Photooxygenation of 1c. A mixture of 200 mg of **1c** and 60 mg of TCA in 50 mL of acetonitrile was irradiated (HPK, GWV filter) under oxygen for 40 min. The solution was filtered from an insoluble solid that was a mixture of TCA and the 1,2-dioxane **12c**. **12c** was recrystallized from benzene/acetonitrile with charcoal treatment: mp 189–191 °C dec; IR (KBr) 2940, 2880, 2794, 1615, 1522, 1445, 1353, 1200, 945, 809, 557 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.47 (br s, 4 H, CH_2CH_2), 2.90 (s, 24 H, $N(CH_3)_2$), 6.43–6.72 and 6.90–7.30 (m, 16 H, arom); ^{13}C NMR ($CDCl_3$) δ 149.6, 132.0, 128.2, 112.1, 85.6, 40.6, 30.8.

Anal. Calcd for $C_{36}H_{44}N_4O_2$: C, 76.6; H, 7.8; N, 9.9. Found: C, 76.5; H, 7.7; N, 9.8.

By the procedure of Ledwith and co-workers,[18] ~10 mg of $Cu(NO_3)_2 \cdot 5H_2O$ (Kodak) was added to a stirred solution of 266 mg (1 mmol) of **1c** in 100 mL of methanol in a flask open to the air. The solution immediately turned dark blue, and a white precipitate formed. After 1 h, the solid was collected by filtration; it was identical in all respects with the 1,2-dioxane **12c** prepared by photooxygenation.

Photooxygenation of 1a in the Presence of Methanol. A mixture of 180 mg (1 mmol) of **1a**, excess TCA, 10^{-3} M sodium methoxide, and 1 M methanol in 50 mL of acetonitrile was irradiated (HPK, GWV filter) under oxygen for 1 h. The solution was filtered from excess TCA, and the solvent was distilled. By NMR analysis, the residue contained unreacted **1a** and a 6:3:1 mixture of 1-hydroperoxy-2-methoxy-1,1-diphenylethane[16] (**13**), benzophenone, and 1-hydroxy-2-methoxy-1,1-diphenylethane (**14**). **13**: ^1H NMR ($CDCl_3$) δ 3.35 (s, 3 H, OCH_3), 4.23 (s, 2 H, CH_2), 7.23 (br s, 10 H, arom).

The product mixture was reduced with excess lithium aluminum hydride in ether, which converted benzophenone to benzhydrol and **13** to **14**. This mixture was then treated with trifluoroacetic anhydride, to give the trifluoroacetate of **14**: ^1H NMR ($CDCl_3/(CF_3CO)_2O$) δ 3.37 (s, 3 H, OCH_3), 4.05 (s, 2 H, CH_2), 7.00–7.50 (m, 10 H, arom).

Registry No. 1a, 530-48-3; **1a**$^{\bullet+}$, 36195-39-8; **1b**, 4356-69-8; **1b**$^{\bullet+}$, 63464-03-9; **1c**, 7478-69-5; **1c**$^{\bullet+}$, 104267-21-2; **2**, 41977-31-5; **3**, 72805-46-0; **4**, 84537-61-1; (*trans*)-**5**, 104267-15-4; (*cis*)-**5**, 104267-16-5; **7**, 104267-17-6; **8**, 104267-18-7; **9**, 54655-89-9; **10**, 41976-80-1; **11**, 104291-11-4; **12a**, 68313-22-4; **12b**, 68313-25-7; **12c**, 93584-77-1; **13**, 104267-19-8; **14**, 14704-09-7; **14** (trifluoroacetate), 104267-20-1; DCA, 1217-45-4; TCA, 80721-78-4; biphenyl, 92-52-4; methanol, 67-56-1; benzophenone, 119-61-9; benzhydrol, 91-01-0.

Cobalt Carbonyl Catalyzed Reactions of Esters and Lactones with Hydrosilane and Carbon Monoxide. A Novel Synthetic Method for the Introduction of the Siloxymethylidene Group[1]

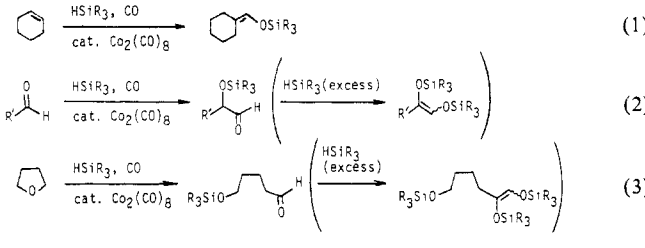
Naoto Chatani, Satoru Fujii, Yasuhiro Yamasaki, Shinji Murai,* and Noboru Sonoda

Contribution from the Department of Applied Chemistry, Faculty of Engineering, Osaka University, Suita, Osaka 565, Japan. *Received June 17, 1986*

Abstract: The catalytic reactions of esters and lactones with hydrosilane and carbon monoxide in the presence of $Co_2(CO)_8$ have been studied in detail with the emphasis being focused on their utility in organic synthesis. The catalytic reaction of secondary alkyl acetates underwent clean incorporation of carbon monoxide to give (siloxymethylidene)alkanes (enol silyl ethers). Lactones of secondary alkyl ester type reacted similarly. The siloxymethylidenation products were converted to aldehydes. Primary alkyl acetates gave several products in a nonselective manner. In the case of tertiary alkyl esters, no incorporation of carbon monoxide took place except for bridgehead alkyl acetates. The mechanism of the catalytic reaction has been proposed, and the importance of the silylcobalt carbonyl, $R_3SiCo(CO)_4$, as the key catalyst species has been suggested. The high affinity of the silicon in $R_3SiCo(CO)_4$ toward the oxygen atom in the ester is suggested to be the driving force for the formation of alkylcobalt carbonyls as the intermediates. This step illustrates a new methodology for the formation of a carbon–transition metal bond.

Carbonyl complexes of transition metals are widely involved as the catalysts in a variety of catalytic reactions in which carbon monoxide is incorporated into an organic substrate. Some of the most commonly used metal complexes may be those containing cobalt. Numerous studies have been done on the cobalt-catalyzed reactions not only because of their role in the commercially important hydroformylation process but also because of their ability to catalyze various types of carbonylation reactions.[2] Mechanistically, migratory insertion of carbon monoxide into a carbon–cobalt bond is the essential step in these reactions.[2] The required carbon–cobalt bond is generally formed by the interaction of a given substrate with $HCo(CO)_n$, the "quintessential catalyst"[3] in the $H_2/CO/Co_2(CO)_8$ system.

On the other hand, two types of catalyst species seem to be important in the new $HSiR_3/CO/Co_2(CO)_8$ system. The reactions of olefins[4] (eq 1) or oxygen-containing compounds such as aldehydes[5] (eq 2) and cyclic ethers[6] (eq 3) with hydrosilane ($HSiR_3$)



(1) For previous papers of this series, see: (a) Murai, T.; Furuta, K.; Kato, S.; Murai, S.; Sonoda, N. *J. Organomet. Chem.* **1986**, *302*, 249. (b) Murai, T.; Kato, S.; Murai, S.; Hatayama, Y.; Sonoda, N. *Tetrahedron Lett.* **1985**, *26*, 2683. (c) Murai, T.; Kato, S.; Murai, S.; Toki, T.; Suzuki, S.; Sonoda, N. *J. Am. Chem. Soc.* **1984**, *106*, 6093. (d) Chatani, N.; Furukawa, H.; Kato, T.; Murai, S.; Sonoda, N. *J. Am. Chem. Soc.* **1984**, *106*, 430. (e) Murai, T.; Hatayama, Y.; Murai, S.; Sonoda, N. *Organometallics* **1983**, *2*, 1883. (f) Chatani, N.; Yamasaki, Y.; Murai, S.; Sonoda, N. *Tetrahedron Lett.* **1983**, *24*, 5649. (g) Chatani, N.; Murai, S.; Sonoda, N. *J. Am. Chem. Soc.* **1983**, *105*, 1370.

(2) For general reviews of cobalt-catalyzed carbonylation reactions, see: (a) Pino, P.; Piacenti, F.; Bianchi, M. In *Organic Syntheses via Metal Carbonyls*; Wender, I., Pino, P., Eds.; Wiley: New York, 1977; Vol. II. (b) Colquhoun, H. W. *Chem. Ind. (London)* **1982**, 747.

(3) For a review under the title of this word, see: Orchin, M. *Acc. Chem. Res.* **1981**, *14*, 259.

(4) (a) Seki, Y.; Hidaka, A.; Murai, S.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 174. (b) Seki, Y.; Murai, S.; Hidaka, A.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 881. (c) Seki, Y.; Hidaka, A.; Makino, S.; Murai, S.; Sonoda, N. *J. Organomet. Chem.* **1977**, *140*, 361.

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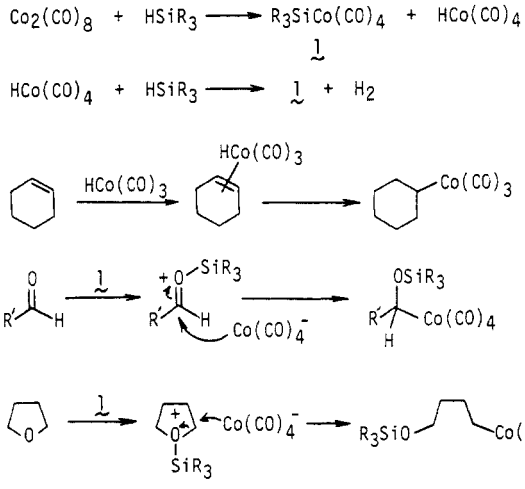
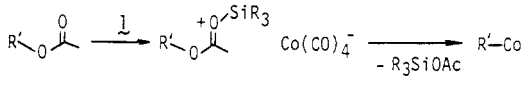
and carbon monoxide have been found to proceed catalytically in the presence of $Co_2(CO)_8$. The key catalyst species responsible for undergoing the initial interaction with a given substrate to form the required carbon–cobalt bond appears to be not only the hydrocobalt carbonyl ($HCo(CO)_3$ or $HCo(CO)_4$) but also the silylcobalt carbonyl ($R_3SiCo(CO)_4$, **1**). These two cobalt carbonyls are generated in situ by the well-established processes 4 and 5.[7] While $HCo(CO)_3$ can interact with an olefin to give an alkylcobalt species (eq 6), the silylcobalt carbonyl **1** has been suggested to react with oxygen-containing compounds to form cobalt complexes containing a carbon–cobalt bond (eq 7 and 8). Processes 6, 7,



and 8 must be involved as the key steps of reactions 1, 2, and 3, respectively. Reactions 7 and 8 illustrate a new methodology for the formation of a carbon–transition metal bond; i.e., the formation of a carbon–cobalt bond can be attained by utilizing the high affinity of the silicon atom in **1** toward the oxygen atom in a substrate. Recently, Gladysz has studied the stoichiometric reaction of $Me_3SiMn(CO)_5$ with oxygen-containing compounds leading to the development of a new efficient method for the formation of carbon–manganese bonds.[8]

To test the applicability and the effectiveness of the methodology described above, we have studied the catalytic reaction of alkyl acetates with hydrosilane and carbon monoxide in the presence of $Co_2(CO)_8$. The analysis based on the above-mentioned concept suggested that activation of an acetoxy group into a better leaving group as shown in eq 9 was highly plausible to occur in a catalytic



process. Thus, development of a new entry to an alkylcobalt tetracarbonyl (eq 9) leading to a new catalytic reaction was expected. Moreover, alkyl acetates are one of the most easily available classes of oxygen-containing compounds, so that incorporation of carbon monoxide into them would lead to a new useful synthetic method.[9] In this paper, the details of the cobalt-catalyzed reactions of alkyl acetates and lactones with hydrosilanes and carbon monoxide are described.[10]

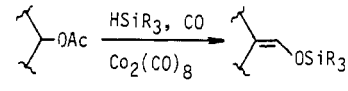
Table I. Catalytic Reaction of Cyclohexyl Acetate (**2**) with $HSiEt_2Me$ and CO[a]

run	catalyst/additive	solvent, temp (°C)	yield, %[b] 3	4
1	$Co_2(CO)_8$	C_6H_6, 100	5	9
2	$Co_2(CO)_8$	C_6H_6, 140	56	21
3	$Co_2(CO)_8$/pyridine[c]	C_6H_6, 140	58	12
4	$Co_2(CO)_8/PPh_3$[d]	C_6H_6, 140	12	0
5	$Co_2(CO)_6(PPh_3)_2$	C_6H_6, 140	28	3
6	$Co_2(CO)_8$	CH_2Cl_2, 140	54	2
7	$Co_2(CO)_8$	C_6H_6, 180	68	4
8	$Co_2(CO)_8$	C_6H_6, 200	75	3
9	$Co_2(CO)_8$	$PhCH_3$, 200	79	e
10	$Me_3SiCo(CO)_4$	C_6H_6, 200	70	e
11	$Co(OAc)_2 \cdot 4H_2O$[f]	C_6H_6, 200	66	e

[a] Reaction conditions: **2** (10 mmol), $HSiEt_2Me$ (30 mmol), CO (50 atm, initial pressure at 25 °C), catalyst (0.4 mmol), and solvent (20 mL) unless otherwise noted. Reaction time was 20 h for runs 1–6 and 6 h for runs 7–11. [b] GLC yield based on **2**. [c] Pyridine (2 mmol) was added. [d] PPh_3 (1 mmol) was added. [e] Less than a few percent. [f] The amount of $HSiEt_2Me$ was 40 mmol.

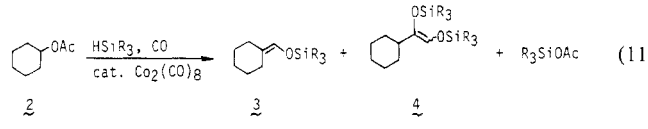
Results and Discussions

The results of the present study may be summarized as follows. Of the alkyl acetates subjected to the $Co_2(CO)_8$-catalyzed reaction with hydrosilane and carbon monoxide, secondary alkyl acetates were found to undergo incorporation of carbon monoxide selectively to give (siloxymethylidene)alkanes (eq 10). The reaction



10 has been studied in detail with particular emphasis focused on its utility in organic synthesis. Related γ-lactones having the secondary alkyl part behaved similarly. On the other hand, primary alkyl acetates suffered from byproducts formation. No incorporation of carbon monoxide took place in the case of tertiary alkyl esters except for those having a specific structure.

Catalytic Reaction of Cyclohexyl Acetate. Cyclohexyl acetate (**2**) was found to react with $HSiR_3$ and carbon monoxide in the presence of a catalytic amount of $Co_2(CO)_8$ to give (siloxymethylidene)cyclohexane **3** and byproducts, (disiloxyvinyl)cyclohexane **4** and R_3SiOAc (eq 11).



Selected results obtained for the catalytic reaction of **2** using $HSiEt_2Me$ as the hydrosilane are shown in Table I. The best result with respect to the yield of **3** and the ratio **3**:**4** was obtained for the reaction carried out under 50 atm of carbon monoxide and at 200 °C in benzene (or toluene) using $Co_2(CO)_8$ as the catalyst (or the catalyst precursor) (runs 8 and 9). The reaction did not take place below 100 °C. An increase in the reaction temperature resulted in an increase in the yield and the selectivity of **3** (runs 1, 2, 7, and 8). Some cobalt complexes, such as $Co_2(CO)_6(PPh_3)_2$ (run 5) and $Co(OAc)_2 \cdot 4H_2O$ (run 11), were also effective as the catalyst but less efficient than $Co_2(CO)_8$ (run 8) or $Me_3SiCo(CO)_4$ (run 10). Under the conditions equivalent to those of runs 2 or 8, various transition-metal complexes, selected mainly from those known to be effective for carbonylation[2,11] and/or hydrosilylation,[12]

(5) (a) Seki, Y.; Murai, S.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 119. (b) Murai, S.; Kato, T.; Sonoda, N.; Seki, Y.; Kawamoto, K. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 393.

(6) Seki, Y.; Murai, S.; Yamamoto, I.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 789.

(7) Chalk, A. J.; Harrod, J. F. *J. Am. Chem. Soc.* **1967**, *8*, 1640. Baay, Y. L.; MacDiarmid, A. G. *Inorg. Chem.* **1969**, *8*, 986. Sisak, A.; Ungrary, F.; Marko, L. *Organometallics* **1986**, *5*, 1019.

(8) (a) Johnson, D. L.; Gladysz, J. A. *J. Am. Chem. Soc.* **1979**, *101*, 6433. (b) Johnson, D. L.; Gladysz, J. A. *Inorg. Chem.* **1981**, *20*, 2508. (c) Marst, M.; Gladysz, J. A. *Organometallics* **1982**, *1*, 1467. (d) Brinkman, K. C.; Gladysz, J. A. *Organometallics* **1984**, *3*, 147. (e) Gladysz, J. A. *Acc. Chem. Res.* **1984**, *17*, 326.

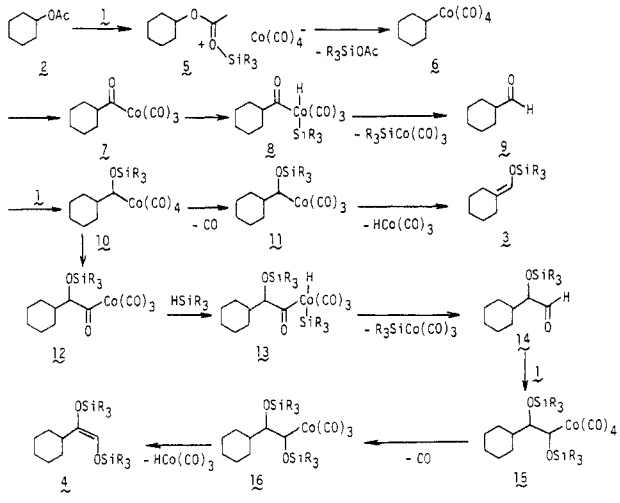
(9) Only little examples have been known about the catalytic reaction of alkyl esters with carbon monoxide. Keister, J. B.; Gentile, R. *J. Organomet. Chem.* **1981**, *222*, 143. Luft, G.; Schrod, M. *J. Mol. Chem.* **1983**, *20*, 175. Wegmann, R. W.; Busby, D. C. *J. Chem. Soc., Chem. Commun.* **1986**, 332. See also ref 2a and 11.

(10) A portion of this study has been communicated; see ref 1g.

(11) Falbe, J. *New Syntheses with Carbon Monoxide*; Springer-Verlag: New York, 1980.

(12) Lukevics, E.; Belyakova, Z. V.; Pomerantseva, M. G.; Voronkov, M. G. *J. Organomet. Chem. Libr.* **1977**, *5*, 1. Speier, J. L. *Adv. Organomet. Chem.* **1979**, *17*, 407.

Scheme I. Proposed Mechanism of the Catalytic Reaction



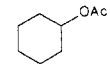
were examined on their ability to catalyze reaction 11. All of the complexes examined, however, showed little or no catalytic activity; these complexes were $Fe(CO)_5$,[13,14] $Fe(CO)_5$/*N*-methylpiperidine,[13] $[CpFe(CO)_2]_2$,[13] $(C_4H_4)Fe(CO)_3$,[13] $FeCl_3$,[13] $Ru_3(CO)_{12}$,[13,14] $RhCl(PPh_3)_3$,[13] $RhCl(CO)(PPh_3)_2$,[13] bis(norbornadienerhodium chloride),[13] $[RhCl(CO)]_2$,[13-15] $[Rh(OAc)_2]_2$,[13] $Rh_6(CO)_{16}$,[13,14] $PdCl_2$,[13,14] $PtCl_2(PPh_3)_2$,[13] $NiCl_2/Et_2S$,[14] and $IrCl(CO)(PPh_3)$.[13,14] The effective range of catalysts for the particular reaction 11 seems to be limited to those containing cobalt (Table I). The cluster complex, $C_6H_5CCo_3(CO)_9$,[16] was not effective in the present reaction.[13] Diethylmethylsilane, $HSiEt_2Me$, was used throughout the present work because of the ease in handling with a hypodermic syringe (bp 78 °C) and the advantage in the NMR assignment of products due to their methyl singlets. Other trialkylhydrosilanes gave similar results in reaction 11 (for example, 82%, 72%, and 58% yields of **3** were obtained from $HSiMe_3$, $HSiEt_3$, and $HSiPh_2Me$, respectively, under the conditions of run 8 in Table I).[17] Alkyl esters such as cyclohexyl formate, benzoate, and pivalate can also be used in place of the acetate **2** in reaction 11. The half-life times of cyclohexyl acetate, formate, benzoate, and pivalate under the conditions used for run 8 in Table I were 1.2, 1.2, 2.1, and 4.5 h, respectively. From the viewpoints of reactivity and availability, alkyl acetates are desirable substrates, especially for synthetic purposes.

The transformation of an alkyl ester shown in eq 10 or 11 has no precedent. Carbon monoxide has been cleanly incorporated into the carbon atom bearing the acetoxy group and appears as part of the siloxymethylidene group of the product. A new carbon–carbon bond has been formed as the result of carbon–oxygen bond cleavage.

Mechanistic Aspects. Although the mechanism of the cobalt carbonyl catalyzed reaction of cyclohexyl acetate with $HSiR_3$ and carbon monoxide (eq 11) is not fully understood yet, reasonable discussion can be made on the basis of the knowledge known about the accepted mechanisms of cobalt-catalyzed carbonylation,[2,3] olefin hydrosilylation,[7,12] and the reaction of olefins with hydrosilanes and carbon monoxide.[18] The latter chemistry has been reinforced by the elegant studies by Gladysz on the stoichiometric reactions of $Me_3SiMn(CO)_5$ with various oxygen-containing compounds.[8] The key catalyst species in the present reaction (eq 11) would be a silylcobalt carbonyl **1**, which could be generated in situ by reactions 4 and 5.

(13) Under the conditions used for run 2 in Table I (at 140 °C).
(14) Under the conditions used for run 8 in Table I (at 200 °C).
(15) A few percent yield of **3** was obtained.
(16) The cluster $C_6H_5CCo_3(CO)_9$ has been known to catalyze hydroformylation of 1-pentene. Pittman, C. U., Jr.; Ryan, R. C. *CHEMTECH* **1978**, *8*, 170.
(17) $HSiMe_3$, $HSiEt_2Me$, and $HSiEt_3$ are commercially available (e.g., Petrarch Systems Co., PA).
(18) For a review, see: Murai, S.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1979**, *18*, 837.

Table II. Cobalt Carbonyl Catalyzed Reactions of Cyclohexene and Cyclohexyl Acetate with $HSiEt_2Me$ and CO[a]

	substrate, mmol	$HSiEt_2Me$, mmol	yield, %[b] 3	4
	30	10	71[c]	0
	10	30	20	0
	30	10	62	2
	10	30	56[d]	21[d]

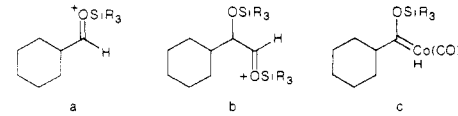
[a] All reactions were conducted by using benzene (20 mL) as a solvent under 50 atm of CO in the presence of $Co_2(CO)_8$ (0.4 mmol) at 140 °C for 20 h. [b] GLC yields based on the limiting substance. [c] Taken from ref 4c. [d] The same reaction listed as run 2 in Table I.

We propose the mechanism for reaction 11 as depicted in Scheme I. The catalytic cycle would begin with the interaction of **1** with the substrate **2** to form an oxonium ion **5** followed by the nucleophilic displacement of the activated acetoxy group by $Co(CO)_4^-$ to give an alkylcobalt complex **6**. These processes illustrate a new entry to alkylcobalt carbonyls. It is interesting to note that the reaction of alkyl carboxylates with Me_3SiI, a reagent analogous to **1** with respect to the point of hard acid (or oxygenophile)–soft base combination, is known to give alkyl iodides.[19] The alkyl migration would convert **6** to an acyl complex **7**, and the oxidative addition of $HSiR_3$ leading to **8** and subsequent reductive elimination from **8** would afford aldehyde **9** as an intermediate. The aldehyde **9** would react again with **1** to give **10** and finally afford the enol silyl ether **3** by β-hydride elimination from **11**.[20a] Another product, **4**, could arise from **10** via the alkyl migration leading to **12** and through the successive steps (**12** → **4**) shown in Scheme I. That the higher reaction temperature favored the selective formation of **3** (see runs 2, 7, and 8 in Table I) would imply that the process from **10** involving β-hydride elimination leading to **3** became relatively faster at the higher temperature than the alkyl migration in **10** to form **12**. Although intermediacy of the aldehydes **9** and **14** has not been substantiated experimentally,[20b] they are suggested as the intermediates in the present reaction since the cobalt-catalyzed reaction of **9** with $HSiEt_2Me$ and carbon monoxide has been already shown to afford **14**,[5b] an aldehyde, and **4**[5a] (eq 2) in addition to **3**.[21] Gladysz has recently reported the reaction of aldehydes with $Me_3SiMn(CO)_5$ to give acyl complexes analogous to **12**.[8a,b,d]

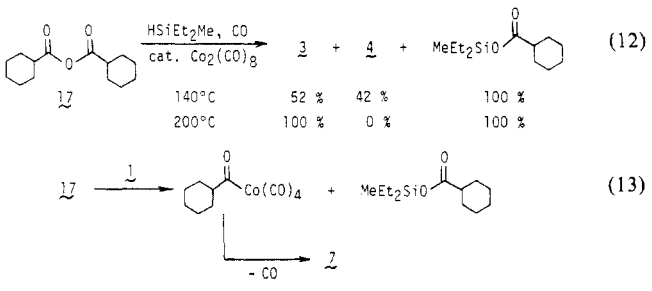
As a control experiment, a different entry to the acyl complex **7** was studied. The reaction of cyclohexanecarboxylic acid anhydride (**17**) with $HSiEt_2Me$ and carbon monoxide in the presence of $Co_2(CO)_8$, under the same conditions used for runs 2 and 8 in Table I, gave the results shown in eq 12. The common intermediate **7** might have been also formed in the catalytic reaction of the anhydride **17** as depicted in eq 13.

A unique feature of the $HSiR_3/CO/Co_2(CO)_8$ system deserves some comments. As has already been described (eq 1 and 11), both cyclohexene and cyclohexyl acetate gave the same product **3** under the same reaction system. This is due to the availability

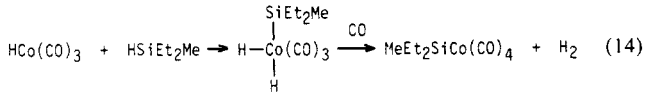
(19) Jung, M. E.; Lyster, M. A. *J. Am. Chem. Soc.* **1977**, *99*, 968. Ho, T.-L.; Olah, G. A. *Synthesis* **1977**, 417. Olah, G. A.; Narang, S. C.; Gupta, B. G. B.; Malhotra, R. *J. Org. Chem.* **1979**, *44*, 1247.
(20) (a) Alternatively, the double bond in **3** or **4** could be formed by the removal of H^+ from a or b, respectively. The oxonium ion a could arise from **9** and **1** or from **10**. (b) An alternative mechanism via a carbenoid complex c in place of **11** may exist. The similar carbenoid complex may be envisioned in place of **15**.



(21) The reaction of **9** (30 mmol) with $HSiEt_2Me$ (10 mmol) and CO (50 atm) in C_6H_6 in the presence of $Co_2(CO)_8/PPh_3$ (0.4 mmol/0.4 mmol) for 20 h at 100 °C gave **3** and **14** in 27% and 54% yields (based on $HSiEt_2Me$), respectively. The similar reaction using **9** (10 mmol) and $HSiEt_2Me$ (30 mmol) at 140 °C gave **3** and **4** in 48% and 48% yields (based on **9**), respectively. See ref 5a and 5b.



of the two kinds of catalyst species, $HCo(CO)_3$ and $R_3SiCo(CO)_4$ (**1**) (see eq 4). Depending on the nature of the substrate, i.e., an olefin or an ester, either of these two can operate as in eq 6 or 9. The results of the catalytic reactions of cyclohexene[4,18] and cyclohexyl acetate under the same reaction conditions are summarized in Table II. The fact that the disiloxyalkene **4** was not formed in the reaction of cyclohexene would imply that the β-elimination process (corresponding to that of **11** going to **3** in Scheme I) might have been facilitated in the presence of an olefin. The use of an excess amount of $HSiEt_2Me$ in the reaction of cyclohexene resulted in almost no reaction. In this case, $HCo(CO)_3$ would have been converted by the reaction with $HSiEt_2Me$ (eq 14) to $MeEt_2SiCo(CO)_3$[22] (or to $MeEt_2SiCo(CO)_4$ in the presence of carbon monoxide), which is not an active catalyst toward an olefin. Thus, $HCo(CO)_3$ would react with either an olefin (eq 6) or a hydrosilane (eq 14 or 5) in a competitive manner.

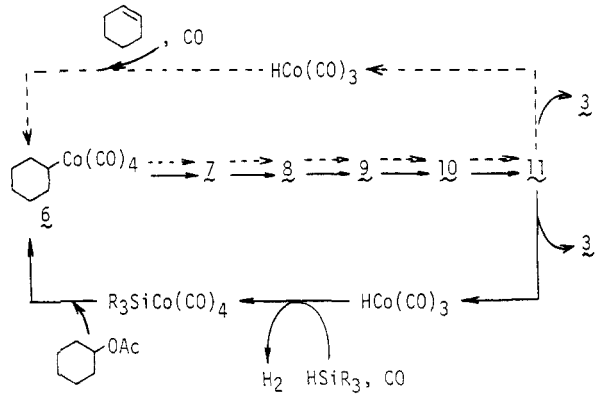


On the other hand, since $HCo(CO)_3$ could react with only the hydrosilane in the reaction of cyclohexyl acetate, the catalytic reaction could proceed irrespective of the molar ratio of an ester to a hydrosilane. Scheme II shows the simplified catalytic cycles suggested for the reactions of cyclohexene and of cyclohexyl acetate. Interestingly, they are different only in the entry to the alkylcobalt complex **6**. This kind of HCo/SiCo selection by merely changing the molar ratio of the reactants will be further discussed for the catalytic reaction of 5-acetoxy-1-hexene (**38**, vide infra).

Catalytic Reaction of Secondary Alkyl Acetates. In the case of secondary alkyl acetates, the cobalt carbonyl catalyzed reaction proceeded in a highly selective manner as has been shown for cyclohexyl acetate (runs 8 and 9 in Table I). The reaction provides a unique synthetic transformation, i.e., introduction of the siloxymethylidene group onto the carbon atom bearing an acetoxy group (eq 10). The reactions with primary and tertiary esters proceeded in somewhat different ways as will be described later.

The results obtained for various secondary alkyl acetates are summarized in Table III. The products obtained were enol silyl ethers, and these compounds are known as extremely versatile intermediates in organic synthesis.[23] Conversion of these products into aldehydes was also studied. Desilylation of the enol silyl ethers with KF/CH_3OH at 25 °C gave the corresponding aldehydes, including Liliar[24] (run 13), in quantitative yields. The overall

Scheme II. Catalytic Cycles for the Reactions of Cyclohexene and Cyclohexyl Acetate



transformation is formally the displacement of an acetoxy group with a formyl group. This is important in relation to the current interests on homologation techniques.[27] When it is appropriate, the conversion to an aldehyde and the subsequent synthetic reaction can be carried out in one operation since the desilylation to an aldehyde is known to take place easily under both basic and acidic conditions.[23] For example, the enol silyl ether **3** reacted with $NaBH_4$ in ethanol (25 °C, 3 h) to give cyclohexanemethanol in 70% yield.

The principal byproducts in the catalytic reaction of secondary alkyl acetates were alkenes obtainable by elimination of acetic acid. For example, cyclododecene was formed from cyclododecyl acetate in 40% yield in addition to the desired enol silyl ether **21** (run 5 in Table III). The higher yield of **22** (run 6 in Table III) may be attributed to the difficulty of β-hydride elimination from the initially formed 2-adamantylcobalt tetracarbonyl similar to **6**.

In the case of an alkyl acetate having an olefinic function in the proper position, intramolecular interception of an acylcobalt carbonyl intermediate by the olefin was expected to take place.[28] The cobalt-catalyzed reaction of *trans*-2-allylcyclopentanyl acetate with $HSiEt_2Me$ (3 equiv) and CO (50 atm, 180 °C, 20 h in C_6H_6) gave a bicyclic compound **37** in 54% yield (eq 15). The acylcobalt complex shown in eq 15 would be formed through S_N2-type displacement of the activated acetoxy group with $Co(CO)_4^-$ followed by successive migratory insertion of carbon monoxide. Since the same type of starting materials as those used in eq 15 can be readily prepared by the reaction of allyl anions with ep-

(22) Anderson, F. R.; Wrighton, M. S. *J. Am. Chem. Soc.* **1984**, *106*, 995.

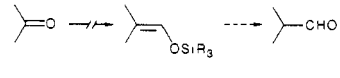
(23) For reviews on synthetic application of enol silyl ethers, see: Rasmussen, J. K. *Synthesis* **1977**, 91. Fleming, I. In *Comprehensive Organic Chemistry*; Jones, D. N., Ed.; Pergamon: Oxford, 1979; Vol. 3, Part 13, pp 584–592. Colvin, E. *Silicon in Organic Synthesis*; Butterworths: London, 1981; pp 198–287. Reetz, M. T. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 96. Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: New York, 1983; pp 206–254. Brownbridge, P. *Synthesis* **1983**, 1.

(24) Liliar is important not only as a perfume component[25] but also as an intermediate for pharmacological active amines.[26]

(25) Heilen, G.; Nissen, A.; Koernig, W.; Horner, M.; Fliege, W.; Boettger, G. Ger. Offen. 2832699; *Chem. Abstr.* **1980**, *93*, 26108. Sokolskii, D. V.; Pak, A. M.; Konuspaev, S. R.; Ginzburg, M. A.; Turganbaeva, S. M.; Pogorelskii, A. P. *Izv. Akad. Nauk SSSR, Ser. Khim.* **1980**, 26; *Chem. Abstr.* **1981**, *94*, 4126. Virgilio, J. A.; Heilweil, E. *Org. Prep. Proced. Int.* **1982**, *14*, 9. Grabbai, A.; De Polo, K. F. Eur. Pat. Appl. 103896; *Chem. Abstr.* **1984**, *101*, 90581. Yamazaki, Y.; Suzuki, T. Eur. Pat. Appl. 119067; *Chem. Abstr.* **1985**, *102*, 61935.

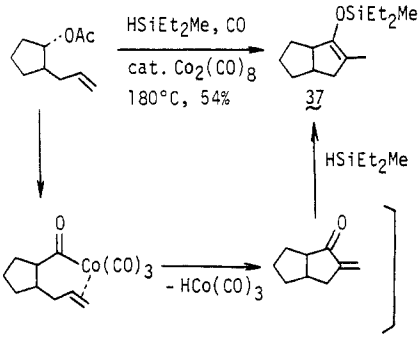
(26) Goetz, N.; Hupfer, L. Ger. Offen. 2830999; *Chem. Abstr.* **1980**, *93*, 95288. Bohnen, K.; Pfiffner, A. Eur. Pat. Appl. 5541; *Chem. Abstr.* **1980**, *93*, 8027. Pommer, E. H.; Himmele, W. Ger. Offen. 2921131; *Chem. Abstr.* **1981**, *94*, 116004. Himmele, W.; Heberle, W.; Kohlmann, F. W.; Wesenberg, W. Ger. Offen. 2921221; *Chem. Abstr.* **1981**, *95*, 7302. Pfiffner, A.; Bohnen, K. Patentschrift (Switz) CH 635076; *Chem. Abstr.* **1983**, *99*, 88056. Rentzea, C.; Buschmann, E.; Meyer, N.; Ammermann, E.; Pommer, E. H. Ger. Offen. 3218394; *Chem. Abstr.* **1983**, *100*, 67982. Himmele, W.; Heberle, W.; Kohlmann, F. W.; Wesenberg, W. Ger. Offen. 3225879; *Chem. Abstr.* **1984**, *101*, 6687.

(27) For a review of the current interest in this type of homologation, see: Martin, S. F. *Synthesis* **1979**, 633. It should be noted that attempts for related conversion of ketonic oxygen to the formyl group via enol silyl ethers have been unsuccessful.



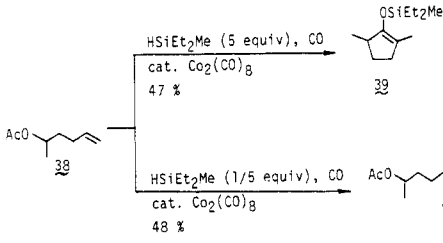
The attempted reactions and reagents used were as follows. (a) $(EtO)_2P(O)CH_2OSiMe_2$-*t*-Bu/LiN(*i*-Pr)$_2$: Kluge, A. F.; Cloudsdale, I. S. *J. Org. Chem.* **1979**, *44*, 4847. (b) $(EtO)_2P(O)CH(Ph)OSiMe_3$/LiN(*i*-Pr)$_2$: Koenigkramer, R. E.; Zimmer, H. *Tetrahedron Lett.* **1980**, *21*, 1017. $PPh_3^+CH_2OSiMe_3I^-$/base: Martin, S. F.; Phillips, G. W.; Puckette, T. A.; Colapret, J. A. *J. Am. Chem. Soc.* **1980**, *102*, 5866.

(28) Cobalt carbonyl mediated cyclization has been known. For a review, see: Mullen, A. *New Synthesis with Carbon Monoxide*; Falbe, J., Ed.; Springer-Verlag: New York, 1980; pp 414–439. See also: Fox, A. L. U.S. Patent 2995607; *Chem. Abstr.* **1962**, *56*, 1363. Heck, R. F. *J. Am. Chem. Soc.* **1963**, *85*, 3116. Garst, M. E.; Lukton, D. *J. Org. Chem.* **1981**, *46*, 4433.



(15)

oxides,[29] the catalytic reaction suggests a new possibility for the preparation of five-membered-ring compounds. Similarly, 5-acetoxy-1-hexene (**38**) gave a cyclized product, **39** (eq 16). In-

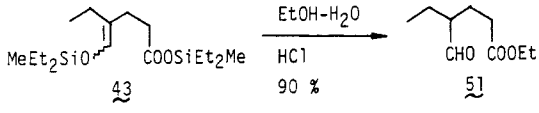


(16)

(17)

terestingly, the reaction course can be controlled by changing the molar ratio of **38** to the hydrosilane. This represents the intramolecular version of the $HCo(CO)_3/R_3SiCo(CO)_4$ selection depicted in Scheme II. Thus, the use of an excess amount of **38** over the hydrosilane gave a different product, **40**, in which carbon monoxide was incorporated into only the olefinic part of the starting olefinic acetate **38** (eq 17).[30]

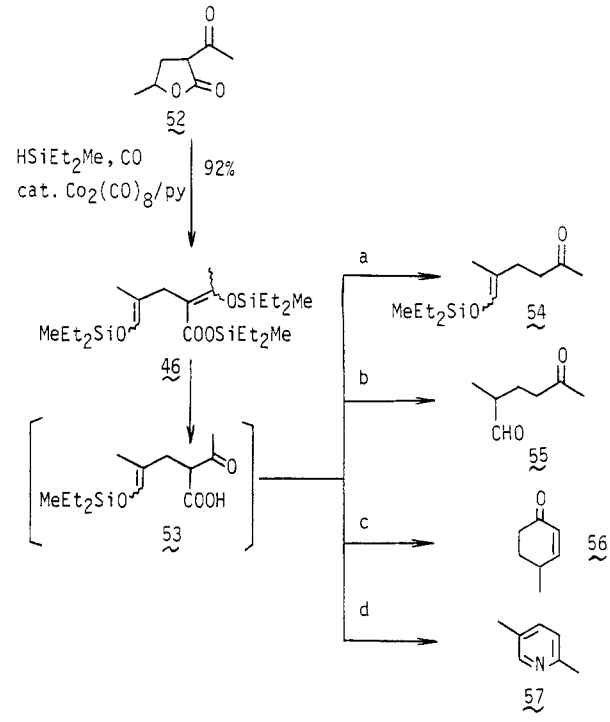
Catalytic Reaction of Lactones. Lactones of the secondary alkyl ester type underwent incorporation of carbon monoxide to give enol silyl ethers. The results obtained for the reactions using a lactone (10 mmol), $HSiEt_2Me$ (30 mmol), CO (50 atm), $Co_2(CO)_8$/pyridine (0.4 mmol/2 mmol), and benzene (20 mL) at 140 °C for 6 h are given in Table IV. In these examples, the leaving group in the carbon–oxygen bond cleavage remained in the product as the silyl ester moieties. The introduced siloxymethylidene group can be also desilylated to a formyl group, an example being shown in eq 18. A new method for the introduction of a carbon-containing functional group onto a five-membered ring is illustrated in run 5 of Table IV.



(18)

The lactones having 2-acetyl, 2-propionyl, or 2-benzoyl groups (runs 6–10) offer additional unique possibilities in organic synthesis. In the catalytic reaction of these lactones, the siloxymethylidene group has been introduced in a usual manner, and at the same time the acyl groups at the 2-position of the lactones were protected in the form of enol silyl ether.[31] Scheme III summarizes the controlled desilylation. Treatment of the trisilylated compound **46** with CH_3OH effected the removal of the two silyl groups of the β-keto ester without affecting the silyl moiety of the siloxymethylidene group. Thus, the generated β-keto acid **53** underwent spontaneous decarboxylation[32] to give 5-(sil-

Scheme III[a]



[a] (a) CH_3OH, reflux, 2 h, 64% from **46**; (b) 1 N HCl/THF, 25 °C, 30 min, 54% from **52** without purification of **46**; (c) 7 N HCl, 25 °C, 12 h, 48% from **52** without purification of **46**; (d) NH_2OH·HCl/CH_3COOH, reflux, 34% from **52** without purification of **46**.

oxymethylidene)-2-hexanone **54**. On the other hand, the complete desilylation (1 N HCl/THF, 25 °C) afforded the 5-keto aldehyde **55**. Such a 5-keto aldehyde as **55** has been known as a useful intermediate for the synthesis of cyclohexenones[33] or pyridines.[34] The reactions leading to cyclohexenone **56** and pyridine **57** via the 5-keto aldehyde **55**, generated in situ (Scheme III), illustrate further the synthetic potential of the products derived from 2-acyl-γ-lactones, **52**.

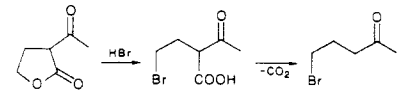
Catalytic Reaction of Primary Alkyl Acetates. *n*-Hexyl acetate reacted with $HSiEt_2Me$ and carbon monoxide in the presence of a catalytic amount of $Co_2(CO)_8$ to give several products which incorporated one, two, and even three molecules of carbon monoxide (eq 19). Under the standard conditions, 200 °C and 50 atm of CO, the expected product **58** became a major component, but considerable amounts of byproducts **24** and **59** were also formed. The formation of branched-chain isomer **24** suggests the isomerization of the primary alkylcobalt intermediate to the secondary isomer.[35] The product distribution of the reaction at a lower temperature (140 °C) may be compared to that observed for cyclohexyl acetate in which incorporation of one molecule of carbon monoxide predominated (Table I). The predominant formation of product **59** with the incorporation of two molecules of carbon monoxide at 140 °C can be attributed to the slower β-hydride elimination from **61** in which the β-hydrogen is a

(29) Letsinger, R. L.; Traynham, J. G.; Bobko, E. *J. Am. Chem. Soc.* **1952**, *74*, 399. Fried, J.; Lin, C. H.; Sih, J. C.; Dalven, P.; Cooper, C. F. *J. Am. Chem. Soc.* **1972**, *94*, 4342. Hegedus, L. S.; Holder, M. S.; Mckearin, J. M. *Organic Syntheses*; Wiley: New York, 1984; Vol. 62, p 48.

(30) In the present reaction the straight-chain isomers predominated while both straight- and branched-chain isomers were obtained from 1-hexene.[4b] This effect of the remote acetoxy group is not understood yet.

(31) Silylation of the 1,3-dicarbonyl group is known to give enol silyl ethers. Pierce, A. E. *Silylation of Organic Compounds*; Pierce Chemical Co.: Rockford, 1968.

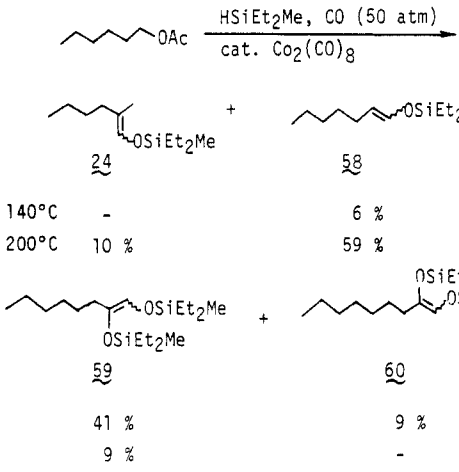
(32) For an example of similar decarboxylation, see: Smith, L. I. *J. Am. Chem. Soc.* **1951**, *73*, 4049.



(33) Baldwin, A. W.; Gawley, R. E. *Tetrahedron Lett.* **1975**, 3969.

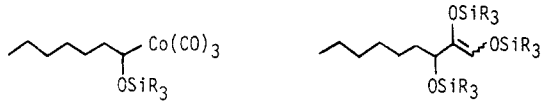
(34) Caccia, G.; Chelucci, G.; Botteghi, C. *Synth. Commun.* **1981**, *11*, 71.

(35) In contrast, the reaction of 2-hexyl acetate (run 9 in Table III) gave less than a few percent yield of straight-chain product **57**. The reason for this difference is not clear. The difference in the nature of the hydrogen atoms available for the β-hydride elimination in each alkylcobalt might be an important factor.

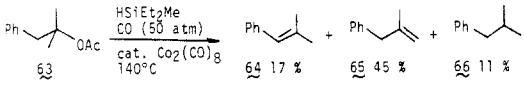


(19)

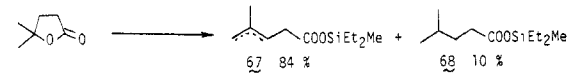
methylene type, rather than elimination from **10** having a β-hydrogen of a methine type. Incorporation of three molecules of carbon monoxide to give **60** is remarkable. The catalyzed reduction of the allylic siloxy group in the presumed intermediate **62** with $HSiEt_2Me$ could lead to the formation of **60**. The formation of **60** indicates a possibility and also a limitation in realizing the proposal on the copolymerization of carbon monoxide and a hydrosilane.[36] Further studies will be needed to understand the product distribution in eq 19. The catalytic reaction of unsubstituted δ-butyrolactone, a lactone of the primary alkyl ester type, proceeded in a similar way as *n*-hexyl acetate to give several products (by GLC), and no effort was made to characterize these products.



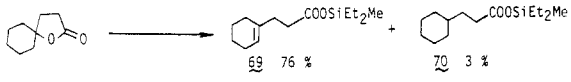
Catalytic Reaction of Tertiary Alkyl Acetates. No carbon monoxide was incorporated to tertiary alkyl esters, as shown in eq 20–22. Such results are not unexpected since only a few examples have been known for the incorporation of carbon monoxide into a tertiary carbon center with the aid of transition metals.[37] Many possibilities may be envisaged for the mechanism



(20)

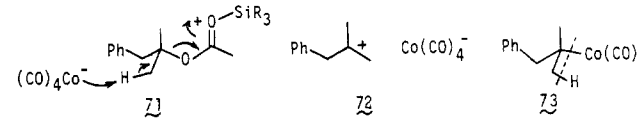


(21)

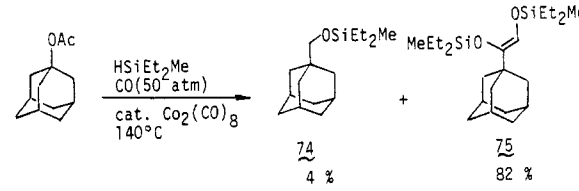


(22)

of the process leading to an alkene from a tertiary alkyl acetate: an E2 process via **71**, an S_N1 process via **72**, or β-hydride elimination from **73**. Although the exact mechanism is not clear, the product distribution in reaction 20 is not likely to be controlled by a typical carbonium ion intermediate **72**, since the yield of the 1-alkene **65** was higher than that of the thermodynamically more stable 2-alkene **64**.[38]

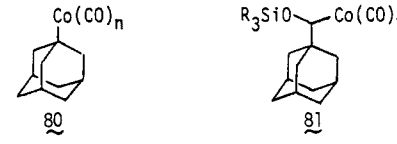


It seemed interesting to study the catalytic reaction of a tertiary alkyl acetate which could not easily undergo the formal elimination of acetic acid to give an alkene according to Bredt's rule.[39] The results obtained for some bridgehead acetates[40] are given in Table V and eq 23. The observations are the first example of a highly



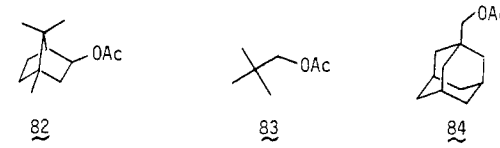
(23)

efficient, transition-metal-catalyzed incorporation of carbon monoxide onto a tertiary carbon center. The difficulty in the β-hydride elimination process from **80**[41] would be a key to the present result. The predominant formation of the product **75**



(corresponding to **4** in Scheme I) with incorporation of two molecules of carbon monoxide may be attributed to the absence of β-hydrogen atom in **81** (compared with **10** in Scheme I). It is worth mentioning that extensive studies have been carried out for the development of preparative methods for various heterocyclic compounds containing adamantyl substituents because of their promising uses in pharmaceutical application.[42] The present reaction (eq 23) will open a new possibility in this field since product **75** contains an enediol disilyl ether moiety which has been known as a useful building block for the preparation of various heterocycles.[43]

Limitations of Catalytic Incorporation of Carbon Monoxide. The catalytic reaction of secondary alkyl acetates and lactones of secondary alkyl ester type proceeds in a highly selective manner. While norbornyl acetates reacted smoothly (runs 7 and 8 in Table III), the reaction of bornyl acetate (**82**) proceeded only sluggishly



to give several products in low yields (not identified). Neopentyl

(36) See eq w in ref 18.

(37) Moreover, the few known examples of carbonylation at a tertiary carbon center were observed as a minor process or took place only sluggishly. (a) Hydroformylation of methyl methacrylate catalyzed by a rhodium complex: Pittman, C. U., Jr.; Honnick, W. D.; Yang, J. J. *J. Org. Chem.* **1980**, *45*, 684 and references cited therein. (b) Carbonylation at tertiary carbon of 2-methyl-1-propene (1% yield) under the hydroformylation (oxo) reaction conditions: Wender, I.; Feldman, J.; Meltin, G.; Gwynn, B. H.; Orchin, M. *J. Am. Chem. Soc.* **1955**, *77*, 5760. (c) Stoichiometric reaction of $HCo(CO)_4$ with 2-methyl-1-propene: Heck, R. F.; Breslow, O. S. *J. Am. Chem. Soc.* **1961**, *83*, 4023. (d) Insertion of carbon monoxide into *tert*-butyl lanthanoid complexes: Evans, W. J.; Wayda, A. L.; Hunter, W. E.; Atwood, J. L. *J. Chem. Soc., Chem. Commun.* **1975**, 706.

(38) Bunnett, J. F.; Sridharan, S. *J. Org. Chem.* **1979**, *44*, 1458. Bunnett, J. F.; Sridharan, S.; Cavin, W. P. *J. Org. Chem.* **1979**, *44*, 1463.

(39) For reviews, see: Buchanan, G. L. *Chem. Soc. Rev.* **1974**, *3*, 41. Shea, K. J. *Tetrahedron* **1980**, *36*, 1683.

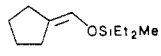
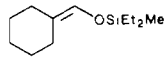
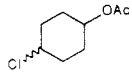
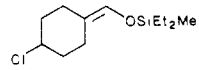
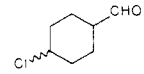
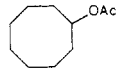
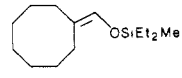
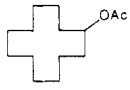
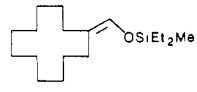
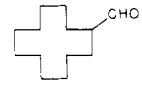
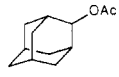
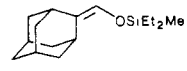
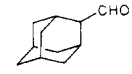
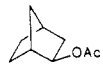
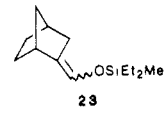
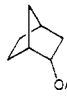
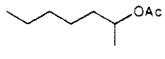
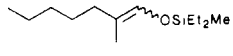
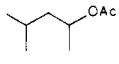
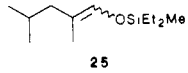
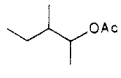
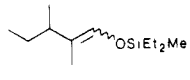
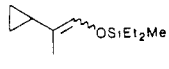
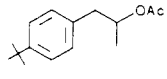
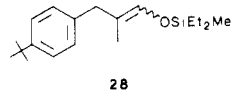
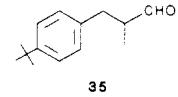
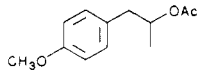
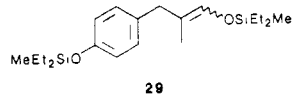
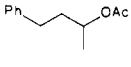
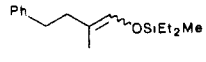
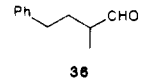
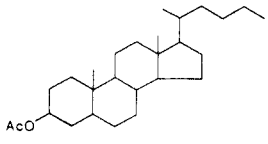
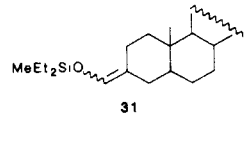
(40) For the synthesis of bridgehead alcohols, see: Aigami, K.; Inamoto, Y.; Takaishi, N.; Fujikura, Y.; Takatsuki, A.; Tamura, G. *J. Med. Chem.* **1976**, *19*, 536. Imanoto, Y.; Aigami, K.; Takaishi, N.; Fujikura, Y.; Ohsugi, M.; Ikeda, H.; Tsuchihashi, K. *J. Med. Chem.* **1979**, *22*, 1207.

(41) For related cobalt complexes, see: Goh, S. H.; Goh, L.-Y. *J. Organomet. Chem.* **1972**, *43*, 401. Bower, B. K.; Tennet, H. G. *J. Am. Chem. Soc.* **1972**, *94*, 2512.

(42) For a review, see: Fort, R. C., Jr. *Adamantane*; Marcel Dekker: New York, 1976. For some recent works, see: Reetz, M. T.; Maier, W. F.; Chatziiosifidis, I.; Giannis, A.; Heimback, H.; Lowe, U. *Chem. Ber.* **1980**, *113*, 3741. Sasaki, T.; Nakanishi, A.; Ohno, M. *J. Org. Chem.* **1982**, *47*, 3219.

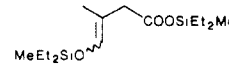
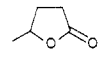
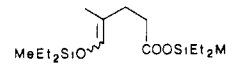
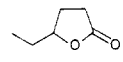
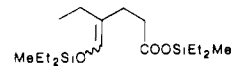
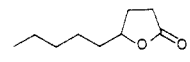
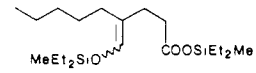
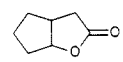
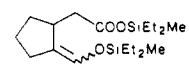
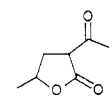
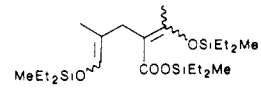
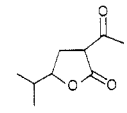
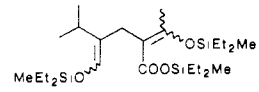
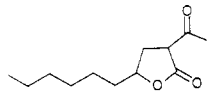
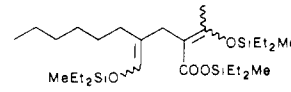
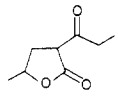
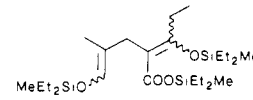
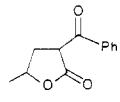
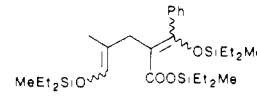
(43) For a review, see: Ruhlmann, K. *Synthesis* **1971**, 236.

Table III. Synthesis of Enol Silyl Ethers from Esters by the Cobalt-Catalyzed Reaction[a]

run	acetate	enol silyl ether	yield, %[b,c]	aldehyde[d]	isolated yield, %
1		 **18**	75		
2	 **2**	 **3**	75		
3		 **19**	60	 **32**	(93)
4		 **20**	68 (57)		
5		 **21**	56 (40)	 **33**	(93)
6		 **22**	95 (90)	 **34**	(82)
7		 **23**	68[e]		
8		**23**	87[e]		
9		 **24**	91 *Z*:*E* = 43:57		
10		 **25**	64 *Z*:*E* = 31:69		
11		 **26**	49 *Z*:*E* = 31:69		
12		 **27**	47[e]		
13		 **28**	63[f] *Z*:*E* = 40:60	 **35**	(85)
14		 **29**	56[g] *Z*:*E* = 30:70		
15		 **30**	67 *Z*:*E* = 27:73	 **36**	(93)
16		 **31**	(65)[d,e]		

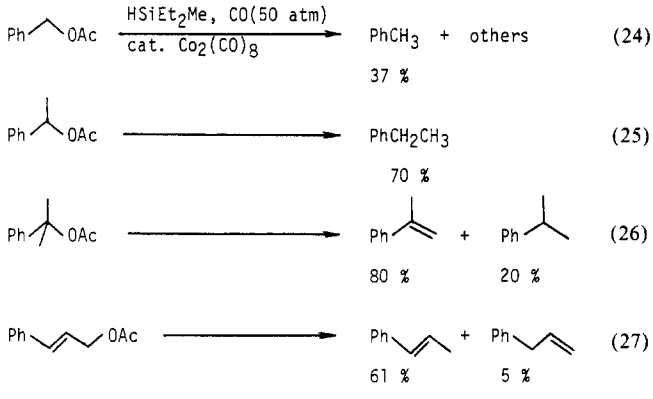
[a] Reaction conditions: an acetate (10 mmol), $HSiEt_2Me$ (30 mmol), CO (50 atm), $Co_2(CO)_8$ (0.4 mmol), C_6H_6 (20 mL), and 6 h unless otherwise noted. [b] GLC yields based on the acetates. Isolated yields are in parentheses. [c] The ratio of stereoisomers was determined by GLC. [d] Yields are of isolated products purified by column chromatography (silica gel). [e] The ratio of stereoisomers was not determined. [f] $HSiEt_2Me$ (50 mmol) and $Co_2(CO)_8$ (0.8 mmol) were used. [g] $HSiEt_2Me$ (70 mmol) and $Co_2(CO)_8$ (0.8 mmol) were used.

Table IV. Synthesis of Enol Silyl Ethers from Lactones by the Cobalt Carbonyl Catalyzed Reaction[a]

run	lactone	enol silyl ether	yield, %[b,c]
1		 **41**	88 (73) Z:E = 48:52
2		 **42**	87 Z:E = 38:62
3		 **43**	67 Z:E = 46:54
4		 **44**	81 (73)[d]
5		 **45**	70[d]
6	 **52**	 **46**	92 (85)[e,f]
7		 **47**	74[e-g]
8		 **48**	81[e-g]
9		 **49**	79[e-g]
10		 **50**	71[e-g]

[a] Reaction conditions: a lactone (10 mmol), $HSiEt_2Me$ (30 mmol), CO (50 atm), $Co_2(CO)_8$ (0.4 mmol), pyridine (2 mmol), C_6H_6 (20 mL), 140 °C, and 6 h unless otherwise noted. [b] GLC yields based on the lactones. Isolated yields are in parentheses. [c] The ratio of stereoisomers was determined by GLC. [d] The ratio of stereoisomers was not determined. [e] For the ratio of stereoisomers, see the Experimental Section. [f] 50 mmol of $HSiEt_2Me$ was used. [g] The reaction was run at 110 °C.

acetate (**83**) and 1-adamantylmethyl acetate (**84**) did not give any detectable amount of products. These results indicate that the present catalytic reaction is somewhat sensitive to steric congestion at the reaction site. Not unexpectedly, phenyl acetate did not react. Benzyl or allylic acetates were reduced probably by $HSiEt_2Me$[44] or less likely by $HCo(CO)_4$.

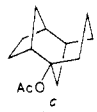
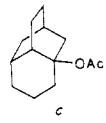


Summary

A new methodology for making carbon–cobalt bonds, by utilizing the high affinity of silicon in $R_3SiCo(CO)_4$ for oxygen, has resulted in the development of new catalytic reactions of alkyl acetates and also lactones with hydrosilane ($HSiR_3$) and carbon monoxide in the presence of $Co_2(CO)_8$. The suggested key catalyst species is (trialkylsilyl)cobalt tetracarbonyl ($R_3SiCo(CO)_4$), which has hard acid–soft base components. The $HSiR_3/CO/Co_2(CO)_8$ system initiates either the $HCo(CO)_3$-based catalytic cycle for olefins or the $R_3SiCo(CO)_4$-based catalytic cycle for esters. These two modes can be controlled, both in the inter- and intramolecularly competitive cases, by simply changing the molar ratio of the substrate (an olefin or an ester function) to the $HSiR_3$ (Scheme II, eq 15–17). It appears that the product distribution in the catalytic reactions is determined by the relative ease of β-elimination of $HCo(CO)_3$ from the alkyl- and/or (α-siloxyalkyl)cobalt carbonyls formed as the intermediates at various stages in the catalytic cycle. The rate of β-hydride elimination seems faster in the order tertiary alkyl > secondary alkyl > primary alkyl for

(44) For a review of reduction with hydrosilane, see: Nagai, Y. *Org. Prep. Proced. Int.* **1980**, *12*, 13.

Table V. Catalytic Reaction of Bridgehead Acetates with $HSiEt_2Me$ and CO[a]

substrate ROAc	product: R–OSiEt$_2$Me	product: R(OSiEt$_2$Me)^b–OSiEt$_2$Me
	**74**, 4%	**75**, 82%
	**76**, 17%	**77**, 78%
	**78**, 19%	**79**, 63%

[a] Reaction conditions: an acetate (2.5 mmol), $HSiEt_2Me$ (12.5 mmol), CO (50 atm), $Co_2(CO)_8$ (0.1 mmol), C_6H_6 (20 mL), 140 °C, and 6 h unless otherwise noted. [b] Only *Z* isomers were formed. [c] Pyridine (1 mmol) was added.

$RCo(CO)_4$ intermediates and also in the order methine > methylene with respect to the β-carbon center. Thus catalytic reactions of secondary alkyl acetates (Table III) and lactones of secondary alkyl ester type (Table IV) and of bridgehead acetates (Table V) underwent selective incorporation of one and two molecules of carbon monoxide, respectively. The latter represents the very rare example of the transition-metal-mediated incorporation of carbon monoxide into a tertiary carbon center. From the viewpoint of organic synthesis, the present catalytic reaction provides a novel method for the introduction of the siloxymethylidene or 1,2-disiloxyvinyl group into carbon atoms bearing an acetoxy group. The products obtained are enol silyl ethers of a type otherwise hardly accessible. Enol silyl ethers are known as extremely useful synthetic intermediates. All of the catalytic transformations described in this paper are unprecedented. The potential of the $HSiR_3/CO/Co_2(CO)_8$ system will be further demonstrated in the forthcoming papers.

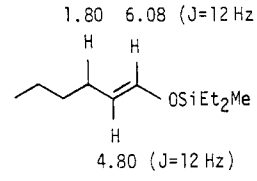
Experimental Section

General Procedures. Boiling points and melting points are uncorrected. Infrared spectra were recorded on a Shimazu IR-400 spectrometer; absorptions are reported in reciprocal centimeters. ^1H NMR were recorded on a JEOL JNM-PS-100 spectrometer and are reported in ppm from internal tetramethylsilane on the δ scale. Data are reported as follows: chemical shift, multiplicity (s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, c = complex, and br = broad), coupling constant (Hz), integration, and interpretation. ^{13}C NMR were recorded on a JEOL JNM-FX-60S spectrometer and are reported in ppm from trimethylsilane (on the δ scale). Mass spectra were recorded on a Hitachi Model RMU-6E. Elemental analyses were performed by Elemental Analyses Section of Osaka University. Analytical GLC was carried out on a Shimazu GC-3BF gas chromatograph, equipped with a flame ionization detector, using a 6-m × 3-mm stainless steel column packed with 5% Silicone OV-1 on 60–80-mesh Chromosorb W. Preparative GLC was performed on a Hitachi 164 gas chromatograph using a 2-m × 10-mm stainless steel column packed with 10% Silicone OV-1 on 60–80-mesh Chromosorb W and 15% DEGS on 60–80-mesh Chromosorb W. Benzene and toluene were distilled from sodium–lead alloy. Dichloromethane was distilled from CaH_2. All solvents were stored under nitrogen. Inorganic chemicals used as the catalysts were commercially obtained from Strem Chemicals, Inc., and were used without further purification except for the following. A cluster complex $C_6H_5CCo_3(CO)_9$ was prepared according to the literature.[45] $Co_2(CO)_8$ was obtained from Strem Chemicals, Inc., and purified by low-temperature recrystallization (*n*-hexane, −20 °C). The alkyl acetates were prepared by the acetylation (Ac_2O/pyridine or CH_3COCl/*N*,*N*-dimethylaniline) of the corresponding alcohols. Most of the alcohols were commercially purchased or prepared by $NaBH_4$ reduction of ketones. *trans*-4-Chlorocyclohexanol,[46] *exo*-norbornanol,[47] and *endo*-norbornanol[48] were prepared by a literature method. 1-(4-*tert*-Butylphenyl)-2-propanol was prepared by the treatment of acetoaldehyde with (4-*tert*-butylbenzyl)magnesium bromide. *trans*-2-Allylcyclopentanol was prepared by the treatment of cyclopentene oxide with allylmagnesium bromide. Lactones used in runs 1–4 of Table IV were commercially available. The lactone used in run 5 of Table IV was prepared by MCPBA oxidation of a corresponding cyclobutanone. Lactones used in runs 6–10[49] of Table IV were prepared according to the literature indicated.

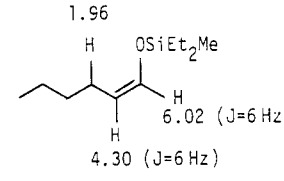
General Procedure for the $Co_2(CO)_8$-Catalyzed Reaction of an Ester or a Lactone with $HSiR_3$ and CO. In a 100-mL stainless steel autoclave were placed a magnetic stirring bar, 0.4 mmol of $Co_2(CO)_8$, 30 mmol of an appropriate hydrosilane $HSiR_3$, 2 mmol of additive (if necessary), 20 mL of benzene, and 10 mmol of an ester (or a lactone) in this order. The autoclave was charged with carbon monoxide to 50 atm at 25 °C and then heated with stirring in an oil bath at 200 or 140 °C and for 6 or 20 h. After the reaction, the autoclave was cooled and depressurized. When appropriate, a few drops of pyridine were added to the mixture, and the mixture was exposed to air for 10 min to precipitate the cobalt-containing compounds. The precipitates were removed by centrifugation. Solvent was evaporated in vacuo, and distillation (bulb-to-bulb and/or fractional distillation) gave an essentially pure sample of the products. When necessary, purification by preparative GLC was carried out. For GLC yields, appropriate hydrocarbons (n-C_nH_{2n+2}) calibrated against purified products obtained in a separate run were added before or immediately after the catalytic reaction. The yields of the products are described in tables or in the text.

Enol silyl ethers **3**,[4c] **18**,[4c] **20**,[4c] **23**,[4c] **24**[4b] and **58**[4b] were already reported. Physical properties of new compounds thus obtained are recorded below.

The assignment of *E* and *Z* isomers of the siloxymethylidene compounds has been based on their ^1H and ^{13}C NMR spectra. There have been several reports on the *E*/*Z* assignment of enol silyl ethers having a β-vinyl proton by using ^1H NMR.[50] However, almost no data seem to be available to our knowledge for the *E*/*Z* assignment of enol silyl ethers which have an α-vinyl proton and two β-alkyl groups such as those obtained in the present study. Consequently, a 30:70 mixture of β-monoalkyl enol silyl ethers **85** and **86** was prepared by House's method B[50a]



85



86

from *n*-hexanal and $MeEt_2SiCl$ (Et_3N/DMF) in 60% combined yield. Isomers separated by preparative GLC showed ^1H NMR chemical shifts as shown above. The assignment of **85** for *E* and **86** for *Z* is straightforward from their coupling constants between α- and β-vinyl protons. In these isomers, γ-methylene protons cis to the siloxy group resonate downfield from those that are trans by 0.16 ppm. Application of this γ-methylene proton shift to the *E*/*Z* assignment of β,β-dialkyl enol silyl ethers leads to the assignment of *E* configuration for the isomers showing γ-methylene protons at higher fields and *Z* configuration for those with lower γ-methylene signals.[51]

^{13}C NMR has been recently used for the *E*/*Z* assignment of enol ethers.[52,53] As in the case of ^1H NMR, there are almost no established

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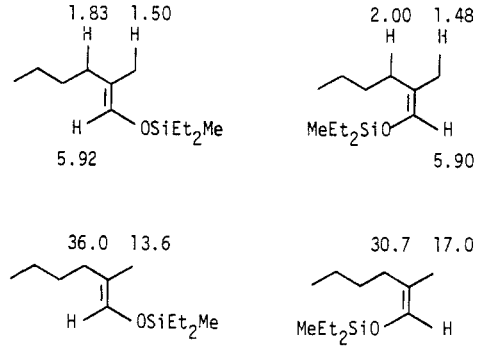
methods using ^{13}C NMR for the E/Z assignment of β,β-dialkyl enol (silyl) ethers. However, a survey of these literatures suggests that a γ-carbon cis to a methoxy group resonates 1–4 ppm upfield than a trans γ-carbon. Crandall has also drawn the same conclusion.[53]



[(4-Chlorocyclohexylidene)methoxy]diethylmethylsilane (19): bp 100–120 °C (5 mmHg); IR (neat) 2930, 2910, 2870, 1680 (C=C), 1450, 1255, 1175, 1140, 1060, 1005, 965, 825, 800, 770 cm^{-1}; NMR (CCl_4) δ 0.10 (s, 3 H, $SiCH_3$), 0.46–0.79 (m, 4 H, $SiCH_2$–), 0.79–1.15 (m, 6 H, $SiCCH_3$), 1.42–2.80 (c, 8 H, $-CH_2-$, $=CCH_2-$), 4.08 (tt, J = 6, 15 Hz, 1 H, ClCH–), 6.01 (s, 1 H, =CH); mass spectrum, m/e (relative intensity) 248 (15, $M^+ + 2$), 246 (38, M^+), 217 (23, $M^+ - Et$), 109 (35), 107 (35), 101 (26), 93 (100), 73 (43). Anal. Calcd for $C_{12}H_{23}OSiCl$: C, 58.39; H, 9.39; Cl, 14.36. Found: C, 58.43; H, 9.67; Cl, 14.29.

[(Cyclododecylidene)methoxy]diethylmethylsilane (21): bp 116–120 °C (0.95 mmHg); IR (neat) 2920, 2870, 2850, 1660 (C=C), 1470, 1450, 1250, 1200, 1180, 1160, 1120, 1000, 960, 850, 830, 820, 800, 770 cm^{-1}; NMR (CCl_4) δ 0.10 (s, 3 H, $SiCH_3$), 0.67 (m, 4 H, $SiCH_3$–), 0.97 (m, 6 H, $SiCCH_3$), 1.90 (t, J = 6 Hz, 2 H, $=CCH_2-$ trans to OSi), 2.08 (t, J = 6 Hz, 2 H, $=CCH_2-$ cis to OSi), 6.01 (s, 1 H, =CH); mass spectrum, m/e (relative intensity) 296 (61, M^+), 267 (21, $M^+ - Et$), 183 (11), 177 (11), 101 (32), 89 (100). Anal. Calcd for $C_{18}H_{36}OSi$: C, 72.90; H, 12.24. Found: C, 72.67; H, 12.40.

Diethylmethyl[(tricyclo[3.3.1.1^{3,7}]decylidene)methoxy]silane (22): bp 103–104.5 °C (0.28 mmHg); IR (neat) 2950, 2900, 2850, 1685 (C=C), 1470, 1465, 1455, 1420, 1390, 1275, 1210, 1140, 1100, 1080, 1005, 860, 815 cm^{-1}; NMR (CCl_4) δ 0.09 (s, 3 H, $SiCH_3$), 0.41–0.77 (m, 4 H, $SiCH_2$–), 0.81–1.13 (m, 6 H, $SiCCH_3$), 1.56–2.07 (c, 12 H, $-CH_2-$, –CH–), 2.19 (m, 1 H, =CCH– trans to OSi), 2.98 (m, 1 H, =CCH– cis to OSi), 5.94 (s, 1 H, =CH); mass spectrum, m/e (relative intensity) 264 (100, M^+), 235 (58, $M^+ - Et$), 101 (17), 89 (29). Anal. Calcd for $C_{16}H_{28}OSi$: C, 72.66; H, 10.68. Found: C, 73.00; H, 11.06.

Diethyl[(2,4-dimethyl-1-pentenyl)oxy]methylsilane (25): bp 92–95 °C (27 mmHg); IR (neat) 2850–2950, 2825, 1670 (C=C), 1460, 1410, 1380, 1360, 1260, 1240, 1150–1180, 1080, 1000, 960, 940, 880, 820, 800, 760, 680 cm^{-1}; NMR (CCl_4) δ 0.09 (s, 3 H, $SiCH_3$), 0.66 (m, 4 H, $SiCH_2$–), 0.77–1.17 (c, 12 H, $SiCCH_3$, $-CH_3$), 1.50 (s, 3 H, $=CCH_3$), 1.68 (m, 2 H, $=CCH_2-$), 1.89 (m, 1 H, –CH–), 5.97 (m, 1 H, =CH); mass spectrum, m/e (relative intensity) 214 (11, M^+), 171 (91), 153 (8), 101 (100). Anal. Calcd for $C_{12}H_{26}OSi$: C, 67.22; H, 12.22. Found: C, 66.95; H, 12.46.

Diethyl[(2,3-dimethyl-1-pentenyl)oxy]methylsilane (26): bp 70–87 °C (23 mmHg); IR (neat) 2950, 2930, 2910, 2870, 1670 (C=C), 1460, 1415, 1380, 1255, 1250, 1175, 1130, 1015, 1005, 970, 860, 835, 800, 770, 760, 685 cm^{-1}; NMR (CCl_4) δ 0.08 (s, 3 H, $SiCH_3$), 0.40–1.52 (c, 22 H, including $=CCH_3$ singlet at 1.40 ppm, $SiCH_2CH_3$, $-CH_3$, $-CH_2-$, –CH–, $=CCH_3$), 5.94 (s, 1 H, =CH); mass spectrum, m/e (relative intensity) 214 (17, M^+), 185 (100, M – Et), 157 (61), 101 (94), 73 (46). Anal. Calcd for $C_{12}H_{26}OSi$: C, 67.22; H, 12.22. Found: C, 67.58; H, 12.48.

[(2-Cyclopropyl-1-propenyl)oxy]diethylmethylsilane (27): bp 100–130 °C (30 mmHg); IR (neat) 3000, 2950, 2900, 2875, 1670 (C=C), 1465, 1420, 1380, 1255, 1240, 1180, 1160, 1050, 1010, 1005, 960, 840, 795, 765, 755 cm^{-1}; NMR (CCl_4) δ [0.09 (s, $SiCH_3$), 0.10 (s, $SiCH_3$), total 3 H], 0.21–1.14 (c, 15 H, $SiCH_2CH_3$, CH_2CHCH_2), [1.13 (s, 1.35 H, =CCH of Z isomer), 1.44 (s, 1.65 H, $=CCH_3$ of E isomer), total 3 H], 1.56–2.01 (m, 1 H, –CH–), 6.06 (s, 1 H, =CH); mass spectrum, m/e (relative intensity) 198 (19, M^+), 185 (10, $M^+ - Et$), 183 (12), 169 (16), 101 (23), 89 (100), 73 (48). Anal. Calcd for $C_{11}H_{22}OSi$: C, 66.60; H, 11.18. Found: C, 66.28; H, 11.40.

Diethyl[[3-[4-(1,1-dimethylethyl)phenyl]-2-methyl-1-propenyl]oxy]methylsilane (28): bp 116–120 °C (0.55 mmHg); IR (neat) 2960, 2910, 2880, 1680 (C=C), 1520, 1465, 1420, 1370, 1260, 1240, 1185, 1155, 1100, 1051, 995, 970, 850, 835, 825, 800, 770, 690 cm^{-1}; NMR (CCl_4) δ [0.12 (s, $SiCH_3$), 0.14 (s, $SiCH_3$), total 3 H], 0.48–0.80 (m, 4 H, $SiCH_3$), 0.84–1.12 (m, 6 H, $SiCCH_3$), 1.28 (s, 9 H, $-C(CH_3)_3$), 1.44 (c, 3 H, $=CCH_3$), [3.06 (s, 1.3 H, $PhCH_2C=$ of E isomer), 3.30 (s, 0.7 H, $PhCH_2C=$ of Z isomer), total 2 H], 6.09 (m, 1 H, =CH), 6.90–7.29 (m, 4 H, aromatic H); mass spectrum, m/e (relative intensity) 304 (100, M^+), 289 (46, $M^+ - Me$), 275 (38, $M^+ - Et$), 247 (62), 145 (50), 101 (50), 89 (62), 73 (81). Anal. Calcd for $C_{19}H_{32}OSi$: C, 74.93; H, 10.59. Found: C, 74.44; H, 10.79.

Diethyl[[3-[4-[(diethylmethylsilyl)oxy]phenyl]-2-methyl-1-propenyl]oxy]methylsilane (29): bp 150–180 °C (3 mmHg, bulb-to-bulb distillation); IR (neat) 2960, 2910, 2880, 1680 (C=C), 1610, 1510, 1465, 1420, 1260, 1190, 1055, 1110, 970, 915, 830, 800, 770, 690 cm^{-1}; NMR (CCl_4) δ 0.12 (s, 3 H, $SiCH_3$), 0.18 (s, 3 H, $SiCH_3$), 0.45–0.81 (m, 8 H, $SiCH_3$–), 0.81–1.17 (m, 12 H, $SiCCH_3$), 1.44 (s, 3 H, $=CCH_3$), [3.06 (s, 1.4 H, $=CCH_2-$ of E isomer), 3.27 (s, 0.6 H, $=CCH_2-$ of Z isomer), total 2 H], 6.12 (m, 1 H, =CH), 6.57–7.07 (m, 4 H, aromatic H); mass spectrum, m/e (relative intensity) 364 (100, M^+), 349 (63, $M^+ - Me$), 335 (19, $M^+ - Et$), 265 (15), 247 (67), 237 (22), 207 (33), 101 (44), 73 (100). Anal. Calcd for $C_{20}H_{36}O_2Si_2$: C, 65.87; H, 9.95. Found: C, 65.78; H, 10.17.

Diethylmethyl[(2-methyl-4-phenyl-1-butenyl)oxy]silane (30): bp 100–120 °C (2 mmHg, bulb-to-bulb distillation); IR (neat) 3030, 2950, 2940, 2910, 2880, 1660 (C=C), 1610, 1500, 1260, 1180, 1160, 1140, 1080, 1010, 970, 850, 835, 770, 750, 700 cm^{-1}; NMR (CCl_4) δ [0.03 (s, $SiCH_3$), 0.06 (s, $SiCH_3$), total 3 H], 0.24–0.78 (m, 4 H, $SiCH_2$–), 0.78–1.11 (m, 6 H, $SiCCH_3$), [1.50 (s, 0.75 H, $=CCH_3$ of Z isomer), 1.56 (s, 2.25 H, $=CCH_3$ of E isomer), total 3 H], 1.71–2.46 (m, 2 H, $=CCH_2-$), 2.64 (t, J = 9 Hz, 2 H, $PhCH_2-$), 5.84–6.05 (m, 1 H, =CH), 6.93–7.32 (m, 5 H, aromatic H); mass spectrum, m/e (relative intensity) 262 (4, M^+), 233 (5, $M^+ - Et$), 143 (9), 101 (80), 91 (17), 89 (14), 73 (46), 61 (100). Anal. Calcd for $C_{16}H_{26}OSi$: C, 73.22; H, 9.99. Found: C, 72.95; H, 10.05.

(Cholestanylidenemethoxy)diethylmethylsilane (31): R_f 0.16 (n-hexane); IR (neat) 2900, 2860, 2830, 1680 (C=C), 1465, 1455, 1450, 1380, 1250, 1160, 1110, 1005, 820, 800, 765 cm^{-1}; NMR (CCl_4) δ 0.08 (s, 3 H, $SiCH_3$), 0.65 (m, 4 H, $SiCH_2$–), 0.77–2.16 (c, 52 H, $SiCCH_3$, steroid flamework), 5.90 (s, 1 H, =CH); mass spectrum, m/e (relative intensity) 500 (100, M^+), 485 (2, $M^+ - Me$), 471 (3, $M^+ - Et$), 171 (12), 101 (14), 73 (17). Anal. Calcd for $C_{33}H_{60}OSi$: C, 79.12; H, 12.07. Found: C, 78.94; H, 12.37.

Diethylmethyl[(2-methylbicyclo[3.3.0]oct-1-en-1-yl)oxy]silane (37): bp 85–87 °C (1 mmHg); IR (neat) 2940, 2910, 2875, 2830, 1690 (C=C), 1460, 1450, 1415, 1385, 1340, 1300, 1285, 1255, 1210, 1160, 1130, 1095, 1075, 1010, 970, 950, 880, 795, 770, 690 cm^{-1}; NMR (CCl_4) δ 0.10 (s, 3 H, $SiCH_3$), 0.42–0.78 (m, 4 H, $SiCH_2$–), 0.78–1.10 (m, 6 H, $SiCCH_3$), 1.10–1.94 (c, with a singlet superimposed at 1.45 ($=CCH_3$), 10 H, $-CH_2-$, –CH–, =CCH–), 2.66–2.98 (c, 1 H, =CCH–); mass spectrum, m/e (relative intensity) 238 (100, M^+), 223 (18, $M^+ - Me$), 209 (44, $M^+ - Et$), 197 (28), 101 (51), 89 (100). Anal. Calcd for $C_{10}H_{26}OSi$: C, 70.52; H, 10.99. Found: C, 70.67; H, 11.21.

Diethyl[(2,5-dimethyl-1-cyclopentenyl)oxy]methylsilane (39): bp 115–120 °C (26 mmHg); IR (neat) 2960, 2800, 1690 (C=C), 1455, 1370, 1325, 1240, 1205, 1090, 1000, 905, 890, 850, 795, 775, 750, 685 cm^{-1}; NMR (CCl_4) δ 0.09 (s, 3 H, $SiCH_3$), 0.42–0.76 (m, 4 H, $SiCH_2$–), 0.76–1.08 (c, 11 H, $SiCCH_3$, $-CH_3$, $-CH_2-$), 1.26 (s, 3 H, $=CCH_3$), 1.65–2.05 (c, 3 H, $=CCH_2-$, =CCH–); mass spectrum, m/e (relative intensity) 212 (60, M^+), 197 (30), 186 (54), 89 (100), 73 (68). Anal. Calcd for $C_{12}H_{24}OSi$: C, 67.86; H, 11.39. Found: C, 67.62; H, 11.62.

[(6-Acetoxy-1-hexenyl)oxy]diethylmethylsilane (40): bp 100–110 °C (0.85 mmHg); IR (neat) 3040, 2960, 2930, 2870, 1740 (C=O), 1660 (C=C), 1460, 1410, 1370, 1235, 1160, 1140, 1080, 1015, 970, 950, 925, 805, 770, 690 cm^{-1}; NMR (CCl_4) δ 0.10 (s, 3 H, $SiCH_3$), 0.38–0.74 (m, 4 H, $SiCH_2$–), 0.74–1.08 (m, 6 H, $SiCCH_3$), 1.12 (d, J = 7 Hz, $-CH_3$), 1.27–1.66 (c, 4 H, $-CH_2-$), 1.66–2.17 (c, with a singlet superimposed at 1.93 ($COCH_3$), 5 H, $=CCH_2-$, $COCH_3$), [4.33 (pseudo t, J = 6 Hz, 0.4 H, C=CH– of Z isomer), 4.60–4.99 (m, with a doublet–triplet superimposed at 4.80 (J = 6, 12 Hz, 0.6 H, C=CH– of E isomer), 1.6 H, C=CH–, OCH–), total 2 H], [6.02 (d, J = 6 Hz, =CH of Z isomer), 6.05 (d, J = 12 Hz, =CH of E isomer), total 1 H]; mass spectrum, m/e (relative intensity) 272 (2, M^+), 213 (14), 161 (100), 157 (25), 131 (97), 101 (76), 89 (54), 73 (46). Anal. Calcd for $C_{14}H_{28}O_3Si$: C, 61.72; H, 10.36. Found: C, 61.59; H, 10.21.

4-[(Diethylmethylsilyl)oxy]-3-methyl-3-butenoic Acid Diethylmethylsilyl Ester (41): bp 123–125 °C (3 mmHg); IR (neat) 2955, 2920, 2860, 1700 (C=O), 1680 (C=C), 1465, 1420, 1335, 1275, 1260, 1240, 1185, 1150, 1010, 965, 835, 800, 770 cm^{-1}; NMR (CCl_4) δ 0.12 (s, 3 H, $SiCH_3$), 0.20 (s, 3 H, $SiCH_3$), 0.44–1.24 (m, 20 H, $SiCH_2CH_3$), 1.60 (m, 3 H, $=CCH_3$), [2.76 (s, 1 H, $=CCH_2CO$ of E isomer), 3.00 (s, 1 H, $=CCH_2CO$ of Z isomer), total 2 H], 6.08 (m, 1 H, =CH); mass spectrum, m/e (relative intensity) 316 (7, M^+), 287 (25, $M^+ - Et$), 193 (100), 101 (90), 91 (83). Anal. Calcd for $C_{15}H_{32}O_3Si_2$: C, 56.91; H, 10.19. Found: C, 56.83; H, 10.35.

5-[(Diethylmethylsilyl)oxy]-4-methyl-4-pentenoic Acid Diethylmethylsilyl Ester (42): bp 117–118 °C (0.35 mmHg); IR (neat) 2940, 2890, 2870, 1720 (C=O), 1660 (C=C), 1460, 1415, 1255, 1180, 1145, 1010, 965, 845, 830, 800, 765 cm^{-1}; NMR (CCl_4) δ 0.10 (s, 3 H, $SiCH_3$), 0.20 (s, 3 H, $SiCH_3$), 0.64–1.24 (m, 20 H, $SiCH_2CH_3$), 1.57 (m, 3 H, $=CCH_3$), 2.03–2.47 (m, 4 H, $=CCH_2-$, $COCH_2-$), [5.98 (m, 0.3 H, =CH), 6.04 (m, 0.7 H, =CH), total 1 H]; mass spectrum, *m/e* 330 (26, M^+), 301 (39, M^+ – Et), 189 (41), 171 (100), 101 (87). Anal. Calcd for $C_{16}H_{34}O_3Si_2$: C, 58.13; H, 10.34. Found: C, 57.87; H, 10.71.

5-[(Diethylmethylsilyl)oxy]-4-ethyl-4-pentenoic Acid Diethylmethylsilyl Ester (43): bp 114 °C (0.38 mmHg); IR (neat) 2940, 2900, 2860, 1710 (C=O), 1660 (C=C), 1460, 1410, 1360, 1250, 1170, 1140, 1060, 1000, 980, 790, 760 cm^{-1}; NMR (CCl_4) δ 0.10 (s, 3 H, $SiCH_3$), 0.20 (s, 3 H, $SiCH_3$), 0.44–1.16 (c, 23 H, $SiCH_2CH_3$, $-CH_3$), 1.72–2.28 (c, 6 H, $=CCH_2-$, $-COCH_2-$), 6.00 (s, 1 H, =CH); mass spectrum, *m/e* (relative intensity) 344 (28, M^+), 315 (43, M^+ – Et), 198 (43), 185 (100), 101 (76). Anal. Calcd for $C_{17}H_{36}O_3Si_2$: C, 59.24; H, 10.53. Found: C, 58.85; H, 10.71.

4-[[(Diethylmethylsilyl)oxy]methylene]nonanoic Acid Diethylmethylsilyl Ester (44): bp 135–140 °C (0.68 mmHg); IR (neat) 2960, 2930, 2880, 1725 (C=O), 1675 (C=C), 1465, 1420, 1385, 1370, 1260, 1150, 1010, 970, 805, 770, 695 cm^{-1}; NMR (CCl_4) δ 0.10 (s, 3 H, $SiCH_3$), 0.19 (s, 3 H, $SiCH_3$), 0.52–1.20 (m, 23 H, $SiCH_2CH_3$, $-CH_3$), 1.20–1.62 (m, 6 H, $-CH_2-$), 1.70–2.40 (m, 6 H, $=CCH_2-$, $COCH_2-$), [6.00 (m, 0.4 H, =CH), 6.07 (m, 0.6 H, =CH), total 1 H]; mass spectrum, *m/e* (relative intensity) 386 (3, M^+), 249 (100), 131 (46), 89 (69). Anal. Calcd for $C_{19}H_{42}O_3Si_2$: C, 62.11; H, 10.95. Found: C, 61.87; H, 11.17.

2-[[(Diethylmethylsilyl)oxy]methylene]cyclopentaneacetic Acid Diethylmethylsilyl Ester (45): bp 110–120 °C (0.4 mmHg, bulb-to-bulb distillation); IR (neat) 2950, 2910, 1875, 1715 (C=O), 1685 (C=C), 1465, 1415, 1360, 1280, 1255, 1180, 1140, 1005, 965, 800, 770, 690 cm^{-1}; NMR (CCl_4) δ 0.09 (s, 3 H, $SiCH_3$), 0.20 (s, 3 H, $SiCH_3$), 0.45–1.14 (m, 20 H, $SiCH_2CH_3$), 1.17–3.15 (c, 9 H, $-CH_2-$, $=CCH_2-$, =CCH–, $COCH_2-$), 6.12 (m, 1 H, =CH); mass spectrum, *m/e* (relative intensity) 356 (12, M^+), 327 (12, M^+ – Et), 210 (50), 197 (100), 101 (62), 73 (87). Anal. Calcd for $C_{18}H_{36}O_3Si_2$: C, 60.62; H, 10.17. Found: C, 60.83; H, 10.35.

5-[(Diethylmethylsilyl)oxy]-2-[1-[(diethylmethylsilyl)oxy]ethylidene]-4-methyl-4-pentenoic Acid Diethylmethylsilyl Ester (46): bp 160–170 °C (1 mmHg, bulb-to-bulb distillation); IR (neat) 2950, 2900, 2870, two strong absorptions with nearly equal intensities at 1680 and 1610 (the trisubstituted C=C at 1680 overlapping with C=CC=O at 1680 and 1610), 1460, 1415, 1380, 1295, 1255, 1210, 1155, 1125, 1065, 1000, 965, 900, 820, 790, 690 cm^{-1}; NMR (CCl_4) δ 0.07 (s, 3 H, $SiCH_3$), 0.21 (s, 6 H, $SiCH_3$), 0.31–1.15 (m, 30 H, $SiCH_2CH_3$), [1.35 (m, 0.6 H, $=CCH_3$ *Z* configuration), 1.47 (m, 2.4 H, $=CCH_3$ *E* configuration), total 3 H], [2.11 (s, 0.3 H, $=C(OSi)CH_3$ cis to COOSi), 2.25 (s, 2.7 H, $=C(OSi)CH_3$ trans to COOSi), total 3 H], [2.79 (s, 1.6 H, $=CCH_2C=$ *E* configuration), 3.07 (s, 0.4 H, $=CCH_2C=$ *Z* configuration), total 2 H], 5.93 (m, 1 H, =CH). Of the above mixture, 90% (100 × 2.7/3) could be accounted for by 5-[(diethylmethylsilyl)oxy]-2(*Z*)-[1-[(diethylmethylsilyl)oxy]ethylidene]-4-methyl-4(*E*)-pentenoic acid diethylmethylsilyl ester, which will be referred to as the (*Z*,*E*)-isomer (δ 1.47, 2.25, 2.79) and the (*Z*,*Z*)-isomer (δ 1.35, 2.25, 3.07), present in a ratio of 75:25 (or 2.4:0.6 or 1.6:0.4). These two isomers corresponded to two major peaks (79:21) in GLC. The absorption at 2.11 (CH_3 cis to COOSi) may indicate the presence of the (*E*,*E*)- and/or (*E*,*Z*)-isomer (total 10%). Mass spectrum, *m/e* (relative intensity) 472 (3, M^+); 443 (26, M^+ – Et), 354 (60), 325 (86), 101 (60), 73 (100). Anal. Calcd for $C_{23}H_{48}O_4Si_3$: C, 58.42; H, 10.23. Found: C, 58.22; H, 10.37.

2-[1-[(Diethylmethylsilyl)oxy]ethylidene]-4-[[(diethylmethylsilyl)oxy]-methylene]-5-methylhexanoic Acid Diethylmethylsilyl Ester (47): bp 160–170 °C (0.6 mmHg, bulb-to-bulb distillation); IR (neat) 2950, 2910, 2875, 1685 (trisubstituted C=C, C=O), 1615 (tetrasubstituted C=C), 1460, 1420, 1380, 1255, 1210, 1150, 1125, 1060, 1020, 965, 840, 790, 690 cm^{-1}; NMR (CCl_4) δ 0.06 (s, 3 H, $SiCH_3$), 0.20 (s, 6 H, $SiCH_3$), 0.39–1.19 (c, 36 H, $SiCH_2CH_3$, $-CH_3$), [1.53 (m, $=CCH_2-$ *Z* configuration), 1.80 (m, $=CCH_2-$ *E* configuration), total 2 H, overlapping with 1 H between δ 1.41 and 1.94 (c, –CH–)], [2.10 (s, 0.15 H, $=C(OSi)CH_3$ cis to COOSi), 2.22 (s, 2.85 H, $=C(OSi)CH_3$ trans to COOSi), total 3 H], [2.49 (s, 1.55 H, $=CCH_2C=$ *E* configuration), 3.03 (s, 0.45 H, $=CCH_2C=$ *Z* configuration), total 2 H], 5.91 (m, 1 H, =CH). Of the above mixture, 95% (100 × 2.85/3) could be accounted for by 2(*Z*)-[1-[(diethylmethylsilyl)oxy]ethylidene]-4(*E*)-[[(diethylmethylsilyl)-oxy]ethylene]pentanoic acid diethylmethylsilyl ester, which will be referred to as the (*Z*,*E*)-isomer (δ 1.80, 2.22, 2.49) and the (*Z*,*Z*)-isomer (δ 1.53, 2.22, 3.03), present in a ratio of 78:22 (1.55:0.45). These two isomers corresponded to two major peaks (78:22) in GLC. The absorption at 2.10 (CH_3 cis to COOSi) may indicate the presence of the (*E*,*E*)- and/or (*E*,*Z*)-isomer (total 5%). Mass spectrum, *m/e* (relative intensity) 514 (17, M^+), 485 (33, M^+ – Et), 396 (100), 369 (60), 367 (56), 101 (94). Anal. Calcd for $C_{26}H_{54}O_4Si_3$: C, 60.64; H, 10.57. Found: C, 60.63; H, 10.65.

2-[1-[(Diethylmethylsilyl)oxy]ethylidene]-4-[[(diethylmethylsilyl)oxy]-methylene]decanoic Acid Diethylmethylsilyl Ester (48): bp 170–180 °C (1.8 mmHg, bulb-to-bulb distillation); IR (neat) 2950, 2920, 2870, 1685 (trisubstituted C=C, C=O), 1620 (tetrasubstituted C=C), 1465, 1420, 1385, 1300, 1260, 1215, 1155, 1130, 1065, 1005, 985, 855, 800, 695 cm^{-1}; NMR (CCl_4) δ 0.06 (s, 3 H, $SiCH_3$), 0.21 (s, 6 H, $SiCH_3$), 0.39–1.10 (c, 33 H, $SiCH_2CH_3$, $-CH_3$), 1.26 (m, 8 H, $-CH_2-$), [1.65 (m, $=CCH_2$ *Z* configuration), 1.92 (m, $=CCH_2$ *E* configuration), total 2 H], [2.10 (s, 0.2 H, $=C(OSi)CH_3$ cis to COOSi), 2.22 (s, 2.8 H, $=C(OSi)CH_3$ trans to COOSi), total 3 H], [2.79 (s, 1.6 H, $=CCH_2C=$ *E* configuration), 3.03 (s, 0.4 H, $=CCH_2C=$ *Z* configuration), total 2 H], 5.91 (m, 1 H, =CH). Of the above mixture, 93% (100 × 2.8/3) could be accounted for by the (*Z*,*E*)-isomer (δ 1.92, 2.22, 2.79) and the (*Z*,*Z*)-isomer (δ 1.65, 2.22, 3.03), present in a ratio of 80:20 (1.6:0.4). These two isomers corresponded to two major peaks (81:19) in GLC. The absorption at 2.10 (CH_3 cis to COOSi) may indicate the presence of (*E*,*E*)- and/or (*E*,*Z*)-isomers (total 7%). Mass spectrum, *m/e* (relative intensity) 542 (6, M^+), 513 (16, M^+ – Et), 424 (51), 397 (29), 395 (22), 227 (19), 101 (19), 89 (100), 73 (92). Anal. Calcd for $C_{28}H_{58}O_4Si_3$: C, 61.93; H, 10.77. Found: C, 61.74; H, 11.02.

5-[(Diethylmethylsilyl)oxy]-2-[1-[(diethylmethylsilyl)oxy]-propylidene]-4-methyl-4-pentenoic Acid Diethylmethylsilyl Ester (49): bp 140–160 °C (0.4 mmHg, bulb-to-bulb distillation); IR (neat) 2950, 2910, 2870, 1715 (C=O), 1685 (trisubstituted C=C), 1610 (tetrasubstituted C=C), 1465, 1420, 1330, 1280, 1255, 1240, 1210, 1155, 1130, 1080, 1060, 1040, 1005, 960, 865, 800, 690 cm^{-1}; NMR (CCl_4) δ [0.06 (s, $SiCH_3$), 0.21 (s, $SiCH_3$), total 9 H], 0.38–1.26 (c, 33 H, $SiCH_2CH_3$, $-CH_3$), [1.26 (s, $=CCH_3$), 1.30 (s, $=CCH_3$), 1.42 (s, $=CCH_3$), 1.50 (s, $=CCH_3$), total 3 H], [2.02 (q, *J* = 7.5 Hz, 0.6 H, $=C(OSi)CH_2-$ cis to COOSi), 2.52 (q, *J* = 7.5 Hz, 1.4 H, $=C(OSi)CH_2-$ trans to COOSi), total 2 H], [2.72 (s, 1.5 H, $=CCH_2-$ *E* configuration), 3.02 (s, 0.5 H, $=CCH_2-$ *Z* configuration), total 2 H], 5.86 (m, 1 H, =CH), the absorptions at δ 1.26, 1.30, 1.42, and 1.50 may indicate that the above mixture contains four stereoisomers, the ratio of which is (*Z*,*E*):(*Z*,*Z*):(*E*,*E*):(*E*,*Z*) = 53:23:17:7 determined by integration of the $=CCH_3$ singlet; mass spectrum, *m/e* (relative intensity) 486 (7, M^+), 457 (28, M^+ – Et), 368 (43), 339 (51), 171 (36), 131 (40), 101 (60), 89 (61), 73 (100). Anal. Calcd for $C_{24}H_{50}O_4Si_3$: C, 59.20; H, 10.35. Found: C, 59.18; H, 10.52.

5-[(Diethylmethylsilyl)oxy]-2-[[(diethylmethylsilyl)oxy]phenyl-methylene]-4-methyl-4-pentenoic Acid Diethylmethylsilyl Ester (50): bp 170–180 °C (0.9 mmHg); IR (neat) 2950, 2900, 2870, 1710 (C=O), 1680 (trisubstituted C=C), 1625 (tetrasubstituted C=C), 1600 (Ph), 1495, 1460, 1415, 1380, 1325, 1250, 1150, 1090, 1000, 980, 850, 795, 770, 700 cm^{-1}; NMR (CCl_4) δ [–0.14 (s, $SiCH_3$), –0.12 (s, $SiCH_3$), 0.10 (s, $SiCH_3$), total 9 H], 0.18–1.22 (c, 30 H, $SiCH_2CH_3$), [1.38 (s, $=CCH_3$), 1.46 (s, $=CCH_3$), 1.54 (s, $=CCH_3$), total 3 H], [2.70 (s, 0.6 H, $=CCH_2C=$), 3.14 (s, 1.1 H, $=CCH_2C=$), 3.42 (s, 0.3 H, $=CCH_2C=$), total 2 H], 5.82–6.10 (m, 1 H, =CH), 6.94–7.50 (m, 5 H, aromatic H); mass spectrum, *m/e* (relative intensity) 534 (3, M^+), 505 (12, M^+ – Et), 416 (53), 387 (25), 273 (47), 207 (21), 171 (35), 101 (83), 73 (100). Anal. Calcd for $C_{28}H_{50}O_3Si_4$: C, 62.86; H, 9.42. Found: C, 62.78; H, 9.71.

4-Methyl-4-pentenoic Acid Diethylmethylsilyl Ester and 4-Methyl-3-pentenoic Acid Diethylmethylsilyl Ester (67): bp 104–108 °C (40 mmHg); IR (neat) 2950, 2900, 2870, 1720 (C=O), 1650 (C=C), 1460, 1415, 1380, 1370, 1320, 1255, 1180, 1060, 1005, 960, 930, 885, 795, 760, 685 cm^{-1}; NMR (CCl_4) δ 0.20 (s, 3 H, $SiCH_3$), 0.68 (m, 4 H, $SiCH_2-$), 0.92 (m, 6 H, $SiCCH_3$), 1.68 (m, 3.6 H, $=CCH_3$), 2.12–2.56 (c, 3 H, $=CCH_2-$, $COCH_2-$), 2.92 (d, *J* = 8 Hz, 0.4 H, $=CCH_2CO$), 4.68 (m, 1.5 H, $=CH_2$), 5.24 (m, 0.2 H, =CH–); mass spectrum, *m/e* (relative intensity) 214 (2, M^+), 199 (5, M^+ – Me), 185 (100, M^+ – Et), 101 (63), 89 (93). Anal. Calcd for $C_{11}H_{22}O_2Si$: C, 61.63; H, 10.35. Found: C, 61.55; H, 10.63.

3-(1-Cyclohexenyl)propanoic Acid Diethylmethylsilyl Ester (69): bp 98–102 °C (0.7 mmHg); IR (neat) 2970, 2930, 2880, 1720 (C=O), 1470, 1450, 1420, 1370, 1350, 1290, 1180, 1010, 970, 800, 770 cm^{-1}; NMR (CCl_4) δ 0.18 (s, 3 H, $SiCH_3$), 0.50–1.06 (m, 10 H, $SiCH_2CH_3$), 1.64 (m, 4 H, $-CH_2-$), 1.90 (m, 4 H, $=CCH_2-$), 2.26 (m, 4 H, $=CCH_2-$, $COCH_2-$), 5.34 (m, 1 H, =CH), NMR analysis showed the complete absence of the *exo*-methylene isomer; mass spectrum, *m/e* (relative intensity) 254 (7, M^+), 225 (100, M^+ – Et), 101 (93), 89 (68). Anal. Calcd for $C_{14}H_{26}O_2Si$: C, 66.08; H, 10.38. Found: C, 65.95; H, 10.43.

Diethylmethyl[[(tricyclo[3.3.1.$1^{3,7}$]decyl)methyl]oxy]silane (74). Spectral data of **74**, which was obtained by preparative GLC, were identified with those of an authentic sample, which was prepared by

$Co_2(CO)_8$-catalyzed silylation of a corresponding alcohol. For an authentic sample obtained by distillation: bp 180–190 °C (2 mmHg, bulb-to-bulb distillation); IR (neat) 2900, 2850, 1465, 1455, 1450, 1415, 1385, 1365, 1345, 1250, 1235, 1155, 1080, 1005, 840, 805, 765 cm^{-1}; NMR (CCl_4) δ 0.00 (s, 3 H, $SiCH_3$), 0.33–0.69 (m, 4 H, $SiCH_2$–), 0.77–1.08 (s, 6 H, $SiCCH_3$), 1.36–1.57 (c, 6 H, $-CH_2-$), 1.57–1.80 (c, 6 H, $-CH_2-$), 1.80–2.05 (c, 3 H, –CH–), 3.05 (s, 2 H, OCH_2–); mass spectrum, *m/e* (relative intensity) 266 (0, M^+), 237 (100, M^+ – Et), 149 (41), 135 (12), 89 (41), 73 (16), 61 (27). Anal. Calcd for $C_{16}H_{30}OSi$: C, 72.11; H, 11.35. Found: C, 71.95; H, 11.47.

Diethyl[[2-[(diethylmethylsilyl)oxy]-2-(tricyclo[3.3.1.1^{3,7}]decyl)-ethenyl]oxy]methylsilane (75): bp 140–158 °C (0.9 mmHg, bulb-to-bulb distillation); IR (neat) 2960, 2940, 2920, 2860, 1685 (C=C), 1460, 1420, 1360, 1260, 1245, 1195, 1150, 1100, 1075, 1050, 1020, 995, 960, 865, 805, 765, 695 cm^{-1}; ^1H NMR (CCl_4) δ 0.08 (s, 3 H, $SiCH_3$), 0.12 (s, 3 H, $SiCH_3$), 0.39–0.81 (m, 8 H, $SiCH_2$–), 0.81–1.07 (m, 12 H, $SiCCH_3$), 1.41–1.81 (c, 12 H, $-CH_2-$), 1.81–2.05 (c, 3 H, –CH–), 5.47 (s, 1 H, =CH); ^{13}C NMR ($CDCl_3$) δ –4.89 ($SiCH_3$), –3.52 ($SiCH_3$), [6.36, 6.70, 7.09, 7.53 ($SiCH_2CH_3$)], 28.57 (–CH–), 36.25 (–C–), [37.23, 38.70 ($-CH_2-$)], 118.99 (=CHOSi), 145.21 (=COSi); mass spectrum, *m/e* (relative intensity) 394 (100, M^+), 365 (17, M^+ – Et), 189 (21), 161 (22), 135 (37), 101 (65), 73 (81). Anal. Calcd for $C_{22}H_{42}O_2Si_2$: C, 66.94; H, 10.73. Found: C, 67.10; H, 10.91.

Diethylmethyl[[(tricyclo[4.3.1.1^{2,5}]undecyl)methyl]oxy]silane (76). The mass spectrum and RRT (GLC relative retention time) of **76**, which was obtained by preparative GLC, were identified with those of an authentic sample, which was prepared by $Co_2(CO)_8$-catalyzed silylation of a corresponding alcohol. For an authentic sample: bp 110–120 °C (0.7 mmHg, bulb-to-bulb distillation); IR (neat) 3040, 2930–2870, 2740, 1480, 1420, 1390, 1260, 1240, 1140, 1120, 1090, 1010, 970, 920, 830, 800, 770, 740, 690 cm^{-1}; NMR (CCl_4) δ 0.00 (s, 3 H, $SiCH_3$), 0.32–0.64 (m, 4 H, $SiCH_2$–), 0.80–2.52 (c, 23 H, $SiCCH_3$, $-CH_2-$, –CH–), 3.08 (ABq, 2 H, J = 8 Hz, OCH_2–); mass spectrum, *m/e* (relative intensity) 280 (1, M^+), 251 (100, M^+ – Et), 161 (24), 149 (15), 89 (100). Anal. Calcd for $C_{17}H_{32}OSi$: C, 72.79; H, 11.50. Found: C, 72.44; H, 11.63.

Diethyl[[2-[(diethylmethylsilyl)oxy]-2-(tricyclo[4.3.1.1^{2,5}]undecyl)-ethenyl]oxy]methylsilane (77): bp 160–170 °C (2 mmHg, bulb-to-bulb distillation); IR (neat) 2940, 2925, 2880, 1680 (C=C), 1470, 1415, 1355, 1270, 1160, 1140, 1080, 1070, 1020, 970, 950, 890, 835, 800, 755, 690 cm^{-1}; ^1H NMR (CCl_4) δ 0.07 (s, 3 H, $SiCH_3$), 0.12 (s, 3 H, $SiCH_3$), 0.45–0.75 (m, 8 H, $SiCH_2$–), 1.15–2.25 (c, 29 H, $SiCCH_3$, $-CH_2-$, –CH–), 5.40 (s, 1 H, =CH); ^{13}C NMR ($CDCl_3$) δ [–4.89, –3.47 ($SiCH_3$)], [6.36, 6.70, 7.05, 7.63 ($SiCH_2CH_3$)], [18.88, 25.98, 27.15, 27.64, 28.62, 32.63, 33.27 ($-CH_2-$)], [31.51, 40.80, 41.49 (–CH–)], 40.22 (–C–), 119.52 (=CHOSi), 144.08 (=COSi); mass spectrum, *m/e* (relative intensity) 408 (57, M^+), 379 (10, M^+ – Et), 365 (10), 339 (50), 279 (33), 189 (10), 161 (20), 149 (10), 133 (10), 105 (15), 101 (37), 73 (100). Anal. Calcd for $C_{23}H_{44}O_2Si_2$: C, 67.58; H, 10.85. Found: C, 67.60; H, 11.01.

Diethylmethyl[[(tricyclo[3.3.2^{3,9}.1]undecyl)methyl]oxy]silane (78). The mass spectrum, IR, and RRT of **78**, which was obtained by preparative GLC, were identified with those of an authentic sample, which was prepared by $Co_2(CO)_8$-catalyzed silylation of a corresponding alcohol. For an authentic sample: bp 100–110 °C (0.5 mmHg, bulb-to-bulb distillation); IR (neat) 2900, 1470, 1420, 1380, 1250, 1120, 1110, 1080, 1010, 960, 840, 800, 760, 735, 685 cm^{-1}; NMR (CCl_4) δ 0.03 (s, 3 H, $SiCH_3$), 0.36–0.66 (m, 4 H, $SiCH_2$–), 0.76–1.96 (c, 23 H, $SiCCH_3$, $-CH_2-$, –CH–), 3.15 (ABq, J = 9 Hz, 2 H, OCH_2–); mass spectrum, *m/e* (relative intensity) 280 (3, M^+), 251 (100, M^+ – Et), 161 (40), 149 (76), 89 (95), 67 (22). Anal. Calcd for $C_{17}H_{32}OSi$: C, 72.79; H, 11.50. Found: C, 72.75; H, 11.64.

Diethyl[[2-[(diethylmethylsilyl)oxy]-2-(tricyclo[3.3.2^{3,9}.1]undecyl)-ethenyl]oxy]methylsilane (79): bp 170–180 °C (1.5 mmHg, bulb-to-bulb distillation); IR (neat) 2900, 2875, 1675 (C=C), 1465, 1410, 1360, 1255, 1135, 1100, 1085, 1075, 1010, 965, 840, 800, 760, 690 cm^{-1}; ^1H NMR (CCl_4) δ 0.12 (s, 6 H, $SiCH_3$), 0.42–0.80 (m, 8 H, $SiCH_2$–), 0.80–2.00 (c, 29 H, $SiCCH_3$, $-CH_2-$, –CH–), 5.75 (s, 1 H, =CH); ^{13}C NMR ($CDCl_3$) δ [–4.89, –3.33 ($SiCH_3$)], [6.36, 6.65, 7.09, 7.73 ($SiCH_2CH_3$)], [14.47, 23.39, 25.64, 31.07, 32.05, 34.30, 38.65 ($-CH_2-$)], [25.25, 31.95, 33.76 (–CH–)], 38.90 (–C–), 120.11 (=CHOSi), 144.04 (=COSi); mass spectrum, *m/e* (relative intensity) 408 (100, M^+), 379 (13, M^+ – Et), 279 (43), 189 (11), 161 (20), 149 (20), 101 (17), 73 (33). Anal. Calcd for $C_{23}H_{44}O_2Si_2$: C, 67.58; H, 10.85. Found: C, 67.20; H, 11.14.

Desilylation of Siloxymethylidenation Products (Enol Silyl Ethers). 3-[4-(1,1-Dimethylethyl)phenyl]-2-methylpropanal (35). An enol silyl ether **28** (530 mg, 1.7 mmol) was added to a solution of KF (130 mg, 2.2 mmol) in CH_3OH (5 mL) under nitrogen. The reaction mixture was stirred at 25 °C for 1 h. The solvent was removed in vacuo, diluted with diethyl ether, and washed with saturated aqueous ammonium chloride. The aqueous layer was extracted with diethyl ether, and the combined organic layer was dried over $CaSO_4$. Removal of solvent in vacuo gave a crude aldehyde **35** (352 mg, 100%, essentially pure by NMR), and chromatography (silica gel, benzene) gave a pure aldehyde **35** (295 mg, 85%) as a colorless oil: IR (neat) 1739 cm^{-1} (C=O); NMR (CCl_4) δ 9.65 (CHO); mass spectrum, *m/e* 204 (M^+).

4-Chlorocyclohexanecarboxaldehyde (32). In a similar manner as described above, treatment of **19** (208 mg, 0.84 mmol) with KF (60 mg, 1 mmol) in CH_3OH (2.5 mL) under nitrogen at 25 °C for 1 h and chromatography gave a 61:39 mixture of stereoisomers of an aldehyde **32** (104 mg, 93%): IR (neat) 1725 cm^{-1} (C=O); NMR (CCl_4) δ 9.48 (CHO); mass spectrum, *m/e* 146 (M^+).

Cyclododecanecarboxaldehyde (33).[54] Treatment of **21** (240 mg, 0.83 mmol) with KF (60 mg, 1 mmol) in CH_3OH (2.5 mL) and chromatography gave **33** (152 mg, 93%): IR (neat) 1720 cm^{-1} (C=O); NMR (CCl_4) δ 9.46 (CHO); mass spectrum, *m/e* 196 (M^+).

Tricyclo[3.3.1.1^{3,7}]decanecarboxaldehyde (34).[55] Treatment of **22** (534 mg, 2 mmol) with KF (130 mg, 2.2 mmol) in CH_3OH (5 mL) and chromatography gave **34** (269 mg, 82%): mp 106–110 °C [lit.[55b] mp 110–114 °C, lit.[55a] mp 99–102 °C]; IR (neat) 1725 cm^{-1} (C=O); NMR (CCl_4) δ 9.60 (CHO); mass spectrum, *m/e* 164 (M^+).

4-Phenyl-2-methylbutanal (36).[56] Treatment of **30** (529 mg, 2 mmol) with KF (130 mg, 2.2 mmol) in CH_3OH (5 mL) and chromatography gave **36** (300 mg, 93%): IR (neat) 1725 cm^{-1} (C=O); NMR (CCl_4) δ 9.52 (CHO); mass spectrum, *m/e* 162 (M^+).

Ethyl 4-Ethyl-5-oxopentanoate (51).[57] Azeotropic distillation from a solution of **43** (690 mg, 2 mmol) in EtOH (15 mL), C_6H_6 (120 mL), and 15% aqueous HCl (5 mL) for 3.5 h resulted in removal of most of the solvent. Chromatography (silica gel, C_6H_6) of the residue gave 1,5-aldehyde ester **51** (310 mg, 90%) as a colorless oil: IR (neat) 1730 cm^{-1} (C=O); NMR (CCl_4) δ 9.45 (CHO); mass spectrum, *m/e* 144 (M^+ – Et).

Diethylmethyl[(2-methyl-5-oxo-1-hexenyl)oxy]silane (54). A solution of **46** (624 mg, 1.3 mmol) in CH_3OH (10 mL) was refluxed under nitrogen. The solvent was removed under reduced pressure, and the residue was chromatographed (silica gel, C_6H_6/Et_2O 4/1) to afford pure **54** (194 mg, 65%) as a colorless oil: IR (neat) 2950, 2900, 2870, 1715 (C=O), 1675 (C=C), 1415, 1360, 1255, 1190, 1150, 1000, 840, 820, 800 cm^{-1}; NMR (CCl_4) δ 0.10 (s, 3 H, $SiCH_3$), 0.66 (m, 4 H, $SiCH_2$–), 0.94 (m, 3 H, $SiCH_3$), 1.54 (s, 3 H, $=CCH_3$), 1.98–2.54 (m, 7 H, including a COCH singlet at δ 2.06 ($COCH_3$, $COCH_2$–, $=CCH_2$–)), 6.04 (m, 1 H, =CH); mass spectrum, *m/e* (relative intensity) 228 (32, M^+), 199 (38, M^+ – Et), 172 (51), 129 (86), 101 (100).

5-Oxo-2-methylhexanal (55).[58] To a solution of **46** (718 mg, 1.5 mmol) in THF (2 mL) was added 1 N HCl (1 mL). The mixture was stirred at 25 °C under nitrogen for 1 h. Diethyl ether was added to the reaction mixture, and the solution was washed with saturated aqueous NaCl. The organic layer was dried over $CaSO_4$ and concentrated in vacuo, and the light-yellow oily residue was chromatographed (silica gel, C_6H_6/Et_2O 9/1) to give pure **55** (71 mg, 60%): IR (neat) 1710 cm^{-1} (C=O); NMR (CCl_4) δ 9.24 (CHO); mass spectrum, *m/e* 128 (M^+).

4-Methyl-2-cyclohexen-1-one (56).[59] After the catalytic reaction of **52** (720 mg, 5 mmol, see run 6 in Table IV), the solvent was removed in vacuo to give crude **46** as a black oil. To 7 N HCl (15 mL) was added crude **46**, without further purification, at 0 °C under nitrogen. The mixture was stirred at room temperature overnight. Diethyl ether was added to the reaction mixture, and the solution was washed with saturated aqueous NaCl and then dried over $CaSO_4$. Removal of the solvent in vacuo and chromatography (silica gel, C_6H_6/Et_2O 4/1) gave **56** (265 mg, 48% yield based on **52**): IR (neat) 1675 cm^{-1} (C=O); NMR (CCl_4) δ 5.80, 6.73 (=CH); mass spectrum, *m/e* 110 (M^+).

2,5-Dimethylpyridine (57).[60a,61a] To crude **46**, which was obtained in a similar manner as described above, were added $NH_2OH{\cdot}HCl$ (1.05 g, 15 mmol) and CH_3COOH (5 mL), and the resulting mixture was stirred under reflux. After 12 h, the bottle was cooled to room temperature, and diethyl ether was added. The aqueous layer was separated, and then diethyl ether was added followed by a NaOH pellet. Enough alkali was

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added to make the aqueous solution strongly alkaline. The organic layer was separated, dried over $MgSO_4$, concentrated in vacuo, and distilled to yield **57** (208 mg, 39% yield based on **52**): NMR (CCl_4) δ 2.23, 2.40 ($-CH_3$).

Reduction of Siloxymethylidenation Product (Enol Silyl Ether) Cyclohexanemethanol.[60b,61b] To a solution of $NaBH_4$ (1 mmol, 40 mg) in ethanol (8 mL) was added **3** (2 mmol, 430 mg). The mixture was stirred at 25 °C under nitrogen for 3 h. Solvent was removed in vacuo. Diethyl ether was added to the residue, and the solution was washed with dilute HCl solution. The organic layer was dried over $CaSO_4$ and concentrated in vacuo. The residue was purified by column chromatography (silica gel, C_6H_6) to give cyclohexanemethanol (160 mg, 70% yield based on **3**): NMR (CCl_4) δ 3.15 (d, J = 5 Hz, OCH_2-).

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Highly Stereocontrolled Synthesis of Some Trioxygenated Cyclohexenes: An Asymmetric Total Synthesis of (−)-Methyl Triacetyl-4-epishikimate

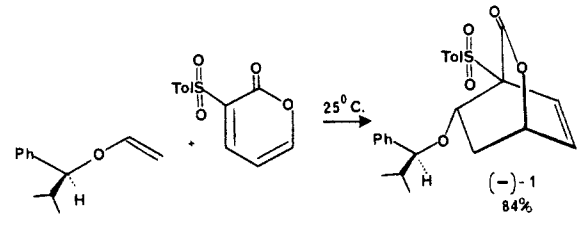
Gary H. Posner* and David G. Wettlaufer

Contribution from the Department of Chemistry, The Johns Hopkins University, Baltimore, Maryland 21218. *Received May 19, 1986*

Abstract: Polyfunctional bicyclic lactone (−)-**1** serves as a chiron for preparation of 3,4,6-trioxygenated cyclohexene (−)-**5a** in 56.6% overall yield and for synthesis of (−)-methyl triacetyl-4-epishikimate, (−)-**12**, in 14 steps and in 23.4% overall yield. 3,4,5-Trioxygenated cyclohexene (−)-**12** is obtained in at least 98% enantiomeric purity.

Many polyoxygenated carbocycles produce potent biological responses, including antimicrobial,[1] antiviral,[1] and antitumor[2] as well as growth-promoting[3] effects. Because of these pronounced biological activities and because of their potential as versatile chemical intermediates, polyoxygenated carbocycles have been the targets of many synthetic efforts.[2a,4]

We recently reported using an α-pyrone sulfone[5] as an an electron-deficient diene in some highly asymmetric Diels–Alder cycloadditions with several chiral, nonracemic alkyl vinyl ethers as electron-rich dienophiles.[6] For example, such an inverse-electron-demand asymmetric (2 + 4) cycloaddition proceeded on a gram scale, as illustrated in eq 1, with formation of adduct (−)-**1**, which was isolated as a single diastereomer in 84% yield. This high level of stereocontrol was especially gratifying and somewhat surprising because the stereogenic center in the reactant alkyl vinyl



(1)

ether is insulated from the reacting vinyl moiety by a freely rotating ether linkage.[7] Chiron[8] (−)-**1** is a richly functionalized bicyclic lactone subject to a variety of chemoselective and stereoselective chemical operations. For example, hydroxylation of the olefinic bond in unsaturated lactone (−)-**1** would produce a *tetra*oxygenated cyclohexane; also the allylic carboxylate functionality within bicyclic lactone (−)-**1** affords opportunities for substitution reactions with various organometallic reagents.[9] We record here conversion of chiron (−)-**1** into some trioxygenated cyclohexenes of defined absolute stereochemistry, and we highlight the utility of chiron (−)-**1** by converting it in 14 steps and in 23.4% overall yield into (−)-methyl triacetyl-4-epishikimate, an intermediate for synthesis of (−)-chorismic acid and analogues. The important shikimate biosynthetic pathway in plants and microorganisms leads from carbohydrates to various aromatic compounds.[10] (−)-Methyl triacetyl-4-epishikimate has been prepared previously by resolution of a racemic precursor[11] and

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