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Tributylmanganate(II)-Mediated Cyclization of Enynes

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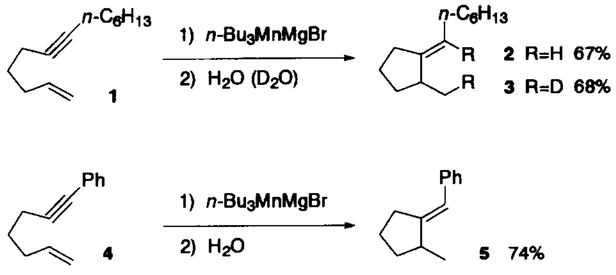
Treatment of enynes with tributylmanganate(II) provided cyclized products containing alkylidene substituents. 1-Tridecen-6-yne or 1-tetradecen-7-yne gave 1-heptylidene-2-methylcyclopentane or 1-heptylidene-2-methylcyclohexane in 67 or 50% yield, respectively upon treatment with tributylmanganate(II). 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 enynes[2] with tributylmanganate in place of triallylmanganate(II).

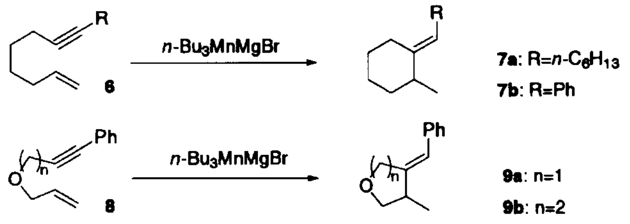
A solution of 1-tridecen-6-yne (**1**) in THF was added to a THF solution of tributylmanganate(II), generated from $MnCl_2$ and three molar amounts of butylmagnesium bromide, at 0 °C. The resulting mixture was stirred for 20 h at 0 °C. Extractive workup followed by silica-gel column purification provided 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]



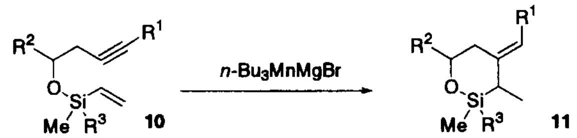
Scheme 1.

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



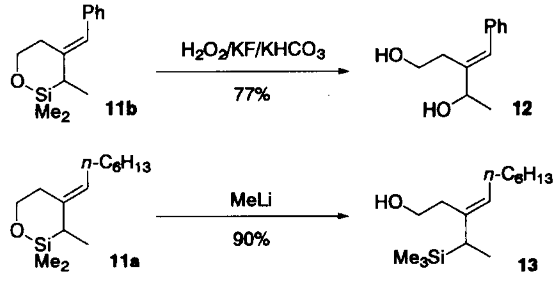
Scheme 2.

Table 1. *n*-$Bu_3MnMgBr$-Mediated Cyclization of Silyl Ether

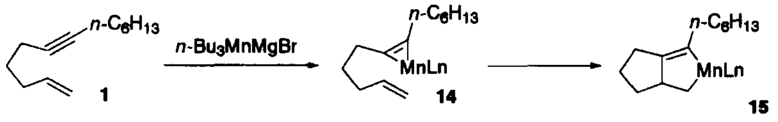


Entry		R^1	R^2	R^3	Product(%)	
1	**10a**	*n*-C_6H_{13}	H	CH_3	**11a**	55
2	**10b**	Ph	H	CH_3	**11b**	57
3	**10c**	*n*-C_6H_{13}	CH_3	CH_3	**11c**	59[a)]
4	**10d**	Ph	CH_3	CH_3	**11d**	59[a)]
5	**10e**	*n*-C_4H_9	Ph	CH_3	**11e**	59[b)]
6	**10f**	*n*-C_6H_{13}	H	Ph	**11f**	40
7	**10g**	Ph	H	Ph	**11g**	44

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



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-siacyclohexanes could be easily converted into diols or allylic silanes. Oxidation of **11b** with hydrogen peroxide in the presence of potassium fluoride and potassium hydrogencarbonate[6] gave 3-benzylidene-1,4-pentanediol (**12**) in 77% yield. An addition of methyllithium 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 D_2O 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 Na_2SO_4 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 ($CDCl_3$) 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); ^{13}C NMR ($CDCl_3$) 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 $C_{14}H_{28}OSi$: 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 ($CDCl_3$) 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); ^{13}C NMR ($CDCl_3$) 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 $C_{14}H_{20}OSi$: 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 ($CDCl_3$) 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); ^{13}C NMR ($CDCl_3$) 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 $C_{15}H_{30}OSi$: C, 70.79; H, 11.88; O, 6.29%.

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3 An addition of I_2 or aldehyde instead of H_2O gave the complex mixture.

4 Allyl propargyl amine such as $PhC{\equiv}CCH_2N(CH_2CH{=}CH_2)_2$ 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 machanism could be a direct cycloaddition reaction between triple bond, double bond, and manganese to give **15** in a single step.

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