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A NEW STEREOSELECTIVE SYNTHESIS OF 2-SUBSTITUTED 1,3-BIS(TRIMETHYLSILYL)PROPENE DERIVATIVES AND THEIR CONVERSION TO CYCLOPENTANE AND CYCLOHEXANE DERIVATIVES

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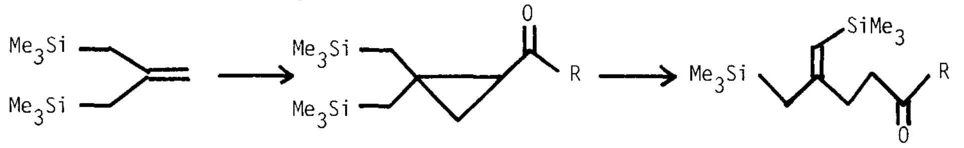
Summary: Ester 2 on treatment with sodium salt of sulfone or sulfoxide afforded 2-substituted 1,3-bis(trimethylsilyl)propene 3 in good yield, from which cyclopentane and cyclohexane derivatives bearing a trimethylsilyl group in the molecules were synthesized.

Silicon-assisted ring opening of cyclopropane derivatives substituted with trimethylsilyl or trimethylsilylmethyl group in the presence of acid has been recognized as one of the important tools for the synthesis of substituted olefins.[1] We reported that 2-(trimethylsilylmethyl) cyclopropyl ketones were smoothly cleaved with boron trifluoride-acetic acid complex under mild conditions to give γ,δ-enones in good yields.[2] In this report we describe an unusual alkylative ring opening of ethyl 2,2-bis(trimethylsilylmethyl)cyclopropanecarboxylate (2) in the basic conditions to give 2-substituted 1,3-bis(trimethylsilyl)propene 3 as shown in Scheme 1.



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2 R=OEt

4 R=$CH_2SO_2C_6H_5$

3a R=$CH_2SO_2C_6H_5$

3b R=$CH_2SO_2CH_3$

3c R=$CH(SO_2C_6H_5)CH_2CH{=}CHCH_2CH_3$

3d R=CH_2SOCH_3

Scheme 1

The ester 2 was prepared quantitatively by the rhodium(II) acetate catalyzed cyclopropanation[3] of allylsilane 1[4] with ethyl diazoacetate in ether, and treated with sodium salt of methyl phenyl sulfone in 1,2-dimethoxyethane and dimethyl sulfoxide at 65° for 2 h. The corresponding β-keto sulfone 4 was not obtained at all but instead the product 3a was stereoselectively produ-

Table I Synthesis of 1,3-Bis(trimethylsilyl)propene **3** from Ester **2**

Nucleophile[a]		Solvent	Conditions	Product	Yield, %[b]
$NaCH_2SO_2C_6H_5$[c]	(2)	DME/DMSO	65°/2h	**3a**	74
$NaCH_2SO_2CH_3$[c]	(4)	DME/DMSO	65°/1h	**3b**	64
$Li_2C(SO_2C_6H_5)$[d] $CH_2CH{=}CHCH_2CH_3$	(1.1)	THF	-78°/1h, then r.t./5h	**3c**	18
$NaCH_2SOCH_3$	(4)	THF/DMSO	0°/40min, then r.t./40min	**3d**	77

a) The amount of nucleophile used relative to **2** was shown in parenthes. b) Isolated yield. c) Prepared by the reaction of sulfone with dimethyl sulfoxide anion. d) Prepared by the reaction of sulfone with *n*-buthyllithium in the presence of tetramethylethylenediamine.

ced in 74% yield under ring opening. **3a**, $C_{19}H_{32}O_3SSi_2$: IR($CHCl_3$) 1720, 1325, 1155 cm^{-1}; ^1H NMR ($CDCl_3$) δ -0.01, 0.05 (each 9H, s), 1.57 (2H, s), 2.1-2.4 (2H, m), 2.7-2.9 (2H, m), 4.14 (2H, s), 5.00 (1H, s), 7.4-7.9 (5H, m); ^{13}C NMR ($CDCl_3$) δ 197.0, 154.6, 138.5 (each s), 133.9, 129.0, 128.0, 123.1 (each d), 66.9, 44.1, 31.1, 30.2 (each t), 0.4, -1.4 (each q). The stereochemistry of the double bond of **3a** was determined by the measurement of the nuclear Overhauser effect (NOE).[5]

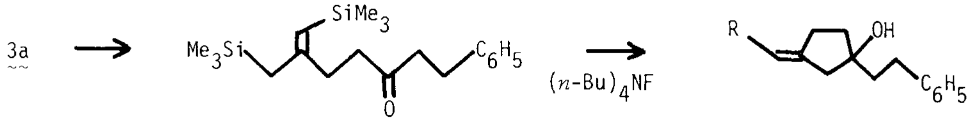
The ring opening of **2** also took place on the reactions with sodium salt of dimethyl sulfone or dimethyl sulfoxide and with dilithio derivative of *cis*-3-hexen-1-yl phenyl sulfone. The results are summarized in Table I.

The first step in the reaction of **2** with sodium anion of methyl phenyl sulfone seems to be the formation of β-keto sulfone **4**. Its ring opening must take place immediately and yield **3a**. The cleavage of the cyclopropyl ring of ester **2** by the reactions with bases did not occur, the starting material being recovered unchanged under the following conditions: DBN/benzene/refluxing; lithium di-isopropylamide/THF/-20°; lithium bis(trimethylsilyl)amide/THF/HMPA/room temperature. Strong bases have usually been used for the abstraction of protons α to silicon, because of their low acidity.[6] Hence one of the important factors of the rapid ring opening of **4** (or its sodium anion) is probably a severe steric strain between the acyl substituent and a trimethylsilylmethyl group in the *cis* relationship.[7]

The 1,3-bis(trimethylsilyl)propenes 3 were shown to be versatile intermediates by the conversions to cyclopentane and cyclohexane derivatives bearing trimethylsilyl group in the molecules. The ketone 5 was prepared from 3a by benzylation (benzyl bromide/sodium hydride/ dimethyl sulfoxide) followed by a reductive cleavage of carbon-sulfur bond[8] (sodium amalgam/ disodium hydrogen phosphate/methanol) in 63% yield. Then, it was subjected to fluoride ion[9] induced cyclization in tetrahydrofuran at room temperature to give cyclopentanol 6 as a major product (54% yield) and 7 as a minor product (16% yield) (Scheme 2). The geometry of the double bond in 6 was tentatively assigned.[10] On the contrary, the attempted Lewis acid catalyzed cyclization of 5 using titanium tetrachloride did not proceed giving a protodesilylation product.

Then an interesting cyclohexane derivative 11 was synthesized from 3a *via* aldehyde 10. On treatment of 3a with m-CPBA in dichloromethane at -78° for 30 min and then at -20° for 1h, a rearranged aldehyde 10 was obtained in quantitative yield. The aldehyde 10 seems to be produced by the rearrangement of carbonium ion 9 stabilized by the two trimethylsilyl groups or by the concerted process from epoxide 8.[11] The unstable aldehyde without purification was subjected to oxidative cyclization using an alkaline hydrogen peroxide in aqueous methanol at room temperature for 4h to afford α,β-epoxy cyclohexanone 11 in one step (60% yield). Its structure and stereochemistry were determined by an X-ray analysis.

We are currently investigating further synthetic utility of 1,3-bis(trimethylsilyl)propene 3.



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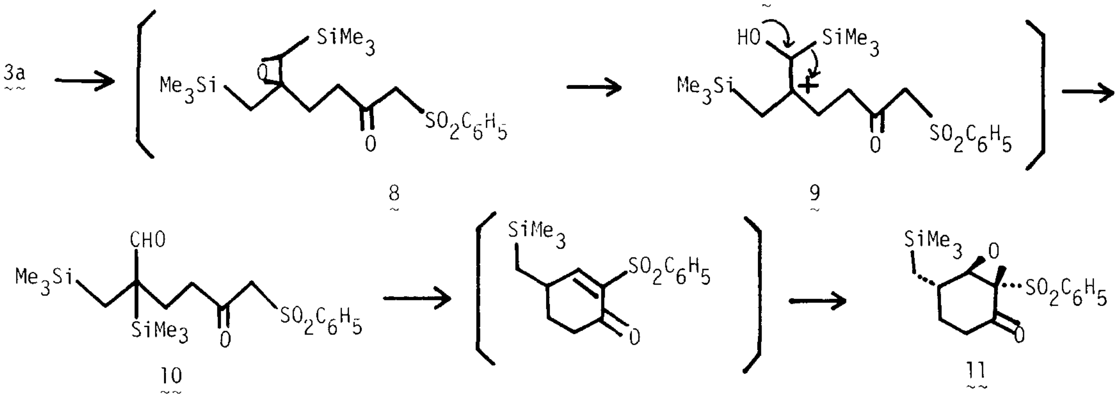
6 R=SiMe3

7 R=H

Scheme 2



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9

10

11

Scheme 3

References and Notes

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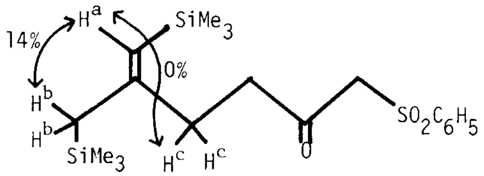
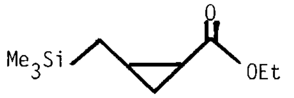
5. A 14% NOE of vinylic proton H^a was observed in the irradiation on H^b protons, while no NOE was observed in the irradiation on H^c protons.



3a

6. Tetramethylsilane can be deprotonated using *n*-buthyllithium in THF containing tetramethylethylenediamine. For reviews of preparation of α-silyl carbanions, see: P. Magnus, *Aldrichimica Acta*, **13**, 43 (1980); E. W. Colvin, "Silicon in Organic Synthesis", Butterworths, London (1981), P. 21-29.
7. The ester **12** [2](a mixture of *cis* and *trans* isomers) on treatment with boron trifluoride-acetic acid complex in refluxing dichloromethane gave the thermodynamically more stable *trans*-**12**, while ester **2** on the same treatment gave allylsilane **13** in good yield even at -78°. These facts also can be explained by a large steric strain in ester **2**.



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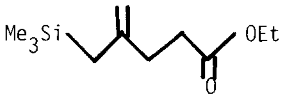

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10. **6**: 'H NMR($CDCl_3$) δ 0.08 (9H, s), 1.7-2.0 (4H, m), 2.1-2.9 (6H, m), 5.40 (1H, quintet, J=2.1 Hz), 7.0-7.4 (5H, m); ^{13}C NMR($CDCl_3$) δ 159.5, 142.5 (each S), 128.4, 128.3, 125.8, 121.3 (each d), 80.5 (s), 50.9, 42.4, 39.6, 31.0, 30.2 (each t), -0.3 (s).
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