J. K. *J. Org. Chem.* **1983**, *48*, 4634. Godschalx, J.; Stille, J. K. *Tetrahedron Lett.* **1980**, *21*, 2599. (c) Trost, B. M.; Keinan, E. *Ibid.* **1980**, *21*, 2595.

(17) (a) Kosugi, M.; Shimizu, Y.; Migita, T. *J. Organomet. Chem.* **1977**, *129*, C36. (b) Merrifield, J. H.; Godschalx, J. P.; Stille, J. K. *Organometallics* **1984**, *3*, 1108. (c) Goliaszewski, A.; Schwartz, J. *Ibid.* **1985**, *4*, 417.

Table IV. Reactions of 9 with Carbon Electrophiles

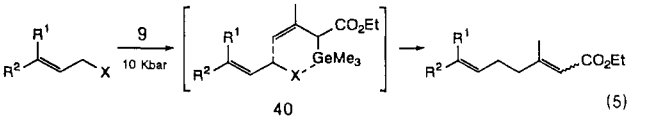
entry	electrophile	Lewis acid	temp, °C; time, h	product	E/Z[a] ratio	isolated yield, %
1	$PhCH(OMe)_2$	$TiCl_4$	−78 → −40; 1	 **31**	9.5/1	87
2	$CH_3(CH_2)_6CH(OMe)_2$	$TiCl_4$	−78 → −35; 1.5	 **32**	5/1	78
3		$TiCl_4$	−78 → −40; 1.5	 **33**	12/1	89
4		TMSOTf	−78 → −40; 1.5	33	7.5/1	91
5	$Me_2C(OMe)_2$	$TiCl_4$	−78 → −35; 1.5	 **34**	3/1	77
6	$MeOCH_2Cl$	$TiCl_4$	−78 → −10; 2	 **35**	3.5/1	38
7	$PhCHBrCH_3$	$ZnBr_2$	−70 → 0; 2	 **36**	1.3/1	45
8	PhCHO	$TiCl_4$	−78; 6	 **37**	4.5/1	37[b]
9		TMSCl	rt, 10 kbar; 48	 **38**	1.2/1	91[c]
10		TMSCl	rt, 10 kbar; 48	 **39**	1.2/1	38[c]

[a] Determined by ^1H NMR. [b] Benzaldehyde was recovered in ca. 50% yield. In entries 6 and 7, the starting materials might be recovered, since these compounds would be transformed during the workup procedure. [c] Small amounts (5–10%) of the α-isomers were formed along with the desired γ-isomers. In entry 10, the starting material may undergo dehydrobromination to give the butadiene derivative.

duce **27** and Pd^0 species. The π-allyl mechanism is supported by the E/Z ratio of **27** (Table III). If the σ-allyl species is the only intermediate involved, the ratio should be the same as those of the starting material **5** (E/Z = 13/87). Experimental results indicate that the ratio is independent of the geometry of **5**, suggesting intermediacy of the π-allylpalladium complex. The reason why the cinnamyl cases give the allylic transposition product **28** is not clear. The π-allylic ligand might be prone to be attacked directly by the soft reagent **5** rather than undergoing the transmetalation step.

Reactions of Germanium-Masked Dienolates with Carbon Electrophiles. We examined the reactions of **9** with a variety of carbon electrophiles and the results are summarized in Table IV. The carbon–carbon bond formation always took place at the γ-position. Acetals reacted regioselectively in high yields (entries 1–5). The stereochemistries of enoates were predominantly E. It is noteworthy that the α,β-unsaturated acetal undergoes regioselective head-to-tail coupling with **9** to give **33** with high E stereoselectivity (entries 3 and 4), since the Lewis acid mediated reactions of allylic acetates frequently result in regiochemical scrambling.[18] Aldehydes and reactive halides also gave the γ-alkylation products in moderate to allowable yields (entries 6–8).

The regioselective allylic–allylic coupling between allylic halides and allylic organometallic reagents is synthetically very important,[19] because the resulting head-to-tail 1,5-diene is useful for terpenoid synthesis. Unfortunately, however, the high reactivity of allylic organometallic reagents often results in low regioselectivity as observed in the Wurtz-type coupling. The stabilization–activation procedure may help to overcome this difficulty. The coupling with dienol trimethylsilyl ether has produced a low regio- and stereoselectivity.[6b] α-Silyl β,γ-unsaturated esters **20** do not react with allyl bromide and dimethylallyl chloride.[3a] The reaction of allylic halides with **9** in the presence of ordinary Lewis acids, such as $TiCl_4$, BF_3, $AlCl_3$, ZnX_2, etc., resulted in the production of complex mixtures, suggesting that the reactivity of **9** is higher than that of **20** (R^2 = H). However, use of TMSCl (trimethylsilyl chloride) at 10 kbar solved this problem;[20] the head-to-tail coupling took place either in high yield (entry 9) or in allowable yield (entry 10) (eq 5). Unfortunately, however,



40 (5)

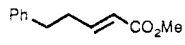
the stereoselectivity of the double bond was low. The reaction may proceed through the six-membered cyclic transition state **40**. A similar transition state is proposed in the high pressure induced coupling between allylic tins

(18) Ghribi, A.; Alexakis, A.; Normant, J. F. *Tetrahedron Lett.* **1984**, *25*, 3079. Hosomi, A.; Endo, M.; Sakurai, H. *Chem. Lett.* **1978**, 499. For the γ-selective reaction of dienoxysilane, see ref 6c.

(19) For example: Yamamoto, Y.; Yatagai, H.; Maruyama, K. *J. Am. Chem. Soc.* **1981**, *103*, 1969, and references cited therein.

(20) For high pressure induced allylic couplings via allyltins, see: Yamamoto, Y.; Maruyama, K.; Matsumoto, K. *J. Chem. Soc., Chem. Commun.* **1984**, 548.

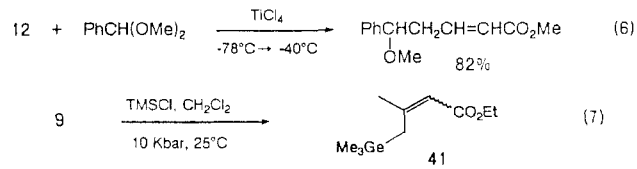
Table V. Reactions of Lithium Dienolates with DEAD

entry	enoate	conditions[a]	product: 42/43 (E/Z of 43)	product: total isolated yield, %
1	11	A	1/>99 (>99/1)	64
2	 44	A	1/>99 (>99/1)	71
3	4	B	1/10 (1/1)	78
4	4	A	1/5 (2/1)	75
5	4	C	1/2.5 (1/1)	86
6	16	B	1/3 (1/2)	87
7	18	B	4/1 (1/1.5)	69
8	18	D	3/1 (10/1)	50

[a] Lithium dienolates were prepared by the following conditions. Condition A: enoate (2 mmol), LDA (1.1 equiv) in HMPA (1.3 equiv) THF, −78 °C, 30 min. Condition B: enoate (2 mmol), LDA (1.1 equiv) in THF, −78 °C, 30 min. Condition C: $ZnCl_2$ (1.1 equiv) was added after generating the lithium enolate according to the procedure B. Condition D: the reaction was carried out by condition B, and then protonated at 0 °C.

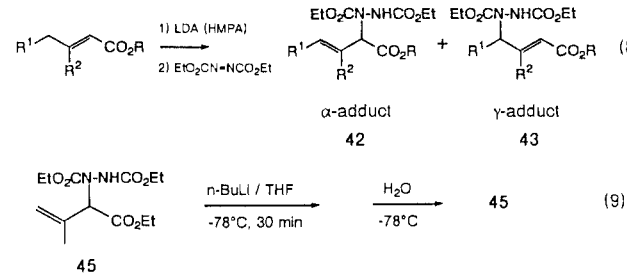
and allylic halides.[21] The coupling did not take place without use of TMSCl. The combination between very weak Lewis acid, TMSCl, and **9** under very high pressure is suitable to activate the coupling reaction. Use of other Lewis acids, such as TMSOTf, Me_2SiCl_2, and $Ti(OEt)_4$, under 10 kbar gave a poor result. Presumably, the Lewis acidity of TMSCl might be enhanced at high pressure to the level enough to activate the allylic–allylic coupling. Irrespective of the precise mechanism for this new coupling, the combination between high pressure and Lewis acids having low Lewis acidity clearly provides a new method for the activation of stabilized Group 14 organometallic compounds.

The γ-regioselectivity was also observed for **12** (eq 6). Although 12 contained small amounts of **13** (**12**/**13** = 75/25), the γ-germylated isomer did not react with electrophiles and recovered without change. Accordingly, the α-germylated compound is more reactive than the γ-germylated isomer. Treatment of **9** with TMSCl in the absence of electrophiles at 10 kbar gave the γ-isomer **41** cleanly (eq 7). Needless to say, **9** was unchanged at 10 kbar in the absence of TMSCl. The coupling between **41** and allylic halides did not take place at 10 kbar. It is clear that (1) the coupling occurs via **9** at high pressure, (2) thermodynamically **41** is more stable than **9**, and (3) TMSCl catayzes the rearrangement of Ge atom from the α-position to the γ-position.



Regioselective Synthesis of Amino Acid Derivatives. The amination reaction of lithium dienolates often produces a mixture of α- and γ-amino acid derivatives. For example, the reaction of the lithium dienolate of β,β-dimethylacryloyl imide with di-*tert*-butyl azodicarboxylate (DBAD) affords a 51% of the α-adduct along with 42% of the γ-isomer.[5] The structures of β,γ-unsaturated α-amino acids and α,β-unsaturated γ-amino acids are frequently found in important biologically active natural and unnatural products, e.g. vinyl glycine,[22] statine,[22] and anthopleurine.[23] Accordingly, we intended to control the regiochemistry in the amination of dienolates.

Before applying the stabilization–activation procedure, we first examined the reaction of lithium dienolates themselves with diethyl azodicarboxylate (DEAD) (eq 8). The result are summarized in Table V. In contrast to the lithium dienolate derived from α,β-unsaturated imide,[5] the dienolates from the enoates (**11**, **44**, **4**, and **16**) gave the γ-amino acid derivatives **43** either exclusively (entries 1 and 2) or predominantly (entries 3–6). The γ-selectivity decreased in the presence of HMPA (cf. entries 3 and 4). The zinc dienolate from **4** gave higher yield than the lithium dienolate, but resulted in lower regio- and stereoselectivity (entry 5). An interesting contrast was observed in the cyclic systems: the five-membered derivative **16** gave the γ-isomer prodominantly, whereas the six-membered enoate **18** produced the α-isomer preferentially (entries 6–8). As mentioned earlier, the condensation of dienolates with aldehydes produces the γ-adduct under thermodynamic control; before protonation the α- and γ-adducts are prone to undergo a facile isomerization. Accordingly, the protonation of the amination reaction was carried out at higher temperature (0 °C) in order to know whether the isomerization between **42** and **43** may take place under the reaction conditions (entry 8). Although the *E*/*Z* ratio of **43** changed remarkably from 1/1.5 to 10/1, the regioisomer ratio was still α-preference. The ratio of **42**/**43** slightly changes at 0 °C but presumably does not change at −78 °C. In order to confirm this point, the isolated α-adduct **45** was treated with *n*-BuLi at −78 °C and quenched after 30 min at this temperature (eq 9). The γ-isomer was not detected, and **45** was recovered in essentially 100% yield. Consequently, the regioisomer ratios are those produced under kinetic control.



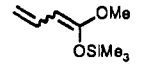
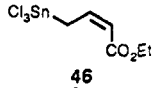
It is clear that certain γ-amino acids are obtained with very high regioselectivity by simply treating lithium dienolates with DEAD. However, the α-isomers from **11**, **44**, **4**, and **16** and the γ-isomer from **18** are not available.

(21) Yamamoto, Y.; Maruyama, K.; Matsumoto, K. *J. Chem. Soc., Chem. Commun.* **1984**, 548.

(22) Fitzner, J. N.; Pratt, D. V.; Hopkins, P. B. *Tetrahedron Lett.* **1985**, *26*, 1959. Hanessian, S.; Sahoo, S. P. *Ibid.* **1984**, *25*, 1984 and references cited therein.

(23) Wagner, I.; Musso, H. *Angew. Chem., Int. Ed. Engl.* **1983**, *22*, 816.

Table VI. Lewis Acid Mediated Reactions of Sn-, Ge-, and Si-Masked Dienolates with DEAD

entry	masked dienolate	Lewis acid	temp, °C; reaction time	product 42/43 (E/Z of 43)	product total isolated yield, %
1		$TiCl_4$	−78; 30 min	1/4 (>99/1)	85
2	**5**	$ZnCl_2$	−78 → 0; 40 min	15/1	80
3	8	*a*	−10; 100 min	10/1	28
4	 **46**	*a*	−10; 30 min	10/1	58
5	**9**	$TiCl_4$	−78 → rt; 2 h	1/>99 (3/1)	71
6	17	$TiCl_4$	−78 → 5; 40 min	1/>99 (8/1)	88
7	**19**	$TiCl_4$	−78 → 0; 30 min	1/>99 (6/1)	55

[a] Lithium dienolate, prepared from the corresponding enoate, was trapped with 1.1 equiv of $SnCl_4$ at −78 °C and then DEAD was added to this mixture (in situ method).

We next examined the Lewis acid mediated reaction of Sn- and Ge-masked dienolates, and the results are summarized in Table VI.

As expected, the Sn-masked dienolates **5**, **8**, and **46** gave the α-adducts **42** with high regioselectivity (entries 2–4), and the Ge-masked dienolates **9**, **17**, and **19** produced the γ-adducts **42** exclusively (entries 5–7). In entries 3 and 4, the lithium enolates were trapped with $SnCl_4$, and then the resulting γ-stannyl α,β-unsaturated esters were treated in situ with DEAD. The in situ method seems to be convenient, since the isolation of the masked enolate is not required. The dienol silyl ether afforded the γ-isomer predominantly, but the regioselectivity was not so high compared with the lithium dienolate itself (cf. Table V, entry 1, vs Table VI, entry 1).

It has been reported that the reaction of azodicarboxylates with simple lithium enolates[24,25] or with ketene silyl acetals[26,27] produces the amino acid derivatives in high yields. However, the regiocontrol on the amination reaction of dienolates has not been achieved by the previous procedure. Here also, the stabilization–activation procedure with Sn and Ge derivatives is proved to be successful for controlling the amination reaction.

Conclusions. It is well known that the reaction of lithium enolates including dienolates with trimethylsilyl chloride gives the corresponding O-silylated enol (or dienol) ethers. The reaction of lithium dienolates with tin chlorides produces the γ-stannylated α,β-unsaturated esters, whereas the reaction of trimethylgermanium halides with certain lithium dienolates gives the α-trimethylgermylated β,γ-unsaturated esters. Therefore, trapping dienolates regioselectively at the three different nucleophilic cites is realized by choosing Si, Ge, and Sn halides as the electrophile. By using these Sn-masked and Ge-masked dienolates, (1) the regio- and diastereoselective aldol condensations with aldehydes, (2) the C–C bond formation at the γ-position with the carbon electrophiles having sp^2-hybridization via palladium-catalyzed reactions, (3) the C–C bond formation at the γ-position with variety of carbon electrophiles via Lewis acid promoted reactions including high pressure reactions, and (4) the regiocontrolled amination reaction with DEAD have been accomplished. The present development clearly provides an synthetic application of the stabilization–activation concept of anionic species with group 14 elements.

Experimental Section

^1H NMR spectra were recorded on a JEOL JNM-PMX 60, a JEOL GSX-270, a Varian XL-200, or a Varian EM-390 spectrometer. The chemical shifts are expressed in parts per million downfield from tetramethylsilane internal standard. ^{13}C NMR spectra were recorded on a Varian XL-200 or a JEOL GSX-270 spectrometer. IR spectra were recorded on a Hitachi Model 215. Mass spectra were recorded on a Hitachi M-52 spectrometer. High-resolution mass spectra were recorded on a JEOL JMS-HX 110. Melting points were determined on a Yamato MP-21 capillary melting point apparatus. Melting points and boiling points stated are uncorrected. The Kugelrohr distillation temperatures are oven temperatures, not boiling points as stated.

Tetrahydrofuran was distilled from sodium benzophenone ketyl under nitrogen. All other solvents were dried and stored over 3-Å molecular sieves. Diisopropylamine was distilled from CaH_2 and stored under nitrogen. Butyllithium in hexane solution was purchased and titrated prior to use. Most commercially supplied chemicals were distilled and stored over molecular sieves.

Ethyl 3-Methyl-4-(tributylstannyl)-2-butenoate (5). In a 200-mL flask with a septum inlet were placed 30 mL of THF and 4.6 mL (34.5 mmol) of diisopropylamine, and the mixture was cooled to −78 °C. A hexane solution of BuLi (1.5 M × 22 mL, 33 mmol) was added, and the mixture was stirred for 15 min. A solution of **4** (4.3 mL, 30 mmol) dissolved in THF (11 mL) was added dropwise through a dropping funnel over 30 min, and then the mixture was stirred for 20 min. Chlorotributylstannane (8.6 mL, 30 mmol) was added, and after 1 h the reaction was warmed to 20 °C. The solvents were removed under reduced pressures, and then hexane was added. All operations were carried out under nitrogen. Lithium chloride was precipitated out, and then hexane solution was separated by using a centrifuge. Removal of the solvent under reduced pressures gave yellow oil. ^1H NMR analysis of this crude product showed the *E*/*Z* ratio of **5** was 13/87. Kugelrohr distillation gave pale-yellow **5** (10.34 g) in 83% yield; bp 165 °C (0.09 mmHg). The *E*/*Z* ratio of this distilled product was against 13/87. The NOE enhancement (20%) was observed between the 3-Me proton and the olefinic 2-H proton of the major isomer of **5**, indicating *Z* geometry. A methylene chloride solution of **5** under Ar could be stored for two months in a refrigerator. When **5** was kept without a solvent for a prolonged time, the self-condensation took place: ^1H NMR of (*Z*)-**5** (CCl_4) δ 0.8–1.6 (m, 30), 1.84 (d, *J* = 1.5 Hz, 3), 2.46 (s, 2), 4.03 (q, *J* = 7.0 Hz, 2), 5.27 (m, 1); (*E*)-**5** (CCl_4) δ 0.8–1.6 (m, 30), 2.10 (m, 3), 2.82 (s, 2), 4.03 (q, *J* = 7.0 Hz, 2), 5.37 (m, 1); ^{13}C NMR of (*Z*)-**5** ($CDCl_3$) δ 10.34, 13.69, 14.52, 22.08, 27.36, 27.86, 28.98, 58.84, 108.70, 163.86, 169.2; IR (neat) 1700, 1620 cm^{-1}.

Ethyl 4-(Chlorodibutylstannyl)-3-methyl-2-butenoate (6) and Ethyl 4-(Butyldichlorostannyl)-3-methyl-2-butenoate (7). A similar procedure as above was used to prepare **6** and **7**. The geometry of the double bond was also determined by NOE experiments. The *E* isomer was not detected by the ^1H NMR analysis (90 MHz) of the crude products: ^1H NMR of **6** (CCl_4) δ 0.8–1.9 (m, 21), 2.09 (d, *J* = 1.5 Hz, 3), 2.38 (s, 2), 4.10 (q, *J* = 7.0 Hz, 2), 5.44 (m, 1); ^1H NMr of **7** (CCl_4) δ 0.97 (t, *J* = 6.8 Hz, 3), 1.30 (t, *J* = 7.0 Hz, 3), 1.1–1.6 (m, 2), 1.73 (m, 2), 2.12 (d, *J* = 1.5 Hz, 3), 2.63 (s, 2), 4.18 (q, *J* = 7.0 Hz, 2), 5.76 (m, 1).

Ethyl 3-Methyl-4-(trichlorostannyl)-2-butenoate (8). In a 100-mL flask with a septum inlet were placed THF (8 mL) and diisopropylamine (1.54 mL, 11.5 mmol) under Ar, and the mixture was cooled to −78 °C. A hexane solution of butyllithium (1.5 M × 7.33 mL, 11 mmol) was added, and the mixture was stired for 10 min. A solution of **4** (1.43 mL, 10 mmol) dissolved in 5 mL of THF was added dropwise. The resulting mixture was stirred for 30 min, and then tin tetrachloride (1.3 mL, 10 mmol) was added. The reaction was allowed to warm to 0 °C, and the solvents were removed under reduced pressures. Dichloromethane was added, and the white precipitate was separated by a glass filter

(24) Evans, D. A.; Britton, T. C.; Dorow, R. L.; Dellaria, J. F. *J. Am. Chem. Soc.* **1986**, *108*, 6395.
(25) Trimble, L. A.; Vederas, J. C. *J. Am.* Chem. *Soc.* **1986**, *108*, 6397.
(26) Gennari, C.; Colombo, L.; Bertolini, G. *J. Am. Chem. Soc.* **1986**, *108*, 6394.
(27) Oppolzer, W.; Moretti, R. *Helv. Chim. Acta* **1986**, *69*, 1923.

(G1, G3). Removal of the solvent gave a yellow oil. ^{1}H NMR analysis (90 MHz) of the crude product revealed that the E/Z ratio was 62/48. Kugelrohr distillation gave **8** as a heavy oil (2.4 g, 68%); bp 150–160 °C (0.2 mmHg). On standing, **8** crystallized, whose ^{1}H NMR revealed that the distilled **8** consisted of the Z isomer, a minor isomer of the crude product. The residue in the distillation flask was the E isomer, which exhibited very high boiling point, presumably owing to the formation of the dimeric compound. The Z isomer exhibited NOE enhancement (20%), whereas the E isomer did not show such enhancement. Apparently, isomerization from the E to Z isomer took place upon heating. The Z isomer must exist as a monomer owing to the intramolecular coordination of the carbonyl oxygen atom to the Lewis acidic tin atom, and thus exhibits lower boiling point. On the other hand, the E isomer must exist as a dimer, since the intramolecular coordination is not possible but instead the intramolecular coordination is involved. A dichloromethane solution of **8** was kept under Ar and used within a week: ^{1}H NMR of **8** (Z) ($CDCl_3$) δ 1.36 (t, J = 7.0 Hz, 3), 2.25 (d, J = 1.5 Hz, 3), 2.92 (s, 2), 4.32 (q, J = 7.0 Hz, 2), 5.86 (m, 1); ^{13}C NMR ($CDCl_3$) δ 11.01, 28.94, 39.12, 63.11, 113.71, 162.14, 179.19; IR (CCl_4) 1645, 1610 cm^{-1}; ^{1}H NMR of the E isomer of **8** (CCl_4) δ 1.30 (t, J = 7.0 Hz, 3), 2.10 (d, J = 1.5 Hz, 3), 2,80 (s, 2), 4.19 (q, J = 7.0 Hz, 2), 5.73 (m, 1); ^{13}C NMR ($CDCl_3$) δ 14.16, 28.87, 40.56, 61.29, 112.62, 164.11, 172.0; IR ($CHCl_3$) 1645, 1610 cm^{-1}.

Ethyl 3-Methyl-2-(trimethylgermyl)-3-butenoate (9). The lithium dienolate **1** was prepared in a 10-mmol scale as described above. To a THF solution of **1** was added chlorotrimethylgermane (1.36 mL, 11 mmol), and the reaction mixture was allowed to warm to 20 °C. Ether and water were added, and the organic layer was separated and dried over anhydrous magnesium sulfate. Removal of the solvents gave a yellow oil (2.374 g, 97%). ^{1}H NMR analysis (90 MHz) revealed that the regioisomer ratio was at least >15:1. Kugelrohr distillation gave colorless **9** (2.132 g) in 87% yield; bp 100 °C (5 mmHg). A dichloromethane solution of **9** under Ar could be stored over 6 months in a refrigerator: ^{1}H NMR of **9** (CCl_4) δ 0.24 (s, 9), 1.24 (t, J = 7.0 Hz, 3), 1.79 (m, 3), 2.87 (s, 1), 4.03 (q, J = 7.0 Hz, 2), 4.75 (m, 1), 4.87 (m, 1); ^{13}C NMR ($CDCl_3$) δ −2.0, 14.5, 23.9, 46.2, 58.8, 111.0, 140.6, 173.1; IR (CCl_4) 1720, 1150 cm^{-1}; MS calcd for $C_{10}H_{20}O_2Ge$ m/z 246.0675, found m/z 246.0665. The γ-isomer of **9** could not be isolated in pure form, but its structure was assigned only by ^{1}H NMR spectra: E isomer (CCl_4) δ 0.24 (s, 9), 1.17 (t, J = 7.0 Hz, 3), 1.73 (m, 3), 2.37 (s, 2), 3.96 (q, J = 7.90 Hz, 2), 5.33 (m, 1); Z isomer (CCl_4) δ 0.24 (s, 9), 1.16 (t, J = 7.0 Hz, 3), 1.73 (s, 2), 2.03 (m, 3), 3.96 (q, J = 7.0 Hz, 2), 5.30 (m, 1); IR (CCl_4) of E and Z isomer 1710 cm^{-1}.

Ethyl 3-Methyl-4-(triphenylgermyl)-2-butenoate (10). The same procedure as above was used. Purification of the product was performed by column chromatography on silica gel: **10** (Z isomer) mp 59–62 °C; ^{1}H NMR ($CDCl_3$) δ 1.22 (t, J = 7.1 Hz, 3), 1.96 (s, 3), 2.62 (s, 2), 4.07 (q, J = 7.1 Hz, 2), 5.54 (s, 1), 7.34–7.48 (m, 15); IR (CCl_4) 1710 cm^{-1}; MS calcd for $C_{25}H_{26}O_2Ge$ m/z 432.1144, found m/z 432.1122. The E isomer and α-regioisomer could not be isolated in pure form.

Methyl 2-(Trimethylgermyl)-3-butenoate (12) and Methyl 4-(Trimethylgermyl)-2-butenoate (13). The same procedure as above was employed except (i) using HMPA (1.3 equiv) as an additive when the lithium dienolate was generated, and (ii) adding a solution of the lithium dienolate to a THF solution of bromotrimethylgermane (inversion addition): ^{1}H NMR of **12** (CCl_4) δ 0.21 (s, 9), 2.89 (d, J = 10.4 Hz, 1), 3.59 (s, 3), 4.74 (m, 1), 4.90 (s, 1), 6.0 (m, 1); IR (CCl_4) 1725, 1640 cm^{-1}; MS 186 (100), 214 (11.8), 216 (17.6), 218 (23.1); ^{1}H NMR of **13** (CCl_4) δ 0.21 (s, 9), 1.82 (dd, J = 1.4, 9.0 Hz, 2), 3.61 (s, 3), 5.53 (dt, J = 1.4, 15.3 Hz, 1), 6.92 (dt, J = 15.3, 9.0 Hz, 1); IR (CCl_4) 1725, 1640, 1205, 1135 cm^{-1}; MS 186 (100), 214 (11.8), 216 (17.6), 218 (23.1).

Methyl 2-Methyl-4-(trimethylgermyl)-2-butenoate (15). The same procedure as above was used except that purification of the product was performed by column chromatography on silica gel: ^{1}H NMR of **15** ($CDCl_3$) δ 0.20 (s, 9), 1.79 (br s, 3), 1.84 (d, J = 9.7 Hz, 2), 3.72 (s, 3), 6.99 (t, J = 9.7 Hz, 1); IR (CCl_4) 1715, 1640, 1275 cm^{-1}; MS 117 (100), 228 (27.8), 230 (18.5), 232 (47.7).

Ethyl 2-(1-Cyclopenten-1-yl)-2-(trimethylgermyl)acetate (17). The same proceudre as above was used: bp 120 °C (1 mmHg) (Kugelrohr); ^{1}H NMR ($CDCl_3$) δ 0.25 (s, 9), 1.25 (t, J = 7.0 Hz, 3), 1.83 (m, 2), 2.2–2.5 (m, 3), 3.11 and 3.13 (s, totally 1, presumably due to rotomer), 4.1 (m, 2), 5.55 (m, 1); ^{13}C NMR ($CDCl_3$) δ −2.0, 14.5, 23.5, 32.4, 36.2, 41.0, 59.7, 124.2, 138.7, 173.3; IR (CCl_4) 1710 cm^{-1}; MS calcd for $C_{12}H_{22}O_2Ge$ m/z 272.0832, found m/z 272.0835.

Ethyl 2-(1-Cyclohexen-1-yl)-2-(trimethylgermyl)acetate (19). The same procedure as above was used: bp 115 °C (0.07 mmHg) (Kugelrohr); ^{1}H NMR ($CDCl_3$) δ 0.24 (s, 9), 1.5–1.65 (m, 4), 1.88 (d, J = 17.5 Hz, 1), 2.02 (m, 2), 2.18 (d, J = 17.5 Hz, 1), 2.85 (s, 1), 3.62 (s, 3), 5.58 (m, 1); ^{13}C NMR ($CDCl_3$) δ −1.8, 22.3, 23.1, 25.4, 29.6, 46.1, 50.9, 122.5, 132.9, 174.1; IR (CCl_4) 1725, 1155 cm^{-1}; MS calcd for $C_{12}H_{22}O_2Ge$ m/z 272.0832, found m/z 272.0826.

Reactions of Tin-Masked Dienolates with Aldehydes. In a 50-mL flask with a septum inlet cooled at −78 °C under Ar were placed 3 mL of dichloromethane, 104 μL (1 mmol) of benzaldehyde, and 0.13 mL of BF_3·OEt_2. After stirring for 10 min at this temperature, a dichloromethane solution of **5** (4.4 mL, 1.5 mmol) was added dropwise, and stirring was continued for 30 min. The reaction was quenched at −78 °C by the addition of methanol and then allowed to warm to 0 °C. Ether and saturated aqueous $NaHCO_3$ solution were added. The organic layer was separated, brined, and dried over anhydrous Na_2SO_4. The diastereoselectivity was determined prior to purification of the products by comparing the integral area ratio at C-2 proton of the stereoisomers. It has been established that J(syn) on the C-2 proton is greater than J(anti).[3d] Isolation of products was performed with column chromatography on silica gel. The reaction in the presence of Bu_4NF was carried out as follows. In a 50-mL flask with a septum inlet cooled at −78 °C under Ar were placed 3 mL of THF, 104 μL (1 mmol) of benzaldehyde, and 1.5 mL of THF solution of Bu_4NF (1.5 mmol), and the mixture was stirred for 10 min. A THF solution of **5** (4 mL, 1.5 mmol) was added. After stirring for 30 min, the reaction was quenched at −78 °C by adding methanol.

Ethyl 2-(1-Hydroxy-1-phenylmethyl)-3-methyl-3-butenoate (R = Ph in 22 and 23). The syn isomer: colorless oil; ^{1}H NMR ($CDCl_3$) δ 1.25 (t, J = 7.1 Hz, 3), 1.58 (s, 3), 3.12 (d, J = 4.8 Hz, 1), 3.37 (d, J = 8.8 Hz, 1), 4.19 (q, J = 7.1 Hz, 2), 4.84 (s, 2), 5.03 (dd, J = 8.8, 4.4 Hz, 1), 7.26–7.33 (m, 5); IR (neat) 3490, 1725 cm^{-1}; MS calcd for $C_{14}H_{18}O_3$ m/z 234.1256, found m/z 234.1255. The anti isomer: colorless oil; ^{1}H NMR ($CDCl_3$) δ 1.06 (t, J = 7.1 Hz, 3), 1.86 (s, 3), 2.55 (d, J = 2.3 Hz, 1), 3.40 (d, J = 8.4 Hz, 1), 3.98 (q, J = 7.1 Hz, 2), 5.05–5.12 (m, 3), 7.26–7.41 (m, 5); IR (neat) 3500, 1725 cm^{-1}; MS calcd for $C_{14}H_{18}O_3$ m/z 234.1256, found m/z 234.1249.

Ethyl 3-hydroxy-2-isopropenylpentanoate (R = Et in 22): colorless oil; ^{1}H NMR (CCl_4) δ 0.95 (t, J = 6.8 Hz, 3), 1.25 (t, J = 7.0 Hz, 3), 1.2–1.7 (m, 2), 1.71 (m, 3), 2.73 (d, J = 4.9 Hz, 1), 2.92 (d, J = 8.7 Hz, 1), 3.78 (m, 1), 4.11 (q, J = 7.0 Hz, 2), 4.86 (m, 2); IR (neat) 3480, 1725 cm^{-1}; MS 128 (100), 186 (M$^+$).

Ethyl 4-ethyl-3-hydroxy-2-isopropenylhexanoate (R = CH(Et)$_2$ in 22): colorless solid; mp 29–30 °C; ^{1}H NMR ($CDCl_3$) δ 0.89 (t, J = 7.2 Hz, 3), 0.92 (t, J = 7.3 Hz, 3), 1.18 (m, 2), 1.27 (t, J = 7.0 Hz, 3), 1.3–1.6 (m, 3), 1.75 (s, 3), 2.54 (d, J = 5.9 Hz, 1), 3.30 (d, J = 9.0 Hz, 1), 4.08 (ddd, J = 5.9, 9.0, 2.8 Hz, 1), 4.18 (q, J = 7.0 Hz, 2), 4.93 (br s, 1), 4.95 (m, 1); IR (neat) 3600, 3530, 1720, 1645 cm^{-1}; MS calcd for $C_{13}H_{24}O_3$ m/z 228.1725, found m/z 228.1704.

Ethyl 3-Hydroxy-2-isopropenyl-5-phenyl-4-pentenoate (R = CH=CHPh in 22 and 23). The syn isomer: yellow oil; ^{1}H NMR ($CDCl_3$) δ 1.27 (t, J = 7.1 Hz, 3), 1.79 (s, 3), 2.95 (d, J = 5.1 Hz, 1), 3.19 (d, J = 8.4 Hz, 1), 4.20 (q, J = 7.1 Hz, 2), 4.68 (ddd, J = 5.1, 6.4, 8.4 Hz, 1), 4.98 (s, 2), 6.18 (dd, J = 6.4, 15.8 Hz, 1), 6.67 (d, J = 15.8 Hz, 1), 7.21–7.39 (m, 5); IR (neat) 3450, 1730, 1650 cm^{-1}; MS calcd for $C_{16}H_{20}O_3$ m/z 260.1413, found m/z 260.1408. The anti isomer: yellow oil; ^{1}H NMR ($CDCl_3$) δ 1.22 (t, J = 7.0 Hz, 3), 1.88 (s, 3), 2.40 (d, J = 3.3 Hz, 1), 3.25 (d, J = 8.0 Hz, 1), 4.13 (q, J = 7.0 Hz, 2), 4.69 (ddd, J = 3.3, 6.6, 8.0 Hz, 1), 5.05 (s, 1), 5.10 (s, 1), 6.22 (dd, J = 15.8, 6.6 Hz, 1), 6.69 (d, J = 15.8 Hz, 1), 7.24–7.39 (m, 5); IR (neat) 3485, 1730, 1650 cm^{-1}; MS calcd for $C_{16}H_{20}O_3$ m/z 260.1413, found m/z 260.1413.

Palladium-Catalyzed Coupling of 5. The reactions of p-bromoacetophenone and 1-bromonaphthalene are representative. In a 20-mL flask with a septum inlet were placed 57.5 mg (0.05 mmol) of $Pd(PPh_3)_4$, 200 mg (1 mmol) of p-bromoacetophenone, and 1.5 mL of benzene under Ar. A benzene solution of **5** (1 mL, 1.2 mmol) was added, and the mixture was kept at 80 °C for 22

h with stirring. The mixture was cooled to room temperature, and 10 mL of ether was added. Palladium was removed by filtration through a short silica gel column. Removal of the solvents gave yellow oil. The E/Z ratio was determined at this stage. Column chromatography with silica gel (40 g) by using hexane–chloroform (10:1, 150 mL) as an eluant was used to isolate the product; 91.0 mg of pure Z isomer and 63.6 mg of a mixture of Z and E isomers were obtained. In a similar flask under Ar were placed 11.2 mg (0.05 mmol) of $Pd(OAc)_2$, 52.5 mg (0.20 mmol) of Ph_3P, 1.5 mL of benzene, and 139 μL (1 mmol) of 1-bromonaphthalene. A benzene solution of **5** (1 mL, 1.5 mmol) was added, and the mixture was kept at 80 °C for 20 h with stirring. The same workup procedure as above was used. The minor E isomers in Table III could not be obtained in a pure form, but obtained as mixture was the Z isomers.

Ethyl 4-Benzoyl-3-methyl-2-butenoate (R = COPh in 27). Z Isomer: colorless oil; ^1H NMR (CCl_4) δ 1.22 (t, J = 6.9 Hz, 3), 1.95 (d, J = 1.5 Hz, 3), 4.06 (q, J = 6.9 Hz, 2), 4.35 (s, 2), 5.78 (s, 1), 7.3–7.5 (m, 3), 7.8–8.0 (m, 2); IR (CCl_4) 1715, 1685 cm^{-1}; MS calcd for $C_{14}H_{16}O_3$ m/z 232.1100, found m/z 232.1104.

Ethyl 3-Methyl-5-oxo-2-dodecenoate (R = $CO(CH_2)_6CH_3$ in 27). Z Isomer: colorless oil; ^1H NMR (CCl_4) δ 0.8–1.8 (m, 16), 1.90 (d, J = 1.5 Hz, 3), 2.43 (t, J = 6.8 Hz, 2), 3.70 (s, 2), 4.07 (q, J = 7.1 Hz, 2), 5.72 (m, 1); IR (neat) 1715, 1740, 1650 cm^{-1}; MS calcd for $C_{15}H_{26}O_3$ m/z 254.1882, found m/z 254.1856.

Ethyl 6-Ethyl-3-methyl-5-oxo-2-decenoate (R = $COCH(Et)(CH_2)_3CH_3$ in 27). Z Isomer: colorless oil; ^1H NMR (CCl_4) δ 0.8–1.8 (m, 17), 1.88 (d, J = 1.5 Hz, 3), 2.35 (m, 1), 3.81 (s, 2), 4.06 (q, J = 6.9 Hz, 2), 5.71 (m, 1); IR (neat) 1715, 1740, 1650 cm^{-1}; MS calcd for $C_{15}H_{26}O_3$ m/z 254.1882, found m/z 254.1912.

Ethyl 3-Methyl-4-phenyl-2-butenoate (R = Ph in 27). Z Isomer: colorless oil; ^1H NMR (CCl_4) δ 1.28 (t, J = 7.0 Hz), 1.76 (m, 3), 4.00 (s, 2), 4.13 (q, J = 7.0 Hz, 2), 5.67 (s, 1), 7.13 (s, 5); IR (neat) 1720, 1655 cm^{-1}; MS calcd for $C_{43}H_{16}O_2$ m/z 204.1150, found m/z 204.1150.

Ethyl 4-(4-Acetylphenyl)-3-methyl-2-butenoate (R = C_6H_4-*p*-$COCH_3$ in 27). Z Isomer: colorless oil; ^1H NMR (CCl_4) δ 1.29 (t, J = 6.9 Hz, 3), 1.77 (d, J = 1.5 Hz, 3), 2.46 (s, 3), 4.03 (s, 2), 4.12 (q, J = 6.9 Hz, 2), 5.70 (m, 1), 7.22 (d, J = 7.8 Hz, 2), 7.73 (d, J = 7.8 Hz, 2); IR (neat) 1710, 1680, 1645, 1600, 1270, 1170 cm^{-1}; MS calcd for $C_{15}H_{18}O_3$ m/z 246.1255, found m/z 246.1257.

Ethyl 3-Methyl-4-(1-naphthyl)-2-butenoate (R = Naphthyl in 27). Z Isomer: colorless oil; ^1H NMR (CCl_4) δ 1.30 (t, J = 6.9 Hz, 3), 1.66 (s, 3), 4.17 (q, J = 6.9 Hz, 2), 4.50 (s, 2), 5.77 (m, 1), 7.2–7.4 (m, 4), 7.5–7.75 (m, 2), 7.9–8.05 (m, 1); IR (neat) 1705, 1640, 1175 cm^{-1}; MS calcd for $C_{17}H_{18}O_2$ m/z 254.1307, found m/z 254.1302.

Ethyl 4-(4-Methoxyphenyl)-3-methyl-2-butenoate (R = C_6H_4-*p*-OMe in 27). Z Isomer; colorless oil; ^1H NMR (CCl_4) δ 1.28 (t, J = 7.2 Hz, 3), 1.75 (d, J = 1.5 Hz, 3), 3.70 (s, 3), 3.88 (s, 2), 4.11 (q, J = 7.2 Hz, 2), 5.60 (m, 1), 6.65 (d, J = 11.1 Hz, 2), 7.02 (d, J = 11.1 Hz, 2); IR (neat) 1710, 1645, 1510, 1250, 1170 cm^{-1}.

Ethyl 3,6-Dimethyl-2,5-heptadienoate (R = $CH{=}C(CH_3)_2$ in 27). Z Isomer; colorless oil; ^1H NMR (CCl_4) δ 1.23 (t, J = 6.9 Hz, 3), 1.69 (br s, 6), 1.81 (d, J = 1.5 Hz, 3), 3.33 (d, J = 7.8 Hz, 2), 4.06 (q, J = 6.9 Hz, 2), 5.07 (t, J = 7.8 Hz, 1), 5.52 (m, 1); IR (neat) 1710, 1655 cm^{-1}.

Ethyl 2-isopropenyl-5-phenyl-4-pentanoate (28): pale yellow oil; ^1H NMR ($CDCl_3$) δ 1.24 (t, J = 7.1 Hz, 3), 1.79 (s, 3), 2.35–2.55 (m, 1), 2.65–2.85 (m, 1), 3.17 (t, J = 7.7 Hz, 1), 4.15 (q, J = 7.1 Hz, 2), 4.93 (s, 2), 6.14 (m, 1), 6.44 (d, J = 15.8 Hz, 1), 7.17–7.34 (m, 5); IR (neat) 1730, 1650, 1450, 1160 cm^{-1}; MS calcd for $C_{16}H_{22}O_2$ m/z 244.1464, found m/z 244.1465.

Reactions of 9 with Carbon Electrophiles. Syntheses of **32** and **38** are representative. In a 20-mL flask with a septum inlet cooled at −78 °C under Ar were placed 2 mL of dichloromethane, 86 mg (0.5 mmol) of octylaldehyde dimethyl acetal dissolved in 1 mL of dichloromethane, and 0.5 mL (0.5 mmol) of dichloromethane solution of $TiCl_4$. The mixture was stirred for 5 min, and 2 mL (0.6 mmol) of dichloromethane solution of **9** was added at −78 °C. The mixture was allowed to warm to −35 °C over 90 min with stirring, and then the reaction was quenched by adding methanol. The mixture was warmed to 0 °C. Ether and saturated aqueous $NaHCO_3$ solution were added. The usual workup gave 147 mg of yellow oil. ^1H NMR analysis of this crude product revealed that the E/Z ratio was 5/1. Purification was carried out by silica gel column chromatography (SiO_2, 15 g, hexane–ether = 30:1 as an eluant), and thus 11.4 mg of the Z isomer of **32**, 87.9 mg of the E isomer, and 6.5 mg of a mixture of E and Z isomers were obtained.

In a 1-mL Teflon tube for high-pressure reaction were placed 98.5 mg (0.5 mmol) of cinnamyl bromide dissolved in 0.5 mL of dichloromethane, 145 mg (0.6 mmol) of **9**, and 64 μL (0.5 mmol) of chlorotrimethylsilane.[28] Extra space of the tube was filled with dichloromethane. The tube was kept under 10 kbar at 25 °C for 48 h, and then the pressure was released. Removal of the solvent followed by column chromatography on silica gel gave **38** (81%) along with the α-isomer (10%).

Ethyl 5-Methoxy-3-methyl-5-phenyl-2-pentenoate (31). E Isomer: colorless oil; ^1H NMR (CCl_4) δ 1.25 (t, J = 7.2 Hz, 3), 2.13 (d, J = 1.5 Hz, 3), 2.27 (dd, J = 12.9, 5.0 Hz, 1), 2.54 (dd, J = 12.0, 7.7 Hz, 1), 3.13 (s, 3), 4.05 (q, J = 7.2 Hz, 2), 4.20 (dd, J = 7.7, 5.0 Hz, 1), 5.53 (m, 1), 7.20 (s, 5); IR (CCl_4) 1715 cm^{-1}; MS 121 (100), 248 (M^+, 0.1).

Ethyl 5-Methoxy-3-methyl-2-dodecenoate (32). E Isomer: colorless oil; ^1H NMR ($CDCl_3$) δ 0.88 (t, J = 6.0 Hz, 3), 1.25–1.46 (m, 15), 2.18 (s, 3), 2.2 (m, 1), 2.37 (dd, J = 13.6, 7.0 Hz, 1), 3.32 (s, 3), 4.15 (q, J = 7.1 Hz, 2), 5.71 (s, 1); IR (CCl_4) 1720, 1645 cm^{-1}; MS calcd for $C_{16}H_{30}O_3$ m/z 270.2195, found m/z 270.2200.

Ethyl 5-Methoxy-3-methyl-7-phenyl-2,6-heptadienoate (33). E Isomer: colorless oil; ^1H NMR ($CDCl_3$) δ 1.27 (t, J = 7.0 Hz, 3), 2.22 (s, 3), 2.37 (dd, J = 7.6, 14.0 Hz, 1), 2.54 (dd, J = 5.9, 14.0 Hz, 1), 3.32 (s, 3), 3.93 (m, 1), 4.14 (q, J = 7.0 Hz, 2), 5.74 (d, J = 1.0 Hz, 1), 6.03 (dd, J = 15.9, 8.0 Hz, 1), 6.56 (d, J = 15.9 Hz, 1), 7.25–7.45 (m, 5); IR (CCl_4) 1720, 1650, 1225, 1150, 1100 cm^{-1}; MS calcd for $C_{17}H_{22}O_2$ m/z 274.1569, found m/z 274.1570.

Ethyl 3,5-Dimethyl-5-methoxy-2-hexenoate (34), Ethyl 5-Hydroxy-3-methyl-5-phenyl-2-pentenoate (37), and Ethyl 3,7-Dimethyl-2,6-octadienoate (39). These structures were determined by comparison with the spectroscopic data of authentic materials.[3a]

Ethyl 5-Methoxy-3-methyl-2-pentenoate (35). E Isomer: colorless oil; ^1H NMR ($CDCl_3$) δ 1.27 (t, J = 6.9 Hz, 3), 2.16 (d, J = 1.5 Hz, 3), 2.34 (t, J = 6.0 Hz, 2), 3.27 (s, 3), 3.45 (t, J = 6.0 Hz, 2), 4.07 (q, J = 6.9 Hz, 2), 5.58 (m, 1); IR (CCl_4) 1720, 1650, 1150 cm^{-1}; MS 127 (100), 172 (M^+, 4.95).

Ethyl 3-Methyl-5-phenyl-2-hexenoate (36). E Isomer: colorless oil; ^1H NMR ($CDCl_3$) δ 1.25 (t, J = 6.9 Hz, 3), 1.25 (d, J = 6.9 Hz, 3), 2.10 (d, J = 1.5 Hz, 3), 2.35 (m, 2), 2.96 (m, 1), 4.05 (q, J = 6.9 Hz, 2), 5.50 (m, 1), 7.12 (m, 5); IR (CCl_4) 1720, 1650 cm^{-1}; MS calcd for $C_{15}H_{20}O_2$ m/z 232.1463, found m/z 232.1456.

Ethyl 3-Methyl-7-phenyl-2,6-heptadienoate (38). E Isomer: pale yellow oil; ^1H NMR ($CDCl_3$) δ 1.27 (t, J = 7.0 Hz, 3), 2.19 (s, 3), 2.25–2.5 (m, 4), 4.14 (q, J = 7.0 Hz, 2), 5.71 (m, 1), 6.16 (dt, J = 15.3, 6.4 Hz, 1), 6.43 (d, J = 15.3 Hz, 1), 7.15–7.5 (m, 5); IR (CCl_4) 1720, 1650, 1225, 1150 cm^{-1}; MS calcd for $C_{16}H_{22}O_2$ m/z 244.1464, found m/z 244.1461.

Methyl 5-Methoxy-5-phenyl-2-pentenoate. E Isomer; colorless needles; mp 44–45 °C; ^1H NMR (CCl_4) δ 2.52 (m, 2), 3.17 (s, 3), 3.65 (s, 3), 4.13 (dd, J = 5.3, 7.4 Hz, 1), 5.70 (dt, J = 15.3, 1.5 Hz, 1), 6.80 (dt, J = 15.3, J = 7.4 Hz, 1), 7.23 (m, 5); IR (CCl_4) 1725 cm^{-1}; MS 121 (100). Anal. Calcd for $C_{13}H_{16}O_3$: C, 70.83; H, 7.32. Found: C, 70.82; H, 7.42.

Reactions with DEAD. The following five reactions are representative. In a 30-mL flask with a septum inlet cooled to −78 °C under Ar were placed 3 mL of THF, 0.32 mL (2.3 mmol) of diisopropylamine, and a hexane solution of BuLi (1.6 M × 1.38 mL, 2.2 mmol). After stirring for 15 min, 0.45 mL (2.6 mmol) of HMPA was added, and the mixture was stirred for 20 min. A THF solution (1.2 mL) of **11** (0.21 mL, 2.0 mmol) was slowly added over 10 min, and then the mixture was stirred for 60 min. A solution of DEAD (0.35 mL, 2.2 mmol) dissolved in 1 mL of dichloromethane, which was cooled at −78 °C prior to addition, was added via a double-ended needle. The reaction was quenched after 3 min by adding methanol. The reaction was allowed to

(28) For the high-pressure equipment, see: Yamamoto, Y.; Saito, K. *J. Chem. Soc., Chem. Commun.* **1989**, 1676 and references cited therein.

warm to 0 °C, and the usual workup gave 557 mg of a yellow oil. ^{1}H NMR analysis of this crude product revealed that only the γ-isomer was formed. Purification with silica gel column chromatography (SiO_2, 10 g) by using hexane–ethyl acetate (4:1) as an eluant gave 351.7 mg (64%) of the γ-adduct (Table V, entry 1).

In a 20-mL flask with a septum inlet under Ar was placed 0.75 mL (0.75 mmol) of $ZnCl_2$–ether solution. The solvent was removed under vacuum, and then 2 mL of dichloromethane and 79 μL (0.5 mmol) of DEAD were added at −78 °C. After stirring for 10 min, a dichloromethane solution (2.5 mL, 0.6 mmol) of **5** was added dropwise. The reaction was allowed to warm to 0 °C over 40 min, and quenched with saturated aqueous $NaHCO_3$ solution. The usual workup gave 334 mg of the yellow oil (Table VI, entry 2). Purification was performed with the same procedure as above.

In a similar flask cooled to −78 °C under Ar were placed 4 mL of dichloromethane and 157 μL (1.0 mmol) of DEAD. A dichloromethane solution of $TiCl_4$ (1.0 mL, 1.0 mmol) was added, and stirring was continued for 10 min. A dichloromethane solution of **17** (1 mL, 1.2 mmol) was added dropwise. The color changed to dark-brown. The reaction was allowed to warm to 5 °C over 40 min and then quenched with saturated aqueous $NaHCO_3$ solution. Isolation of the product was carried out as described above (Table VI, entry 6).

In a similar flask were placed 2 mL of THF, 0.32 mL (2.3 mmol) of diisopropylamine, and BuLi–hexane solution (1.46 mL × 1.5 M, 2.2 mmol) at −78 °C. After stirring for 15 min, 322 mg (2.0 mmol) of **18** dissolved in 1 mL of THF was added dropwise over 10 min. The mixture was stirred for 60 min at this temperature. A dichloromethane (1 mL) solution of DEAD (0.35 mL, 2.2 mmol), cooled at −78 °C in a separate flask, was added via a double-ended needle. The reaction was quenched after 3 min by adding methanol. The usual workup and purification afforded 459 mg of the product (69%) (Table V, entry 7).

In a similar flask cooled to −78 °C were placed 3 mL of THF, 0.32 mL (2.3 mmol) of diisopropylamine, and BuLi–hexane solution (1.5 M × 1.46 mL, 2.2 mmol). After stirring for 15 min, 0.45 mL (2.6 mmol) of HMPA was added. The mixture was stirred for 20 min. A solution of **11** (212 μL, 2.0 mmol) dissolved in 1.5 mL of THF was added dropwise over 15 min, and stirring was continued for 35 min. $SnCl_4$ (0.28 mL, 2.2 mmol) was added, and the mixture was warmed to −10 °C over 5 min. The tin masked **46** was formed at this stage. A solution of DEAD (0.35 mL, 2.2 mmol) dissolved in 1 mL of THF was added. After stirring for 30 min, the reaction mixture was again cooled to −78 °C, and then quenched with methanol. The usual workup and purification gave 318 mg of the α-adduct (58%) (Table VI, entry 4).

Methyl 4-(*N*,*N*′-bis(ethoxycarbonyl)hydrazino)-2-butenoate (R = Me, R^1 = R^2 = H in 43): colorless oil; ^{1}H NMR ($CDCl_3$) δ 1.27 (t, *J* = 7.0 Hz, 6), 3.75 (s, 3), 4.20 (q, *J* = 7.0 Hz, 4), 4.29 (m, 2), 5.97 (d, *J* = 15.7 Hz, 1), 6.81 (br s, 1), 6.91 (dt, *J* = 15.7, 5.7 Hz, 1); IR (CCl_4) 3400, 1760, 1730 cm^{-1}; MS calcd for $C_{11}H_{18}N_2O_6$ *m*/*z* 274.1165, found *m*/*z* 274.1168.

Methyl 2-(*N*,*N*′-bis(ethoxycarbonyl)hydrazino)-3-butenoate (R = Me, R^1 = R^2 = H in 42): colorless oil; ^{1}H NMR ($CDCl_3$) δ 1.27 (t, *J* = 7.0 Hz, 3), 1.28 (t, *J* = 7.0 Hz, 3), 3.78 (s, 3), 4.15–4.25 (m, 4), 5.37–5.45 (m, 3), 5.94 (m, 1), 6.77 (br s, 1); IR (CCl_4) 3400, 1760, 1745, 1725 cm^{-1}; MS calcd for $C_{11}H_{18}N_2O_6$ *m*/*z* 274.1165, found *m*/*z* 274.1170.

Methyl 4-(*N*,*N*′-bis(ethoxycarbonyl)hydrazino)-5-phenyl-2-pentenoate (R = Me, R^1 = CH$_2$Ph, R^2 = H in 43): colorless needles; mp 101–103 °C recrystallized from ethyl acetate–hexane; ^{1}H NMR ($CDCl_3$) δ 1.19 (t, *J* = 6.9 Hz, 3), 1.27 (t, *J* = 7.0 Hz, 3), 2.97 (dd, *J* = 13.5, 6.9 Hz, 1). 3.11 (br s, 1), 3.72 (s, 3), 4.05–4.25 (m, 4), 5.03 (br s, 1), 5.90 (d, *J* = 15.7 Hz, 1), 6.19 (br s, 1), 6.96 (dd, *J* = 6.9, 15.7 Hz, 1), 7.15–7.35 (m, 5); IR (CCl_4) 3400, 1765, 1725 cm^{-1}; MS calcd for $C_{18}H_{24}N_2O_6$ *m*/*z* 364.1634, found *m*/*z* 364.1588.

Ethyl 2-(*N*,*N*′-bis(ethoxycarbonyl)hydrazino)-3-methyl-3-butenoate (R = Et, R^1 = H, R^2 = Me in 42): colorless oil; ^{1}H NMR ($CDCl_3$) δ 1.2–1.3 (m, 9), 1.94 (s, 3), 4.1–4.3 (m, 6), 4.83 (s, 1), 5.13 (s, 1), 5.34 (br s, 1), 6.9 (br, 1); IR (CCl_4) 3425, 1760, 1740, 1725 cm^{-1}; MS calcd for $C_{13}H_{22}N_2O_6$ *m*/*z* 302.1478, found *m*/*z* 302.1478.

Ethyl 4-(*N*,*N*′-Bis(ethoxycarbonyl)hydrazino)-3-methyl-2-butenoate (R = Et, R^1 = H, R^2 = Me in 43). *E* Isomer: colorless oil; ^{1}H NMR ($CDCl_3$) δ 1.2–1.3 (m, 9), 2.14 (s, 3), 4.1–4.2 (m, 8), 5.73 (s, 1), 6.6 (br s, 1); IR (CCl_4) 3300, 1760, 1725 cm^{-1}; MS calcd for $C_{13}H_{22}N_2O_6$ *m*/*z* 302.1478, found *m*/*z* 302.1476. *Z* Isomer: colorless oil; ^{1}H NMR ($CDCl_3$) δ 1.2–1.3 (m, 9), 1.95 (br s, 3), 4.1–4.2 (m, 6), 4.73 (s, 2), 5.81 (s, 1), 6.6 (br s, 1); MS calcd for $C_{13}H_{22}N_2O_6$ *m*/*z* 302.1478, found *m*/*z* 302.1476.

Ethyl 2-(*N*,*N*′-bis(ethoxycarbonyl)hydrazino)-2-(1-cyclopent-1-yl)acetate (R = Et, R^1–R^2 = (CH$_2$)$_3$ in 42): colorless oil; ^{1}H NMR ($CDCl_3$) δ 1.2–1.35 (m, 9), 1.88 (m, 2), 2.25–2.4 (m, 3), 2.60 (m, 1), 4.1–4.3 (m, 6), 5.43 (br s, 1), 5.66 (br s, 1), 6.83 (br s, 1); IR (CCl_4) 3415, 1760, 1740, 1725 cm^{-1}; MS calcd for $C_{15}H_{24}N_2O_6$ *m*/*z* 328.1635, found *m*/*z* 328.1637.

Ethyl 2-(*N*,*N*′-Bis(ethoxycarbonyl)hydrazino)-1-cyclopentylideneacetate (R = Et, R^1–R^2 = (CH$_2$)$_3$ in 43). *E* Isomer: colorless needles; mp 82–84 °C from ether–hexane; ^{1}H NMR ($CDCl_3$) δ 1.25–1.35 (m, 9), 1.56 (m, 1), 1.69 (m, 1), 1.91 (m, 1), 2.07 (m, 1), 2.65 (m, 1), 2.97 (dd, *J* = 7.0, 19.7 Hz, 1), 4.1–4.25 (m, 6), 5.15 (br s, 1), 5.69 (br s, 1), 6.29 (br s, 1); IR (CCl_4) 3400, 1765, 1720 cm^{-1}; MS calcd for $C_{15}H_{24}N_2O_6$ *m*/*z* 328.1635, found *m*/*z* 328.1632. *Z* Isomer: colorless oil; ^{1}H NMR ($CDCl_3$) δ 1.2–1.3 (m, 9), 1.43 (m, 1), 1.91 (m, 1), 2.25 (m, 2), 2.39 (dd, *J* = 6.5, 17.0 Hz, 1), 2.65 (br, 1), 4.07–4.24 (m, 6), 4.7–5.0 (br, 1), 5.92 (br s, 1), 6.8–7.4 (br, 1); IR (CCl_4) 3415, 1750, 1710, 1655 cm^{-1}; MS calcd for $C_{15}H_{24}N_2O_6$ *m*/*z* 328.1635, found *m*/*z* 328.1634.

Ethyl 2-(*N*,*N*′-bis(ethoxycarbonyl)hydrazino)-2-(1-cyclohexen-1-yl)acetate (R = Et, R^1–R^2 = (CH$_2$)$_4$ in 42): colorless oil; ^{1}H NMR ($CDCl_3$) δ 1.2–1.3 (m, 6), 1.5–1.75 (br, 4), 1.9–2.1 (br, 3), 2.36 (br d, *J* = 16.5 Hz, 1), 3.74 (s, 3), 4.05–4.3 (m, 4), 5.28 (br, 1), 5.53 (br s, 1), 6.6–6.8 (br, 1); IR (CCl_4) 3425, 1760, 1740, 1720 cm^{-1}; MS calcd for $C_{15}H_{24}N_2O_6$ *m*/*z* 328.1635, found *m*/*z* 328.1636.

Ethyl 2-(*N*,*N*′-Bis(ethoxycarbonyl)hydrazino)-1-cyclohexylideneacetate (R = Et, R^1–R^2 = (CH$_2$)$_4$ in 43). *E* Isomer; colorless needles from ether–hexane; mp 116–118 °C; ^{1}H NMR ($CDCl_3$) δ 1.2–1.3 (m, 6), 1.6 (m, 3), 1.8–1.95 (m, 3), 2.14 (m, 1), 3.69 (s, 3), 3.94 (d, *J* = 13.2 Hz, 1), 4.15–4.25 (m, 4), 4.67 (br s, 1), 5.47 (br s, 1), 6.34 (br s, 1); IR (CCl_4) 3425, 1760, 1740, 1725 cm^{-1}; MS calcd for $C_{16}H_{26}N_2O_6$ *m*/*z* 342.1789, found *m*/*z* 342.1789. *Z* Isomer: colorless oil; ^{1}H NMR ($CDCl_3$) δ 1.2–1.3 (m, 6), 1.6 (br, 4), 1.85 (m, 1), 1.9 (m, 1), 2.2 (m, 1), 2.4 (br, 1), 3.67 (s, 3), 4.1–4.25 (m, 4), 5.13 (br s, 1), 5.70 (s, 1), 6.82 (br s, 1); IR (CCl_4) 3370, 1760, 1725 cm^{-1}; MS calcd for $C_{16}H_{26}N_2O_6$ *m*/*z* 342.1789, found *m*/*z* 342.1789.

Supplementary Material Available: ^{1}H NMR spectra for **5–10**, **12**, **13**, **15**, **17**, **19**, **22**, **23**, **27**, **28**, **31–33**, **35**, **36**, **38**, methyl 5-methoxy-5-phenyl-2-pentenoate, **42**, and **43** (38 pages). Ordering information is given on any current masthead page.