

Tributylmanganate(II)-Mediated Cyclization of Enynes

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Treatment of enynes with tributylmanganate(II) provided cyclized products containing alkylidene substituents. 1-Tridecen-6-yne or 1-tetradecen-7-yne gave 1-heptylidene-2-methylcyclopentane or 1-heptylidene-2-methylcyclohexane in 67 or 50% yield, respectively upon treatment with tributylmanganate(II). The reaction of dimethylvinylsilyl ether of 3-decyn-1-ol with tributylmanganate(II) afforded 4-heptylidene-2,2,3-trimethyl-1-oxa-2-silacyclohexane in good yield.

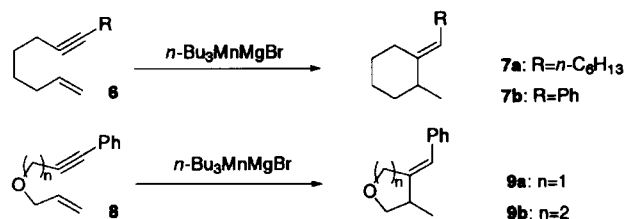
Recently we have reported an intramolecular cycloaddition reaction of diynes, enynes, and dienes with triallylmanganate(II).¹ In the reaction of diynes and enynes, part of the allylic group was used to construct the cyclized products. Here we describe the cyclization reaction of enynes² with tributylmanganate in place of triallylmanganate(II).

A solution of 1-tridecen-6-yne (**1**) in THF was added to a THF solution of tributylmanganate(II), generated from MnCl_2 and three molar amounts of butylmagnesium bromide, at 0 °C. The resulting mixture was stirred for 20 h at 0 °C. Extractive workup followed by silica-gel column purification provided 1-heptylidene-2-methylcyclopentane (**2**) as a single stereoisomer (*E* only) in 67% yield (Scheme 1). An addition of D_2O before quenching the reaction afforded the corresponding deuterated cyclopentane (**3**, 92% *d*-2).³ Under the same reaction conditions, 1-phenyl-6-hepten-1-yne (**4**) provided 1-benzylidene-2-methylcyclopentane (**5**) in 74% yield.

Treatment of 1,7-enynes such as 1-tetradecene-7-yne (**6a**) and 1-phenyl-7-octen-1-yne (**6b**) with tributylmanganate(II) gave the corresponding 1-alkylidene-2-methylcyclohexane

7a and **7b** in 50 and 51% yields, respectively. In contrast, allyl propargylic ether **8a** and allyl homopropargylic ether **8b** provided cyclic ether derivatives **9a** and **9b** in only 25 and 12% yields, respectively (Scheme 2). The main products were propargylic alcohol and homopropargylic alcohol which could be generated by an attack of tributylmanganate(II) on the allylic ether moiety.^{4,5}

Next, the tributylmanganate(II)-promoted cyclization reaction of silyl ethers was studied. Starting silyl ethers **10** were prepared from dimethylvinylsilyl chloride and the corresponding homopropargylic alcohol. Treatment of dimethylvinylsilyl ether of 3-decyn-1-ol (**10a**) with tributylmanganate(II) in THF at 25 °C for 5 h provided 4-heptylidene-2,2,3-trimethyl-1-oxa-2-silacyclohexane (**11a**) in 55% yield. The representative results are shown in Table 1. The silyl ethers **10c** and **10d** which have been prepared from secondary homopropargylic alcohol afforded the 1-oxa-2-silacyclohexane derivatives as 4:1 isomeric mixtures. In contrasts, the silyl ether **10e** which has phenyl substituent in place of methyl group of **10c** and **10d** gave the corresponding cyclized product **11e** as a single stereoisomer. The



Scheme 2.

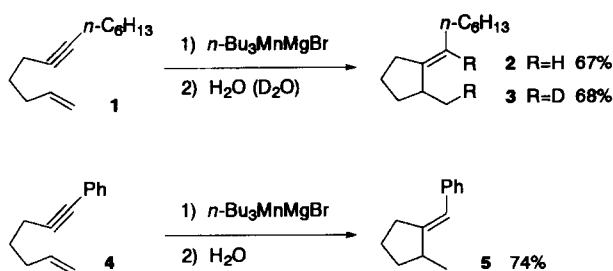
Table 1. $n\text{-Bu}_3\text{MnMgBr}$ -Mediated Cyclization of Silyl Ether

$$\begin{array}{ccc}
 \text{R}^2 & & \text{R}^1 \\
 | & & | \\
 \text{CH}_2 & \text{---} & \text{C} \equiv \text{C} \\
 | & & | \\
 \text{O} & \text{---} & \text{Si} \\
 | & & | \\
 \text{Me} & & \text{R}^3
 \end{array}
 \xrightarrow{n\text{-Bu}_3\text{MnMgBr}}
 \begin{array}{ccc}
 \text{R}^2 & & \text{R}^1 \\
 | & & | \\
 \text{CH}_2 & \text{---} & \text{C} = \text{C} \\
 | & & | \\
 \text{O} & \text{---} & \text{Si} \\
 | & & | \\
 \text{Me} & & \text{R}^3
 \end{array}$$

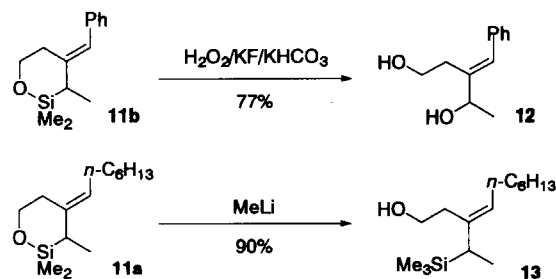
10 **11**

Entry		R ¹	R ²	R ³	Product(%)
1	10a	<i>n</i> -C ₆ H ₁₃	H	CH ₃	11a 55
2	10b	Ph	H	CH ₃	11b 57
3	10c	<i>n</i> -C ₆ H ₁₃	CH ₃	CH ₃	11c 59 ^{a)}
4	10d	Ph	CH ₃	CH ₃	11d 59 ^{a)}
5	10e	<i>n</i> -C ₄ H ₉	Ph	CH ₃	11e 59 ^{b)}
6	10f	<i>n</i> -C ₆ H ₁₃	H	Ph	11f 40
7	10g	Ph	H	Ph	11g 44

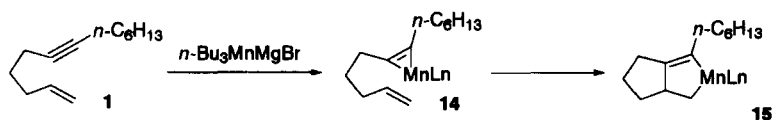
a) Mixture of diastereomers (4 : 1). b) Single isomer.



Scheme 1.



Scheme 3.



Scheme 4.

substrates **10f** and **10g** bearing a phenyl group on the silicon atom in place of a methyl group also provided the corresponding cyclized products **11f** and **11g** in moderate yields. The distance between double bond and triple bond played an important role. Thus, the silyl ethers of propargylic alcohol and 4-alkyn-1-ol gave no cyclized products upon treatment with tributylmanganate(II).

The cyclized product 1-oxa-2-silacyclohexanes could be easily converted into diols or allylic silanes. Oxidation of **11b** with hydrogen peroxide in the presence of potassium fluoride and potassium hydrogencarbonate⁶ gave 3-benzylidene-1,4-pentanediol (**12**) in 77% yield. An addition of methylolithium to **11a** afforded allylic silane **13** in 90% yield (Scheme 3).

Although the mechanism for the cyclization reaction has not yet been clarified, we assume the following mechanism (Scheme 4).⁷ Reaction of **1** with tributylmanganate(II) would provide manganese alkyne complex **14**. Then insertion of olefinic moiety into carbon–manganese bond could give manganacyclopentene **15**. Quenching the intermediate **15** with D₂O would provide stereo-defined cyclopentane **3**.

Experimental

General Procedure for the Reaction of Enyne with Tributylmanganate(II). Under argon atmosphere, a suspension of manganese(II) chloride (0.20 g, 1.6 mmol) in THF (5.0 mL) was sonicated for 10 min. Butylmagnesium bromide (1.03 M THF solution, 1 M = 1 mol dm⁻³, 4.7 mL, 4.8 mmol) was added at 0 °C to the suspension to give clear brown solution. After the solution had been stirred at 0 °C for 20 min, a solution of 1-tridecen-6-yne (143 mg, 0.8 mmol) in THF (5.0 mL) was added. The resulting solution was stirred for 20 h at 0 °C and poured into water. The product was extracted with hexane (20 mL × 3) and the combined organic layer was dried over anhydrous Na₂SO₄ and then concentrated in vacuo. Purification of the residual oil by silica-gel column chromatography provided 1-heptylidene-2-methylcyclopentane (**2**, 95 mg) in 67% yield. The physical data of the compounds **2**,⁸ **5**,⁹ **7b**,⁸ **9a**,⁸ and **9b**⁸ were identical with authentic samples obtained according to the literature.

4-Heptylidene-2,2,3-trimethyl-1-oxa-2-silacyclohexane (11a): IR (neat) 2952, 2920, 2854, 1649, 1462, 1452, 1377, 1253, 1160, 1092, 1043, 969, 922, 874, 825, 783, 721, 670, 645 cm⁻¹; ¹H NMR (CDCl₃) δ = 4.98 (t, *J* = 7.2 Hz, 1H), 3.97 (dt, *J* = 11.5, 4.2 Hz, 1H), 3.70 (dt, *J* = 7.5, 3.3 Hz, 1H), 2.58 (dt, *J* = 13.8, 3.3 Hz, 1H), 2.00–2.09 (m, 3H), 1.67 (q, *J* = 7.2 Hz, 1H), 1.20–1.40 (m, 8H), 1.01 (d, *J* = 6.9 Hz, 3H), 0.88 (t, *J* = 6.9 Hz, 3H), 0.18 (s, 3H), 0.00 (s, 3H); ¹³C NMR (CDCl₃) δ = -6.59, -2.57, 11.33, 13.96, 22.56, 27.59, 28.91, 30.45, 30.79, 31.70, 33.35, 65.63, 120.22, 139.20. Found: C, 69.67; H, 12.03%. Calcd for C₁₄H₂₈OSi: C, 69.93; H, 11.74%; O, 6.65%.

4-Benzylidene-2,2,3-trimethyl-1-oxa-2-silacyclohexane (11b):

IR (neat) 3076, 3054, 3020, 2954, 2922, 2862, 1635, 1600, 1496, 1461, 1445, 1253, 1151, 1090, 1045, 1029, 968, 933, 911, 881, 852, 826, 778, 741, 724, 699, 648 cm⁻¹; ¹H NMR (CDCl₃) δ = 7.29–7.34 (m, 2H), 7.16–7.21 (m, 3H), 6.15 (s, 1H), 4.07 (dt, *J* = 10.8, 4.2 Hz, 1H), 3.87 (dt, *J* = 10.8, 2.7 Hz, 1H), 2.84 (dt, *J* = 9.9, 2.7 Hz, 1H), 2.17 (dt, *J* = 12.3, 4.8 Hz, 1H), 1.88 (q, *J* = 7.2 Hz, 1H), 1.17 (d, *J* = 7.2 Hz, 3H), 0.26 (s, 3H), 0.09 (s, 3H); ¹³C NMR (CDCl₃) δ = -6.45, -2.52, 11.17, 31.93, 33.91, 55.89, 120.62, 125.88, 128.20, 128.90, 138.94, 143.57. Found: C, 72.47; H, 8.74%. Calcd for C₁₄H₂₀OSi: C, 72.36; H, 8.67%; O, 6.88%.

4-Heptylidene-2,2,3,6-tetramethyl-1-oxa-2-silacyclohexane (11c):

IR (neat) 2956, 2922, 2854, 1651, 1462, 1405, 1377, 1341, 1251, 1155, 1125, 1111, 1042, 998, 972, 903, 887, 836, 785, 723, 686, 651 cm⁻¹; ¹H NMR (CDCl₃) δ = 4.92 (t, *J* = 7.2 Hz, 1H), 3.75–3.85 (m, 1H), 2.66 (dd, *J* = 13.2, 2.1 Hz, 1H), 2.00–2.08 (m, 3H), 1.57–1.69 (m, 1H), 1.18–1.40 (m, 11H), 0.98 (d, *J* = 7.2 Hz, 3H), 0.89 (t, *J* = 6.9 Hz, 3H), 0.20 (s, 3H), -0.04 (s, 3H); ¹³C NMR (CDCl₃) δ = -6.89, -2.11, 10.50, 13.97, 22.57, 24.57, 27.64, 28.92, 30.08, 30.49, 31.71, 41.35, 71.62, 119.57, 138.93. Found: C, 70.64; H, 12.07%. Calcd for C₁₅H₃₀OSi: C, 70.79; H, 11.88; O, 6.29%.

References

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- 3 An addition of I₂ or aldehyde instead of H₂O gave the complex mixture.
- 4 Allyl propargyl amine such as PhC≡CCH₂N(CH₂CH=CH₂)₂ afforded the corresponding pyrrolidine derivative in 55% yield.
- 5 Diynes such as 1,7-diphenyl-1,6-heptadiyne and 5,5-bis(methoxymethyl)-2,7-nonadiyne gave complex mixtures upon treatment with tributylmanganate(II). Meanwhile, 4,4-bis(methoxymethyl)-1,6-heptadiene was recovered unchanged.
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- 7 An alternative mechanism could be a direct cycloaddition reaction between triple bond, double bond, and manganese to give **15** in a single step.
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