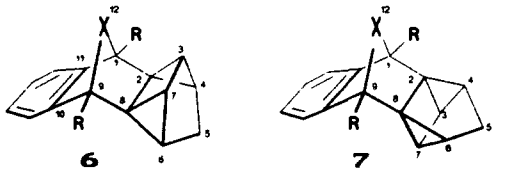
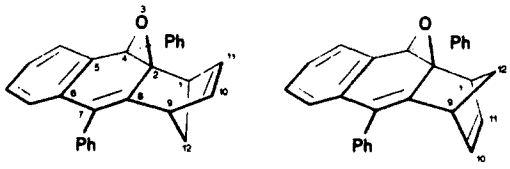
soluble in ether than **6a** and could be purified from that solvent, whereas **6a** was obtained pure after several crystallization from acetonitrile. The structure of **6a** was determined by X-ray diffraction[16] and is depicted in Figure 1.[17]



6 **7**

a: X = O, R = Ph; **b**: X = NMe, R = Me

8 **9**



10 **11**

At 83:17, the ratio of **6a** to **7a** (total yield 36%) remained practically unchanged when the reaction sequence was carried out with **3g** instead of **3k**. The result is in accord with **2** as the common intermediate.

In two further experiments, a solution of **3i** in THF/pentane was allowed to warm from −78 °C to room temperature in the presence of 1,2,3-trimethylisoindole and, respectively, of 2,5-dimethylfuran. In the first case, aqueous workup afforded a 65% yield of adduct **6b**;[8,18] NMR spectroscopy of the crude material did not provide any evidence for the formation of the syn isomer **7b**. With dimethylfuran as a trap for **2**, a 3:1 mixture of **8** and **9**[19] was obtained in 23% yield as a liquid, the components of which could not be separated.

So far, several attempts at isomerizing the quadricyclanes **6a** and **7a** to the corresponding oxasesquinorbornatrienes were unsuccessful. After chromatography of **6a** or **7a** on a silica gel column, the epoxides **10**[20] and, respectively, **11**[21] were obtained as main products. In addition, **11** was formed after refluxing a solution of **7a** in acetonitrile for 1 h. Presumably, these rearrangements are effected by electrophilic catalysis via cationic intermediates. The structure of **11** was established by X-ray crystallography.[22]

Acknowledgment. This work was supported by the Deutsche Forschungsgemeinschaft and by the Fonds der Chemischen Industrie.

Supplementary Material Available: Tables of atomic positional parameters, anisotropic thermal parameters, hydrogen atom positions, bond distances, and bond angles of **6a** and additional spectroscopic information for **4g**, **4k**, **3k**, **6a**, **7a**, **6b**, **10**, **11** (5 pages). Ordering information is given on any current masthead page.

(15) **7a**: mp 186.5–188 °C; ^{13}C NMR ($CDCl_3$) δ 16.20 (d, C-3, C-7), 27.57 (d, C-4, C-6), 36.48 (t, C-5), 40.59 (s, C-2, C-8), 89.39 (s, C-1, C-9), 118.74, 126.40, 126.47, 127.83, 128.32, (5 d), 137.17, 148.71 (2 s).

(16) X-ray crystal data of **6a** ($C_{27}H_{20}O$): M = 360.460; monoclinic; space group = $P2_1$; Z = 2; a (pm) = 801.4 (2); b (pm) = 835.4 (2); c (pm) = 1396.4 (4); β = 91.18 (2)°; V (nm^3) = 0.934 62; D_{calcd} (g cm^{-3}) = 1.281. The data were collected on an Enraf-Nonius CAD-4 diffractometer using Mo Kα radiation. A total of 2792 refections ($\pm h,\pm k,l$) were collected in the range $4° < 2\theta < 46°$ with 1322 having $I > 2\sigma(I)$ being used in the structure refinement by full-matrix least-squares techniques (252 variables). Final R = 0.0286, R_w = 0.0243.

(17) Molecules of quadricyclane frameworks related to *syn*-sesquinorbornatrienes have recently been synthesized: Paquette, L. A.; Künzer, H.; Kesselmayer, M. A. *J. Am. Chem. Soc.* **1988**, *110*, 6521.

(18) **6b**: waxy solid, mp 46–52 °C; ^{13}C NMR (C_6D_6) δ 11.54 (q, CCH_3), 15.39 (d, C-3, C-7), 22.14 (d, C-2, C-8), 29.62 (NCH_3), 68.12 (s, C-1, C-9), 119.16, 126.12 (2 d), 146.02 (s).

(19) **8**: ^{13}C NMR ($CDCl_3$) δ 10.08 (d, C-3, C-7), 15.42 (q, CH_3), 24.20 (d, C-4, C-6), 36.35 (t, C-5), 40.33 (s, C-2, C-8), 84.98 (s, C-1, C-9), 135.47 (d, C-10, C-11). **9**: ^{13}C NMR ($CDCl_3$) δ 14.99 (d, C-3, C-7), 16.29 (q, CH_3), 24.41 (d, C-4, C-6), 37.72 (t, C-5), 39.20 (s, C-2, C-8), 86.21 (s, C-1, C-9), 138.30 (d, C-10, C-11).

(20) **10**: mp 193–196 °C; ^{13}C NMR ($CDCl_3$) δ 43.65, 48.67 (2 d, C-1, C-9), 50.46 (t, C-9), 68.66, 78.34 (2 s, C-2, C-4).

(21) **11**: mp 180.5–182 °C; ^{13}C NMR ($CDCl_3$) δ 46.10, 46.83 (2 d, C-1, C-9), 52.61 (t, C-12), 67.93, 76.78 (2 s, C-2 C-4).

(22) Details on the X-ray structure of **11** will be published at a later point.

Stereodivergent Synthesis of 1,2-Diol Derivatives via α-Alkoxy Organolead Compounds. S_E2-Retention Pathway

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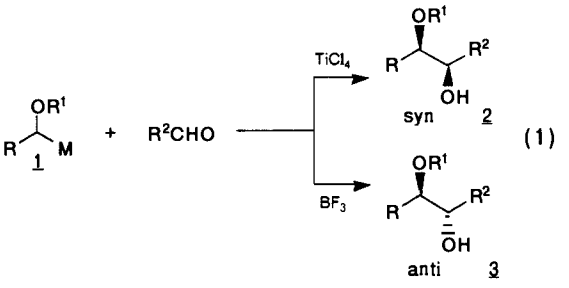
Received April 3, 1990

α-Alkoxy organometallic compounds (**1**; M = Sn,[1] Li,[1,2] MgX,[3] CuX[4]) are versatile reagents in organic synthesis. However, access to 1,2-diols via these reagents produces some difficulties. For example, the condensation of **1** (M = Li, MgBr, CuX) with benzaldehyde produces a low syn diastereoselectivity especially in the case of primary and secondary R groups.[3] Previously, we reported that tetraalkyllead compounds react smoothly with aldehydes.[5] If functionalized alkyl groups could be transferred stereoselectively to aldehydes in addition to such a simple alkyl group transfer, the synthetic utility of our Pb method would be enhanced. Accordingly, we prepared, for the first time, α-alkoxy organolead compounds **1** (M = Pb) and investigated the condensation of **1** (M = Pb) with aldehydes. Here, we report that (i) the stereodivergent synthesis of 1,2-diol derivatives is accomplished by the condensation of **1** (M = Pb) with aldehydes by merely changing Lewis acids (eq 1) and also (ii) the reaction proceeds through S_E2-retention.



(1)

α-Methoxy organolead compounds **5**[6] were prepared by transmetalation of the corresponding α-methoxy organostannanes **4**[7] with *n*-butyllithium followed by trapping with *n*-Bu_3PbBr at

(1) (a) Pereyre, M.; Quintard, J.-P.; Rahm, A. *Tin in Organic Synthesis*; Butterworth: London, 1987. (b) Sawyer, J. S.; Kucerovy, A.; Macdonald, T. L.; McGarvey, G. J. *J. Am. Chem. Soc.* **1988**, *110*, 842.

(2) (a) Cohen, T.; Maty, J. R. *J. Am. Chem. Soc.* **1980**, *102*, 6900. (b) Cohen, T.; Lin, M.-T. *J. Am. Chem. Soc.* **1984**, *106*, 1130.

(3) McGarvey, G. J.; Kimura, M. *J. Org. Chem.* **1982**, *47*, 5420.

(4) (a) Linderman, R. J.; Godfrey, A. *J. Am. Chem. Soc.* **1988**, *110*, 6249. (b) Linderman, R. J.; Godfrey, A. Home, K. *Tetrahedron* **1989**, *45*, 495.

(5) Yamamoto, Y.; Yamada, J. *J. Am. Chem. Soc.* **1987**, 109, 4395.

(6) ^{1}H NMR ($CDCl_3$, 270 MHz): **5a**, PbC*H*(OMe)CH_2 δ 4.370 (1 H, dd, J = 5.5 and 7.5 Hz), ^{207}Pb satellites gave $J_{H,Pb}$ = 82 Hz; **5b**, PbC*H*(OMe)CH δ 4.185 (1 H, d, J = 6.0 Hz), ^{207}Pb satellites gave $J_{H,Pb}$ = 74 Hz.

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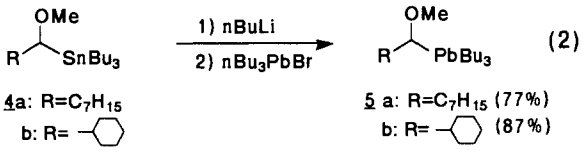
Table I. Stereodivergent Synthesis of 1,2-Diol Derivatives[a]

entry	reagent	R^2CHO R^2	reactn conditns: Lewis acid	reactn conditns: temp, °C	isomer ratio[b] **2:3**	isolated yield, %
1	**4a**	Ph	$TiCl_4$[c]	−78 → rt[d]	95:5	28
2	**5a**	Ph	$TiCl_4$	−78	99:1	90
3	**5a**	C_7H_{15}	$TiCl_4$	−78	99:1	84
4	**5a**	C_6H_{11}	$TiCl_4$	−78	99.5:0.5	94
5	**5b**	C_7H_{15}	$TiCl_4$	−78 → −20	97:3	63
6	**5b**	*i*-Pr	$TiCl_4$	−78 → −20	99:1	64
7	**5a**	C_7H_{15}	$BF_3{\cdot}OEt_2$[e]	−78 → 0	39:61	60
8	**5a**[f]	C_7H_{15}	$BF_3{\cdot}OEt_2$	−78 → 0	39:61	95
9	**5a**	C_7H_{15}	$BF_3{\cdot}OBu_2$	−78 → 0	30:70	49
10	**5a**	C_6H_{11}	$BF_3{\cdot}OEt_2$	−78 → 0	20:80	58
11	**5b**	C_7H_{15}	$BF_3{\cdot}OEt_2$	−78 → 0	18:82	54
12	**5b**	*i*-Pr	$BF_3{\cdot}OEt_2$	−78 → 0	14:86	49
13	**5b**	C_6H_{11}	$BF_3{\cdot}OEt_2$	−78 → 0	11:89	43

[a] All reactions were carried out on a 0.5-mmol scale under nitrogen as described previously.[5] [b] Determined by GLC analysis. [c] When $TiCl_4$ was used as a Lewis acid, 1.2 equiv of $TiCl_4$ for R^2CHO was added. [d] Room temperature. [e] When $BF_3{\cdot}OR_2$ was used as a Lewis acid, 2.5 equiv of $BF_3{\cdot}OR_2$ for R^2CHO was added. [f] Three equivalents of **5a** for R^2CHO was used.

−78 °C (eq 2). α-Methoxy organoleads **5** were able to be purified by column chromatography with silica gel immersed in 0.5% Et_3N/*n*-hexane by using 1.3% AcOEt/*n*-hexane as an eluent. The purification should be carried out within a short period, since the compounds were prone to gradually decompose at room temperature.



The results of reactions of α-methoxy organometallics with various aldehydes are summarized in Table I. First, the reaction of both **4a** and **5a** with benzaldehyde in the presence of $TiCl_4$ was examined (entries 1 and 2). The reaction of **4a** was sluggish and produced a mixture of the syn form (**2**) and the anti form (**3**) in a ratio of 95:5 (entry 1), whereas the condensation of **5a** was rapid and afforded very high syn selectivity (**2**:**3** = 99:1) in high yield (entry 2). Such a high diastereoselectivity cannot be attained by ordinary α-alkoxy organometallic compounds.[3] Similarly, the syn isomer (**2**) could be obtained with very high diastereoselectivities by the condensation of **5a** with octanal and cyclohexanecarboxaldehyde (entries 3 and 4). However, the reaction of **5b** was somewhat slow in comparison with that of **5a** (entries 5 and 6).

Further, in the presence of $BF_3{\cdot}OEt_2$, the anti isomer was afforded preferentially in the condensation of **5a** with octanal (entry 7). The chemical yield in entry 7 was 60%. However, use of excess **5a** gave the desired product in 95% yield with the same anti selectivity (entry 8). When $BF_3{\cdot}OBu_2$ was used instead of $BF_3{\cdot}OEt_2$ as a Lewis acid, the anti selectivity was enhanced (entry 9). Moreover, the anti selectivity was enhanced when either cyclohexanecarboxaldehyde or **5b** was employed (entries 10–13). Until now, the anti diastereoselection has not been achieved by using conventional α-alkoxy organometallic compounds such as Li, Mg, Cu, and Sn derivatives.[1-4,7] Demethylation of the methyl ethers proceeded quite nicely according to the literature procedure.[8]

The syn selectivity in the $TiCl_4$-mediated reactions can be accounted for by intermolecular chelation, whereas the anti selectivity in the BF_3-mediated reactions can be explained by nonchelation control. As shown in Figure 1, the transition states A and C are sterically favored over the diastereomeric transition states B and D, respectively. However, it is not clear whether the Lewis acid promoted reactions proceed via S_E2-retention or S_E2-inversion. Accordingly, we prepared the optically active α-methoxy organolead compound and examined the reaction with an aldehyde in order to clarify the mechanism and to develop an asymmetric synthetic procedure for 1,2-diols.

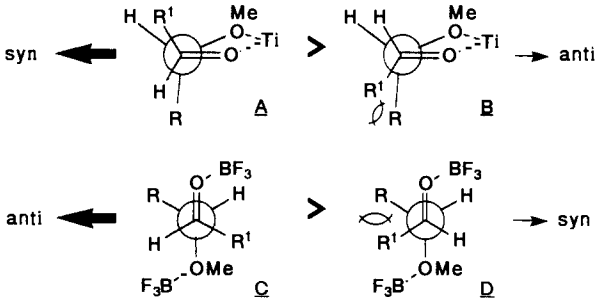
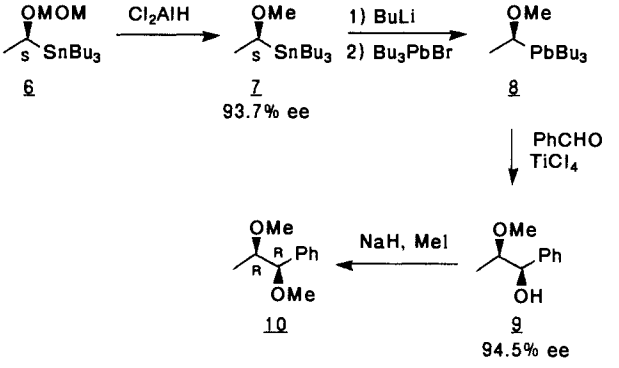


Figure 1. Chelation control and nonchelation control.

Scheme I



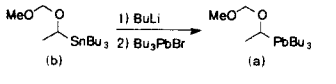
Reduction of (*S*)-**6**[9] with Cl_2AlH afforded the (*S*)-α-methoxy organostannane **7** ($[\alpha]^{20}_D$ +32.3°; *c* 0.78, $CHCl_3$) with 93.7% ee in 94% yield (Scheme I). Conversion of **7** into **8** was carried out according to the previously described procedure (79% yield). The absolute configuration of **8**[10] must be the *S* form, since it has been reported that this procedure, transmetalation followed by trapping with electrophiles, proceeds with retention of configuration.[9a,11]

(7) Still, W. C. *J. Am. Chem. Soc.* **1978**, *100*, 1481.
(8) Node, M.; Nishide, K.; Fuji, K.; Fujita, E. *J. Org. Chem.* **1980**, *45*, 4275.

(9) This compound ($[\alpha]^{20}_D$ +23.7°; *c* 1.31, $CHCl_3$) was prepared via chromatographic resolution of the corresponding (*R*)-(+)-MTPA ester according to the literature: (a) Still, W. C.; Sreekumar, C. *J. Am. Chem. Soc.* **1980**, *102*, 1201. It has been known that the absolute configuration of (+)-**6** is the *S* form: (b) Chen, P. C.-M.; Chong, J. M. *J. Org. Chem.* **1988**, *53*, 5584.

(10) We did not measure the optical rotation of **8**, since it was prone to decompose very slowly on standing. The reliable data was obtained with the compound a (ref 11).

(11) The MOM lead reagent **a**, obtained from **b**, was more stable than **8**. The lanthanide-induced [(+)-Eu(hfc)$_3$] shifts of the O*Me* for the *R* and *S* enantiomers of **a** exhibited the same tendency as those of **b**: Sullivan, G. R.; Ciavarella, D.; Mosher, H. S. *J. Org. Chem.* **1974**, *39*, 2411. This result indicates that **a** has the same configuration as **b** and supports Still's observation[9a] and our conclusion that conversion of α-alkoxy organostannanes into α-alkoxy organoleads proceeds with retention.



Condensation of **8** with benzaldehyde in the presence of $TiCl_4$ gave the syn isomer **9** predominantly (93:7) in 90% yield. The optical purity of **9** was 94.5% ee.[12] The absolute configuration of **9** was determined by transformation of **9** into dimethyl ether **10** ($[\alpha]^{24}_D$ -83.8°; *c* 0.370, EtOH). (-)-**10** could be assigned as the *R,R* form in comparison with the authentic sample ($[\alpha]^{24}_D$ +101.0°; *c* 0.015, EtOH) derived from the *S,S* diol.[12] Accordingly, it is clear that the $TiCl_4$-mediated reaction of **8** proceeds through retention.

We are now in a position to prepare 1,2-diols in a stereodivergent and enantioselective way via the newly developed α-methoxy organolead reagents. Further, the S_E2-retention mechanism is established. We are actively pursuing research of the Pb-mediated new synthetic reactions.

Acknowledgment. We thank Professor M. Hirama of our department for providing us with an authentic sample of the *S,S* diol.

(12) The optical purity was determined by ^1H NMR (270 MHz) analysis of the corresponding MTPA ester. The optical purity of **9** does not correlate to the rotational data given for **10**. This is due to the difference in concentration, and thus the purity determined by ^1H NMR analysis is more reliable than that by the rotation.

Ready Access to α-(Triorganosilyl)methylene β-Lactones by Means of Rhodium-Catalyzed Cyclocarbonylation of Substituted Propargyl Alcohols

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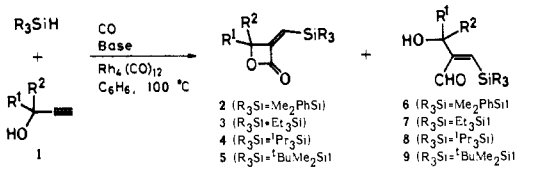
Received February 5, 1990

The incorporation of carbon monoxide in the synthesis of α-methylene γ-lactones has been of interest because it is one of the most elegant examples of the synthetic application of transition-metal complexes.[1] In particular, palladium-catalyzed cyclocarbonylation of homopropargyl alcohols is attractive because of the easy access to starting materials and the mildness of reaction conditions.[1a,b] α-Methylene β-lactones, however, are not formed by an analogous carbonylation of propargyl type alcohols.[2] Despite their simple structure it is astonishing that these compounds are constructed by an extremely limited number of methods.[3] Recently, we reported a rhodium-catalyzed silylformylation of alkynes.[4] The efficacy of the catalyst prompted us to apply this reaction to lactone formation. We report herein a successful cyclocarbonylation of acetylenic alcohols to form α-(triorganosilyl)methylene β-, γ-, and δ-lactones with the assistance of an appropriate base and $Rh_4(CO)_{12}$.

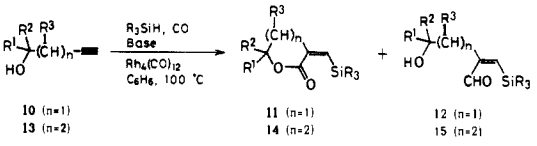
Carbonylation of a mixture of 1 equiv each of 2-methyl-3-butyn-2-ol (**1c**), Me_2PhSiH, and Et_3N gave α-silylmethylene β-lactone **2c**[5] (43%) and 3-silylpropenal **6c**[5] (52%) in the presence of a catalytic amount of $Rh_4(CO)_{12}$. The structure of the β-lactones is unambiguously confirmed by the IR spectrum, which showed a strong $\nu_{C=O}$ absorption at 1820 cm^{-1}. In the absence of Et_3N, however, **6c** was the sole product (94%). On the other hand, 2-propyn-1-ol (**1a**) gave **6a** (83%) selectively even in the presence of Et_3N. This preliminary finding suggests that the propensity for β-lactone formation depends on both steric and electronic factors. In fact, the ratio of β-lactone to 3-silylpropenal was remarkably affected by the silane and base employed in the carbonylation of **1c** (entries 5-9 in Table I). A dramatic improvement of the selectivity for β-lactone was attained by the use of either a bulkier silane, such as ^{t}BuMe$_2$SiH, or a stronger base, such as 1,8-diazabicyclo[5.4.0]undec-7-ene (DBU). On the basis of this information, suitable conditions to form **5b** (R_3Si = ^{t}BuMe$_2$Si) from the less substituted **1b** were found by the combined use of ^{t}BuMe$_2$SiH and 0.1 equiv of DBU. Spiro type β-lactones were also obtained by this method. These results are summarized in Table I.



(1)

γ-Lactone **11** is derived from homopropargyl type alcohols **10** by a similar operation even more easily than **2**. A γ-lactone **11a**[5] ($R^1 = R^2 = R^3 = H$, $R_3Si = Me_2PhSi$) (90%) was obtained selectively with the aid of $Rh_4(CO)_{12}$ in the carbonylation of a mixture of 1 equiv each of 3-butyn-1-ol (**10a**), Me_2PhSiH, and Et_3N. 1-(2-Propynyl)cyclohexan-1-ol (**10b**) and *trans*-2-ethynylcyclohexan-1-ol (**10c**) were converted to the corresponding lactones, **11b** (87%)[5] and **11c** (87%),[5,8] respectively, under analogous conditions. This simple operation is also applicable to the synthesis of six-membered α-silylmethylene lactones, although a combined use of ^{t}BuMe$_2$SiH and Et_3N is again required for the selective formation of δ-lactone **14**[5] ($R^1 = R^2 = R^3 = H$, R_3Si = ^{t}BuMe$_2$Si) (84%) in the carbonylation of 4-pentyn-1-ol **13**.

Carbonylation of **1** without a base, however, results in the formation of **6** selectively. The trimethylsilyl ether of **1** is converted to the trimethylsilyl ether of **6** by a similar carbonylation, which is an alternative method to give **6** as the sole product. The latter is the route of choice for selective synthesis of **12** or **15**. The results suggest that the presence of the adjacent hydroxyl group is crucial and silylation[6] of the hydroxyl group prior to carbonylation should be strictly avoided for the selective cyclocarbonylation of **1**, **10**, and **13**.



(2)

It should be stressed that the present modified silylformylation provides an effective route to strained α-silylmethylene β-lactones **2-5** by means of the carbonylation of **1**. The result is quite different from the previous reports that butenolides are formed by the reaction of the acetylenic triple bond with 2 equiv of CO in the presence of $Rh_4(CO)_{12}$.[9] In fact, the carbonylation of **1f**

(1) (a) Murray, T. F.; Norton, J. R. *J. Am. Chem. Soc.* **1979**, *101*, 4107-4119. (b) Murray, T. F.; Samsel, E. G.; Varma, V.; Norton, J. R. *J. Am. Chem. Soc.* **1981**, *103*, 7520-7528. (c) Tsuji, Y.; Kondo, T.; Watanabe, Y. *J. Mol. Catal.* **1987**, *40*, 295-304. (d) Matsuda, I. *Chem. Lett.* **1978**, 773-776. (e) Semmelhack, M. F.; Brickner, S. J. *J. Am. Chem. Soc.* **1981**, *103*, 3945-3947. (f) Martin, L. D.; Stille, J. K. *J. Org. Chem.* **1982**, *47*, 3630-3633.

(2) (a) Rosenthal, R. W.; Schwartzman, L. H.; Greco, N. P.; Roper, R. *J. Org. Chem.* **1963**, *28*, 2835-2838. (b) Nogi, T.; Tsuji, J. *Tetrahedron* **1969**, *25*, 4099-4108. (c) Larock, R.; Riefling, B.; Fellows, C. A. *J. Org. Chem.* **1978**, *43*, 131-137. (d) Buchwald, S. L.; Fang, Q.; King, S. M. *Tetrahedron Lett.* **1988**, *29*, 3445-3448.

(3) Adam, W.; Hasemann, L.; Prechtl, F. *Angew. Chem., Int. Ed. Engl.* **1988**, *27*, 1536-1537.

(4) Matsuda, I.; Ogiso, A.; Sato, S.; Izumi, Y. *J. Am. Chem. Soc.* **1989**, *111*, 2332-2333.

(5) All these compounds were identified by ^1H NMR, ^{13}C NMR, and IR spectra. All new compounds gave satisfactory combustion analyses.

(6) (a) Gilman, H.; Dunn, G. E.; Hartzfeld, H.; Smith, A. G. *J. Am. Chem. Soc.* **1955**, *77*, 1287-1288. (b) Sommer, L. H.; Lyons, J. E. *J. Am. Chem. Soc.* **1967**, *89*, 1521-1522.

(7) The isolated lactones (**2-5**, **11**, and **14**) show the *Z* geometry in the exocyclic double bond unless otherwise noted. The assignment of *Z* and *E* geometry is based on the chemical shift value of the vinyl proton. An appreciable low-field shift is observed in the *E* isomer (e.g., δ 6.47 and 7.05 for (*Z*)- and (*E*)-**11c**, respectively).

(8) For the trimethylsilyl analogue, see: (a) Bachi, M. D.; Bosch, E. *Tetrahedron Lett.* **1986**, *27*, 641-644. (b) Nozaki, K.; Oshima, K.; Utimoto, K. *Tetrahedron Lett.* **1988**, *29*, 6127-6128.

0002-7863/90/1512-6120$02.50/0