A Synthetic Equivalent for the Butadienyl Carbonium Ion: Use of 4-(Trimethylsilyl)but-2-ynal for Preparation of 1,3-Dienes and Macroexpansion of Cyclic Ketones

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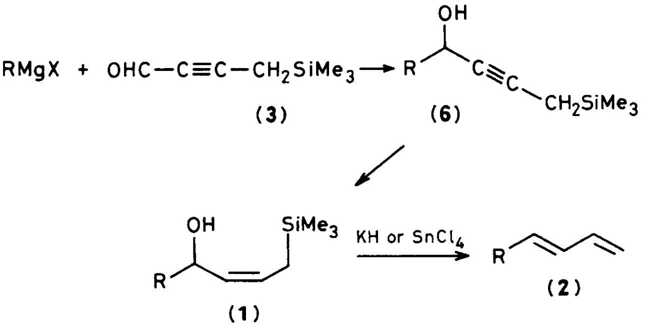
4-(Trimethylsilyl)but-2-ynal (**3**) is a synthetic equivalent for the butadienyl carbonium ion and can be used for preparation of terminal 1,3-dienes and for macroexpansion of cyclic ketones.

Fragmentation of β-hydroxysilanes is a well-established[1] reaction for making carbon–carbon double bonds. We report that the vinylogous counterpart of this process is a general and efficient route to 1,3-dienes[2] [(**1**) → (**2**); Scheme 1] having the stereochemistry shown. The starting materials (**1**) are accessible from 4-(trimethylsilyl)but-2-ynal (**3**), a substance which behaves (see below) as a synthetic equivalent for the butadienyl carbonium ion.

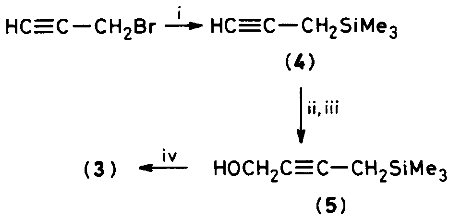
Aldehyde (**3**) is easily prepared (Scheme 2) from the known[3] silane (**4**) by hydroxymethylation (**4**) → (**5**) (79%) and oxidation† (**5**) → (**3**). The aldehyde (**3**)[4] [^{1}H n.m.r. (200 MHz, $CDCl_3$) δ 0.05 (s, 9H), 1.65 (d, 2H), 9.04 (t, 1H); i.r. (neat) 2200, 1665, 1250, 850 cm^{-1}] is sensitive and is best used within 24 h. The crude material from the oxidation was taken up in dry hexane and treated directly at room temperature with a diethyl ether solution of a Grignard reagent. We routinely used an excess (approximately 3-fold) of the aldehyde and found that it reacts cleanly and rapidly (<0.5 h) (Scheme 1 and Table 1). The resulting acetylenic alcohols (**6**) undergo efficient semihydrogenation (**6**) → (**1**) over Lindlar catalyst[5] in hexane. The products [*e.g.*, (**1a**), (**1b**), see Table 1] should have (*Z*) double bond geometry from the mode of formation and, in the case of (**1a**), this assumption was proved by appropriate ^{1}H n.m.r. decoupling experiments which gave ^3J(HC=CH) as 10 Hz. Alkenes (**1a**) and (**1b**), when treated with KH in THF (room temp., 15 min), were converted efficiently into dienes (**2a**) and (**2b**). Each diene was a single isomer (^{13}C n.m.r., 100.62 MHz) and had (*E*) geometry on the basis of ^3J(HC=CH) values of 14.9 and 16.1 Hz, respectively.[6]



Scheme 1

Aldehyde (**3**) also reacts in an aldol fashion with ketone enolates (see Table 1). These were generated in diethyl ether by the action of MeLi on trimethylsilyl enol ethers and converted, arbitrarily, into zinc enolates by addition of 0.5 mol (per mol silyl enol ether) of $ZnCl_2$ in diethyl ether.[7] The resulting aldols (**6c**)—(**6f**) were isolated in the yields shown after reaction periods of 10—20 min at room temperature. Each aldol was a mixture of diastereoisomers, but this fact is not relevant to the overall transformation [*e.g.*, (**6c**) ($n = 1$) → (**1c**) → (**2c**)]. The acetylenic aldols underwent semihydrogenation (5% Pd on $BaSO_4$ in pyridine[8]) in very high yields (see Table 1) to (**1c**)—(**1f**). Reaction of these olefins with KH in THF was unpromising, but the desired conversion into the corresponding dienes (**2c**)—(**2f**) took place rapidly when $SnCl_4$ (2 mol per mol alcohol[9]) was added to cold (0 to −20 °C) solutions of the individual alcohols in CH_2Cl_2. The reaction appears to proceed more cleanly at lower temperatures and the products have only (*E*)-geometry [^3J(HC=CH) *ca.* 15 Hz].

α-Butadienyl ketones are useful intermediates for macroexpansion.[10] For example, the cyclohexanone (**2c**) (Table 1)



Scheme 2. *Reagents:* i, Mg, Me_3SiCl; ii, BuLi, tetrahydrofuran (THF); iii, $[CH_2O]_n$, room temp., 12 h; iv, pyridinium chlorochromate, CH_2Cl_2, room temp., 1 h.

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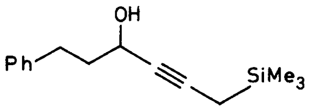
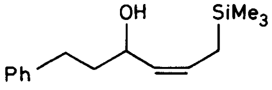
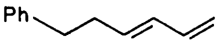
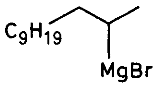
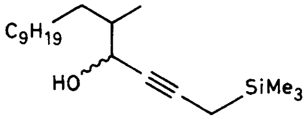
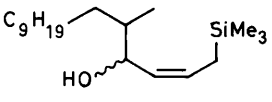
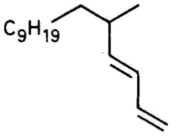
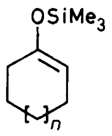
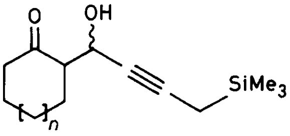
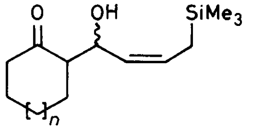
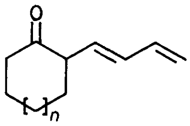
† T.l.c. showed complete reaction, but a reliable yield was not measured because the product evaporates on attempts to remove all the solvent.

Table 1. Reactions of (**3**) as a synthetic equivalent for the butadienyl carbonium ion (Scheme 2).[a]

Reagent	Condensation Product (Yield %)	Hydrogenation Product (Yield %)	Diene (Yield %)
$PhCH_2CH_2MgCl$	 (**6a**) (79%)	 (**1a**) (96%)	 (**2a**) (74%)
	 (**6b**) (60%)	 (**1b**) (95%)	 (**2b**) (84%)
			
n = 1,	(**6c**) (76%)	(**1c**) (96%)	(**2c**) (69%)
n = 2,	(**6d**) (85%)	(**1d**) (97%)	(**2d**) (80%)
n = 7,[b]	(**6e**) (78%)	(**1e**) (96%)	(**2e**) (78%)
n = 8,[b]	(**6f**) (70%)	(**1f**) (95%)	(**2f**) (73%)

[a] All yields refer to pure, isolated compounds. [b] The silyl enol ether was a mixture of *Z* and *E* isomers.

has been converted[10a] (Scheme 3) into the 14-membered carbocycle (**8c**; R = K) and then into the corresponding ketone (**9c**). Surprisingly,[11] the C(1) epimer of (**7c**) also gave[10a] only (**9c**). We examined macroexpansion of (**7d**; R = H) and (**7e**; R = H) and found that attempts to induce the process with KH did not work properly.‡ However, we have found a successful alternative: The bis(butadienyl) alcohols were prepared (Scheme 3) by treatment of (**2d**) and (**2e**) with butadienyllithium§ in THF (−78 °C, 30 min). We did not detect any isomer (*i.e.*, with 1α,2β stereochemistry) of (**7d**; R = H) but, in the case of the 12-membered ring (**2e**), two easily separable isomers [(**7e**), (**7e′**); R = H] were produced in a ratio of 3 : 1. We silylated the compounds [Me_3SiCl, $(Me_3Si)_2NH$, room temp., 20 min] and found that the products (**7d**; R = $SiMe_3$), 53% overall from (**2d**), and (**7e**; R = $SiMe_3$), 95% from major alcohol, rearranged smoothly on heating under nitrogen (200 °C, 15 min). Conversion (**7e**; R = $SiMe_3$) → (**8e**; R = $SiMe_3$) gave a single (^{13}C n.m.r., 100.62 MHz) product (95%) which afforded the non-conjugated ketone (**9e**) (79%) on treatment with MeLi (1.1 equiv.) and tetramethylethylenediamine (TMEDA) (1 equiv.) in diethyl ether (room temp., 30 min) followed by quenching with acetic acid.

Similar thermolysis of the minor isomer (**7e′**; R = $SiMe_3$, 1α,2β stereochemistry), 96% from the minor alcohol, gave (91%) two isomeric silyl enol ethers that correspond to (**8e**) but are expected to have 1*Z*, 3*E*, 7*E*, 9*Z* and 1*E*, 3*E*, 7*E*, 9*E* geometries (see below). Thermolysis of (**7d**; R = $SiMe_3$) gave (**8d**; R = $SiMe_3$) (88%) containing 9% of residual (**7d**; R = $SiMe_3$).¶ Treatment of this mixture with MeLi–TMEDA gave (**9d**) (85%) as a single isomer (^{13}C n.m.r., 100.62 MHz) and hydrogenation over 5% Pd/C in ethyl acetate afforded (95%) cyclopentadecanone (Exaltone[13]) as a homogeneous (g.l.c., ^{13}C n.m.r.), white, crystalline solid.

The stereochemistries shown for (**7d, e, e′**), (**8d, e**), and (**9d, e**) are tentative assignments made by analogy[11] and on the assumption that the transition states for ring expansion are chair-like. The degree of stereochemical homogeneity of our products is readily understood on this basis: (**7e**) is expected to provide a *single* enol ether, (**7e′**) should give a mixture of two geometric isomers, and (**7d**) is predicted to yield a *single* ketone rather than a pair of geometric isomers.

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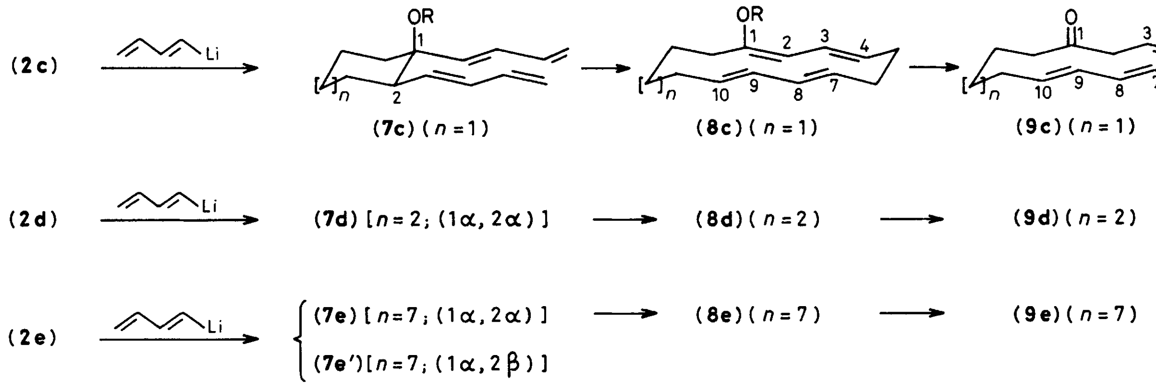
‡ With (**7e**) the total reaction product contained (relatively) too many vinyl protons. With (**7d**) many products were formed.

§ (*E*)-Butadienyl-lithium was generated from (*E*)-butadienyltributylstannane (2.5 mol) and BuLi (1 mol) in hexane (−78 °C, 15 min). The pure (^{13}C n.m.r., 100.62 MHz) stannane was made by hydrostannylation (ref. 12) of propyn-2-ol followed by oxidation (MnO_2, CH_2Cl_2, room temp., 24 h; 74% corrected for starting material recovered by chromatography) of the *distilled* hydrostannylation product. The resulting aldehyde [1 : 17 mixture (^1H n.m.r., 400 MHz) of *Z* and *E* isomers] was treated with triphenylphosphine methylide (ref. 10a) and the final product appeared pure by ^{13}C n.m.r. (signal to noise ratio *ca.* 100 for most intense peak). The hydrostannylation has been studied in detail (ref. 12) and it is important to follow the reported procedure.

¶ We did not establish whether this is the result of incomplete rearrangement or of an equilibrium.



Scheme 3. The diagrams are not meant to imply preferred conformations. Yields, which refer to pure, isolated compounds are given in the text. Yield of (**7e**) + (**7e′**) (R = H): 76%. The senior group (Sequence Rule) at C(1) defined the α-face.

In summary, the acetylenic aldehyde (**3**) is a convenient precursor to terminal dienes and it can be used for ring expansion of ketones by 8 carbon atoms.

Acknowledgement of financial support is made to the Natural Sciences and Engineering Research Council of Canada. We thank Christine Brzezowski for a sample of cyclotridecanone.

Received, 7th December 1983; Com. 1591

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