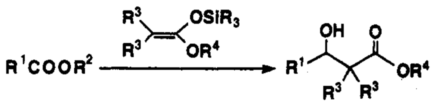
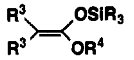
Table I. Boron Trifluoride Mediated Aldol Reaction of Trialkylsilyl Ketene Acetals with the Intermediate Generated by the DIBALH Reduction of Carboxylic Acid Esters

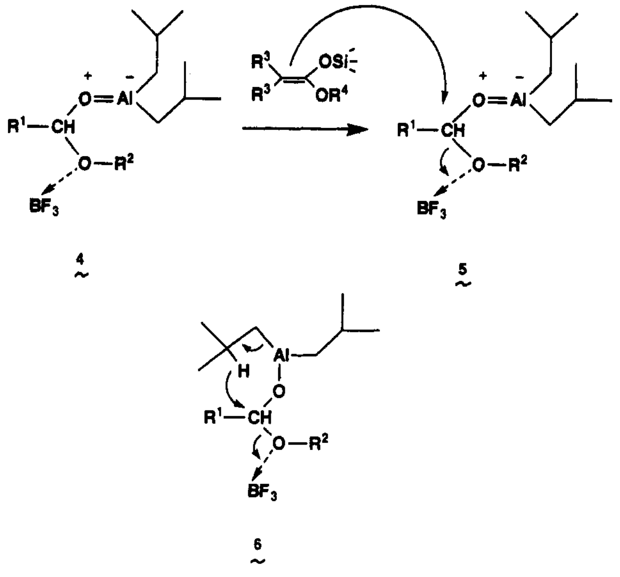


entry	R′COOR²					β-hydroxy ester product[a] (% yield)
	R^1	R^2	R^3	R^4	R(Si)	
1	Me	Me	H	Ph	TMS	**3a** (65)
2	Me	Me	Me	Et	TMS	**3b** (70)
3	*i*-Pr	Et	H	Ph	TMS	**3c** (69)
4	*i*-Pr	Et	Me	Et	TMS	**3d** (77)
5	*s*-Bu	Me	H	Ph	TMS	**3e** (75)
6	*s*-Bu	Me	Me	Et	TMS	**3f** (66)
7	Bn	Me	H	Et	TBDMS	**3g** (85)
8	Bn	Me	Me	Et	TMS	**3h** (70)
9	Ph_2CH	Me	H	Et	TBDMS	**3i** (60)
10	Ph_2CH	Me	Me	Et	TMS	**3j** (86)
11	Ph	Me	H	Et	TBDMS	**3k** (5)
12	Ph	Me	Me	Et	TMS	**3l** (31)

[a] Aliphatic esters (entries 1–10) gave products of overreduction, i.e., the alcohols derived from the acyl fragment of the ester starting material, in yields of 5–10%, whereas methyl benzoate (entries 11 and 12) gave benzyl alcohol in ca. 50% yield.

is very clean, and the only byproduct is the alcohol (5–10% yield) that results from overreduction of the starting ester. The less reactive allylsilane produced only a 25% yield under the BF_3 conditions; however, the performance of other Lewis acids in the reaction has not been examined for purposes of optimizing the yield. Thus, the one-pot conversion of a carboxylic acid ester to a β-hydroxy carboxylic acid ester of greater chain length has been achieved.[7] *What is described here is therefore of considerable synthetic value.* Unfortunately, esters of aromatic acids do not give aldol adducts in sufficiently high yields. For example, methyl benzoate (entries 11 and 12) gives the expected adduct in only low yield, along with a large amount of benzyl alcohol (ca. 50%). α,β-Unsaturated esters like methyl acrylate also give low yield of the desired products.

Scheme II



4

5

6

The reaction seems to occur when species **2** is activated by preferential coordination of BF_3 with the oxygen atom of the alkoxy group. Coordination of BF_3 with the oxygen atom of the carbon–oxygen–aluminum linkage is not favored because the basicity of that oxygen atom is lowered by the development of Al–O double bond character (Scheme II).[8] The alcohol byproduct is obviously the result of a BF_3-assisted Meerwein–Ponndorf–Verley reduction, which probably takes place in the manner indicated in structure **6**.

The details of the mechanism of the reaction are still being elucidated. Nevertheless, effects directed toward the asymmetric synthesis of β-hydroxy carboxylic acid esters by way of the reaction of esters which incorporate a chiral alcohol moiety are now in progress.

Supplementary Material Available: Additional experimental details section and the ^1H NMR, ^{13}C NMR, and IR spectra of **3a–3l** and **7** (7 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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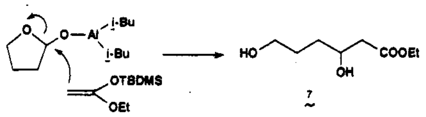
(7) The reaction of γ-butyrolactone under the conditions described here yields the dihydroxy carboxylic acid **7** (30%) as a major product.



7

What is unusual about this result is that it was reported that the BF_3-promoted reaction of γ-lactols with silylated nucleophiles gives the corresponding substituted tetrahydrofurans. No products of ring opening were detected. See: Schmitt, A; Reissig, H. -U. *Synlett* **1990**, 40.

(8) A reviewer has suggested that the structure of the complex **4** might be better represented as an oxygen-bridged dimer rather than as a monomer which processses an aluminum–oxygen double bond.

Regioselective Incorporation of CO into Enamines by Rhodium-Catalyzed Reaction with a Hydrosilane and CO

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Summary: In the presence of $[RhCl(CO)_2]_2$, the reaction of enamines with a hydrosilane and carbon monoxide (140 °C, 50 atm of CO) resulted in regioselective incorporation of CO into the α-carbon atom to give α-(siloxymethylene) amines, which can be easily converted into α-siloxy ketones by hydrolysis.

In a series of studies on new catalytic reactions of

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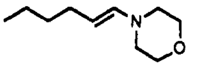
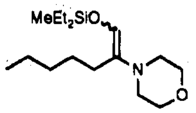
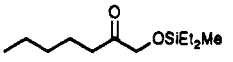
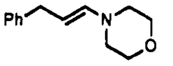
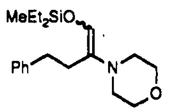
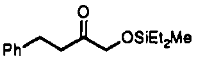
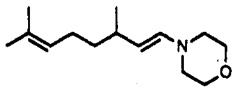
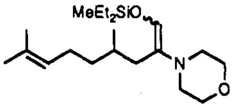
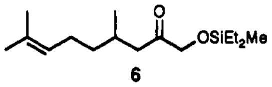
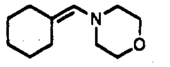
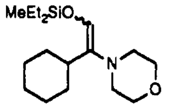
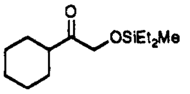
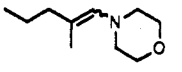
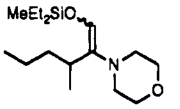
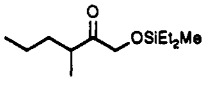
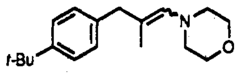
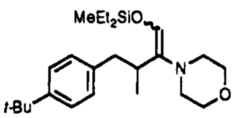
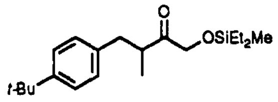
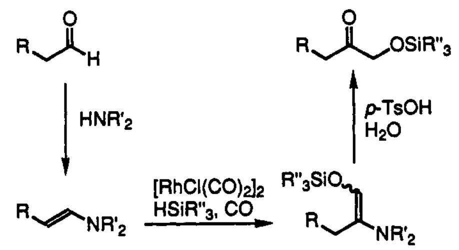
Table I. $[RhCl(CO)_2]_2$-Catalyzed Reaction of Enamines with $HSiEt_2Me$ and CO[a]

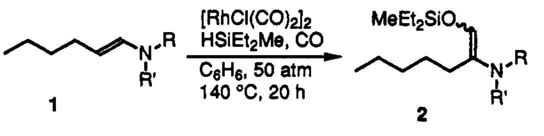
entry	enamine	time, h	α-(siloxymethylene) amine	yield,[b] %	α-siloxy ketone[c]	yield,[d] %
1	 1c	20	 2c	62 (75), $E/Z = 84/16$	 4	~100
2	 1d	72	 2d	74 (91), $E/Z = 81/19$	 5	~100
3	 1e	72	 2e	72, $E/Z = 81/19$	 6	~100
4	 1f	72	 2f	65 (72), $E/Z = 52/48$	 7	~100
5	 1g (E/Z = 63/37)	72	 2g	57, $E/Z = 61/39$	 8	~100
6	 1h (E/Z = 65/35)	120	 2h	21, $E/Z = 51/49$	 9	~100

[a] Reaction conditions: enamine (2.5 mmol), $HSiEt_2Me$ (7.5 mmol), $[RhCl(CO)_2]_2$ (0.05 mmol), CO (50 atm), C_6H_6 (5 mL), 140 °C. [b] Isolated yields based on enamines. GC yields are in parentheses. E/Z ratio was determined by ^1H NMR. [c] Reaction conditions: α-(siloxymethylene) amine (1.5 mmol), TsOH (0.1 mmol), H_2O (10 mL), 70 °C, 1 day. [d] Isolated crude yields based on α-(siloxymethylene) amine.

$HSiR_3/CO/Co_2(CO)_8$,[1] we have reported that the reaction of terminal olefins with a hydrosilane and carbon monoxide catalyzed by $Co_2(CO)_8$ produced a regioisomeric mixture of enol silyl ethers.[2] Although interesting, the reaction is not attractive as a synthetic method since (1) it lacks regiochemical control for incorporation of CO and (2) a high ratio of olefins to hydrosilane is required. These limitations have prompted us to search for another transition-metal-catalyzed reaction of functionalized olefins with a hydrosilane and CO. In this paper, we wish to report that rhodium complexes catalyze the reaction of enamines with $HSiEt_2Me$ (3 equiv) and CO.[3] The overall process outlined in Scheme I provides a simple route for the conversion of an aldehyde to an α-siloxy ketone, which often requires multistep sequences.

Scheme I





1 2 (1)

1a: R= R'= Et 2a: 32 %
1b: R= Me, R'= $PhCH_2$ 2b: 25 %
1c: R= R'= $(CH_2CH_2)_2O$ 2c: 75 %

The reactions of some enamines derived from hexanal (in eq 1)[4,5] were carried out with $HSiEt_2Me$ (3 equiv) in benzene at 140 °C under 50 atm (initial pressure at 25 °C) of CO in the presence of $[RhCl(CO)_2]_2$ (2 mol %) as a catalyst. Incorporation of CO into the enamines 1 took place regioselectively to afford α-(siloxymethylene) amines 2. Morpholine enamine 1c gave a higher yield of the product (75% yield) compared with 1a and 1b. A wide range of transition-metal complexes were examined for their catalytic activity for the reaction of 1c. While $Fe(CO)_5$, $Co_2(CO)_8$, $Ru_3(CO)_{12}$, and $RhCl(PPh_3)_3$ were not effective, some rhodium complexes $(Me_5C_5RhCl)_2$ (65% yield) and $Rh_6(CO)_{16}$ (75% yield) showed catalytic activity. Since $[RhCl(CO)_2]_2$ gave higher yields it was chosen as the

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[1] For recent papers in this series, see: (a) Chatani, N.; Kajikawa, Y.; Nishimura, H.; Murai, S. *Organometallics* **1991**, *10*, 21. (b) Chatani, N.; Sano, T.; Ohe, K.; Kawasaki, Y.; Murai, S. *J. Org. Chem.* **1990**, *55*, 5923.

[2] (a) Seki, Y.; Murai, S.; Hidaka, A.; Sonoda, N. *Angew. Chem., Int. Ed. Engl.* **1977**, *16*, 881. (b) Seki, Y.; Hidaka, A.; Makino, S.; Murai, S.; Sonoda, N. *J. Organomet. Chem.* **1977**, *140*, 361. (c) Seki, Y.; Kawamoto, K.; Chatani, N.; Hidaka, A.; Sonoda, N.; Ohe, K.; Kawasaki, Y.; Murai, S. *J. Organomet. Chem.* **1991**, *403*, 73.

[3] The $[RhCl(CO)_2]_2$-catalyzed reaction of 1-hexene, styrene, cyclohexene, butyl vinyl ether, and phenyl vinyl sulfide with $HSiEt_2Me$ and CO (50 atm, 140 °C in benzene for 20 h) did not result in CO incorporation, with only hydrosilation products being formed in low yields.

[4] All new compounds were characterized by NMR, IR, and mass spectral data and by elemental analyses or high-resolution mass spectra. See supplementary material.

[5] α-(Siloxymethylene) amines 2a–c were moisture sensitive, so that some were converted into α-(siloxymethyl) amines 3a–c by hydrogenation (1 atm of H_2, Pd/C, benzene, 25 °C, 1 day) for characterization.

best catalyst, and morpholine enamines were used as substrates.

The results of the reaction of morpholine enamines derived from various aldehydes are summarized in Table I.[6] While a product **2d** was obtained in only 14% yield using a reaction time of 20 h, a prolonged reaction (72 h) led to an increase in the yield of **2d** (entry 2). The carbon–carbon double bond in **1e** remained intact under the reaction conditions (entry 3). The reaction of trisubstituted enamines **1f–h** also gave α-(siloxymethylene) amines **2f–h**, respectively, but in somewhat lower yields (entries 4–6). Attempted improvement of the yield of **2h** was not successful even at prolonged reaction times (120 h). In contrast to enamines, the reaction of enamides and enimides with $HSiEt_2Me$ and CO did not result in incorporation of CO, with only the substrates being recovered.[7]

Importantly, the enamine function in the products can be easily hydrolyzed to a carbonyl group. Treatment of α-(siloxymethylene) amines **2c–h** with aqueous acid (H_2O/TsOH, 70 °C, 1 day) gave α-siloxy ketones **4–9** in quantitative yields.

To the best of our knowledge, the rhodium-catalyzed reaction of enamines with a hydrosilane and CO represents a first example of incorporation of CO into enamines. Regioselective incorporation of CO into the α-carbon atom of enamines gives α-(siloxymethylene) amines, which are amenable to further synthetic elaboration.[8] Moreover, the present reaction provides an efficient route from aldehydes to α-siloxy ketones[9] (Scheme I).

Acknowledgment. This work was supported in part by Grants from the Ministry of Education, Science, and Culture, Japan. We thank the Instrumental Analysis Center, Faculty of Engineering, Osaka University for the use of the facilities.

Supplementary Material Available: Typical experimental procedures, spectral data of products, and spectra (^{13}C NMR of **2c–h**, **3a,b**, **8**, and **9**) (19 pages). Ordering information is given on any current masthead page.

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(6) A typical experimental procedure is illustrated below for the reaction of 4-(1-hexenyl)morpholine (**1c**). In a 100-mL stainless steel autoclave were placed **1c** (423 mg, 2.5 mmol), $HSiEt_2Me$ (766 mg, 7.5 mmol), $[RhCl(CO)_2]_2$ (19 mg, 0.05 mmol), and 5 mL of benzene. The autoclave was charged with carbon monoxide to 50 atm at 25 °C and then heated with stirring at 140 °C for 20 h. GC analysis showed that 4-[1-(diethylmethylsiloxy)-1-hepten-2-yl]morpholine (**2c**) was obtained in 75% yield. Kugelrohr distillation (140 °C (5 Torr)) gave pure **2c** in 62% yield.

(7) Hydroformylations of enamides and enimides are known. See: (a) Sato, S. *Nippon Kagaku Zasshi* **1969**, *90*, 404; *Chem. Abstr.* **1969**, *71*, 21828. (b) Becker, Y.; Eisenstadt, A.; Stille, J. K. *J. Org. Chem.* **1980**, *45*, 2145. (c) Cavinato, G.; Toniolo, L.; Botteghi, C.; Gladiali, S. *J. Organomet. Chem.* **1982**, *229*, 93. (d) Delogu, G.; Faedda, G.; Gladiali, S. *J. Organomet. Chem.* **1984**, *268*, 167. Attempted hydroformylation of **1c** ($[RhCl(CO)_2]_2$, H_2/CO (1:1) 50 atm, benzene, 140 °C) resulted in hydrogenation, not carbonylation.

(8) α-(Siloxymethylene) amines obtained here have both enol silyl ether and enamine moieties. For reviews on the synthetic application of enol silyl ethers, see: (a) Fleming, I. In *Comprehensive Organic Chemistry*; Jones, D. N., Ed.; Pergamon: Oxford, 1979; Vol. 3, Part 13, pp 584–592. (b) Colvin, E. W. *Silicon in Organic Synthesis*; Butterworths: London, 1981; pp 198–287. (c) Weber, W. P. *Silicon Reagents for Organic Synthesis*; Springer-Verlag: New York, 1983; pp 206–254. For reviews on the synthetic applications of enamines, see: (d) Cook, A. G. *Enamines: Synthesis, Structure, and Reactions*; Marcel Dekker: New York, 1969. (e) Tietze, L. F.; Eicher, T. *Reacktionen und Synthesen*; Thieme Verlag: Stuttgart, 1981.

(9) For other syntheses of α-hydroxy ketone derivatives, see: (a) Rubottom, G. M.; Vazquez, M. A.; Pelegrina, D. R. *Tetrahedron Lett.* **1974**, 4319. (b) Hassner, A.; Reuss, R. H.; Pinnick, H. W. *J. Org. Chem.* **1975**, *40*, 3247. (c) Wissner, A. *Tetrahedron Lett.* **1978**, 2748. (d) Rubottom, G. M.; Gruber, J. M. *J. Org. Chem.* **1978**, *43*, 1599. (e) McCormic, J. P.; Tomasik, W.; Johnson, M. W. *Tetrahedron Lett.* **1981**, *22*, 607. (f) Lee, T. V.; Toczek, J. *Tetrahedron Lett.* **1982**, *23*, 2917. (g) Davis, F. A.; Sheppard, A. C. *J. Org. Chem.* **1987**, *52*, 954. (h) Moriatry, R. M.; Duncan, M. P.; Prakash, O. *J. Chem. Soc., Perkin Trans. 1* **1987**, 1781. (i) Tanaka, T.; Yamada, T.; Rhode, O.; Mukaiyama, T. *Chem. Lett.* **1991**, 281.

[2 + 1] Cycloaddition of (*E*)-1-(Phenylseleno)-2-(trimethylsilyl)ethene. Novel Cyclopropane Ring Formation by a 1,2-Shift of a Trimethylsilyl Group

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Received August 6, 1991

Summary: Reaction of (*E*)-1-(phenylseleno)-2-(trimethylsilyl)ethene (**1**) with vinyl ketones **2a–d** in the presence of $SnCl_4$ gave cyclopropane products by a formal [2 + 1] cycloaddition accompanied by 1,2-silicon migration rather than [2 + 2] cycloaddition.

Development of methods for synthesis of cyclopropane derivatives has attracted much attention,[1] since they are useful intermediates in organic synthesis owing to ring strain[2] and because many natural products include three-membered rings.[3] In this paper, we describe a novel one-step [2 + 1] cycloaddition synthesis of cyclopropanes using (*E*)-1-(phenylseleno)-2-(trimethylsilyl)ethene (**1**).

Recently, several studies on the [2 + 2] cycloaddition reactions of sulfur-substituted olefins activated by electron-withdrawing groups and Lewis acid promoters have been reported.[4] Since **1** should be activated by a combination of the α-seleno[5] and the β-silicon cation stabilization effects,[6] we expected that [2 + 2] cycloaddition

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(1) For reviews, see: *The Chemistry of the Cyclopropyl Group*, Rappoport, Z., Ed.; John Wiley and Sons: New York, 1987.

(2) For reviews, see: (a) *Small Ring Compounds in Organic Synthesis* I, II, III, IV; de Meijere, A., Ed.; Springer-Verlag: New York, 1986, 1987, 1988, 1990. (b) de Meijere, A.; Wessjohann, L. *Synlett* **1990**, 20.

(3) For reviews, see: (a) Corey, E. J.; Cheng, X. *The Logic of Chemical Synthesis*; John Wiley and Sons: New York, 1989. (b) Thomas, A. F.; Bessiere, Y. The Synthesis of Monoterpenes, 1980–1986. In *The Total Synthesis of Natural Products*; Apsimon, J., Ed.; John Wiley and Sons: New York, 1988; Vol. 7.

(4) (a) Takeda, T.; Fujii, T.; Morita, K.; Fujiwara, T. *Chem. Lett.* **1986**, 1311. (b) Hayashi, Y.; Narasaka, K. *Chem. Lett.* **1989**, 793. (c) Hayashi, Y.; Narasaka, K. *Chem. Lett.* **1990**, 1295. (d) Hayashi, Y.; Niihata, S.; Narasaka, K. *Chem. Lett.* **1990**, 2091.

(5) (a) McClelland, R. A.; Leung, M. *J. Org. Chem.* **1980**, *45*, 187. (b) Hevesi, H.; Piquard, J. L. *J. Am. Chem. Soc.* **1981**, *103*, 870. (c) Halazy, S.; Hevesi, L. *J. Org. Chem.* **1983**, *48*, 5242. (d) Nsunda, K. M.; Hevesi, L. *Tetrahedron Lett.* **1984**, *25*, 4441.

(6) For β-silicon stabilization of a carbonium ion, see: (a) Jarvie, A. W. *Organomet. Chem. Rev., Sect. A* **1970**, *6*, 153. (b) Cooke, M.; Eaborn, C.; Walton, D. R. M. *J. Organomet. Chem.* **1970**, *24*, 301. (c) Bourne, A. J.; Jarvie, A. W. P. *Ibid.* **1970**, *24*, 335. (d) Taylor, T. G.; Berwin, H. J.; Jetkunica, J.; Hall, M. L. *Pure Appl. Chem.* **1972**, *30*, 599.

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