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Synthesis of 1-Allyloxy-1-siloxycyclopropanes and 1-Propargyloxy-1-siloxycyclopropanes

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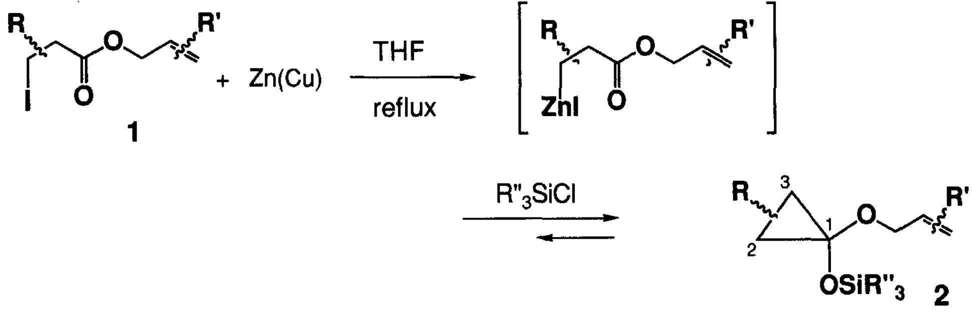
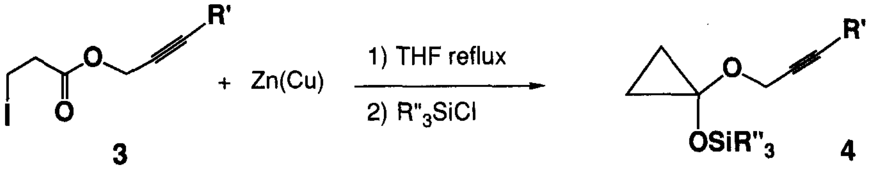
Summary: 1-Allyloxy-1-siloxycyclopropanes (**2**) and 1-propargyloxy-1-siloxycycloporpanes (**4**) were synthesized from ally β-iodopropionates (**1**) and propargyl β-iodopropionates (**3**), respectively, by treatment with zinc-copper couple and silylating agents.

Because of its strain, unique hybridization, and rigid structure, cyclopropane has been a molecule of continuing interest for both synthetic and theoretical organic chemists.[1] In order to investigate an intramolecular interaction between C=C double bond and C_1- C_2 and/or C_1- C_3 σ-bonds, 1-allyloxy-1-siloxycyclopropane (**2**) was required as a probe. These σ-bonds are expected to be weakened by the ketal oxygen atoms (n_O - $\sigma^*_{C\text{-}C}$ overlap).[2]



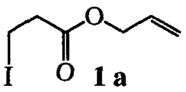
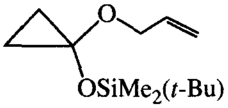
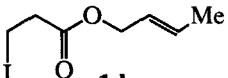
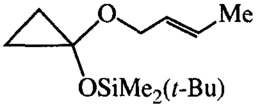
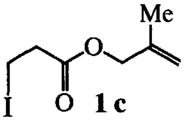
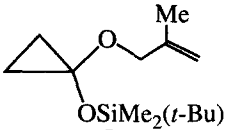
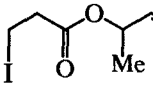
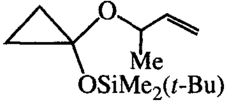
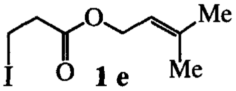
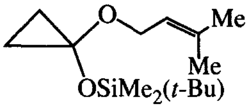
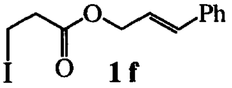
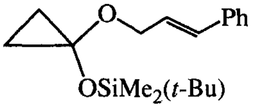
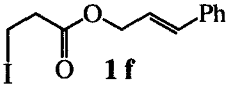
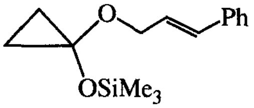
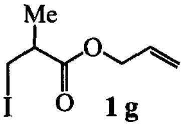
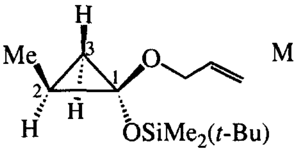
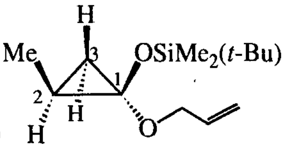
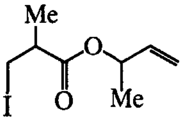
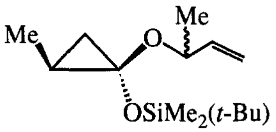
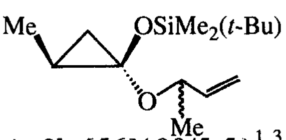
(1)



(2)

The preparation of **2** seemed to be straightforward, as similar saturated hydrocarbon analogs, e.g., 1-ethoxy-1-trimethylsiloxycyclopropane, widely utilized for many

Table I. Synthesis of 1-Allyloxy-1-siloxycyclopropanes (2)

run	starting iodide		product 2 [% isolated yield]{bp.°C/mmHg}	
1	 1a	1) Zn,THF reflux 2) $t\text{-}BuMe_2SiCl$		2a [56]{71/6.0}
2	 1b	1) Zn,THF reflux 2) $t\text{-}BuMe_2SiCl$		2b [58]{100/13.0}
3	 1c	1) Zn,THF reflux 2) $t\text{-}BuMe_2SiCl$		2c [66]{77/3.3}
4	 1d	1) Zn,THF reflux 2) $t\text{-}BuMe_2SiCl$		2d [42]{91/8.0}[1]
5	 1e	1) Zn,THF reflux 2) $t\text{-}BuMe_2SiCl$		2e [33]{60/2.0}[1]
6	 1f	1) Zn,THF reflux 2) $t\text{-}BuMe_2SiCl$		2f [50]{120/0.08}[1]
7	 1f	1) Zn,THF reflux 2) Me_3SiCl		2f' [30]
8	 1g	1) Zn,THF reflux 2) $t\text{-}BuMe_2SiCl$	 trans-2g  cis-2g	[56]{84/2.0}[1,2]
9	 1h	1) Zn,THF reflux 2) $t\text{-}BuMe_2SiCl$	 trans-2h  cis-2h	[56]{90/5.5}[1,3]

1) kugelrohr oven temperature

2) trans-2g: cis-2g = 12 : 1

3) four diastereomers of trans-2h (3.4 : 2.0) and cis-2h (1.3 : 1)

purposes,[3] are readily available by the method of Salaün.[4] An application of the method to allylic esters (e.g., allyl and cinnamyl β-chloropropionates), however, resulted in the formation of an intractable mixture of polymeric products.[5]

Here we describe a modification of Salaün's cyclopropanone ketal synthesis using zinc as the reducing metal. This method is applicable for the preparation of 1-allyloxy-1-siloxy- (**2**) and 1-propargyloxy-1-siloxycyclopropane derivatives (**4**) (equations 1 and 2).

The utility of the present method may be augmented by the ease of the reactions, performed on a scale of a few mmol to 100 mmol, and by the wide tolerance of substituents on both cyclopropane ring moiety and the allylic moiety (Table I).

The utility is also indicated by the stereoselective formation of **2g** (ca. 12 : 1). This makes sharp contrast to the observation that almost 1:1 stereoisomeric mixture of 1-alkoxy-1-trimethylsiloxy-2-methylcyclopropanes was obtained by the Salaün's method.[6] The structure of the major isomer was determined to be *trans*, i. e., C_2-methyl and *tert*-butyldimethylsiloxy groups are *trans* to each other, since a positive NOE was observed between allylic protons and one of the C_3-methylene protons, *cis* with respect to C_2-Me, characteristically appearing at the higher-field region (δ 0.43, d.d, J = 5.1 and 5.9 Hz) than the other two cyclopropane ring protons.[7]

In most cases, the yield are moderate (40 - 60%), but still acceptable. The moderate yield may owe its origin to the equilibrium of the product **2** with the β-zinc ester intermediate (equation 1). Synthetic use of this reverse process was developed by Kuwajima and Nakamura.[4b,4c]

The present method is also applicable for the synthesis of 1-propargyloxy-1-siloxycyclopropanes [**4a** (R' = Me): 56% isolated yield, bp. 77°C/1.3 mmHg; **4b** (R' = H): 24% isolated yield, bp. oven temp. 90°C/1.5 mmHg]. The formation of **4b**, though being albeit in low yield, suggests that the proton exchange between β-CH_2-Zn and the acetylenic proton is rather slow under the reaction conditions.

The *tert*-butyldimethylsilyl derivatives listed in Table I are stable for shelf-storage at an ambient temperature and could be purified by means of column chromatography and distillation under reduced pressure. The trimethylsilyl derivatives are thermally stable, but rather unstable toward hydrolysis: e.g., **2f'** completely decomposed during purification over silica gel and could be isolated in 30% yield over a basic alumina (grade III, hexane - benzene 5:1 eluent).

General Procedure for Preparation of 1-Allyloxy-1-siloxy-cyclopropane (2) and 1-Propargyloxy-1-siloxycyclopropane (4). A flask containing zinc-copper couple[8] (5.77 g, 88 mmol) and a magnetic stirring bar was purged with argon. Into this were added THF (80 mL) and **2** or **4** (80 mmol) successively in one portion via syringes. The mixture was stirred vigorously and refluxed for 4 h. Then a solution of *tert*-butyldimethylsilyl chloride (18.1 g, 120 mmol) in 30 mL of THF was added in one portion via a syringe at 35°C. At the same temperature the mixture was stirred overnight and then cooled and transferred into ether (500 mL) - cold aq. K_2CO_3 (33 g, 240 mmol in 300 mL of H_2O). Quick separation, drying over $MgSO_4$, and evaporation of the solvents, followed by distillation under reduced pressure provided almost pure **2** or **4**. Further purification was undertaken, if necessary, by means of column chromatography over silica gel (hexane - benzene eluent). Yields and boiling points for **2** are given in Table I. VPC (SiDC550) of **2** and **4**, except for **2h**, showed sharp single peaks. The diastereomers of **2h** were poorly separated and appeared as a broad single peak.

Studies focused on the origin of the stereoselectivity for the cyclopropanation are under progress. Study on a through-space σ-π interaction (e.g., a skeletal rearrangement of **2** catalyzed by Pd(II)) is reported in the accompanying paper.

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References and Notes

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(5) Although not verified, the polymerization may be initiated by an intramolecular addition of a radical species, formed at the β-position of the ester **1** by a single electron reduction with Na or Li, to the allylic double bond.

(6) Nakamura, E.; Oshino, H.; Kuwajima, I. *J. Am. Chem. Soc.* **1986**, *108*, 3745.

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