For **37**: 74%; mp 163–164 °C; ^{1}H NMR δ 7.31 (m, 5 H), 6.94 (s, 1 H), 6.27 (d, 1 H, O*H*), 5.49 (d, 1 H), 1.56 (s, 9 H), 1.36 (s, 9 H); IR (KBr) 3400 (br), 1595, 1550 cm^{-1}; FDMS, m^+/e 378 ($C_{20}H_{26}O_2{}^{80}Se$). Anal. Calcd for $C_{20}H_{26}O_2Se$: C, 63.7; H, 6.9. Found: C, 64.0; H, 7.1.

For **38**: 80%; mp 178–179 °C; ^{1}H NMR δ 7.27 (m, 5 H), 7.06 (s, 1 H), 6.34 (d, 1 H, O*H*), 5.41 (d, 1 H), 1.55 (s, 9 H), 1.32 (s, 9 H); IR (KBr) 3400 (br), 1595 cm^{-1}; FDMS, m^+/e 428 ($C_{20}H_{26}O_2{}^{130}Te$). Anal. Calcd for $C_{20}H_{26}O_2Te$: C, 56.4; H, 6.2. Found: C, 56.8; H, 6.1.

Preparation of Carboxylic Acid Derivatives 39 and 40. Lithiated **20** and **21** were prepared on a 5-mmol scale as described. Carbon dioxide was bubbled into the reaction mixtures at −78 °C until the color of the reaction mixture faded. The reaction mixtures were poured into 100 mL of 0.1 M NaOH solution. The aqueous layer was extracted with dichloromethane (3 × 25 mL). The aqueous layer was acidified with cold 10% HCl. The acid layer was extracted with dichloromethane (3 × 50 mL). The combined extracts of the acidic layer were washed with brine, dried over sodium sulfate, and concentrated. The oily, white solids were recrystallized from acetonitrile.

For **39**: mp 165 °C dec; ^{1}H NMR δ 8.2 (br s, 1 H), 7.10 (s, 1 H), 1.55 (s, 9 H), 1.39 (s, 9 H); IR (KBr) 3000 (br), 1740, 1607, 1590 cm^{-1}; FDMS, m^+/e 268 ($C_{14}H_{20}O_3S$).

For **40**: mp 165 °C dec; ^{1}H NMR δ 8.96 (br s, 1 H), 7.15 (s, 1 H), 1.52 (s, 9 H), 1.36 (s, 9 H); IR (KBr) 2900 (br), 1730, 1580 cm^{-1}; FDMS, m^+/e 316 ($C_{14}H_{20}O_3{}^{80}Se$) and 360 (dicarboxylic acid, $C_{15}H_{20}O_5{}^{80}Se$). Anal. Calcd for $C_{14}H_{20}O_3Se$: C, 53.3; H, 6.4. Calcd for $C_{15}H_{20}O_5Se$: C, 50.1; H, 5.6. Found: C, 52.7; H, 6.2.

Preparation of Iodothiapyranone 42. Compound **20** was lithiated on a 5-mmol scale as described. Iodine (1.75 g, 6.90 mmol) was dissolved in 10 mL of a 2:1 mixture of hexanes and THF. The resulting solution was added dropwise via syringe to lithiated **20**. The resulting mixture was stirred for 2 h at −78 °C and was then warmed to ambient temperature. The reaction mixture was poured into 150 mL of ether. The resulting mixture was washed with brine, 5% sodium bisulfite solution (2 × 50 mL), and brine, was dried over sodium sulfate, and was concentrated. The residue was purified by chromatography on silica gel eluted with dichloromethane to give 0.20 g (17%) of the iodide.

For **42**: mp 108–111 °C; ^{1}H NMR δ 6.96 (s, 1 H), 1.70 (s, 9 H), 1.39 (s, 9 H). Anal. Calcd for $C_{13}H_{19}IOS$: C, 44.6; H, 5.5. Found: C, 44.7; H, 5.5.

Preparation of Chromium Carbene Complexes 43–46. The lithiated pyranones or flavones were transferred via cannula to a −78 °C slurry of chromium hexacarbonyl (equimolar with pyranone or flavone) in tetrahydrofuran (5 mL/mmol). The resulting mixture was stirred at −78 °C for 1 h, was warmed to −40 °C for 1 h, and was then warmed to 0 °C until the chromium hexacarbonyl was consumed (1–5 h). The reaction mixture was recooled to −78 °C, and a 50% molar excess of methyl triflate was added via syringe. The carbene reactions were concentrated under vacuum at room temperature or below. The residue was dissolved in a minimal amount of dichloromethane. Pentane was then added, precipitating an orange solid. The precipitate was collected and then purified by chromatography on silica gel using 2:1 dichloromethane–pentane as eluent.

For **43**: mp 101–104 °C dec; ^{1}H NMR δ 8.26 (d × d, 1 H), 7.75 (t × d, 1 H), 7.58 (d, 1 H), 7.54 (m, 5 H), 7.46 (t, 1 H), 4.57 (br s, 3 H); IR (KBr) 2060 (sharp), 1950 (br), 1620, 1610, 1550 cm^{-1}; FDMS, m^+/e 456 ($C_{22}H_{12}CrO_8$). Anal. Calcd for $C_{22}H_{12}CrO_8$: C, 57.9; H, 2.7. Found: C, 57.7; H, 3.0.

For **44**: mp 104–107 °C dec; ^{1}H NMR δ 8.58 (d, 1 H), 7.68 (t × d, 1 H), 7.57 (m, 5 H), 7.52 (d, 1 H), 7.44 (t, 1 H), 4.55 (br s, 3 H); IR (KBr) 2030 (sharp), 1990, 1935 (br), 1610, 1590 cm^{-1}; FDMS, m^+/e 472 ($C_{22}H_{12}CrO_7S$).

For **45**: mp 93 °C dec; ^{1}H NMR δ 6.89 (s, 1 H), 4.30 (br s, 3 H), 1.45 (s, 9 H), 1.37 (s, 9 H); IR (KBr) 2030 (sharp), 1990, 1925 (br), 1600 cm^{-1}; FDMS, m^+/e 458 ($C_{20}H_{22}CrO_7S$). Anal. Calcd for $C_{20}H_{22}CrO_7S$: C, 52.4; H, 4.8. Found: C, 52.6; H, 4.9.

For **46**: ^{1}H NMR δ 4.30 (s, 3 H), 1.39 (s, 9 H); IR (KBr) 2160, 2060, 1930 cm^{-1}.

For **48**: ^{1}H NMR ($CDCl_3$) δ 6.39 (s, 1 H), 4.02 (heptet, 1 H, J = 6.8 Hz), 3.46 (heptet, 1 H, J = 6.8 Hz), 2.22 (s, 3 H), 1.44 (d, 6 H, J = 6.8 Hz), 1.19 (s, 9 H), 1.16 (d, 6 H, J = 6.8 Hz); IR (KBr) 2960, 2920, 2865, 1628, 1435, 1328 cm^{-1}; FDMS, m^+/e 305 ($C_{14}H_{27}SeNO$).

Registry No. **3**, 491-38-3; **3** (2,3-dideuterated deriv), 112763-63-0; **4**, 491-39-4; **4** (2,3-dideuterated deriv), 112763-64-1; **5**, 84144-56-9; **5** (2,3-dideuterated deriv), 112763-65-2; **6**, 112763-66-3; **6** (2,3-dideuterated deriv), 112763-67-4; **8**, 112763-68-5; **9**, 112763-69-6; **10**, 525-82-6; **11**, 784-62-3; **12**, 4512-97-4; **13**, 80697-47-8; **14**, 71972-66-2; **15**, 33928-00-6; **16**, 112763-70-9; **17**, 112763-71-0; **18**, 112763-72-1; **19**, 55107-13-6; **20**, 76874-66-3; **21**, 104698-68-2; **22**, 86029-92-7; **23**, 112763-73-2; **24**, 112763-74-3; **25**, 112763-75-4; **26**, 112763-76-5; **27**, 112763-77-6; **28**, 112763-78-7; **29**, 112763-79-8; **30**, 112763-80-1; **31**, 112763-81-2; **32**, 112763-82-3; **33**, 112763-83-4; **34**, 112763-84-5; **35**, 112763-85-6; **36**, 112763-86-7; **37**, 112763-87-8; **38**, 112763-88-9; **39**, 112763-89-0; **40**, 112763-90-3; **42**, 112763-91-4; **43**, 112763-93-6; **44**, 112763-94-7; **45**, 112763-95-8; **46**, 112763-96-9; **48**, 112763-92-5; $Cr(CO)_6$, 13007-92-6.

Trisubstituted (Stannylmethyl)lithium as a Methylene Double Anion Equivalent. Reaction with Esters[1]

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Trisubstituted (stannylmethyl)lithium reacts with electrophiles as a methylene double anion equivalent to produce enolates from esters. The reaction mechanism is discussed.

Inspired by the established reputation of organosilicon chemistry in the field of organic synthesis,[2] a growing interest in the chemistry of group IV organometal compounds other than silicon has emerged in recent years. Among them, an increasing number of studies have been reported on the application of organotin compounds as a synthetic tool.[3] Generally it has been believed that the silyl and stannyl compounds behave similarly; both metals stabilize the neighboring carbanion due to the participation

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(1) Preliminary report: Sato, T.; Matsuoka, H.; Igarashi, T.; Murayama, E. *Tetrahedron Lett.* **1986**, *27*, 4339.
(2) Larson, G. L. *J. Organomet. Chem.* **1984**, *274*, 29.
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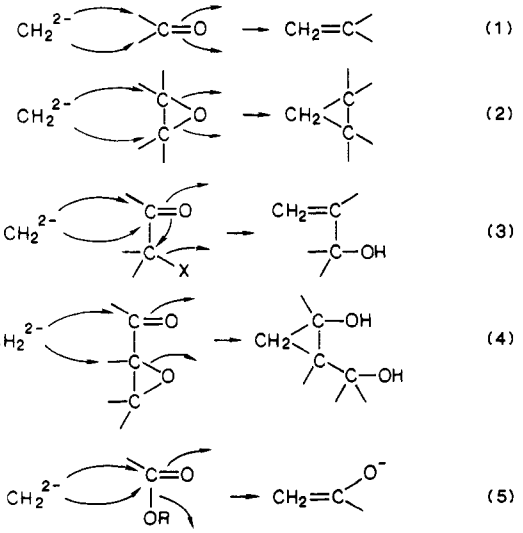
0022-3263/88/1953-1207$01.50/0

of d orbitals, impart anionic character to the neighboring carbon due to the positive nature of the metals, and produce stable compounds having the metal–lithium bond, in which the group IV atoms behave as nucleophiles. However, there are still many reactions in which a large difference is observed between these two metal compounds. Citing a few examples, the stannyllithium is much more accessible to the reaction site with less steric interference than the corresponding silyl derivative due to the longer carbon–metal bond,[4] and γ-silyl alcohols give alkenes upon treatment with acid, while the corresponding stannyl alcohols cyclize to give cyclopropanes.[5]

Because of the electropositive character of the tin atom as compared with carbon atom, the tin–carbon bond is polarized, furnishing carbanionic character to the tin-bearing carbon.[6] The polarization, however, is not strong enough to induce a spontaneous reaction with ordinary electrophiles such as carbonyl compounds, and the bond heterolysis proceeds only with the assistance of nucleophilic attack of some nucleophiles to the metal atom and/or of the presence of an appropriate electron-withdrawing group in the organic moiety. Therefore, if we could set up a system of anionic species containing the tin–carbon bonds, they could interact in two ways with electrophiles having twofold leaving ability: first as an explicit carbanion and second as a latent carbanion.

We now report that an α-(stannylmethyl)lithium species (1) conformed to the requirement and underwent a unique type of reaction.[7] As shown in Scheme I, if the two-stage reaction of reagent 1 with a substrate of type 2 proceeds successively in one pot, the net reaction is a replacement of two leaving groups by a methylene group. Therefore, stannyl reagent 1 could be regarded as a methylene double anion equivalent (3). In our previous papers,[7] we reported on the reaction of 1 with several electrophiles. It was found that the stannyl compound was a versatile reagent for the preparation of α-olefins from carbonyl compounds (eq 1),



(1)

(2)

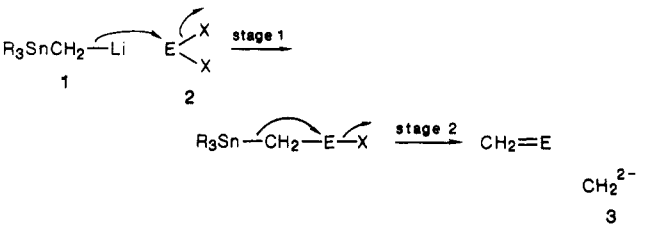
(3)

(4)

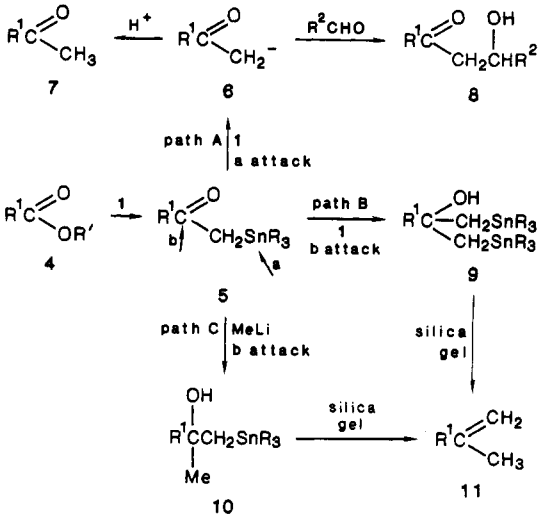
(5)

cyclopropanes from oxiranes (eq 2), allyl alcohols from α-chloro ketones (eq 3), and cyclopropanols from epoxy ketones (eq 4). Evidently, all these results are explicit examples of the equivalence of reagent 1 to the methylene

Scheme I



Scheme II



double anion. As a continuation of the study, we carried out the reaction of the stannyl reagent with esters.

The reaction of conventional organometals with esters of simple alcohols usually produces tertiary alcohols because the primarily produced ketones are more reactive toward the reagent than the starting esters. Since ketones belong to one of the most important categories of organic compounds, it is desirable to find a method of terminating the reaction at the stage of the ketone formation. One of the most successful methods for this purpose is to adopt appropriate precautions to stabilize the ketonic intermediate, as an enolate for instance, and several direct ketone preparations from esters by manipulating the solvent system or alcohol moiety in the ester have been designed according to this concept.[8]

Quite reasonably, we could expect that the reaction of the methylene double anion with an ester would lead to the direct formation of an enolate, thus excluding the possibility of further reaction (eq 5). The expectation was actually realized, and we could prepare methyl ketones or aldols directly from esters.

The reagents used in the present study were prepared in the following ways. Reagent A: $Me_3SnCH_2SnMe_3$ + BuLi. Reagent B: $Me_3SnCH_2SnMe_3$ + MeLi. Reagent C: Ph_3SnCH_2I + BuLi. Reagent D: Bu_3SnCH_2I + BuLi.

The reaction was carried out with 2 equiv of the reagent for 1 equiv of the ester, and, upon quenching the reaction with protonic acid, methyl ketones were isolated as the main products as shown in Table I. While not all the reactions reported in Table I have been optimized, the reaction is generally acceptable as a synthetic method of ketones from esters. The use of 2 equiv of the reagent was a requisite; with lesser amounts of reagent, more of the starting ester was recovered. The reaction is assumed to proceed via α-stannyl ketone 5 as the primary product

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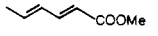
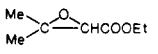
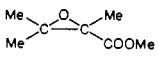
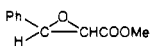
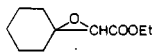
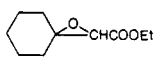
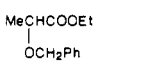
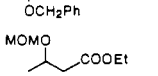
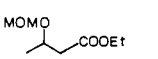
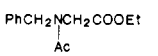
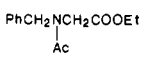
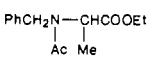
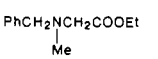
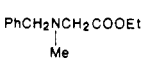
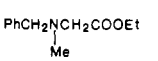
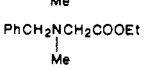
(5) Fleming, I.; Urch, C. J. *J. Organomet. Chem.* **1985**, *285*, 173.
(6) Hudec, J. *J. Chem. Soc., Perkin Trans 1* **1975**, 1020.
(7) (a) Murayama, E.; Kikuchi, T.; Sasaki, K.; Sootome, N.; Sato, T. *Chem. Lett.* **1984**, *1873*. (b) Murayama, E.; Kikuchi, T.; Nishio, H.; Uematsu, M.; Sasaki, K.; Sootome, N.; Sato, T. *Nippon Kagaku Kaishi* (*J. Chem. Soc. Jpn.*) **1985**, 350. (c) Sato, T.; Kikuchi, T.; Sootome, N.; Murayama, E. *Tetrahedron Lett.* **1985**, *26*, 2205.
(8) Kim, S.; Lee, J. I. *J. Chem. Soc., Chem. Commun.* **1981**, 1231. Huet, F.; Emptoz, G.; Jubier, A. *Tetrahedron* **1973**, *29*, 479.

Table I. Preparation of Ketones from Esters

run	esters	reagent	methyl ketone	other
1	$Me(CH_2)_6COOEt$	A	58	**11** (32)
2	$Me(CH_2)_6COOEt$	C	57	**13** (tr)
3	$Me(CH_2)_6COOMe$	D	68	**4** (9)
4	$Me(CH_2)_6COOMe$	C	73	**13** (tr)
5	PhCOOEt	A	84	
6	PhCOOEt	C	21	
7	c-C_6H_{11}COOMe	A	48	
8	c-C_6H_{11}COOMe	C	15	
9	PhCH=CHCOOEt	C	80	
10		C	85	
11		A	80	**4** (13)
12		A	12	
13		A	51	
14		A	82	**11** (16)
15		C	10	**4** (26)
16		A	75	**11** (11)
17		A	40	**11** (20)
18		C	29	**13** (9) **4** (15)
19		A	34	**11** (4) **4** (60)
20		C	20	**4** (46)
21		A	29	**11** (13) **4** (53)
22		A	35	**10** (7)[a] **4** (7)
23		B	63	**10** (2) **4** (9)
24		C	39	**4** (61)
25		D	44	**11** (tr) **14** (tr) **4** (5)

[a] Contains some butylated derivative, see text.

(Scheme II), followed by the attack of the second molecule of the reagent at the tin atom in **5** to produce enolate **6** (a attack, path A). The second step seemed to be faster than the first step, thus leaving part of the starting material intact, when less than 2 equiv of the reagent was used. This contrasts to the reaction of an α-silyl carbanion with an ester, which terminates at the stage of α-silyl ketone formation without[9] or with[10] proton abstraction or produces allylsilanes.[11] The reaction of the silyl carbanion proceeds satisfactorily only with aliphatic esters branched at the α-position or with aromatic esters. In contrast to the reaction of the silyl counterpart, the present reaction proceeded quite smoothly even with straight-chain alkanoic esters having no substituents (runs 1–4).

All the reactions occurred only at the ester group even with substrates having other functional groups. No conjugate addition was observed with unsaturated esters (runs 9 and 10). In contrast to the reaction of **1** with α,β-epoxy ketones, where the oxirane was cleaved in the reaction,[7c] the ring system remained intact in the present reaction (runs 11–15). Also, there appeared to be no indication that the amide group was involved directly in the reaction, as evident from the results of runs 19–21. Due to unknown reasons, however, large amounts of the starting esters **4** remained even if a threefold excess of the reagent was used. We speculate that a possible abstraction of an α-proton might be responsible for this observation.

In case of L-lactate (run 16), there might be a possibility of α-proton abstraction from the resulting hydroxy ketone with an ultimate racemization of the product. However, it was confirmed that there was no racemization during the reaction, since the analysis of the product by chiral column chromatography indicated that the product was 100% optically pure. When the present reaction was run with the optically active β-hydroxy ester, prepared easily by asymmetric reduction of the corresponding keto esters using bakers' yeast,[12] the corresponding β-hydroxy ketone was obtained (run 17). In contrast to the reaction with α-hydroxy ester, there is no need to worry about the racemization during the reaction. Actually, the optical purity of 4-hydroxy-2-pentanone, prepared from the corresponding ester in run 17 followed by the deprotection, was almost the same as that of the starting ester (ca. 70%), referring to the reported value of the optical activity of this hydroxy ketone.[13]

Although the present reaction produced methyl ketones in fair to good yields, the reaction was sometimes accompanied by an olefin formation, which is included in Table I. In our preliminary paper,[1] we assumed that the olefins could be formed through attack of the second molecule of the reagent on the carbonyl group in **5** (b attack, path B, Scheme II), to give bis-stannyl compounds **9**, which decomposed to give the olefins **11** during the workup procedure. Actually, no olefinic protons were observed in the NMR spectrum of the crude material prior to silica gel chromatography. In order to confirm the reaction pathway, we attempted to isolate the olefin precursor. Although, in most cases, the precursors were quite unstable toward silica gel chromatography, we found that the intermediate from *N*-methyl-*N*-benzylglycine ester (runs 22 and 23) was exceptionally stable. Since NMR spectral evidence of the crude product in run 22 suggested that a part of the methyl groups on the tin atom in the product had been replaced by a *n*-butyl group when reagent A was employed, we used methyllithium, instead of *n*-butyllithium, for the reagent preparation (reagent B). Under these conditions (run 23), we succeeded in the isolation of an olefin precursor in a pure state. The tin-containing intermediate, however, proved to be tertiary alcohol **10**, instead of the expected bis-stannyl derivative **9**. This intermediate actually produced the olefin **11** upon treatment with silica gel at 80 °C for 1 h.

These observations led us to propose a different scheme for the possible reaction pathway of the olefin formation. Since we have observed in the present and previous studies that the methyl group on the tin atom could be replaced by an *n*-butyl group when *n*-butyllithium was used as a reagent, it is quite understandable that some amount of methyllithium would be present in the reaction medium, which reacted with the stannyl ketone **5** to produce **10** (path C). Alternatively, the methyllithium could react with ester **4** to produce a methyl ketone, which then reacted with the stannyl carbanion **1** to afford **10**. The latter possibility is more likely since we could also identify di-

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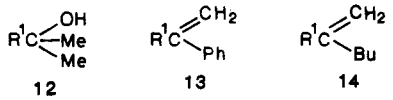
methyl tertiary alcohol **12** as a minor product. Path C



12 **13** **14**

seems to be more plausible than path B for the olefin formation, since we could isolate a phenyl group containing olefin (**13**) in case of the reactions using triphenylstannyl reagent (reagent C) in runs 2, 4, and 18. Apparently, the exchange of the substituents on the tin atom actually occurred, thus affording phenyllithium. Although these observations are in favor of path C for the olefin formation, we could not rule out path B since methyl olefin **11** as well as butyl olefin **14** was also identified in the reaction using reagent D (run 25). Presumably both reaction paths might be operative simultaneously.

When the reaction products of the esters with **1** were treated with carbonyl compounds in the same pot, aldols were obtained. The results are shown in Table II. In cases of the conventional aldol reaction starting from aliphatic methyl ketones, the attainment of the regioselectivity becomes a major problem. Evidently, no such problem arises in the present reaction, because we could obtain the aldol product without any contamination of the alternative regioisomer (runs 28–30).

Although the chromatographic and spectroscopic analyses of the products in runs 30–32 gave no hint of the presence of more than one stereoisomer, the addition of a shift reagent induced the splitting of the doublet of the methyl signal in the lactate moiety. In view of the integrated areas of the signals, we assigned the diastereomer ratio as shown in Table II. However, the absolute stereochemistry has not been determined.

The enolates obtained from the lactate and β-hydroxy ester are promising as key intermediates for the synthesis of optically active compounds. Since the selectivity of the chiral induction in the aldol moiety is not quite satisfactory at the moment, we are now manipulating the reaction conditions to improve the selectivity.

Experimental Section

General Procedure and Instrumentation. GLC experiments were carried out on a 2.5 m × 3 mm stainless steel column packed with silicone SE 30 or Carbowax 20 M on silanized Chromosorb W. Preparative TLC was carried out on DC-Alufolien Kieselgel 60 F_{254}, Art. 5554, using solvents as indicated. Column chromatography was carried out on Kieselgel 60, Art. 7734 (70–230-mesh ASTM) using solvents as indicated. Unless otherwise stated, all the spectroscopic data were determined on a pure sample obtained by distillation, preparative TLC, or column chromatography. ^{1}H NMR spectra (60 MHz) were recorded on a Hitachi R-24 or JEOL PMX 60 SI spectrometer. ^{1}H NMR (90 MHz) and ^{13}C NMR spectra were measured on a Hitachi JNM-PMX 60 S R-90 H spectrometer. GC-MS spectra were taken on a Shimadzu QP-1000 mass spectrometer and high resolution mass spectra on a JEOL DX-300 mass spectrometer. IR spectra were recorded on a Shimadzu IR-400 spectrometer.

All of the ^{1}H NMR signals of the methyl group on the tin atom at $\delta \sim 0$ ppm were accompanied by splitting signals of ^{117}Sn (7.54% abundance, J = 51 Hz) and ^{119}Sn (8.62% abundance, J = 53 Hz).[14]

Preparation of the Reagent. The reagents were prepared by adding solution I to solution II at −78 °C (for reagents A and B) or at −50 °C (for reagents C and D) and stirring for 10 min at this temperature (Chart I). The resulting solutions were directly used for in next step.

General Procedure for the Reaction of 1 with Ester. To a reagent solution (2 equiv) prepared as shown above was added a solution of ester in THF (0.5 M, 1 equiv, for the reagents A or B) or in Et_2O (0.1 M, 1 equiv, for the reagent C or D) at −78 °C or at −50 °C, respectively, and the solution was stirred for 1–5 h at −78 °C. The reaction mixture was quenched with brine, and the product was extracted with ether or chloroform. After being dried over Na_2SO_4, the extract was concentrated in vacuo. The remaining material was kept on a silica gel column for 1 h at room temperature to decompose the tin-containing intermediate. After washing off the tin-containing byproducts with CCl_4, the products were eluted with ethyl acetate. The eluate was concentrated in vacuo and purified by column chromatography or TLC.

Table II. Preparation of Aldols from Esters

run	ester	carbonyl compound	reagent	aldol	diastereomer ratio
26	PhCOOEt	PhCHO	A	71	
27	PhCOOEt	EtCHO	A	86	
28	n-C_7H_{15}COOMe	PhCHO	C	98	
29	n-C_7H_{15}COOMe	EtCHO	C	66	
30	MeCHCOOEt (OCH$_2$Ph)	PhCHO	A	60	2:1
31	MeCHCOOEt (OCH$_2$Ph)	MeCHO	A	60	3.2:1
32	MeCHCOOEt (OCH$_2$Ph)	EtCHO	A	66	4.5:1
33	MeCHCOOEt (OCH$_2$Ph)	HCHO	A	51	

Chart I

reagent	solution I	solution II
A	n-BuLi/hexane (1.5 M, 2.0–3.0 equiv)	$Me_3SnCH_2SnMe_3$/THF (0.5 M, 2.0–3.0 equiv)
B	MeLi/hexane (1.4 M, 3.0 equiv)	$Me_3SnCH_2SnMe_3$/THF (0.5 M, 3.0 equiv)
C	n-BuLi/hexane (1.5 M, 2.0–3.0 equiv)	Ph_3SnCH_2I/Et_2O (0.1 M, 2.0–3.0 equiv)
D	n-BuLi/hexane (1.5 M, 2.0–2.5 equiv)	Bu_3SnCH_2I/Et_2O (0.1 M, 2.0–2.5 equiv)

Reaction of Ethyl Octanoate (Run 1). The reaction was carried out for 1 h by using reagent A (0.2-mmol scale of substrate (35 mg)). The analysis of the crude material by NMR using tetrachloroethane (TCE) indicated that the product was a mixture of **7** (58%) and **11** (32%). Both compounds were separated by TLC. For **7** ($R^1 = C_7H_{15}$): MS, m/z 142 (M^+), 127, 99, 85, 84, 82, 71, 59, 58 (base peak); ^{1}H NMR, identical with reported data;[15] IR ν_{max} 2920, 2855, 1709, 1360, 1160 cm^{-1}. For **11** ($R^1 = C_7H_{15}$): MS, m/z 140 (M^+), 125, 112, 97, 84, 69, 56 (base peak); ^{1}H NMR δ 0.95 (dist t, 3 H), 1.25 (m, 10 H), 1.8 (s, 3 H), 2.00 (t, J = 7 Hz, 2 H), 4.80 (s, 2 H); IR, ν_{max} 3070, 2925, 2850, 1460, 885 cm^{-1}; exact mass, calcd for $C_{10}H_{20}$ (M) 140.1565, obsd 140.1574.

Reaction of Methyl Octanoate (Runs 3 and 4). The reaction was carried out for 2 h by using reagent C (0.3-mmol scale of the substrate (47.5 mg)). The analysis of the crude material by NMR using TCE indicated that the product was a mixture of **7** (73%) and **13** (trace). Column chromatography ($CHCl_3$) gave pure **7**. In the same way, the reaction using reagent D was carried out for 1 h (1.0-mmol scale of the substrate (158 mg)). Column chromatography (AcOEt/hexane (1/6)) gave a pure sample of **7** ($R^1 = C_7H_{15}$, 96 mg, 68%) and the starting material (15 mg, 9%). For **13** ($R^1 = C_7H_{15}$): MS, m/z 202 (M^+), 131, 118 (base peak), 103, 91, 77; ^{1}H NMR δ 0.90–1.55 (m), 2.47 (t, J = 7 Hz, 2 H), 4.95 (d, J = 3 Hz, 1 H), 5.17 (d, J = 3 Hz, 1 H), 7.17 (b s); exact mass, calcd for $C_{15}H_{22}$ (M) 202.1721, obsd 202.1750.

Reaction of Ethyl Benzoate (Run 5). The reaction was carried out for 2 h by using reagent A (0.2-mmol scale of the substrate (30 mg)). TLC purification ($CHCl_3$) gave a pure sample of acetophenone (24 mg, 84%).

Reaction of Methyl Cyclohexanecarboxylate (Run 7). The reaction was carried out for 1 h by using reagent A (0.25-mmol

(14) Poller, R. C. *The Chemistry of Organotin Compounds*; Academic Press: New York, 1973; p 234.

(15) *The Aldlich Library of NMR Spectra*; Aldrich Chemical Co., Vol. II, 1974; p 110B.

scale of the substrate (35.5 mg)). The analysis of the crude material by NMR using TCE indicated that the product was pure acetylcyclohexane (48%).

Reaction of Ethyl Cinnamate (Run 9). The reaction was carried out for 2 h by using reagent C (0.3-mmol scale of the substrate (52.9 mg)). TLC purification ($CHCl_3$) gave pure benzalacetone (35 mg, 80%).

Reaction of Methyl 2,4-Hexadienoate (Run 10). The reaction was carried out for 2 h by using reagent C (0.5-mmol scale of the substrate (63 mg)). Flash column chromatography ($CHCl_3$) gave a pure sample of **7** ($R^1 = C_5H_7$, 47 mg, 85%): MS, m/z 110 (M^+), 95 (base peak), 77, 67, 65; ^1H NMR δ 1.87 (d, J = 5.0 Hz, 3 H), 2.13 (s, 3 H), 5.30–6.23 (m, 4 H); exact mass, calcd for $C_7H_{10}O$ (M) 110.0731, obsd 110.0729.

Reaction of Ethyl 2,3-Epoxy-3-methylbutanoate (Run 11). The reaction was carried for 3 h by using reagent A (0.5-mmol scale of the substrate (72 mg)). The analysis of the crude material by NMR using TCE indicated no signals except those of **7** ($R^1 = C_4H_7O$, 80%) and the starting material (13%). A pure sample of **7** was obtained by preparative TLC ($CHCl_3$). This was identical with the authentic sample prepared by the known method.[16]

Reaction of Methyl 2,3-Epoxy-2,3-dimethylbutanoate (Run 12). The reaction was carried out for 3 h by using reagent A (1.0-mmol scale of the substrate (144 mg)). The analysis of the crude material by NMR using TCE indicated that the product was **7** ($R^1 = C_5H_9O$, 12%): MS, m/z 128 (M^+), 113, 86, 71 (base peak); ^1H NMR δ 1.21 (s, 3 H), 1.33 (s, 3 H), 1.36 (s, 3 H), 2.10 (s, 3 H); exact mass, calcd for $C_7H_{12}O_2$ (M) 128.0837, obsd 128.0867.

Reaction of Methyl 2,3-Epoxy-3-phenylpropanoate (Run 13). The reaction was carried out for 3 h by using reagent A (0.5-mmol) scale of the substrate (89 mg)). The analysis of the crude material by NMR using TCE indicated that the product was pure **7** ($R^1 = C_8H_9O$, 51%): ^1H NMR δ 2.03 (s, 3 H), 3.30 (d, J = 2.0 Hz, 1 H), 3.94 (d, J = 2.0 Hz, 1 H), 7.07–7.58 (br s, 5 H).

Reaction of 1-Cyclohexyl-2-(ethoxycarbonyl)oxirane (Run 14). The reaction was carried out for 3 h by using reagent A (1.0-mmol scale of the substrate (184 mg)). TLC purification ($CHCl_3$) gave **7** (127 mg, 82%) and **11** (24 mg, 16%). For **7** ($R^1 = C_7H_{11}O$): MS, m/z 154 (M^+), 112, 111, 98, 81, 79, 55, 43 (base peak); ^1H NMR δ 1.55 (br s, 10 H), 2.12 (s, 3 H), 3.18 (s, 1 H); IR, ν_{max} 2940, 2860, 1720 cm^{-1}; exact mass, calcd $C_9H_{14}O_2$ (M) 154.0993, obsd 154.1019. For **11** ($R^1 = C_7H_{11}O$): MS, m/z 152 (M^+), 137, 123, 109, 81, 79 (base peak), 71; ^1H NMR δ 1.31–1.72 (m, 10 H), 1.80 (br s, 3 H), 2.96 (br s, 1 H), 4.84 (br s, 2 H); exact mass, calcd $C_{10}H_{16}O$ (M) 152.1201, obsd 152.1231.

Reaction of Ethyl *O*-Benzyl-L-lactate (Run 16). The reaction was carried out for 3 min by using reagent A (1.0-mmol scale of the substrate (208 mg)). TLC separation ($CHCl_3$) gave pure samples of **7** (134 mg, 75%) and **11** (19 mg, 11%). For **7** ($R^1 = C_9H_{11}O$): $[\alpha]_D$ -29.6° [The ketone showed a single peak at R_f 17.5 min on HPLC using a chiral column (CHIRALCEL OB, hexane/2-propanol (9/1)) while the corresponding ketone prepared from the racemic lactate showed another peak at R_f 23.5 min]; MS, m/z 135 (M^+ – COMe), 107, 92, 91 (base peak), 77, 72, 65, 43; ^1H NMR δ 1.27 (d, J = 7.0 Hz, 3 H), 2.08 (s, 3 H), 3.75 (q, J = 7.0 Hz, 1 H), 4.46 (s, 2 H), 7.25 (br s, 5 H); IR ν_{max} 3000–2800, 1720 cm^{-1}; exact mass, calcd $C_{11}H_{14}O_2$ (M) 178.0949, obsd 178.0994. For **11** ($R^1 = C_9H_{11}O$): MS, m/z 161 (M^+ – Me), 107, 91 (base peak), 77, 70; ^1H NMR δ 1.26 (d, J = 7.0 Hz, 3 H), 1.69 (br s, 3 H), 3.83 (q, J = 7.0 Hz, 1 H), 4.10–4.39 (AB q, J = 12 Hz, 2 H), 4.83 (br s, 2 H), 7.08–7.34 (m, 5 H); IR ν_{max} 2950–2860, 1450, 1370 cm^{-1}; exact mass, calcd for $C_{12}H_{16}O$ (M) 176.1201, obsd 176.1224.

Reaction of Ethyl (*S*)-3-(Methoxymethoxy)butanoate (Runs 17 and 18). The reaction was carried out for 1 h by using reagent A (1.0-mmol scale of the substrate (78.4% optical purity,[17] 176 mg)). The analysis of the crude material (155 mg) on GLC indicated that the product was a mixture of **7** (40%) and **11** (20%). Pure samples of **7** and **11** were obtained by preparative TLC ($CHCl_3$). In the same way, the reaction was carried out for 4 h by using reagent C (1.0-mmol scale of the substrate (176 mg)). TLC purification ($CHCl_3$) gave **7** (42 mg, 29%), **13** (9%), and the starting material (15%). The deprotection of **7** was carried out by using 4 M HCl in H_2O/THF (8:1) to give (*S*)-4-hydroxy-2-pentanone in 58% yield, which showed an identical NMR spectrum with that reported.[13] The $[\alpha]_D$ value of +17.7° (c 0.0073) corresponded to 75.3% optical purity in view of the reported value of the pure enantiomer of $[\alpha]_D$ +23.5°.[13] For **7** ($R^1 = C_5H_{11}O_2$): MS, m/z 131 (M^+ – Me), 115, 101, 85, 71, 45 (base peak); ^1H NMR, δ 1.16 (d, J = 6.4 Hz, 3 H), 2.10 (s, 3 H), 2.44 (d, J = 6.4 Hz, 1 H), 2.58 (d, J = 6.4 Hz, 1 H), 3.28 (s, 3 H), 4.08 (sextet, J = 6.4 Hz, 1 H), 4.54 (s, 2 H); IR, ν_{max} 3010–2760, 1710, 1040 cm^{-1}; exact mass, calcd for $C_6H_{11}O_3$ (M – Me) 131.0708, obsd 131.0706. For **11** ($R^1 = C_5H_{11}O_2$): MS, m/z 113 (M^+ – OMe), 100, 89, 55, 45 (base peak); ^1H NMR δ 1.07 (d, J = 6.4 Hz, 3 H), 1.67, (br s, 3 H), 1.80–2.35 (m, 2 H), 3.19 (s, 3 H), 3.72 (q, J = 6.4 Hz, 1 H), 4.46 (s, 2 H), 4.63 (br s, 2 H); IR, ν_{max} 3030–2800, 1460, 1380, 1055 cm^{-1}; exact mass, calcd for $C_7H_{13}O$ (M – OMe) 113.0966, obsd 113.0969. For **13** ($R^1 = C_5H_{11}O_2$): MS, m/z 175 (M^+ – OMe), 174, 146, 131 (base peak), 117, 103, 89, 77; ^1H NMR δ 1.08 (d, J = 6.4 Hz, 3 H), 2.42 (dd, J = 6.4 Hz and 13 Hz, 1 H), 2.86 (dd, J = 6.4 Hz and 13 Hz, 1 H), 3.20 (s, 3 H), 3.69 (sextet, J = 6.4 Hz, 1 H), 4.44 (s, 2 H), 5.04 (br s, 1 H), 5.23 (d, J = 3.0 Hz, 1 H), 7.00–7.58 (m, 5 H); IR, ν_{max} 2940, 1440, 1380, 1035 cm^{-1}; exact mass, calcd for $C_{12}H_{15}O$ (M – OMe) 175.1123, obsd 175.1104.

Reaction of Ethyl *N*-Acetyl-*N*-benzylaminoacetate (Run 19). The reaction was carried out for 5 h by using reagent A (0.4-mmol scale of the substrate (94 mg)). The analysis of crude material (88 mg) on GLC showed three peaks corresponding to **7**, **11**, and the starting material **4**. In view of the relative peak areas, the yields of the products were calculated as 34%, 4%, and 60%, respectively. TLC purification (AcOEt/hexane (2/1)) gave each fraction in a pure state, while the olefin precursor was not isolated. For **7** ($R^1 = C_{10}H_{12}NO$): MS, m/z 205 (M^+), 162, 120 (base peak), 91, 43; ^1H NMR δ 1.98 (s, 3 H), 2.04 (s, 3 H), 3.90 (br s, 2 H), 4.45 (br s, 2 H), 7.13 (br s, 5 H); exact mass, calcd for $C_{12}H_{15}NO_2$ (M) 205.1103, obsd 205.1112. For **11** ($R^1 = C_{10}H_{12}NO$): MS, m/z 203 (base peak), 148, 120, 106, 91, 65; exact mass, calcd for $C_{13}H_{17}NO$ (M) 203.1311, obsd 203.1325.

Reaction of Ethyl *N*-Acetyl-*N*-benzyl-2-aminopropanoate (Run 21). The reaction was carried out for 5 h by using reagent A (0.77-mmol scale of the substrate (190 mg)). The analysis of crude material (181 mg) on GLC showed three peaks corresponding to **7** (29%), **11** (13%), and the starting material (53%). TLC purification (AcOEt/hexane (2:1)) gave the products in pure states. For **7** ($R^1 = C_{11}H_{14}NO$): MS, m/z 219 (M^+), 202, 176, 134, 106, 91 (base peak), 65; ^1H NMR δ 1.20 (d, J = 7.0 Hz, 3 H), 2.00 (s, 3 H), 2.05 (s, 3 H), 4.20 (q, J = 7.0 Hz, 1 H), 4.34–4.60 (m, 2 H), 7.15 (br s, 5 H); exact mass, calcd for $C_{11}H_{14}NO$ (M – COMe) 176.1075, obsd 176.1086. For **11** ($R^1 = C_{11}H_{14}O$): MS, m/z 217 (M^+), 148, 106, 91 (base peak), 84, 65; exact mass, calcd for $C_{14}H_{19}NO$ (M) 217.1466, obsd 217.1467.

Reaction of Ethyl *N*-Benzyl-*N*-methylaminoacetate (Runs 23 and 25). The reaction was carried out for 5 h by using reagent B (1.0-mmol scale of the substrate (207 mg)). Column chromatography (AcOEt/hexane (1/3)) gave pure samples of **7** (110 mg, 63%), **10** (7 mg, 2%), and the starting material **4** (10%). In the same way, the reaction using reagent D (0.5-mmol scale), gave **7** (39 mg, 44%), **11** (trace), **12** (trace), and the starting material (5 mg, 5%) by column chromatography (AcOEt/hexane (1/3)). For **7** ($R^1 = C_9H_{12}N$): MS, m/z 177 (M^+), 134, 91 (base peak), 65; ^1H NMR δ 2.10 (s, 3 H), 2.25 (s, 3 H), 3.00 (s, 2 H), 3.50 (s, 2 H), 7.15 (s, 5 H); exact mass, calcd for $C_{11}H_{15}NO$ (M) 177.1154, obsd 177.1141. For **10** ($R^1 = C_9H_{12}N$, R = CH_3): ^1H NMR δ 0.50 (s, 9 H), 1.05 (s, 2 H), 1.15 (s, 3 H), 2.25 (s, 3 H), 2.40 (s, 2 H), 2.62 (br s, 1 H), 3.55 (s, 2 H), 7.15 (s, 5 H); IR, ν_{max} 3600–3100, 3030, 2950, 2840, 2770, 1742, 1495, 1450, 1360, 1300, 1255, 1115, 700 cm^{-1}. For **12** ($R^1 = C_9H_{12}N$): MS, m/z 217 (M^+), 134, 120, 91 (base peak), 65, 55; exact mass, calcd for $C_{15}H_{23}N$ (M) 217.1830, obsd 217.1815.

When a solution of **10** in CCl_4 was treated with silica gel at 80 °C for 1 h, the olefin **11** ($R^1 = C_9H_{12}N$) was obtained: MS, m/z 175 (M^+), 134, 120, 91 (base peak), 65; ^1H NMR δ 1.75 (s, 3 H), 2.10 (s, 3 H), 2.84 (s, 2 H), 3.39 (s, 2 H), 4.82 (br s, 2 H), 7.20 (s, 5 H); exact mass, calcd for $C_{12}H_{17}N$ (M) 175.1361, obsd 175.1373.

General Procedure for the Aldol Condensation. To reagent A or reagent C (2 equiv) was added a solution of the ester (1 equiv) in THF or in Et_2O, respectively, at −78 °C. After 0.5–2 h of

(16) Payne, G. B. *J. Org. Chem.* **1958**, *23*, 310.
(17) Sugai, T.; Fujita, M.; Mori, K. *Nippon Kagaku Kaishi* (*J. Chem. Soc. Jpn.*) **1983**, 1315.

stirring, the aldehyde (1-3 equiv) was added to the reaction mixture, and the solution was stirred for another 1.5-2 h at -78 °C. The reaction mixture was quenched with NH_4Cl (saturated aqueous) at this temperature, and the product was extracted with ether or chloroform. After being dried over Na_2SO_4, the extract was concentrated in vacuo. The tin-containing byproduct was removed on a silica gel column (CCl_4), and the product was eluted with ethyl acetate. The eluate was concentrated in vacuo and purified by column chromatography or TLC.

Reaction of Ethyl Benzoate with Benzaldehyde (Run 26). The reaction was carried out by using reagent A (0.5-mmol scale of the ester (75 mg)) and the aldehyde (53 mg, 0.5 mmol). The analysis of the crude material by NMR using TCE indicated that the product was the aldol 8 ($R^1 = R^2 = C_6H_5$, 71%). Purification by column chromatography ($CHCl_3$) gave a pure sample: ^1H NMR δ 3.16 (d, J = 7.0 Hz, 2 H), 5.20 (t, J = 6.4 Hz, 1 H), 7.00-8.10 (m, 10 H).

Reaction of Ethyl Benzoate with Propanal (Run 27). The reaction was carried out by using reagent A (1.0-mmol scale of the ester (150 mg)) and the aldehyde (58 mg, 1.0 mmol). Purification by column chromatography ($CHCl_3$) gave the aldol 8 ($R^1 = C_6H_5$, $R^2 = C_2H_5$, 153 mg, 86%): ^1H NMR δ 1.00 (dist t, J = 6.4 Hz, 3 H), 1.21-1.72 (m, 2 H), 3.00 (d, J = 6.0 Hz, 2 H), 3.53 (br s, 1 H), 3.80-4.25 (m, 1 H), 7.40-7.90 (m, 5 H); IR, ν_{max} 3680-3130, 2970, 2930, 2880, 1670, 1595, 1450, 1210 cm^{-1}. The product was identical with the authentic sample prepared by the LDA-induced aldol reaction of acetophenone and propanal.

Reaction of Methyl Octanoate with Benzaldehyde (Run 28). The reaction was carried out by using reagent C (0.5-mmol scale of the ester (71 mg)) and the aldehyde (53 mg, 0.5 mmol). Purification by column chromatography ($CHCl_3$) gave the aldol 8 ($R^1 = C_7H_{15}$, $R^2 = C_6H_5$, 122 mg, 98%): MS, m/z 164 ($M^+ - C_6H_{12}$), 107 (base peak), 79, 77, 73; ^1H NMR δ 0.93-1.30 (m, 13 H), 2.20 (dist t, J = 7.0 Hz, 2 H), 2.60 (d, J = 5.0 Hz, 1 H), 2.64 (d, J = 8.0 Hz, 1 H), 3.59 (br s, 1 H), 5.00 (dd, J = 5.0 Hz and 8.0 Hz, 1 H), 7.20 (m, 5 H); IR ν_{max} 3630-3130, 3070, 2960, 2930, 2880, 2860, 1710, 1455, 1050 cm^{-1}. The product was identical with an authentic sample prepared from 2-nonanone and benzaldehyde using LDA.

Reaction of Methyl Octanoate with Propanal (Run 29). The reaction was carried out by using reagent C (0.5-mmol scale of the ester (74 mg)) and the aldehyde (78.3 mg, 1.35 mmol). Analysis of the crude material by NMR using TCE indicated that the product was the aldol 8 ($R^1 = C_7H_{15}$, $R^2 = C_2H_5$, 66%). Purification by column chromatography ($CHCl_3$) gave a pure sample: ^1H NMR δ 0.90-1.30 (m, 18 H), 2.40 (m, 4 H), 2.85 (br s, 1 H), 3.87 (m, 1 H).

Reaction of Ethyl *O*-Benzyl-L-lactate with Benzaldehyde (Run 30). The reaction was carried out by using reagent A (0.5-mmol scale of the ester (104 mg)) and the aldehyde (159 mg, 1.5 mmol). The crude material was first separated by TLC ($CHCl_3$) into two layers (R_f 0.5, 0.2), and the lower layer was further purified by TLC (Et_2O/hexane (1/1)) to give a pure sample of 8 ($R^1 = C_9H_{11}O$, $R^2 = C_6H_5$, 67 mg, 60%). For 8: ^1H NMR δ 1.22 (d, J = 7.0 Hz, 3 H), 2.71-2.98 (m, 2 H), 3.43 (br s, 1 H), 3.76 (q, J = 7.0 Hz, 1 H), 4.41 (br s, 2 H), 4.88-5.19 (m, 1 H), 7.14-7.32 (s, 10 H).

Dehydration of 8 (49 mg, 0.17 mmol) was carried out by using a catalytic amount of $TsOH-H_2O$ in benzene (2 mL) at room temperature for 73 h. The column chromatography ($CHCl_3$) gave 2-(benzyloxy)-5-phenyl-4-penten-3-one (34 mg, 74%): ^1H NMR δ 1.35 (d, J = 7.0 Hz, 3 H), 3.97 (q, J = 7.0 Hz, 1 H), 4.46 (s, 2 H), 6.88-7.82 (m, 12 H).

Reaction of Ethyl *O*-Benzyl-L-lactate with Ethanal (Run 31). The reaction was carried out by using reagent A (0.5-mmol scale of the ester (104 mg)) and the aldehyde (66 mg, 1.5 mmol). The crude material was first separated into two layers (R_f 0.6, 0.1) by TLC ($CHCl_3$), and the lower layer was further purified by TLC (Et_2O/hexane (1/1)) to give a pure sample of 8 ($R^1 = C_9H_{11}O$, $R^2 = CH_3$, 67 mg, 60%): ^1H NMR δ 1.18 (d, J = 7.0 Hz, 3 H), 1.33 (d, J = 7.0 Hz, 3 H), 2.53-2.75 (m, 2 H), 2.75 (br s, 1 H), 3.80 (q, J = 7.0 Hz, 1 H), 3.93-4.31 (m, 1 H), 4.48 (s, 2 H), 7.26 (s, 5 H).

Reaction of Ethyl *O*-Benzyl-L-lactate with Propanal (Run 32). The reaction was carried out by using reagent A (0.5-mmol scale of the ester (104 mg)) and the aldehyde (87 mg, 1.5 mmol). The crude material was first separated into two layers (R_f 0.6, 0.1) by TLC ($CHCl_3$) and the lower layer was further purified by TLC (Et_2O/hexane (1/1)) to give 8 ($R^1 = C_9H_{11}O$, $R^2 = C_2H_5$, 78 mg, 66%): ^1H NMR δ 0.93-1.51 (m, 8 H), 2.60-2.66 (m, 2 H), 3.19 (br s, 1 H), 3.70-4.30 (m, 2 H), 4.56 (s, 2 H), 7.20 (s, 5 H).

Reaction of Ethyl *O*-Benzyl-L-lactate with Formaldehyde (Run 33). The reaction was carried out by using reagent A (0.5-mmol scale of the ester (104 mg)) and an excess of the aldehyde, which was prepared by heating paraformaldehyde. TLC purification (Et_2O/hexane (1/1)) gave 8 (53 mg, 51%), 7 (10 mg, 10%), and 11 (20 mg, 22%). For 8 ($R^1 = C_9H_{11}O$, R^2 = H): MS, m/z 135 ($M^+ - COC_2H_4OH$), 91 (base peak), 77, 73, 66, 55, 45, 43; ^1H NMR δ 1.26 (d, J = 7.0 Hz, 3 H), 2.50-2.71 (m, 2 H), 2.75 (br s, 1 H), 3.53-3.96 (m, 3 H), 4.40 (s, 2 H), 7.20 (br s, 5 H).

Ultrasound in Organic Synthesis. 13.[1] Some Fundamental Aspects of the Sonochemical Barbier Reaction

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The Barbier reaction of benzaldehyde, *n*-heptyl bromide, and lithium was effected under various sonochemical conditions. The rate of formation of 1-phenyloctanol depends strongly on the intensity of the ultrasonic waves and the temperature. For both parameters, an optimum is observed. An unusual variation of rate with temperature is evidenced, which reveals that the reaction is not mass-transport controlled. Electron microscopy examination of the metal shows the very important activation role of the acoustic waves, through the cavitation phenomenon.

Introduction

After a long period of scattered research, synthetic sonochemistry is presently the subject of more systematic works and applications especially in the case of heterogeneous reactions. The efficiency of ultrasonic waves in promoting various processes has been established,[2] but most of the works dealing with synthetically useful reactions are essentially descriptive. The physical and phys-

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(2) For recent examples, see: (a) Boudjouk, P. *J. Chem. Educ.* **1986**, *63*, 427-429. (b) Suslick, K. S.; Casadonte, D. J. *J. Am. Chem. Soc.* **1987**, *109*, 3459-3461. (c) Henglein, A. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1985**, *40B*, 100-107. (d) Davidson, R. S.; Patel, A. M.; Safdar, A.; Thornthwaitre, D. *Tetrahedron Lett.* **1983**, *24*, 5907-5910. (e) Yamashita, J.; Inoue, Y.; Kondo, T.; Hashimoto, H. *Chem. Lett.* **1986**, 407-408. (f) Brown, H. C.; Racherla, U. S. *Tetrahedron Lett.* **1985**, *26*, 2187-2190. (g) Luche, J. L.; Damiano, J. C. *J. Am. Chem. Soc.* **1980**, *102*, 7926-7928.

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