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MICHAEL ADDITION-PETERSON OLEFINATION SEQUENCE OF METHYL 2-(TRIMETHYLSILYL)ACRYLATE AS A CONVENIENT METHOD FOR CONSECUTIVE FORMATION OF CARBON-CARBON SINGLE AND DOUBLE BONDS

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A convenient method for the consecutive formation of carbon-carbon single and double bonds is presented with the example of the Peterson olefination of the carbanions resulted from the Michael addition of organometallics to methyl 2-(trimethylsilyl)acrylate.

The introduction of two carbon side-chains at both the α and β positions of electron-withdrawing substituent has been important as a key step in the elaboration of complex natural products.1) One of the most simple processes for this purpose consists of the Michael addition of organometallics to the olefins bearing an electron-withdrawing substituent and the followed nucleophilic reaction of the resulting carbanions.2) However, the Michael addition-aldol reaction sequence is not always a smooth reaction since both the reactions can be reversed.3)

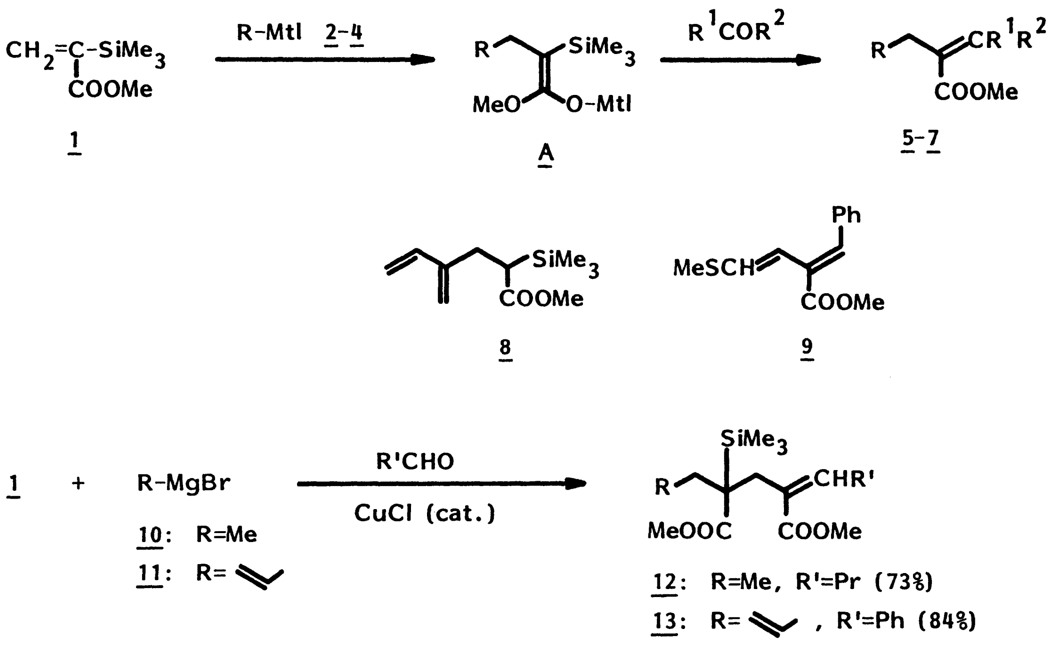
The condensation of α-silyl-substituted carbanions with aldehydes and ketones leading to the irreversible formation of olefins has found wide applications in organic synthesis as the Peterson olefination.4) Accordingly the Peterson reaction of the α-silyl carbanions resulted from the Michael addition to vinylsilanes5) may offer a general process for the consecutive formation of carbon-carbon single and double bonds at the β and α positions of the olefins.6) In order to equilibrate the Michael addition between the vinylsilanes and a variety of organometallics in favor for the adduct, an ester group will be effectively introduced to the α-position of vinylsilanes as the substituent capable of stabilizing the resulting α-silyl carbanions.7)

The present communication presents the Michael addition-Peterson olefination sequence of methyl 2-(trimethylsilyl)acrylate.

The reaction of methyl 2-(trimethylsilyl)acrylate 1 8) with phenylmagnesium bromide 2 (1.1 equiv.) in the presence of CuCl (0.5 mol%) in dry ether was carried out under nitrogen at -15 °C for 1 h, and then the mixture was treated with benzaldehyde (1 equiv.). The hydrolytic work-up and the chromatographic purification over silica gel gave methyl 2-benzyl-3-phenylacrylate 5a in 80% yield as a mixture of the E- and Z-isomers (E/Z = 1/4)9) as shown in Scheme 1 and Table 1.

Apparently this reaction involves the initial formation of a magnesium enolate A (R=Ph, Mtl=MgBr) from the Michael addition of 2 to 1 and the subsequent Peterson reaction with benzaldehyde leading to 5a. This effective Peterson olefination of the magnesium enolate A should be emphasized since the α-silyl carbanions formed by the addition of a Grignard reagent to activated vinylsilanes have failed in the nucleophilic additions to a carbonyl group.10) The E/Z ratio does not seem important in this case as it is known that the similar olefination using a lithio(trimethylsilyl)acetate and benzaldehyde gives the E- and Z-isomers of olefins whose ratios vary depending upon the reaction conditions.11, 12) In the absence of CuCl, a slightly lower yield of 5a was obtained.

Instead of benzaldehyde, such carbonyl compounds as pivalaldehyde, cinnamaldehyde, crotonaldehyde, acetone, and cyclohexanone could be successfully employed giving 5b to 5f in fair to good yields (Table 1). The E- and Z-isomers were easily separated from each other through a silica gel chromatography.

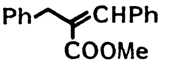
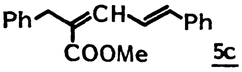
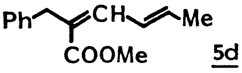
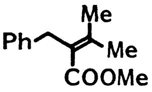
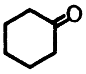
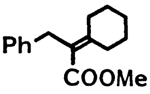
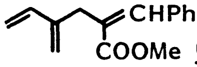
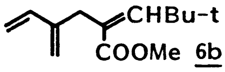
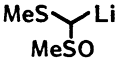
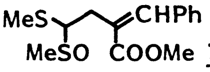
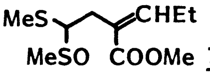
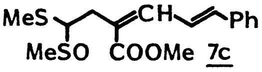


Scheme 1.

For the introduction of additional functionalities, 2-lithio-1,3-butadiene 3 13) and methyl lithio(methylsulfinyl)methyl sulfide 4 were allowed to add to 1 giving 6 and 7, respectively, after the treatment of the resulting carbanions with several aldehydes (Table 1). The reaction of 1 with 3 and then with cyclohexanone or 3-pentanone afforded only the Michael adduct 8 (52 or 71% yield respectively) which was also formed together with 6b, indicating that the α-silyl carbanion A (R=Ph, Mtl=MgBr) derived from 2 is much reactive to carbonyl compounds than A (R=1,3-butadien-2-yl, Mtl=Li) from 3. The products 7 readily eliminated MeSOH on heating to afford vinyl thioethers as shown with an example of the thermolysis of 7a into 9 that was isolated as a mixture of E- and Z-isomers in 90% yield.

When alkyl Grignard reagents were used as the Michael donors,14) other kinds of products were obtained as shown with an example for the formation of 12 in the reaction with methylmagnesium iodide 10 in the presence of CuCl (Scheme 1). Although it is clear that two molecule of 1 has participated in the reaction, the

Table 1. Michael Addition-Peterson Olefination Sequence of Methyl 2-(Trimethylsilyl)acrylate 1

R-Mtl	R^1COR^2	Conditions[a)]		Products		Yield[b)]	E/Z
		Michael	Peterson			%	
PhMgBr 2	PhCHO	A	D		5a	80	1/4
2	t-BuCHO	A	D		5b	54	3/2
2	PhCH$\overset{t}{=}$CHCHO	A	D		5c	63	9/11
2	MeCH$\overset{t}{=}$CHCHO	A	D		5d	59	3/7
2	MeCOMe	A	D		5e	73	-
2		A	D		5f	40	-
 3	PhCHO	B	E		6a	74	2/1
3	t-BuCHO	B	E		6b	47[c)]	Z only
3	PhCH$\overset{t}{=}$CHCHO	B	E		6c	45	1/3
 4	PhCHO	C	F		7a	90	E only
4	EtCHO	C	F		7b	72	1/1
4	PhCH$\overset{t}{=}$CHCHO	C	F		7c	71	E only

a) A: 1 + 2 (1.1 equiv.) + CuCl (0.5 mol%) in ether at -15 °C for 1 h; B: 1 + 3 (1.1 equiv.) + TMEDA (2 equiv.) in ether at -78 °C for 0.5 h; C: 1 + 4 (1.1 equiv.) in THF at -78 °C for 1 h; D-F: Carbonyl compounds (1 equiv.) were added at -15 °C (D) or -78 °C (E, F) and then the reactions were performed at room temperature for 0.5 h (D), 2 h (E), or 12-15 h (F).

b) Isolated yields. c) The Michael adduct 8 was also obtained in 24% yield.

detail of the reaction mechanism has not been confirmed yet.[15)] The similar reaction using vinylmagnesium bromide 11 provided 13 in an excellent yield.

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9) All the new compounds reported herein gave the satisfactory elemental analyses as well as the spectral data. The assignment of the E- and Z-isomers was based on the chemical shifts of the β-hydrogens of unsaturated ester moieties.

10) It has been reported that the magnesium reagents resulted from the Michael addition of isopropylmagnesium chloride to activated vinylsilanes reduce a carbonyl group into an alcohol (Refs. 1a and 2g). The present reaction provides the first example for the Peterson reaction of the magnesium enolate resulted from the Michael addition.

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12) The study on the stereoselection of this reaction is now in progress.

13) The reagent 3 was generated by the treatment of 2-(1,3-butadienyl)tributyltin with butyllithium. The detail of the procedure will be soon published.

14) The use of isopropylmagnesium bromide as the Michael acceptor both in the presence or absence of a catalytic amount of CuCl gave the similar result.

15) A probable mechanism is the double Michael addition followed by the Peterson olefination.

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