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PREPARATION AND REACTIONS OF 2-SUBSTITUTED 3-TRIMETHYLSILYL-4-EN-1-ONE SYSTEM

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Summary Various 3-trimethylsilyl-4-en-1-one types of compounds have been prepared by using 3-trimethylsilylallyl alcohol. Some of them can be efficiently converted into the corresponding cyclization products, 3-cyclopenten-1-ols, or dienone types of compounds.

Allylsilanes have recently been employed in various aspects as useful synthetic intermediates because of high regioselectivity observed in their reactions with various electrophiles.[1] However, it appears to be quite difficult to prepare the substituted allylsilanes with high regioselectivity by the usual methods using the corresponding allyl anionic species because of their intrinsic ambident character.

In this paper, we wish to describe on the regiospecific synthesis of 2-substituted 3-trimethylsilyl-4-en-1-one type of compounds and their reactions.

3-Trimethylsilylallylalcohol 1 could be prepared easily by treating propargyl alcohol with 2 eq of methylmagnesium iodide and chlorotrimethylsilane, followed by reduction of acetylenic bond with lithium aluminium hydride.[2] Claisen rearrangement reaction took place to afford the corresponding 3-trimethylsilyl-4-en-1-one types of compounds in good yield on heating various vinyl ethers with 3-trimethylsilylallyl alcohol (1.5 eq) in the presence of a catalytic amount of p-toluenesulfonic acid (ca. 0.003 eq) in an appropriate solvent. In this reaction, higher temperature or prolonged period was usually required probably because of steric crowdness of trimethylsilyl group.[3]

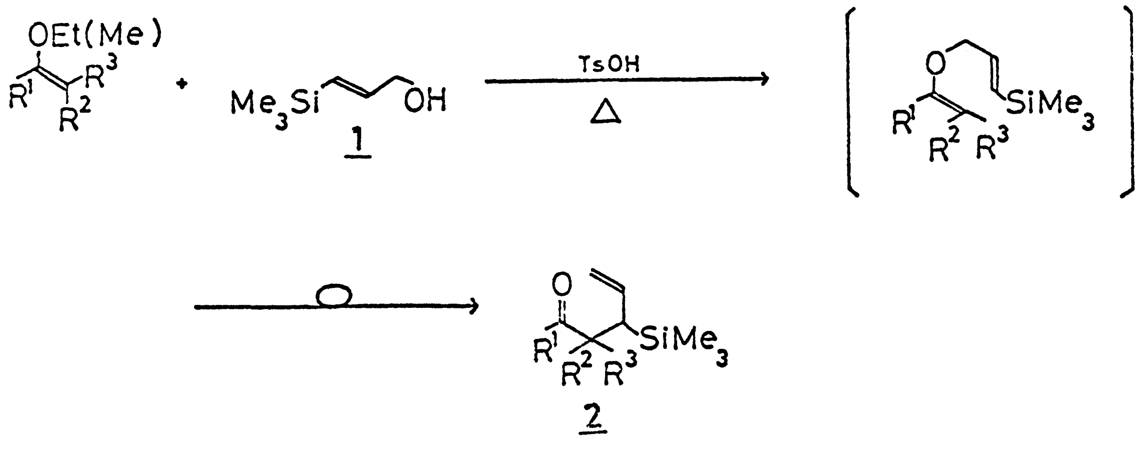
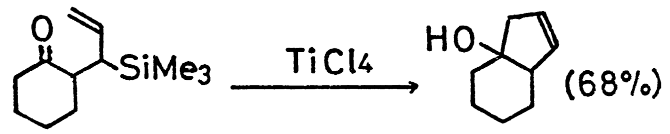


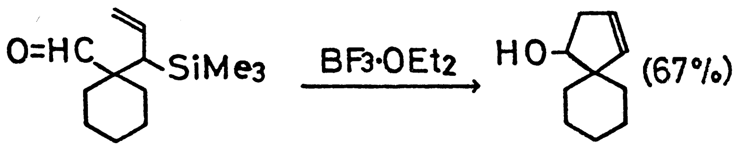
Table. Preparation of 3-Trimethylsilyl-4-en-1-ones 2.[a]

	Vinyl Ether	Period (hr)	Product (b.p., °C/Torr.)	Yield,%
a.	1-Ethoxy-1-cyclohexene	5.5[b]	2-(1-Trimethylsilyl)cyclohexanone (69-73/0.6)	70
b.	1-Methoxy-1-cyclooctene	2.5[b]	2-(1-Trimethylsilylallyl)cyclooctanone (113-5/2.7)	76
c.	1-Methoxy-1-cyclododecene	1.0[b]	2-(1-Trimethylsilylallyl)cyclododecanone (126-130/0.2)	83
d.	5-Methoxy-4-nonene	1.0[b]	3-Trimethylsilyl-4-propyl-1-nonen-5-one (87-90/0.6)	79
e.	Ethoxymethylenecyclohexene	12[c]	2-(1-Trimethylsilylallyl)cyclohexane-carboxaldehyde (128-131/14)	84
f.	1-Ethoxy-2-ethyl-1-hexene	15[c]	3-Trimethylsilyl-2-butyl-2-ethyl-4-penten-1-al (112-4/2.7)	80

a) Satisfactory spectral and analytical data were obtained for all of the products. b) The reaction was carried out in xylene. c) The reaction was carried out in *n*-decane.

Intramolecular cyclization reaction of allylsilane moiety with carbonyl group was also attempted for construction of bicyclic or spirocyclic system.[4] However, on contrary to the expectation, the reactivity for cyclization has been found to be highly sensitive toward substitution pattern around carbonyl and allylsilane functionalities. Thus, 2a and 2e undergo facile intramolecular addition reaction to afford the corresponding cyclization products even under very mild reaction conditions (in methylene chloride at -78°C for a few minutes) as shown in the following equations, but 2b, 2c, and 2d are almost inert under such reaction conditions. Even under more severe reaction conditions (at room temperature for several hours), the corresponding cyclization products were formed only in less than 10% yield and most of the starting materials were recovered. Surprisingly, aldehyde functionalities have also been found not always to react with allylsilane group under the effect of a Lewis acid. For example, 2f remained

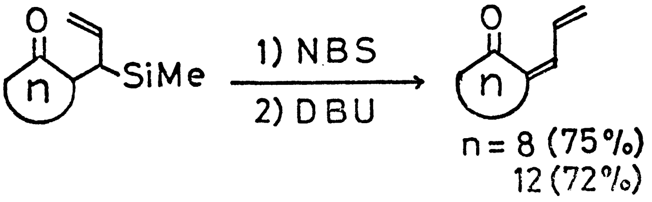




almost unchanged under the reaction conditions usually employed,[1b] and gave the expected cyclization product in only very low yield (ca. 20%) on treating with 1 eq of stannic chloride at room temperature for several hours.

Thus, the intramolecular cyclization reaction of 3-trimethylsilyl-4-en-1-one system appears to be controlled remarkably by subtle steric effects around both of functionalities, but may be applicable efficiently for the synthesis of bicyclo[4.3.0]nonene and spiro[4.5]nonene ring system.

Although the cyclization reaction of 2 could not be generalized for various ring system as shown above, 3-trimethylsilyl-4-en-1-one type of compounds 2 can be employed for the preparation of another type of synthetically versatile reagents. Thus, treatment of 2 with N-bromosuccinimide (1.1 eq) and then with diazabicycloundecene (DBU) successively, was found to lead to the formation of the corresponding dienone type of product 3 in good yield as shown in the following equations.[5]



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Precise procedures of typical examples are given below.

2-(1-Trimethylsilyl)cyclooctanone. 1-Methoxycyclooctene (8.41 g, 60 mmol) and 3-trimethylsilylallylalcohol (11.73 g, 90 mmol) were heated for 2.5 hr in xylene (60 ml) in the presence of p-toluenesulfonic acid (20 mg). Then, the reaction mixture was washed with satd. aq $NaHCO_3$ solution. From the organic layer, the solvent was removed in vacuo and the residual oil was distilled to give the title compound. The product exhibited the following spectral data. nmr (CCl_4)(benzene as internal standard); δ 0.00 (s, 9H), 1.0∿2.9 (m, 14H), 4.67 (d.d., J = 3 and 6 Hz, 1H), 4.73 (d.d., J = 3 and 10 Hz, 1H), and 5.23∿5.93 (m, 1H). ir (neat); 3070, 1703, 1626, 1250, and 850 cm^{-1}.

α-Propenylidenecyclooctanone. N-Bromosuccinimide (385 mg, 2.16 mmol) was added to THF (6 ml) solution of 2-(1-trimethylsilylallyl)cyclooctanone (482 mg, 2.02 mmol) at -78°C under argon atmosphere. After stirring for 40 min at that temperature, 1,8-diazabicycloundecene (615 mg, 2.00 mmol) was added to the solution and it was stirred for 2 hr at -40°C and then for 2 hr at 0°C. The reaction mixture was poured into buffer (KH_2PO_4-NaOH) solution and was extracted with ether. Removal of the solvent and separation of the residual oil by tlc afforded the title compound (m.p. 26∿26.5°C, 249 mg, 75%). The product exhibited the following spectral data. nmr(CCl_4)(tetramethylsilane as internal standard); δ 1.06∿2.20 (m, 8H), 2.30∿2.93 (m, 4H), 5.30∿5.83 (m, 2H), and 6.27∿7.13 (m, 2H). ir(neat); 3080, 3040, 1670, 1610, and 1575 cm^{-1}.

α-Propenylidenecyclododecanone. This compound (m.p. 71~2°C) was also prepared in 72% yield by an essentially same procedure. nmr(CCl_4); δ 0.7∿2.0 (m, 16H), 2.2∿2.9 (m, 4H), 5.13∿5.87 (m, 2H), and 6.30∿7.08 (m, 2H). ir(KBr); 1650, 1625, and 1580 cm^{-1}.

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