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.

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[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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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.

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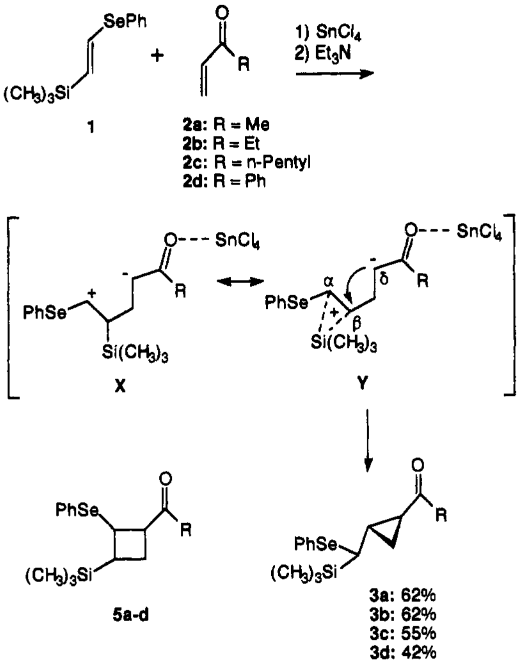
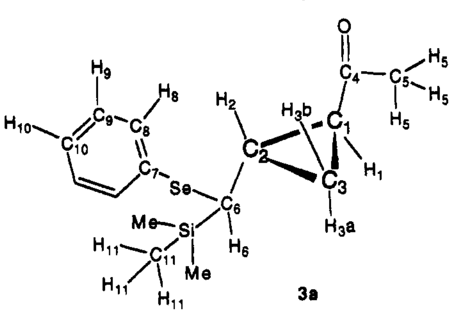
Scheme I



reactions of 1 with vinyl ketones in the presence of Lewis acids would occur readily. Surprisingly, instead of four-membered ring formation, an unexpected cyclopropanation resulted via a 1,2-shift of the trimethylsilyl group[7,8] (Scheme I). The structure of the products was established by spectral data and conversion to the cyclopropane-containing natural product (±)-rothrockene (4).[9] Cyclopropane ring closure presumably occurs via a zwitterionic intermediate which is stabilized by interaction with the adjacent carbon–silicon bond. This is the first example of a 1,2-silicon shift leading to cyclopropanation.

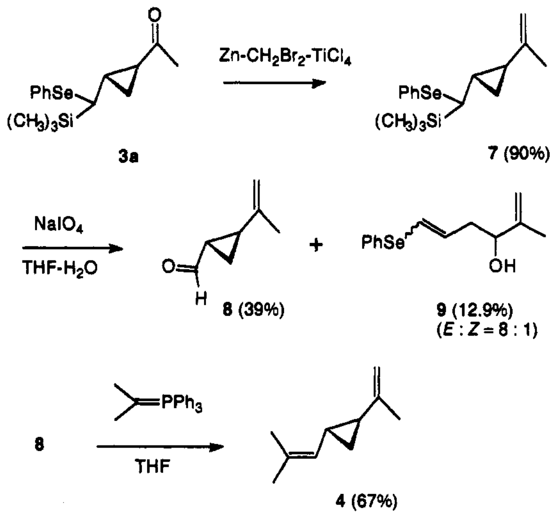
Table I. ^1H and ^{13}C NMR Spectra of 3a



3a

^1H	δ (ppm)	J_{HH} (Hz)	^{13}C	δ (ppm)	$^1J_{CH}$ (Hz)
H_{11}	0.166 (s, 9 H)		C_{11}	-1.897	120 (q)
H_{3a}	0.747 (ddd, 1 H)	3.97 6.37 8.19	C_3	19.72	164 (t)
H_{3b}	1.32 (ddd, 1 H)	3.97 4.56 8.63			
H_1	1.53 (ddd, 1 H)	4.17 4.56 8.19	C_1	29.98	163 (d)
H_2	1.72 (dddd, 1 H)	4.17 6.37 8.63 10.7	C_2	29.91	163 (d)
H_5	1.93 (s, 3 H)		C_5	30.43	127 (q)
H_6	2.09 (d, 1 H)	10.7	C_6	36.26	129 (d)
$H_{9,10}$	7.24–7.30 (m, 3 H)		$C_{8,9,10}$	127.5	161 (d)
				129.1	164 (d)
H_8	7.55–7.59 (m, 2 H)			134.4	163 (d)
			C_7	130.6	(s)
			C_4	207.7	(s)

Scheme II



In the presence of $SnCl_4$ (1.5 equiv for 2a–c and 2.4 equiv for 2d), the reaction of 1[10] (1 equiv) and vinyl ketones 2a–d (1.3 equiv) was carried out in CH_2Cl_2 at −78 °C for 3 h.[11] Quenching with triethylamine (2.3–6.9 equiv) gave products **3a–d** (**3a** 62%, **3b** 62%, **3c** 55%, **3d** 42%) which are isomers of the expected four-membered compounds **5a–d**. However, the presence of a saturated cyclobutyl ketone moiety is incompatible with the observed IR spectra (1692–1698 cm^{-1}) of **3a–c**. An alternative reaction pathway is three-membered formation via a 1,2-silicon migration to give cyclopropane derivatives (Scheme I). The IR spectra agree with the cyclopropyl ketone structures **3a–d**. The structure of **3a** was established by ^1H NMR, ^{13}C NMR, $^{13}C/^1H$ COSY, long-range $^{13}C/^1H$ COSY, and 2D-NOESY spectra. All data are in complete agreement with the cyclopropane structure (Table I). The observation that H_1, H_2, H_{3a}, and H_{3b} are coupled to each other while H_6 is coupled only with H_2 supports structure **3a** (see numbering of H and C atoms in Table I). $^1J_{CH}$ values (J = 163–164 Hz ($C_{1,2,3}$)) in the ^{13}C NMR spectrum, which are characteristic of cyclopropanes, also support structure **3a**. The existence of long-range coupling, $^3J_{CH}$, C_6–Si–C_{11}–H_{11}, and $^3J_{CH}$, C_7–Se–C_6–H_6, indicates that Se and Si atoms reside on the same carbon (C_6). The assignment of the trans stereochemistry of the acetyl and CH(SePh)-

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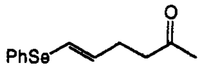
($SiMe_3$) groups is based on 2D-NOESY. The relative configuration at C_2 and C_6 could not be determined from the NMR spectra.

The reaction of **1** and **2a** with $SnCl_4$ in CH_2Cl_2 (−78 °C, 3 h), followed by quenching with water instead of triethylamine gave **3a** (51%) and the Michael adduct (*E*)-6-(phenylseleno)-5-hexen-2-one (**6**) (8%). The NMR spectra of the cycloadducts **3b–d** are also in complete agreement with the cyclopropane structures.



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The structure of **3a** was confirmed by a three-step conversion to the three-membered natural product, (±)-rothrockene (**4**)[9] (Scheme II). Methylenation of the carbonyl group of **3a** by Zn–CH_2Br_2–$TiCl_4$[12] gave **7** in 90% yield. Olefin **7** was oxidized with $NaIO_4$ in THF–H_2O solution at room temperature to give the sila-Pummerer products **8** and **9**.[13] Aldehyde **8** was obtained in 39% yield as a major product along with the ring-opened byproduct **9** (12.9% yield, $E/Z = 8/1$). Wittig reaction of **8** with isopropylidene–triphenylphosphorane in THF gave (±)-rothrockene (**4**) in 67% yield. The spectral data of **4** are in accord with the reported data.[9]

The observed preference for cyclopropanation instead of four-membered ring formation is rationalized as follows. In the first step, the nucleophilic vinyl selenide **1** attacks the electrophilic olefins **2a–d** activated by a Lewis acid to give carbonium ion X in Scheme I. The regioselectivity of this reaction with respect to selenium is the same as it is in the reaction of **1** or 1-(phenylseleno)-1-(trimethylsilyl)ethene (**10**) and unsaturated acid chlorides in the presence of Lewis acids.[14,10] Furthermore, the zwitterionic intermediate X is stabilized by interaction with the adjacent carbon-silicon bond ("β-silicon effect") to give a silicon-bridged carbocation Y. Nucleophilic attack of C_δ at the kinetically favored C_β position rather than at C_α generates the cyclopropane ring as a result of a 1,2-shift of the trimethylsilyl group (Scheme I).

To our knowledge, this is the first example of a 1,2-silicon migration giving rise to a cyclopropane ring. The synthetic utility of the unsymmetrically substituted cyclopropane products is demonstrated by the synthesis of (±)-rothrockene (**4**). Further studies are under way in our laboratory so as to determine why the Se–Si combination leads to a strained three-membered ring and to carry out further applications of this novel cyclopropanation.

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Supplementary Material Available: Experimental details and spectral data for **3a–d**, **4**, and **6–9**, ^1H, ^{13}C, $^{13}C/^1H$ COSY, long-range $^{13}C/^1H$ COSY, and 2D-NOESY actual spectra of **3a**, and ^1H and ^{13}C NMR actual spectra of **4** (19 pages). Ordering information is given on any current masthead page.

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Carbonyl-Protected β-Lithio Aldehydes and Ketones via Reductive Lithiation. A General Preparative Method for Remarkably Versatile Homoenolate Equivalents

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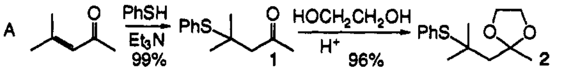
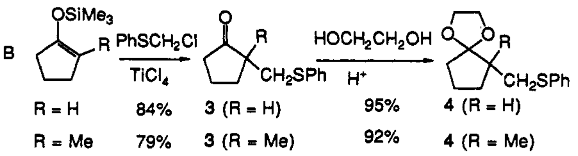
Summary: A general procedure for producing homoenolate equivalents consists of reductive lithiation, induced by 4,4′-di-*tert*-butylbiphenylide, of carbonyl-protected β-(phenylthio) carbonyl compounds prepared in turn by thiophenol addition to enones or the alkylation of silyl enol ethers by α-chlorothioethers.

Although homoenolate anions and their synthetic equivalents have been long recognized as potentially powerful synthons,[1] there are as yet no general methods available for their preparation. We now present the most general and versatile preparative method for homoenolate equivalents. It is based on the reductive lithiation[2] of carbonyl-protected β-(phenylthio) aldehydes and ketones. The key is the ease with which the substituted β-(phenylthio) carbonyl compounds are prepared. One method (A) involves the nearly quantitative 1,4 addition of thiophenol to α,β-unsaturated aldehydes and ketones[3] as shown for mesityl oxide in eq 1. Another involves alkylation[4] of the enol silyl ethers[5] of ketones with β-chloro



(1)



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