Pergamon

SCIENCE DIRECT®

Tetrahedron 59 (2003) 9661–9668

TETRAHEDRON

Formation of manganese–alkyne complexes mediated by trialkylmanganates and their application

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Received 4 August 2003; accepted 18 September 2003

Abstract—Treatment of dodec-6-yne with triallylmanganate in the presence of 1,3,5-trimethylbenzene provides (*Z*)-dodec-6-ene. An addition of D_2O before quenching the reaction affords the corresponding dideuterated alkene. The result suggests the existence of the manganese–alkyne complex as an intermediate. Treatment of methyl propargyl ethers as alkynes with tributylmanganate generates propargylmanganese species. The reaction of non-2-ynyl tetrahydropyran-2-yl ether with tributylmanganate provides tetradec-7-yn-1,5-diol and 6-hexylocta-6,7-dien-1,5-diol.

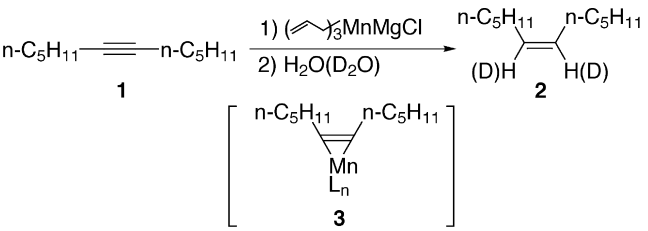
1. Introduction

Recently transition metal–alkyne complexes have received much attention. Among them, the Group IV and V metals such as Ti,[1] Zr,[2] Nb,[3] and Ta[4] have been extensively studied because of the unique properties and usefulness of their alkyne complexes as synthetic intermediates. In contrast, there are few reports on the utilization of manganese (Group VII)–alkyne complexes for organic synthesis. Here we describe a generation (but not isolated) of manganese–alkyne complexes by treatment of alkynes with triallylmanganate in the presence of aromatic compounds such as 1,3,5-trimethylbenzene. In addition, we wish to report that the reaction of propargyl ethers with tributylmanganate provides propargylmanganese species via manganese–alkyne complexes.

2. Results and discussion

2.1. Formation of manganese–alkyne complexes mediated by triallylmanganate

A solution of dodec-6-yne (**1**) in THF was added to a solution of triallylmanganate (1.5 equiv.), which was prepared in situ by mixing allylmagnesium chloride and manganese chloride in a 3:1 ratio in THF at 0°C. After stirring at 25°C for 23 h, aqueous workup of the reaction mixture provided (*Z*)-dodec-6-ene (**2**) in 50% yield (Scheme 1). An addition of D_2O before quenching the reaction afforded the corresponding dideuterated alkene (>99% *d*-2).[5] The result suggests the existence of the manganese–alkyne complex **3** as an intermediate.[6]



Scheme 1.

Then, the reaction of dodec-6-yne (**1**) with triallylmanganate was examined in the presence of various aromatic compounds. Treatment of dodec-6-yne (**1**) with triallylmanganate (1.5 equiv.) in THF at 25°C in the presence of benzene, hexamethylbenzene, 1,3,5-trimethoxybenzene, or 1,3,5-trimethylbenzene (2.0 equiv.) gave (*Z*)-dodec-6-ene (**2**) in 52, 53, 60, or 80% yield, respectively, after aqueous workup. Among aromatic compounds examined, 1,3,5-trimethylbenzene proved to be the best as an additive to stabilize the manganese–alkyne complex **3**. The amount of the additive affected the yield of (*Z*)-dodec-6-ene (**2**). For instance, the use of 4.0 or 15.0 equiv. of 1,3,5-trimethylbenzene provided (*Z*)-dodec-6-ene (**2**) in 80 or 26% yield, respectively.

Next, the reaction of the intermediary manganese–alkyne complex **3** with various electrophiles was studied. In contrast to Group IV and V metal–alkyne complexes which react with carbonyl groups effectively, manganese–alkyne

Keywords: manganese–alkyne complex; diyne; tetrahydronaphthalene; allylation; acetals.
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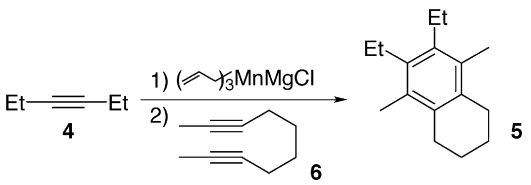
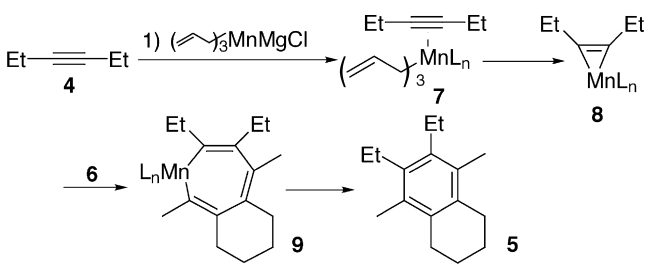
doi:10.1016/j.tet.2003.09.077

complex **3** did not react with aldehydes and ketones. Thus, an addition of benzaldehyde (6.0 equiv.) to the reaction mixture, generated from dodec-6-yne (**1**) and triallylmanganate, resulted in a recovery of dodec-6-yne (**1**) (67%) along with 1-phenylbut-3-en-1-ol, which was generated by allylation of benzaldehyde. The desired adduct, 1-phenyl-2-pentyloct-2-en-1-ol could not be detected in the reaction mixture. An addition of 1,7-diyne **6** instead of carbonyl compounds, however, afforded a tetrahydronaphthalene derivative in moderate yield. Treatment of hex-3-yne (**4**) with triallylmanganate in the presence of 1,3,5-trimethylbenzene followed by an addition of deca-2,8-diyne (**6**) gave tetrahydronaphthalene derivative **5** in 20% yield along with hexaethylbenzene (20%).[7] The yield of tetrahydronaphthalene derivative **5** was improved up to 44% by an addition of triallylmanganate to a mixture of **4** and deca-2,8-diyne (**6**) in the presence of 1,3,5-trimethylbenzene (Scheme 2).



Scheme 2.

We assume the following reaction mechanism (Scheme 3). An interaction of triallylmanganate with hex-3-yne (**4**) would produce π-complex **7** which would afford manganese–alkyne complex **8**. Manganese–alkyne complex **8** would be stabilized by the coordination of 1,3,5-trimethylbenzene. An addition of deca-2,8-diyne (**6**) replaces the 1,3,5-trimethylbenzene as a coordinating ligand. The reaction of deca-2,8-diyne (**6**) with manganese–alkyne complex **8** would provide manganacycloheptatriene **9**, which would produce tetrahydronaphthalene derivative **5** and Mn(0) species.[8]



Scheme 3.

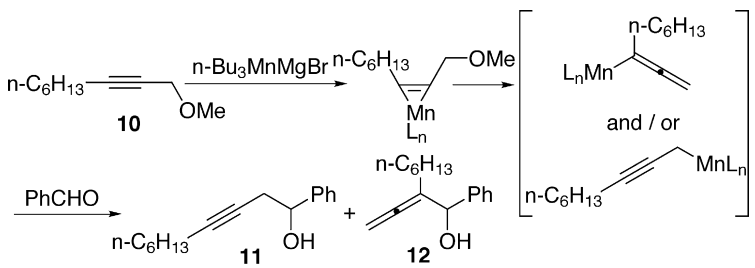
2.2. Transformation of propargyl tetrahydropyranyl ether into 1,5-diol by means of trialkylmanganate

We next picked up propargyl ethers as alkynes. Treatment of methyl propargyl ether **10** with tributylmanganate,[9] derived from 1.0 equiv. of manganese chloride and 3.0 equiv. of butylmagnesium bromide, followed by an addition of benzaldehyde afforded a mixture of homopropargyl alcohol **11** in 22% yield and allenylated product **12** in 18% yield (Scheme 4).[10]

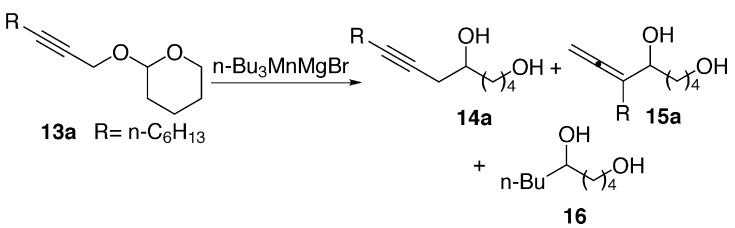
Then, non-2-ynyl tetrahydropyran-2-yl ether (**13a**) was chosen as a substrate instead of methyl propargyl ether **10**. Tributylmanganate (1.0 equiv.) and HMPA (3.0 equiv.) were added to a solution of **13a** in THF at 0°C and the resulting mixture was stirred for 23 h at 25°C. Extractive workup followed by silica-gel column purification provided homopropargyl alcohol, tetradec-7-yn-1,5-diol (**14a**) (36%), allenylated product, 6-hexylocta-6,7-dien-1,5-diol (**15a**) (23%), and nonan-1,5-diol (**16**) (24%) (Scheme 5).

The reactions of various propargyl tetrahydropyranyl ethers were examined under the same conditions. The results are shown in Table 1. Treatment of propargyl tetrahydropyranyl ether **13b**, generated from a primary propargyl alcohol, with tributylmanganate afforded a mixture of homopropargyl alcohol **14b** and allenylated product **15b** in addition to butylated product **16**. The product distribution heavily depended on the nature of the starting materials. The acetals, **13c**, **13d**, and **13e**, which were derived from secondary propargyl alcohols, gave only homopropargyl alcohols **14** without contamination by **15**.

We propose the following reaction mechanism. Oxidative

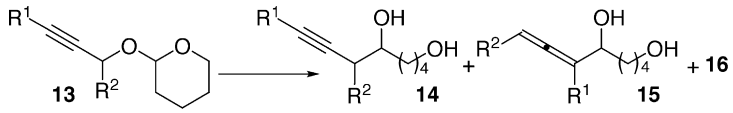


Scheme 4.

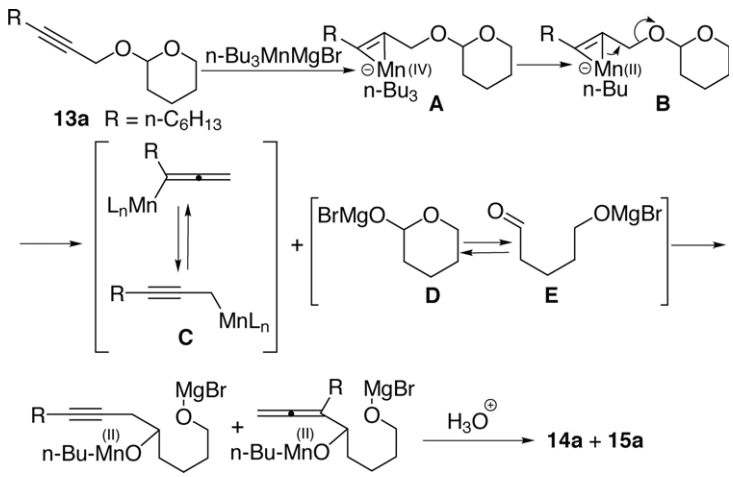


Scheme 5.

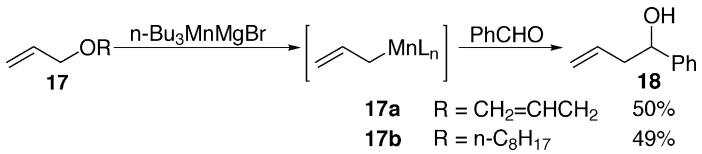
Table 1. Reaction of propargyl tetrahydropyranyl ethers with tributylmanganate



Entry	Substrate **13**		Product/Yield (%)		
	R^1	R^2	**14**	**15**	**16**
1	**13a**: R^1=*n*-C_6H_{13}	R^2=H	36	23	24
2	**13b**: R^1=Me_3Si	R^2=H	46	28	16
3	**13c**: R^1=Me_3Si	R^2=CH_3	50	–	3
4	**13d**: R^1=*n*-C_6H_{13}	R^2=CH_3	61	–	12
5	**13e**: R^1=*n*-C_6H_{13}	R^2=CH_2=CH	63	–	6



Scheme 6.

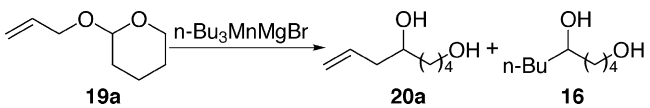


Scheme 7.

addition of manganate (Mn(II)) to the triple bond of **13a** would give manganese–alkyne complex (Mn(IV)) **A** which would be transformed into Mn(II) species **B** by reductive elimination under departure of *n*-Bu–*n*-Bu.[11] Elimination of magnesium oxide from **B** would provide manganese species **C** and a magnesium salt of δ-lactol **D**, which is equilibrated with aldehyde **E**. Recombination[12] of manganese species and aldehyde **E** would afford tetradec-7-yn-1,5-diol (**14a**) and 6-hexylocta-6,7-dien-1,5-diol (**15a**) (Scheme 6).

Then, we also examined the reaction of allyl ethers with tributylmanganate. Treatment of diallyl ether (**17a**) or allyl octyl ether (**17b**) with tributylmanganate, followed by an addition of benzaldehyde afforded 1-phenylbut-3-en-1-ol (**18**) in 50 or 49% yield, respectively (Scheme 7).[13]

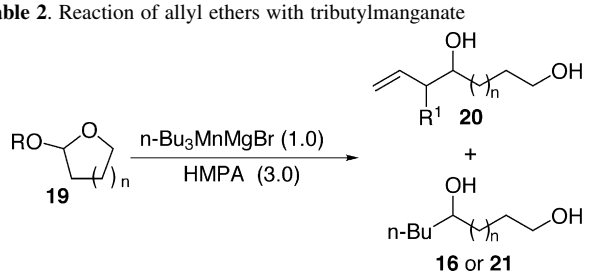
We next investigated the reaction of allyl tetrahydropyran-2-yl ether (**19a**). Tributylmanganate[14] (1.0 equiv.) was added to a solution of **19a** in THF at 0°C and the resulting mixture was stirred for 12 h at 25°C. Extractive workup followed by silica-gel column purification provided oct-7-en-1,5-diol[15] (**20a**) (55%) along with nonan-1,5-diol (**16**) (3%). An addition of 3.0 equiv. of HMPA increased the yield of **20a** up to 84% (Scheme 8).



Scheme 8.

Table 2 summarizes the reaction of various tetrahydropyranyl and tetrahydrofuranyl ethers under the same reaction conditions. Several comments are worth noting. (1) Crotyl ether **19c** provided the same product, 6-methyloct-7-en-1,5-diol (**20b**), as 1-methylprop-2-enyl ether **19b**. None of an isomeric product, non-7-en-1,5-diol, could be detected in the reaction mixture. Cinnamyl ether **19d** and its isomer **19e** gave a trace of 8-phenyloct-7-en-1,5-diol in <3% yield in addition to **20d**. (2) The yield of **20b** was much higher in the case of reaction of **19b** compared to the

Table 2. Reaction of allyl ethers with tributylmanganate



Entry	Substrate **19**		Product/Yield (%)			
	R	*n*	**20**		**16** or **21**	
1	**19a**: CH_2=$CHCH_2$	2	**20a**: R^1=H	84	**16**	3
2	**19b**: CH_2=$CHCH(CH_3)$	2	**20b**: R^1=CH_3	72	**16**	4
3	**19c**: CH_3CH=$CHCH_2$	2	**20b**: R^1=CH_3	14	**16**	2
4	**19d**: PhCH=$CHCH_2$	2	**20d**: R^1=Ph	35	**16**	3
5	**19e**: CH_2=CH(Ph)	2	**20d**: R^1=Ph	46	**16**	3
6	**19f**: CH_2=$CHCH_2$	1	**20f**: R^1=H	70	**21**	13
7	**19g**: CH_2=$CHCH(CH_3)$	1	**20g**: R^1=CH_3	57	**21**	14
8	**19h**: PhCH=$CHCH_2$	1	**20h**: R^1=Ph	44	**21**	8

reaction of **19c** as the starting material. An attack of manganate on an alkenic moiety might be impeded by the methyl substituent in the case of **19c**. (3) Whereas the reaction of tetrahydropyranyl ethers with tributylmanganate afforded a butylated byproduct **16** in only <4% yield, the reaction of tetrahydrofuranyl ethers gave slightly more a butylated byproduct **21** in 8–14% yield.

This transformation can be achieved by the use of a catalytic amount of manganese chloride. For instance, an addition of **19a** to a solution of butylmagnesium bromide (3.0 equiv.) in THF containing HMPA (3.0 equiv.) and manganese chloride catalyst (10 mol%) gave **20a** in 80% yield after 12 h at 25°C. 1-Methylprop-2-enyl tetrahydropyran-2-yl ether (**19b**) also provided the corresponding 1,5-diol **20b** in 66% yield. A byproduct, nonan-1,5-diol (**16**), was obtained in 3–8% yield along with the desired allylated products. In the case of the reaction of the propargyl acetals a catalytic reaction also proceeded smoothly. For instance, an addition of **13c** or **13f** to a THF solution of butylmagnesium bromide (3.0 equiv.) in the presence of manganese chloride (10 mol%) provided homopropargyl alcohol **14c** or **14f** in good yield, respectively, along with **16** (3%) or **21** (13%) (Scheme 9).

3. Conclusion

We found that treatment of dodec-6-yne with triallylmanganate, prepared in situ by mixing allylmagnesium chloride and manganese chloride in a 3:1 ratio in THF at 0°C, provided a manganese–alkyne complex. The reaction of the manganese–alkyne complex with 1,7-diyne induced [2+2+2] cyclization and provided a tetrahydronaphthalene derivative. In the reaction of propargyl ethers with tributylmanganate, propargylmanganese species were obtained via manganese–alkyne complexes. Treatment of a propargyl tetrahydropyranyl ether gave a mixture of a homopropargyl alcohol and an allenylated alcohol.

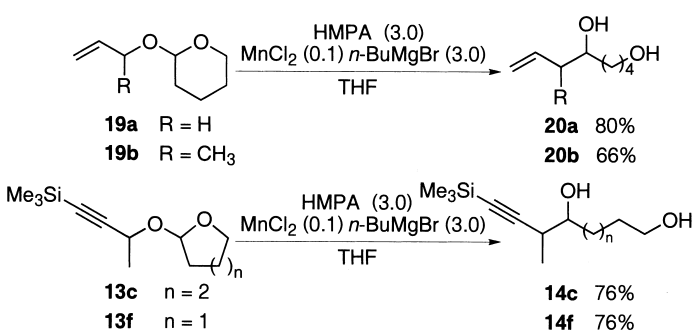
4. Experimental

NMR spectra (^{1}H and ^{13}C) were recorded on a Varian GEMINI 300 spectrometer in $CDCl_3$; tetramethylsilane (TMS) was used as an internal standard. IR spectra were determined on a SHIMADZU FTIR-8200PC spectrometer Mass spectra were determined on a JEOL Mstation 700 spectrometer. Silica gel (Wakogel 200 mesh) was used for column chromatography. The analyses were carried out at the Elemental Analysis Center of Kyoto University. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. Tetrahydrofuran (THF) was freshly distilled from sodium benzophenone ketyl before use. Anhydrous manganese(II) chloride purchased from Aldrich was heated at 160°C for 2 h prior to use.

4.1. General procedure for the reaction of dodec-6-yne (1) with triallylmanganate

Dodec-6-yne (**1**, 166 mg, 1.0 mmol) was added to a THF solution of triallylmanganate, generated from $MnCl_2$ (188 mg, 1.5 mmol), allylmagnesium chloride (1.51 M THF solution, 3.0 mL, 4.5 mmol) and 1,3,5-trimethylbenzene (0.28 mL, 2.0 mmol) at 0°C under argon atmosphere. The resulting mixture was stirred at 25°C for 23 h. The reaction was quenched with H_2O. Extractive workup followed by purification gave (*Z*)-dodec-6-ene (**2**) in 80% yield.

4.1.1. [2+2+2] Cyclization of deca-2,8-diyne (6) with the manganese–alkyne complex. In a flask equipped with a balloon filled with argon, allylmagnesium chloride (1.51 M THF solution, 3.0 mL, 4.5 mmol) and 1,3,5-trimethylbenzene (0.28 mL, 2.0 mmol) were added to a suspension of $MnCl_2$ (188 mg, 1.5 mmol, sonicated for 30 min) in THF at 0°C. After being stirred for 30 min, a solution of hex-3-yne (**4**, 0.34 mL, 3.0 mmol) and deca-2,8-diyne (**6**, 0.13 g,



Scheme 9.

1.0 mmol) in THF (2 mL) was added and the resulting mixture was stirred at 25°C for 16.5 h. The mixture was poured into 1 M HCl and extracted with hexane (20 mL×3). GC analysis indicated that tetrahdronaphthalene derivative **5** was obtained in 44% yield.

4.1.2. 6,7-Diethyl-5,8-dimethyl-1,2,3,4-tetrahydronaphthalene (5). Mp 33°C IR (neat) 3419, 2874, 1732, 1434, 1020, 839 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.15 (t, J=7.6 Hz, 6H), 1.75–1.82 (m, 4H), 2.18 (s, 6H), 2.61–2.63 (m, 4H), 2.70 (q, J=7.6 Hz, 4H); ^{13}C NMR ($CDCl_3$) δ 14.92, 15.07, 22.86, 23.27, 28.37, 131.79, 133.48, 137.12. Found: C, 88.96; H, 11.31%. Calcd for $C_{16}H_{24}$: C, 88.82; H, 11.18%.

4.2. General procedure for the reaction of non-2-ynyl tetrahydropyran-2-yl ether (13a) with tributylmanganate

Manganese(II) chloride (125 mg, 1.0 mmol) was sonicated in THF (10 mL) under argon atmosphere for 20 min. Butylmagnesium bromide (1.03 M THF solution, 2.9 mL, 3.0 mmol) and HMPA (0.52 mL, 3.0 mmol) were added to the suspension of $MnCl_2$ in THF at 0°C. The mixture turned into a clear brown solution and then was stirred for 20 min at 0°C. A solution of **13a** (0.22 g, 1.0 mmol) in THF (2 mL) was added at 0°C and the mixture was stirred at 25°C for 23 h. The mixture was poured into water. Extractive workup followed by purification gave tetradec-7-yn-1,5-diol (**14a**, 82 mg) in 36% yield, 6-hexylocta-6,7-dien-1,5-diol (**15a**, 52 mg) in 23% yield, and nonan-1,5-diol (**16**, 38 mg) in 24% yield.

Compounds **20a**[15] and **20b**[15] are found in the literature.

4.2.1. Tetradec-7-yn-1,5-diol (14a). IR (neat) 3306, 2858, 1956, 1456, 1317, 1030, 916,842 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, J=6.9 Hz, 3H), 1.20–1.80 (m, 16H), 2.16 (ddt, J=6.9, 4.8, 2.4 Hz, 2H), 2.27 (ddt, J=16.5, 6.9, 2.4 Hz, 1H), 2.40 (ddt, J=16.5, 4.8, 2.4 Hz, IH), 3.66 (t, J=6.6 Hz, 2H), 3.63–3.74 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 14.03, 18.74, 21.76, 22.53, 27.74, 28.54, 28.94, 31.30, 32.28, 35.58, 62.16, 70.05, 76.12, 82.88. This compound was converted to its diacetate **14a′** to obtain an analytically pure sample.

4.2.2. 1,5-Diacetoxytetradec-7-yne (14a′). IR (neat) 2932, 2860, 1740, 1435, 1371, 1240, 1030 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, J=6.9 Hz, 3H), 1.20–1.60 (m, 10H), 1.65–1.80 (m, 4H), 2.04 (s, 3H), 2.06 (s, 3H), 2.10–2.16 (m, 2H), 2.40–2.43 (m, 2H), 4.05 (t, J=6.6 Hz, 2H), 4.85–4.93 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 14.05, 18.69, 20.93, 21.13, 21.18, 22.56, 24.26, 28.38, 28.47, 28.84, 31.32, 32.62, 64.14, 74.07, 74.96, 82.49, 170.26, 170.79. Found: C, 69.60; H, 9.87%. Calcd for $C_{18}H_{30}O_4$ C, 69.64; H, 9.74%.

4.2.3. 6-Hexylocta-6,7-dien-1,5-diol (15a). IR (neat) 3306, 2858, 1956, 1456, 1030, 916, 843 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.87 (t, J=6.6 Hz, 3H), 1.20–1.70 (m, 16H), 1.90–2.10 (m, 2H), 3.65 (t, J=6.3 Hz, 2H), 4.00–4.05 (m, 1H), 4.83–4.87 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 14.09, 21.79, 22.63, 27.61, 27.82, 29.09, 31.71, 32.33, 35.07, 62.31, 71.69, 78.21, 107.35, 204.13. This compound was converted to its diacetate **15a′** to obtain an analytically pure sample.

4.2.4. 4,8-Diacetoxy-3-hexylocta-1,2-diene (15a′). IR (neat) 2932, 2860, 1958, 1732, 1445, 1371, 1234, 1020, 954 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, J=6.9 Hz, 3H), 1.20–1.50 (m, 10H), 1.60–1.73 (m, 4H), 1.90–2.00 (m, 2H), 2.04 (s, 3H), 2.06 (s, 3H), 4.05 (t, J=6.6 Hz, 2H), 4.80–4.84 (m, 2H), 5.21 (t, J=6.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.09, 20.96, 21.16, 21.99, 22.62, 27.42, 28.13, 28.28, 28.95, 31.67, 32.41, 64.18, 73.73, 77.86, 103.37, 170.23, 170.83, 205.74. Found: C, 69.65; H, 9.62%. Calcd for $C_{18}H_{30}O_4$: C, 69.64; H, 9.74%.

4.2.5. 8-Trimethylsiloct-7-yn-1,5-diol (14b). IR (neat) 3267, 2869, 2176, 1423, 1430, 1011, 842 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.15 (s, 9H), 1.40–1.70 (m, 7H), 2.10 (bs, 1H), 2.35 (dd, J=16.8, 6.9 Hz, 1H), 2.46 (dd, J=16.8, 4.8 Hz, 1H), 3.60–3.70 (m, 2H), 3.70–3.80 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 0.11, 21.69, 28.84, 32.19, 35.59, 62.11, 69.67, 87.05, 103.43. This compound was converted to its diacetate **14b′** to obtain an analytically pure sample.

4.2.6. 4,8-Diacetoxy-l-trimethylsiloct-l-yne (14b′). IR (neat) 2957, 2179, 1732, 1435, 1371, 1242, 1030, 845, 762 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.14 (s, 9H), 1.30–1.50 (m, 2H), 1.58–1.78 (m, 4H), 2.04 (s, 3H), 2.06 (s, 3H), 2.45 (dd, J=17.1, 6.3 Hz, 1H), 2.51 (dd, J=17.1, 6.0 Hz, 1H), 4.05 (t, J=6.9 Hz, 2H), 4.88–4.97 (m,1H); ^{13}C NMR ($CDCl_3$) δ −0.07, 20.85, 20.97, 21.59, 25.30, 28.26, 32.64, 63.98, 71.39, 86.85, 101.84, 170.05, 170.65. Found: C, 60.48; H, 9.05%. Calcd for $C_{15}H_{26}O_4Si$: C, 60.37; H, 8.78%.

4.2.7. 6-Trimethylsilylocta-6,7-dien-1,5-diol (15b). IR (neat) 3302, 2866, 1927, 1408, 1248, 1014, 812 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.15 (s, 9H), 1.40–1.80 (m, 8H), 3.65 (t, J=6.3 Hz, 2H), 4.14–4.20 (m, 1H), 4.49–4.59 (m, 2H); ^{13}C NMR ($CDCl_3$) δ −0.79, 21.86, 32.32, 37.36, 62.39, 70.38, 71.63, 100.47, 206.97. This compound was converted to its diacetate **15b′** to obtain an analytically pure sample.

4.2.8. 4,8-Diacetoxy-3-trimethylsilylocta-1,2-diene (15b′). IR (neat) 2955, 1931, 1738, 1369, 1240, 1020, 842, 758 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.13 (s, 9H), 1.30–1.50 (m, 2H), 1.55–1.75 (m, 4H), 2.04 (s, 3H), 2.05 (s, 3H), 4.04 (t, J=6.6 Hz, 2H), 4.50–4.51 (m, 2H), 5.29–5.35 (m, 1H); ^{13}C NMR ($CDCl_3$) δ −0.84, 20.99, 21.26, 22.02, 28.28, 34.61, 64.21, 71.11, 72.87, 96.43, 169.98, 170.86, 208.83. Found: C, 60.31; H, 8.61%. Calcd for $C_{15}H_{26}O_4Si$: C, 60.37; H, 8.78%.

4.2.9. 6-Methyl-8-trimethylsiloct-7-yn-1,5-diol (14c, 60/40 diastereomeric mixture). IR (neat) 3346, 2878, 2166, 1250, 1057, 989, 918, 843, 759 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.15 (s, 9H), 1.16 (d, J=6.9 Hz, 1.20H), 1.20 (d, J=6.9 Hz, 1.80H), 1.38–1.50 (m, 6H), 1.76 (s, 2H), 2.50–2.65 (m, 1H), 3.38–3.43 (m, 0.60H), 3.52–3.57 (m, 0.40H), 3.66 (t, J=6.3 Hz, 1.20H), 3.67 (t, J=6.6 Hz, 0.80H); ^{13}C NMR ($CDCl_3$) δ 0.26, 15.80, 17.46, 22.01, 22.10, 32.55, 32.58, 33.18, 34.00, 34.31, 34.61, 62.74, 73.98, 74.08, 86.68, 87.61, 107.38, 108.58. Found: C, 62.87; H, 10.69%. Calcd for $C_{12}H_{24}O_2Si$: C, 63.10; H, 10.59%.

4.2.10. 6-Methyltetradec-7-yn-1,5-diol (14d, 23/77 diastereomeric mixture). IR (neat) 3354, 2932, 2860, 1458, 1436, 1377, 1056, 1004, 920 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, J=6.6 Hz, 3H), 1.12 (d, J=6.9 Hz, 0.69H), 1.17 (d,

J=6.6 Hz, 2.31H), 1.20–1.70 (m, 14H), 1.90–2.10 (m, 2H), 2.12–2.19 (m, 2H), 2.40–2.54 (m, 1H), 3.34–3.40 (m, 0.77H), 3.48–3.52 (m, 0.23H), 3.65 (t, J=6.0 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.91, 16.30, 17.76, 18.64, 21.96, 22.02, 22.45, 28.44, 28.95, 31.23, 32.50, 33.03, 33.16, 33.24, 34.55, 62.52, 74.41, 80.45, 81.66, 82.68, 83.56. This compound was converted to its diacetate **14d′** to obtain an analytically pure sample.

4.2.11. 1,5-Diacetoxy-6-methyltetradec-7-yne (14d′). IR (neat) 2934, 2360, 1740, 1369, 1240, 1022, 970 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J=6.6 Hz, 3H), 1.10 (d, J=7.2 Hz, 3H), 1.20–1.80 (m, 14H), 2.03 (s, 3H), 2.07 (s, 3H), 2.10–2.15 (m, 2H), 2.63–2.69 (m, 1H), 4.04 (t, J=6.6 Hz, 2H), 4.81–4.87 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 13.91, 16.78, 17.60, 18.65, 20.80, 20.93, 22.11, 22.49, 28.39, 28.92, 30.19, 30.96, 31.28, 64.18, 75.53, 80.24, 82.35, 170.61, 170.92. Found: C, 70.24; H, 10.11%. Calcd for $C_{19}H_{32}O_4$: C, 70.33; H, 9.94%.

4.2.12. 6-Vinyltetradec-7-yn-1,5-diol (14e). IR (neat) 3350, 2931, 2860, 1640, 1402, 1329, 920 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.89 (t, J=6.9 Hz, 3H), 1.20–1.70 (m, 16H), 2.22 (dt, J=6.9, 2.4 Hz, 2H), 3.15 (m, 1H), 3.55 (m, 1H), 3.70 (m, 2H), 5.21 (dt, J=10.2, 1.5 Hz, IH), 5.39 (dt, J=17.1, 1.5 Hz, 1H), 5.81 (ddd, J=17.1, 10.2, 6.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.12, 18.85, 22.08, 22.61, 28.61, 28.99, 31.35, 32.56, 34.30, 43.46, 62.70, 73.23, 76.44, 86.52, 117.26, 135.29. This compound was converted to its diacetate **14e′** to obtain an analytically pure sample.

4.2.13. 4,8-Diacetoxy-3-(oct-l-ynyl)oct-1-ene (14e′). IR (neat) 2932, 2860, 1744, 1371, 1238, 1026, 924 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.88 (t, J=6.9 Hz, 3H), 1.20–1.80 (m, 14H), 2.03 (s, 3H), 2.05 (s, 3H), 2.20 (dt, J=7.2, 2.4 Hz, 2H), 3.30–3.36 (m, 1H), 4.04 (t, J=6.6 Hz, 2H), 4.96 (dt, J=8.7, 4.8 Hz, 1H), 5.15–5.21 (m, 1H), 5.34–5.42 (m, 1H), 5.60–5.81 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 14.14, 18.85, 21.06, 21.16, 22.23, 22.65, 28.41, 28.56, 28.96, 30.93, 31.39, 40.16, 64.26, 74.49, 76.16, 85.70, 117.41, 133.85, 170.45, 170.95. Found: C, 71.47; H, 9.66%. Calcd for $C_{20}H_{32}O_4$: C, 71.39; H, 9.59%.

4.2.14. 5-Methyl-7-trimethylsilylhept-6-yn-1,4-diol (14f, 67/33 diastereomeric mixture). IR (neat) 3333, 2878, 2166, 1452, 1249, 1053, 842, 759 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.14 (s, 6H), 0.15 (s, 3H), 1.16 (d, J=6.9 Hz, 0.99H), 1.17 (d, J=6.9 Hz, 2.01H), 1.50–1.80 (m, 4H), 2.10–2.40 (bs, 2H), 2.56 (dq, J=6.9, 5.4 Hz, 0.33H), 2.59 (dq, J=6.9, 5.4 Hz, 0.67H), 3.41–3.48 (m, 0.33H), 3.54–3.60 (m, 0.67H), 3.65–3.76 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 0.26, 15.94, 17.37, 29.36, 29.44, 30.88, 31.73, 34.11, 34.51, 62.92, 62.99, 74.17, 74.25, 86.78, 107.34, 108.49. This compound was converted to its diacetate **14f′** to obtain an analytically pure sample.

4.2.15. 4,7-Diacetoxy-3-methyl-l-trimethylsilylhept-1-yne (14f′, 67/33 diastereomeric mixture). IR (neat) 2990, 2169, 1738, 1371, 1236, 1024, 844, 761 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.14 (s, 9H), 1.14 (d, J=7.2 Hz, 0.99H), 1.15 (d, J=7.2 Hz, 2.01H), 1.60–1.90 (m, 4H), 2.04 (s, 3H), 2.07 (s, 3H), 2.68 (dq, J=7.2, 0.3 Hz, 0.67H), 2.74 (dq, J=7.2, 5.1 Hz, 0.33H), 4.06 (t, J=6.3 Hz, 2H), 4.79–4.88 (m, 0.67H), 4.88–4.95 (m, 0.33H); ^{13}C NMR ($CDCl_3$) δ 0.09, 0.12, 16.32, 17.31, 21.25, 21.83, 24.57, 25.90, 28.02, 28.15, 31.09, 31.75, 62.29, 64.05, 74.07, 75.68, 86.66, 87.00, 107.23, 107.81, 170.81, 171.70. Found: C, 60.41; H, 8.56%. Ca1cd for $C_{15}H_{26}O_4Si$: C, 60.34; H, 8.78%.

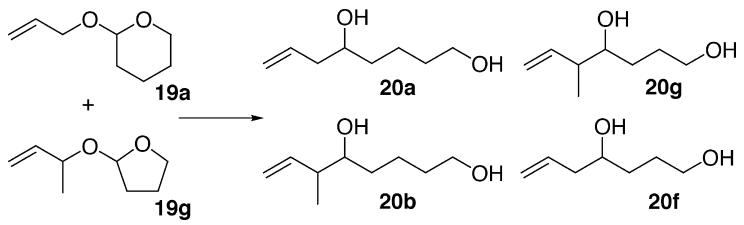
4.2.16. 6-Methyloct-7-en-1,5-diol (20b, 55/45 diastereomeric mixture). IR (neat) 3333, 3078, 2870, 1639, 1418, 1339, 1263, 999, 966 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.02 (d, J=6.9 Hz, 1.65H), 1.03 (d, J=6.9 Hz, 1.35H), 1.35–2.00 (m, 8H), 2.18–2.30 (m, 0.45H), 2.22–2.35 (m, 0.55H), 3.38–3.42 (m, 0.45H), 3.48–3.50 (m, 0.55H), 3.65 (t, J=6.0 Hz, 2H), 5.04–5.14 (m, 2H), 5.68–5.84 (m, 1H); ^{13}C NMR ($CDCl_{13}$) δ 14.26, 16.34, 21.94, 22.32, 32.57, 32.61, 33.58, 33.71, 43.59, 44.25, 62.67, 74.53, 74.59, 115.20, 116.27, 140.18, 140.82. Found: C, 68.20; H, 11.69%. Calcd for $C_9H_{18}O_2$: C, 68.31; H, 11.47%.

4.2.17. 6-Phenyloct-7-en-1,5-diol (20d, 74/26 diastereomeric mixture). IR (neat) 3352, 2937, 2866, 1638, 1601, 1493, 1452, 1001, 918, 759, 702 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.25–1.80 (m, 8H), 3.24 (dd, J=9.0, 9.0 Hz, 0.74H), 3.31 (dd, J=8.7, 8.7 Hz, 0.26H), 3.59 (t, J=6.0 Hz, 1.48H), 3.64 (t, J=6.0 Hz, 0.52H), 3.77–3.83 (m, 0.74H), 3.83–3.92 (m, 0.26H), 5.10–5.16 (m, 0.52H), 5.19–5.25 (m, 1.48H), 6.04 (ddd, J=17.4, 9.9, 8.7 Hz, 0.74H), 6.12 (ddd, J=16.8, 10.5, 9.0 Hz, 0.26H), 7.10–7.35 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 21.89, 32.45, 32.56, 33.92, 34.01, 57.40, 57.50, 62.65, 73.81, 74.11, 116.73, 117.86, 126.58, 126.80, 127.84, 128.35, 128.60, 128.68, 138.18, 138.52, 140.73, 141.40. Found: C, 76.28; H, 9.04%. Calcd for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15%.

4.2.18. Hept-6-en-1,5-diol (20f). IR (neat) 3308, 2872, 1641, 1435, 1346, 1009, 914 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.46–1.54 (m, 1H), 1.60–1.80 (m, 3H), 2.15–2.32 (m, 2H), 2.60–3.20 (m, 2H), 3.60–3.80 (m, 3H), 5.10–5.15 (m, 2H), 5.76–5.91 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 28.98, 33.66, 41.95, 62.61, 70.72, 117.64, 134.82. Found: C, 76.28; H, 9.04%. Calcd for $C_{14}H_{20}O_2$: C, 76.33; H, 9.15% This compound was converted to its diacetate **20f′** to obtain an analytically pure sample.

4.2.19. 4,7-Diacetoxyhept-1-ene (20f′). IR (neat) 3080, 2958, 1738, 1643, 1439, 1371, 1238, 1024, 997 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.60–1.80 (m, 4H), 2.02 (s, 3H), 2.03 (s, 3H), 2.27–2.33 (m, 2H), 4.04 (t, J=6.3 Hz, 2H), 4.88–4.96 (m, 1H), 5.03–5.10 (m, 2H), 5.65–5.80 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 20.83, 21.05, 24.62, 30.03, 38.57, 64.05, 72.73, 117.77, 133.41, 170.55, 170.92. Found: C, 61.41; H, 8.46%. Calcd for $C_{11}H_{18}O_4$: C, 61.66; H, 8.47%.

4.2.20. 5-Methylhept-6-en-1,4-diol (20g, 58/42 diastereomeric mixture). IR (neat) 3305, 2874, 1639, 1417, 999, 914 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 1.03 (d, J=6.6 Hz, 1.26H), 1.04 (d, J=6.9 Hz, 1. 74H), 1.20–1.80 (m, 4H), 2.20–2.40 (m, 3H), 3.39–3.45 (m, 0.42H), 3.48–3.54 (m, 0.58H), 3.60–3.73 (m, 2H), 5.05–5.15 (m, 2H), 5.68–5.85 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 14.88, 16.12, 29.26, 29.47, 31.05, 31.24, 43.86, 44.16, 62.64, 74.67, 74.82, 114.88, 115.82, 140.22, 140.83. Found: C, 66.37; H, 11.09%. Calcd for $C_8H_{16}O_2$: C, 66.63; H, 11.18%.



Scheme 10.

4.2.21. 5-Phenylhept-6-en-1,4-diol (20h, 56/44 diastereomeric mixture). IR (neat) 3354, 2874, 1637, 1001, 918, 759 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.30–1.90 (m, 4H), 1.95 (bs, 2H), 3.25 (dd, J=8.6, 8.6 Hz, 0.56H), 3.32 (dd, J=8.6, 8.6 Hz, 0.44H), 3.54–3.65 (m, 1.12H), 3.60–3.72 (m, 0.88H), 3.83 (dt, J=6.0, 3.0 Hz, 0.56H), 3.90 (dt, J=9.3, 2.7 Hz, 0.44H), 5.10–5.25 (m, 2H), 5.97–6.18 (m, 1H), 7.18–7.38 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 29.19, 31.52, 31.56, 57.31, 62.68, 73.95, 74.17, 116.66, 117.60, 126.50, 126.69, 127.84, 128.29, 128.53, 128.58, 138.24, 138.33, 140.82, 141.40. This compound was converted to its diacetate **20h′** to obtain an analytically pure sample.

4.2.22. 4,7-Diacetoxy-3-phenylhept-1-ene (20h′, 57/43 diastereomeric mixture). IR (neat) 3062, 1738, 1639, 1494, 1369, 1238, 1026, 923 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.40–1.80 (m, 4H), 1.85 (s, 1.29H), 1.97 (s, 1.71H), 2.02 (s, 1.29H), 2.04 (s, 1.71H), 3.39 (dd, J=8.4, 8.4 Hz, 0.57H), 3.50 (dd, J=8.4, 8.4 Hz, 0.43H), 3.96 (m, 1.14H), 4.03 (m, 0.86H), 5.05–5.18 (m, 2H), 5.22–5.30 (m, 1H), 5.95–6.08 (m, 1H) 7.18–7.36 (m, 5H); ^{13}C NMR ($CDCl_3$) δ 20.88, 20.95, 21.00, 21.20, 24.57, 24.66, 28.65, 28.71, 54.56, 55.15, 63.88, 64.01, 75.15, 116.80, 117.27, 126.62, 126.80, 127.89, 128.25, 128.64, 137.23, 137.78, 140.15, 140.47, 170.30, 170.53, 170.78, 170.84. Found: C, 70.55; H, 7.78%. Calcd for $C_{17}H_{22}O_4$: C, 70.32; H, 7.64%.

Acknowledgements

Financial support by Grant-in-Aids for Scientific from the Ministry of Education, Culture, Sports, Science, and Technology, Japan, is acknowledged. T. N. thanks the JSPS Research Fellowship for Young Scientists.

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12. Recombination of manganese species and aldehyde **E** proceeds intermoleculary. Thus, treatment of a mixture of **19a** (0.5 mmol) and **19g** (0.5 mmol) with tributylmanganate (1.0 mmol) provided the intermolecular addition products **20b** and **20f** in addition to the intramolecular addition products **20a** and **20g**. The ratio of these compounds was **20a/20b/20f/20g**=42:24:14:20 (Scheme 10).
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14. Triethylmanganate ($Et_3MnMgBr$) was also effective as tributylmanganate. However, trimethylmanganate derived from $MnCl_2$ and MeMgI was not effective for the transformation. For instance, treatment of **19f** with Me_3MnMgI gave a methylated product (1,4-pentanediol) in only 13% in addition to unidentified complex products. The use of *n*-Bu_3MnLi derived from *n*-BuLi instead of *n*-BuMgBr afforded **20f** in only 31% yield along with **21** (7%).
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