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A NEW SYNTHETIC METHOD FOR β-TRIMETHYLSILYL-α,β-UNSATURATED CARBONYL COMPOUNDS EMPLOYING 1-METHOXY-3-PHENYLTHIO-3-TRIMETHYLSILYL-1-PROPENE

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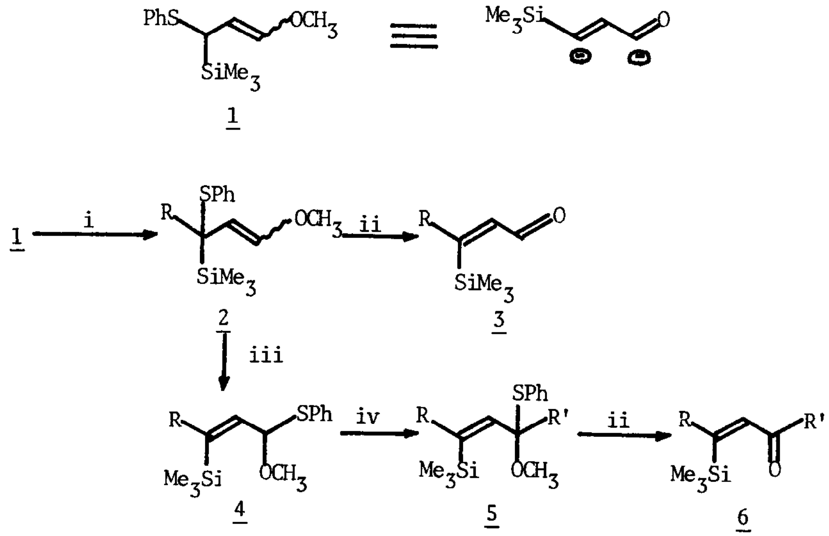
Summary: A new synthetic method for functionally substituted β-trimethylsilyl-α,β-unsaturated carbonyl compounds from 1-methoxy-3-phenylthio-3-trimethylsilyl-1-propene is described.

β-Trimethylsilyl-α,β-unsaturated carbonyl compounds have proven to be attractive because of both their unique spectral properties and synthetic utilities, though there have appeared only a few general synthetic methods for them.1)

Due to their synthetic utilities, a variety of ambident allylic anions have received much attention.2) Among them, of special interest is an ambident allylic anion stabilized with both sulfur and oxygen because of its possibility of incorporation of electrophiles in a completely regioselective manner.3)

We wish to report here that the allylic sulfide 1 4) is a new homoenolate dianion equivalent3c) with a trimethylsilyl group which would make a various type of β-trimethylsilyl-α,β-unsaturated carbonyl compounds available. Our synthetic course is shown in Scheme.

Scheme

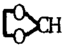


i) n-BuLi, TMEDA, HMPA, RX, THF ii) $NaIO_4$, dioxane-water iii) SiO_2-hexane
iv) n-BuLi, HMPA, R'X, THF

Alkylation of 1 results in an exclusive formation of α-adduct 2 that can be converted into 3 on treatment with $NaIO_4$ via a [2,3]-sigmatropic rearrangement. On the other hand, a novel silica gel-promoted thioallylic rearrangement of 2 followed by α-alkylation of resultant 4 enables incorporation of two electrophiles in the desired position in 1. Another notable feature of the present method consists in a mild oxidation process, thus functionally substituted products 3 or 6 being successfully obtained.

Reaction of the carbanion of 1 (n-BuLi, TMEDA, -20 °C, 0.5 h) with various alkyl halides in the presence of HMPA took place smoothly at -78 °C for 0.5 h and at -40 °C for 1 h, providing 2 in good yields. Sequential desulfurization of 2 thus obtained occurred easily through oxidation with $NaIO_4$ (1.2 eq) in dioxane-water (5:1) at room temperature for 1 h to afford 3. On the other hand, the thioallylic rearrangement of 2 took place with ease on heating a hexane solution of 2 (1.0 mmol) under reflux for 4 h in the presence of silica gel (flame dried in vacuo, 2.0 g). The newly formed allylic sulfide 4, pure enough without purification, was treated with n-BuLi (1.2 eq) in THF at -40 °C for 1 h followed by HMPA (1.2 eq) and alkyl halides (1.2 eq) at -40 °C for 1 h to afford 5. Crude 5 thus obtained was treated with $NaIO_4$ in the same manner mentioned above to give 6 in good yields. These results are summarized in Table.

Table Conversion of 1 into 3 or 6

entry	RX	R'X	Yield (%)[a]			
			2	3	4	6[b]
1	$CH_2=CHCH_2Br$		69[c]	62		
2	$THPO(CH_2)_3Br$	$n\text{-}C_6H_{13}Br$	79	72	89	62
3	$CH_2=CH(CH_2)_9I$	$THPO(CH_2)_3Br$	75	80	88	56
4	$n\text{-}C_6H_{13}Br$	$THPO(CH_2)_3Br$	80[d]	75	92	55
5	$n\text{-}C_6H_{13}Br$	$CH(CH_2)_2Cl$	80[d]	75	83	48

a) Isolated yield after column chromatography (silica gel). b) Yield based on 4. c) Isolated yield after distillation (Kugelrohr temp. 100 °C/0.6 mmHg). d) Isolated yield after distillation (Kugelrohr temp. 130 °C/0.6 mmHg).

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