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Stannylformylation of Vinylcyclopropanes Accompanied by Radical Ring-Opening

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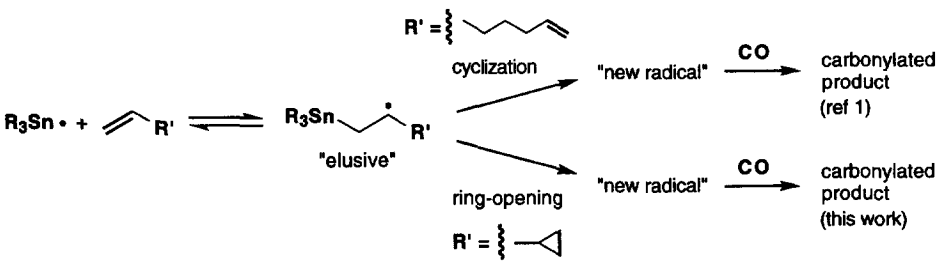
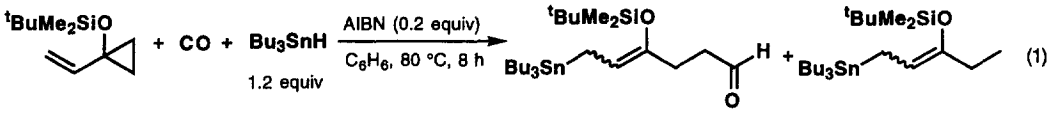
Abstract: Treatment of vinylcyclopropanes with CO in the presence of Bu_3SnH and AIBN (catalytic) leads to a stannylformylated product via a cyclopropylcarbinyl radical opening to a homoallylic radical.

In a previous communication, we reported free-radical mediated stannylformylation of 1,6-dienes accompanied by five-membered radical ring-closure.[1] As shown in the former study, for stannylcarbonylation of olefinic compounds to be successful, the initially generated radical, formed by the addition of stannyl radical to the alkene must be sequenced by a "rapid" event such as a 5-hexenyl cyclization. This is a necessary requirement to overcome the reversibility of the stannyl radical addition step as illustrated in Scheme 1. As the ring-opening of cyclopropylcarbinyl radical[2] is known to be considerably faster ($k_{ring\ opening}$ = 1.2 x 10^8 s^{-1}, $k_{ring\ closure}$ = 2.0 x 10^4 s^{-1} at 37 °C)[2b] than 5-*exo* cyclization, we believed that the use of vinylcyclopropanes would also be promising. In this letter, we wish to report that vinylcyclopropanes can successfully participate in free-radical mediated stannylformylation affording γ,δ-unsaturated aldehydes possessing an ε-stannyl group.



Scheme 1. Concept for Two Types of Stannylformylation of Alkenes

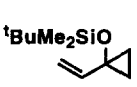
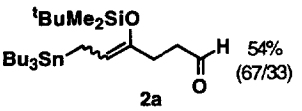
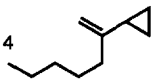
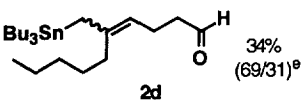
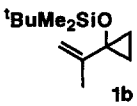
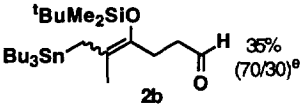
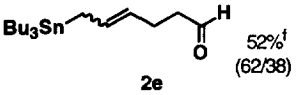
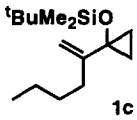
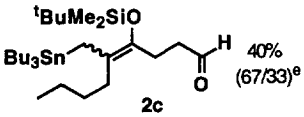
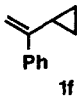
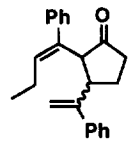
The reaction of 1-siloxy-1-vinylcyclopropane **1a** (0.05 M in benzene) with Bu_3SnH (1.2 equiv) and AIBN (0.2 equiv) at 90 atm of CO afforded the desired stannylformylation product **2a** in 34% yield along with hydrostannylation product **3a**[3] in 25% yield (eq 1). By employing a lower concentration of **1a** (0.03 M) and a higher CO pressure (110 atm), the reaction resulted in an increased yield of **2a** (54%). Unfortunately, however, further dilution was ineffective in improving this reaction due to poor chain propagation.



1a	0.05 M	90 atm	**2a** (E/Z)	34% (65/35)	**3a** (E/Z) 25% (50/50)
	0.03 M	90 atm		46% (67/33)	15% (59/41)
	0.03 M	110 atm		54% (67/33)	12% (43/57)

Table 1 summarizes some of our results in the stannylformylation of various vinylcyclopropanes.[4] Stannylformylation of vinylcyclopropanes **1d** and **1e** gave **2d** and **2e**, respectively (runs 4 and 5). Similarly, alkyl substituted 1-siloxy-1-vinylcyclopropane **1b** and **1c** were converted to ε-stannyl substituted γ-siloxy-γ,δ-unsaturated aldehydes **2b** and **2c**, respectively (runs 2 and 3).

Table 1. Stannylformylation of Vinylcyclopropanes[a]

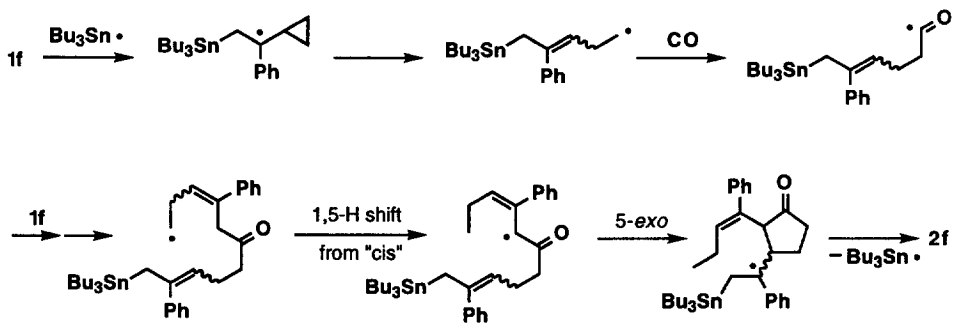
run	vinylcyclo-propanes, 1	products, 2	yields[b] (E/Z)[c]	run	vinylcyclo-propanes, 1	products, 2	yields[b] (E/Z)[c]
1	 **1a**	 **2a**	54% (67/33)	4	 **1d**	 **2d**	34% (69/31)[e]
2	 **1b**	 **2b**	35% (70/30)[e]	5	 **1e**	 **2e**	52%[f] (62/38)
3	 **1c**	 **2c**	40% (67/33)[e]	6[d]	 **1f**	 **2f**	21%[g] (61/39)[h]

[a]Reactions were conducted on a 0.5 mmol scale of **1** (runs 1-4; [**1**] = 0.03-0.1 M, Bu_3SnH 1.1-1.2 equiv, CO 95-110 atm, AIBN 0.2 equiv) or a 1.0 mmol scale of Bu_3SnH (runs 5 and 6; [**1**] = 0.1-0.15 M, Bu_3SnH 0.33 equiv, CO 90 atm, AIBN 0.067-0.1 equiv) in benzene at 80 °C for 8 h. [b]Isolated yields by HPLC. Isolated yields of ring-opening/reduction products: 12% (run 1), 27% (run 2), 31% (run 3), 20% (run 4), 23% (run 5), 10% (run 6). [c]Determined by ^{1}H-NMR spectroscopy. [d]Bu_3SnH (10%) was recovered. [e]Regiochemistry not assigned. [f]Yield based on Bu_3SnH [g]Regiochemistry of double bond in **2f** was confirmed by NOE experiments, see footnote 5. [h]Trans/cis.

Unlike 1-siloxy-1-vinylcyclopropane **1a**,[5,6] 1-(1'-siloxyethenyl)cyclopropane **1g** was essentially inert toward the tin radical mediated ring-opening. PM3 semi-empirical molecular orbital calculation of the difference in heats of formation of the cyclopropylcarbinyl radical ring-opening suggests that the energy gain from the α-siloxycyclopropylcarbinyl radical is ca. 8 kcal/mol smaller than that from β-siloxycyclopropylcarbinyl radical, in support of this observation.

1g

Interestingly, attempted stannylformylation of (1-phenylethenyl)cyclopropane (**1f**) led to a cyclopentanone **2f**, comprizing CO and two molecules of **1f** rather than the expected stannylformylation product (run 6).[7] A possible rationale to account for this unusual reaction is provided in Scheme 2. Thus, the intermediate acyl radical, arising from stannylative ring-opening and subsequent CO trapping of the vinylcyclopropane, experiences addition to a second molecule of **1f**.[8] The observed cyclopentanone arises following a 1,5-H shift, 5-*exo* cyclization, and finally expulsion of a stannyl radical. We are currently engaged in optimizing this unusual [3+1+1] annulation reaction.



Scheme 2. Possible Reaction Pathway for the Formation of Cyclopentanone **2f** from **1f**

In summary, we have demonstrated that free-radical stannylformylation of vinylcyclopropanes provides a synthetically useful ring-opened carbonylated products. Although as observed in the stannylformylation of 1,6-dienes,[1] formylation/reduction ratios are relatively low compared with formylation of alkyl halides[9] carried out under similar conditions (concentration and CO pressure), the reaction provides a unique entry to allyltin compounds possessing a formyl group in ε-position.

Acknowledgment. We thank the Instrumental Analysis Center, Faculty of Engineering, Osaka University, for assistance in obtaining 600 MHz NMR and mass spectra. Financial support of this work through a Grant-in-Aid for Scientific Research, the Ministry of Education, is gratefully acknowledged. We acknowledge Dr. Claudio F. Sturino for helpful discussion.

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2. (a) Bowry, V. W.; Lusztyk, J.; Ingold, K. U. *J. Am. Chem. Soc.* **1991**, *113*, 5687-5698. (b) Bowry, V. W.; Ingold, K. U. *J. Am. Chem. Soc.* **1991**, *113*, 5699-5707. (c) Nonhebel, D. C. *Chem. Soc. Rev.* **1993**, 347-359. (d) Newcomb, M. *Tetrahedron* **1993**, *49*, 1151-1176. (b) Beckwith, A. L. J.; Bowry, V. W. *J. Am. Chem. Soc.* **1994**, *116*, 2710-2716. (e) Feldman, K. S. *Synlett* **1995**, 217-225.
3. For radical-mediated hydrostannylation of vinylcyclopropanes, see: Ratier, M.; Pereyre, M. *Tetrahedron Lett.* **1976**, 2273-2276.
4. **General procedure for stannylformylation of 1:** Benzene (10 mL), 1-*tert*-butyldimethylsiloxy-1-vinylcyclopropane (**1a**, 62 mg, 0.30 mmol), tributyltin hydride (106 mg, 0.36 mmol), and AIBN (11 mg, 0.06 mmol) were placed in a 50-mL stainless steel autoclave lined with a round bottomed glass tube. The autoclave was closed, purged twice with carbon monoxide, and then pressurized with 110 atm of CO and was heated, with stirring, at 80 °C for 8 h. After excess CO was discharged at room temperature, the benzene was evaporated. HPLC (seven cycles, GPC columns using $CHCl_3$ as an eluant) gave 84 mg (54%) of 4-*tert*-butyldimethylsiloxy-6-tributylstannyl-4-hexenal (**2a**): ^{1}H-NMR ($CDCl_3$, 270 MHz) E isomer: δ 0.11 (s, E 6H), 0.13 (s, Z 6H), 0.79-0.95 (m, E 18H+ Z 18H), 1.25-1.60 (m, E 20H+Z 20H), 2.30-2.42 (m, E 2H+Z 2H), 2.50-2.62 (m, E 2H+Z 2H), 4.60 (t, J = 8.9 Hz, E 1H), 4.79 (t, J = 8.9 Hz, Z 1H), 9.76 (s, Z 1H), 9.80 (s, E 1H); ^{13}C-NMR ($CDCl_3$, 68 MHz) δ -3.85 (Z), -4.41 (E), 7.40 (Z), 7.92 (E), 9.25 (E), 9.33 (Z), 13.68 (E+Z), 18.00 (E), 18.26 (Z), 23.69 (E+Z), 25.75 (E), 25.86 (Z), 27.39 (E+Z), 29.16 (Z), 29.21 (E), 41.31 (E), 41.95 (Z), 106.69 (E), 107.68 (Z), 144.46 (Z), 145.29 (E), 202.10 (Z), 202.46 (E); IR (a mixture of isomers; neat) 1728 cm^{-1} ($\nu_{C=O}$), 1654 cm^{-1} ($\nu_{C=C}$); EIHRMS calcd for $C_{20}H_{41}O_2SiSn$ (M^+-Bu) m/z 461.1898, found, E isomer 461.1878, Z isomer 461.1887. E/Z determination is based on ^{13}C-NMR data, see: Heathcock, C. H.; Buse, C. T.; Kleschick, W. A.; Pirrung, M. C.; Sohn, J. E.; Lampe, J. *J. Org. Chem.* **1980**, *45*, 1066-1081.
5. For other synthetic utility of **1a**, see: Ryu, I.; Ikura, K.; Tamura, Y.; Maenaka, J.; Ogawa, A.; Sonoda, N. *Synlett* **1994**, 941-942.
6. For the use of **1a** for radical polymerization, see: Mizukami, S.; Kihara, N.; Endo, T. *J. Am. Chem. Soc.* **1994**, *116*, 6453-6454.
7. *trans*-2-(1-Phenyl-1-butenyl)-3-(1-phenyl-1-ethenyl)cyclopentanone (**2f**): ^{1}H-NMR ($CDCl_3$, 600 MHz): δ 0.92 (t, J = 7.5 Hz, 3H), 1.55 (ddd, J = 3.2, 9.8, 19.9 Hz, 1H), 1.87 (dd-like, J ~ 7.3, 12.8 Hz, 1H), 1.89 (dd-like, J ~ 7.4, 12.8 Hz, 1H), 2.03 (dd, J = 9.0, 18.0 Hz, 1H), 2.05 (dd, J = 8.9, 19.9 Hz, 1H), 2.38 (dd, J = 7.7, 18.0 Hz, 1H), 2.98 (dt, J = 5.3, 11.8 Hz, 1H, β-methine), 3.08 (d, J = 11.8 Hz, 1H, α-methine), 5.20 (s, 1H), 5.27 (s, 1H), 5.59 (t, J = 7.4 Hz, 1H), 6.96-7.03 (m, 2H), 7.15-7.18 (m, 2H), 7.21-7.30 (m, 6H); ^{13}C-NMR ($CDCl_3$, 150 MHz) δ 14.36 (q), 22.49 (t), 28.02 (t), 38.31 (t), 45.70 (d), 63.87 (d), 112.98 (t), 126.93 (d), 127.39 (d), 127.97 (d), 128.09 (d), 128.21 (d), 129.05 (d), 135.81 (s), 136.18 (d), 139.20 (s), 141.81 (s), 150.20 (s), 217.41 (s); IR (a mixture of isomers; neat) 1742 cm^{-1} ($\nu_{C=O}$), 1670, 1628 cm^{-1} ($\nu_{C=C}$); EIHRMS calcd for $C_{23}H_{24}O$ m/z 316.1827, found, 316.1831. The regiochemistry of double bond was confirmed based on NOE experiments, in which an enhancement (2.8%) of vinyl proton signal (5.59 ppm) was observed when the ortho proton of phenyl group was irradiated. The chemical shift of two methine proton signals for minor isomer was observed at lower field (β: 3.14 and α: 3.51 ppm) compared with those of major isomer, supporting the major isomer being *trans*.
8. Higher reactivity of acyl radical to **1f** relative to **1e** can be explained by lower LUMO of **1f** (LUMO of **1e**: 1.02 eV, LUMO of **1f**: 0.18 eV, by PM3).
9. Ryu, I.; Kusano, K.; Ogawa, A.; Kambe, N.; Sonoda, N. *J. Am. Chem. Soc.* **1990**, *112*, 1295-1297.

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