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Triethylaluminum Catalyzed Ring Opening Reaction of 1-Acetyl-2-[(trimethylsilyl)-methyl]cyclobutanes. Stereoselective Preparation of (Z)-Enol Trimethylsilyl Ethers

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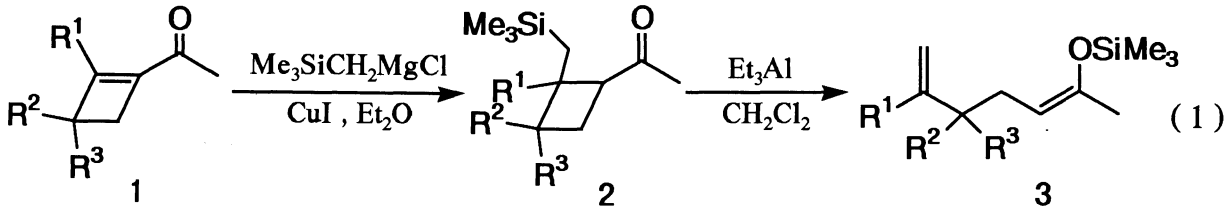
The triethylaluminum catalyzed ring opening reaction of 1-acetyl-2-[(trimethylsilyl)methyl]cyclobutanes gave (Z)-6-(trimethylsiloxy)-1,5-heptadienes stereoselectively. The starting materials were easily prepared by the 1,4-addition of (trimethylsilyl)methylmagnesium chloride to 1-cyclobutenyl ketones.

Enol silyl ethers of ketones are useful synthetic reagents for regioselective carbon-carbon bond formation and the precursors of functionalized ketones.[1] Since the geometry of the enolate essentially influences the stereochemical outcome of aldol condensation[2] and enol silyl ethers are easily converted to the corresponding boron enolates stereospecifically,[3] various methods have been developed for the regio and stereoselective synthesis of enol silyl ethers.[4,5] However, some of them are not applicable to unsymmetric ketones because the processes include the enolization of carbonyl compounds.

In this communication, we wish to report the regio and stereoselective synthesis of (Z)-6-(trimethylsiloxy)-1,5-heptadienes (**3**) by the triethylaluminum catalyzed ring opening reaction of 1-acetyl-2-[(trimethylsilyl)-methyl]cyclobutanes (**2**) (Eq. 1).

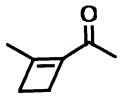
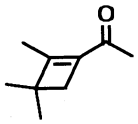
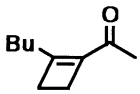
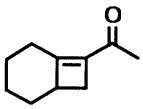
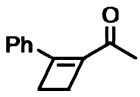


(1)

The present method consists of the conjugate addition of (trimethylsilyl)methylmagnesium chloride to 1-cyclobutenyl ketones (**1**)[6] and the ring opening reaction of the resulting cyclobutyl ketones (**2**). The first part of the present preparation was performed by the treatment of 1-cyclobutenyl ketones (**1**) with diorganocuprate (1.2 equiv.) prepared from (trimethylsilyl)methylmagnesium chloride and CuI (-30 °C, 30 min) in ether to give the adducts (**2**) in good yields (Table 1). The NMR spectra indicated that all the adducts (**2**) were mixtures of diastereomers and they could not be separated each other by silica gel chromatography. The two diastereomers (**2e** and **2e'**), however, were isolated when 1-acetyl-2-phenylcyclobutene (**1e**) was used.

Concerning the stereochemistry of the enol silyl ethers (**3**), we expected that the Z-isomers would be preferentially produced regardless of the stereochemistry of the starting materials (**2**) because the stereochemical course of the reaction would depend only on the conformation of acetyl group of **2**. As depicted in Eq. 2, the

Table 1. Preparation of 1-acetyl-2-[(trimethylsilyl)methyl]cyclobutanes (2)

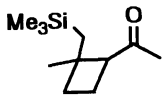
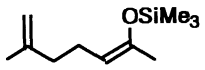
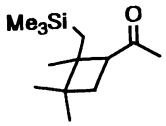
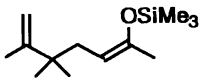
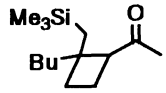
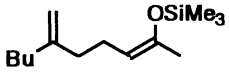
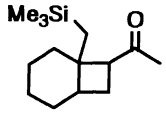
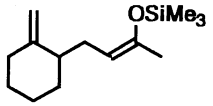
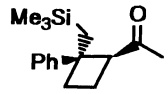
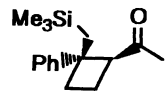
Entry	Cyclobutenyl ketone (1)		Temp °C	Time h	Product [a] (Yield / %)
1		**1a**	-50	0.5	**2a** (82)
2		**1b**	-78	3	**2b** (73)
3		**1c**	-78	overnight	**2c** (82)
4		**1d**	-50	5	**2d** (79)
5		**1e**	-78--30	4	**2e** (34)[b] **2e'** (32)b)

a) All compounds were identified by IR and NMR spectra. b) Both isomers (**2e** and **2e'**) were separated each other by TLC.

overlap of the p-orbital of carbonyl group and the breaking σ-orbital must be maintained during the reaction. Consequently, the carbonyl group or methyl group of acetyl moiety and the methylene of cyclobutane ring must be eclipsed. The transition state (**B**) which affords E-isomer is less stable than **A** because of the repulsion between methyl group and a hydrogen atom attached β to acetyl group.

Then we examined the ring opening reaction using the diastereomeric mixtures of **2** and found that triethylaluminum was an efficient catalyst for the present transformation. As was expected, (Z)-enol silyl ethers (**3a-d**) were selectively produced when **2** was treated with a catalytic amount of triethylaluminum (5 or 10 mol%) att 0–15 °C in CH_2Cl_2 (Table 2). The stereochemistry of **3** was determined by the comparison with the mixtures of E and Z isomers of authentic samples prepared by the reaction of α-lithiosulfones with acetyltrimethylsilane reported by Reich et al.[5] Since the isomerization of E-**3a** to Z-**3a** was not observed under the present reaction conditions, it is reasonable to assume that the present reaction is a kinetically controlled process. It was observed that trans-**2** isomerized to cis-**2** in the reaction carried out at low temperature (-30 °C). This fact may suggest that the migration of trimethylsilyl group from carbon to carbonyl oxygen proceeds via the most stable cyclic transition state of cis-isomer depicted in Fig. 1 even when trans-**2** was employed.

Table 2. Ring opening reaction of 1-acetyl-2-[(trimethylsilyl)methyl]cyclobutanes (2)[a]

Entry	Cyclobutyl ketone (2)		Et_3Al (equiv.)	Temp °C	Time h	Product [b](Isolated yield / %)		E : Z
1		**2a**	0.1	0–15	20		**3a** (82)	Z[c]
2		**2b**	0.1	0–15	21		**3b** (78)[d]	Z[e]
3		**2c**	0.1	0–15	15		**3c** (77)	Z[c]
4		**2d**	0.05	0	1		**3d** (78)	Z[c]
5		**2e**	0.1	0	0.5		**3e** (78)	13 : 87[f]
6		**2e'**	0.05	0	1		**3e** (82)	14 : 86[f]

a) All reactions were performed with a same procedure as described in the text, unless otherwise noted. b) The structures of enol silyl ethers (3) were supported by IR and NMR spectra and comparison with the authentic samples (mixture of stereoisomers)[5] c) The E-isomer could not be detected by NMR spectrum and GLC analysis. d) The structure of **3b** was identified by IR and NMR spectra and comparison with the authentic samples prepared by the reaction of 5,5,6-trimethyl-6-hepten-2-one with trimethylsilyl trifluoromethanesulfonate in the presence of triethylamine.[7] e) The E-isomer could not be detected by NMR spectrum. f) Determined by NMR spectrum.

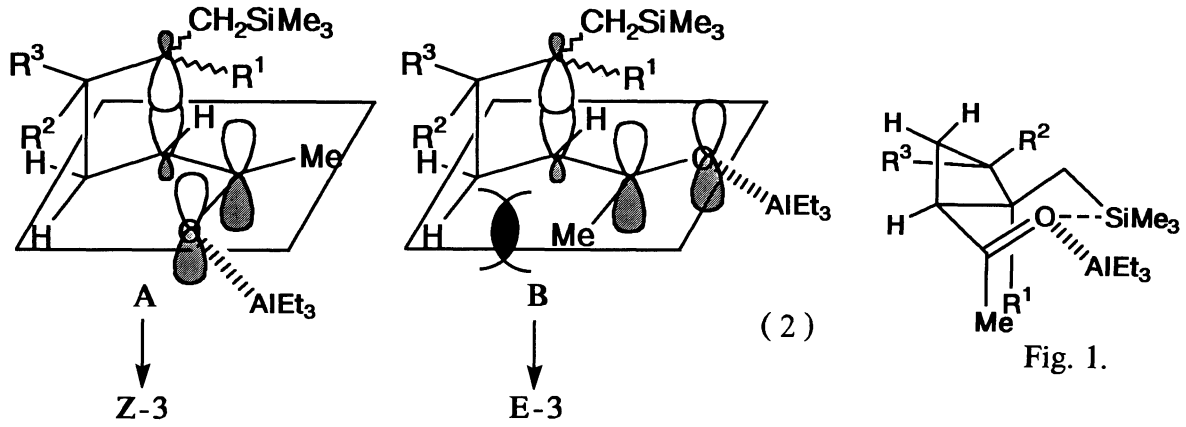


Fig. 1.

A typical experimental procedure is as follows: To a CH_2Cl_2 (5 ml) solution of 1-acetyl-2-butyl-2-(trimethylsilyl)methylcyclobutane (**2c**) (241 mg, 1 mmol) was added a hexane solution of triethylaluminum (0.1 mmol) at 0 °C. The reaction mixture was stirred at 0–15 °C for 15 h. The reaction was quenched by addition of saturated $NaHCO_3$ aqueous solution. The organic material was extracted with CH_2Cl_2 and the extract was dried over K_2CO_3. After evaporation of the solvent, the residue was purified by column chromatography (aluminum oxide deactivated with 15% water, hexane) to afford (Z)-2-butyl-6-(trimethylsiloxy)-1,5-heptadiene (**3c**) (185 mg) in 77% yield.

Concerning the rearrangement of trimethylsilyl group, the silyl group shifts from carbon to alkoxide oxygen are well known.[8] However, no migration of trimethylsilyl group from carbon to carbonyl oxygen except for the thermal or Lewis acid promoted isomerization of β-silyl ketones to enol silyl ethers[9] has been reported. It should be noted that the present reaction is the first example of 1,6-migration of trimethylsilyl group to the carbonyl oxygen and provides a useful method for the stereoselective preparation of unsaturated enol silyl ethers.

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