Pergamon

Tetrahedron 57 (2001) 10063–10069

TETRAHEDRON

Synthesis of trisubstituted and tetrasubstituted alkenes via a manganate-induced migration–elimination process

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Received 13 September 2001; accepted 25 October 2001

Abstract—Preparation of alkenes via a manganate-induced alkylation–elimination sequence was investigated. The reaction of 2-alkoxy-1,1-dibromoalkanes with trialkylmanganates afforded disubstituted or trisubstituted alkenes. Treatment of 2-alkoxy-1,1,1-tribromoalkanes with trialkylmanganates provided trisubstituted or tetrasubstituted alkenes through bromine–metal exchange, transfer of two alkyl groups from manganese to carbon, and successive elimination of metal and the β-alkoxy moieties.

1. Introduction

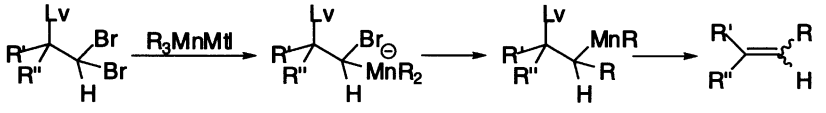
Alkenes are useful building blocks in a number of synthetic applications including epoxidation, hydroxylation, dihydroxylation, haloetherification, and so forth. Alkenes with various substitution patterns are found in the structure of numerous natural products and pharmaceutical agents. Therefore, the stereoselective synthesis of polysubstituted alkenes is a very important issue in synthetic chemistry.[1] For alkene synthesis, one can use the condensation-type reaction of carbonyl compounds such as the Wittig reaction,[2] or related reactions.[3,4] However, the condensation-type reaction is not effective for the synthesis of tetrasubstituted alkenes due to the steric demand of the products. The McMurry coupling reaction is useful only to prepare cyclic alkenes or symmetric alkenes, in which all substituents are identical.[5] The transition metal-catalyzed coupling reaction using alkenyl halides or alkenyl metals as precursors is a powerful means to access trisubstituted alkenes.[6] However, it is often difficult to prepare trialkyl-substituted alkenyl halides or alkenyl metals regio- and stereoselectively.[7] Consequently, the protocol is scarcely utilized for the synthesis of tetrasubstituted alkenes.[8,9]

We have reported that treatment of *gem*-dibromoalkanes or trialkyl(dibromomethyl)silanes with trialkylmanganates, derived from manganese(II) chloride and 3.0 equiv. of Grignard reagents or alkyllithiums,[10,11] provided alkylated alkenes or (*E*)-alkenylsilanes in good yields, respectively.[12] Then, we anticipated that the reaction of di- and tribromoalkanes bearing a leaving group with trialkylmanganates could be applied to prepare tri- and tetrasubstituted alkenes according to Scheme 1. Bromine–manganese exchange followed by 1,2-migration of an alkyl group and sequential elimination of manganese and the leaving group would afford the desired alkenes. Here, we wish to report that treatment of these bromides with trialkylmanganates provided the alkylated or dialkylated polysubstituted alkenes in one-step.

2. Results and discussion

We have reported that the reaction of 1,1-dibromo-2-(*t*-butyldimethylsiloxy)-2-phenylethane (**1a**) with tributylmanganate afforded 1-phenyl-1-hexene (**2**) in only 38% yield (Scheme 2).[12] After further investigation, we found that the use of *n*-Bu_3MnLi in place of *n*-$Bu_3MnMgBr$ improved the yield of **2** up to 85% yield.

Table 1 shows the results of the reaction of various dibromoalkanes with manganates. Several comments are worth noting. (1) The substituents on silicon had no significant influence on the yield of the product (entries 1 and 2).



Scheme 1.

Keywords: manganese and compounds; alkenes; halogens and compounds; migration.

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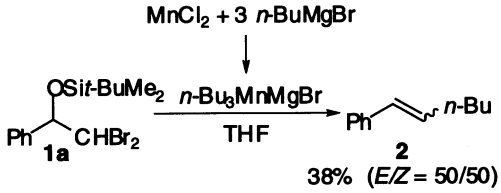
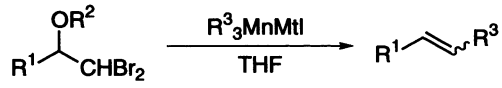


Scheme 2.

Table 1. The reaction of dibromoalkanes with trialkylmanganate



Entry	R^1	R^2	$R^3{}_nMnMtl$	Yield (%)[a]	*E*/*Z*
1	Ph	Si*t*-BuMe$_2$ (**1a**)	*n*-Bu$_3$MnLi	85 (**2**)	50/50
2	Ph	SiMe$_3$ (**1b**)	*n*-Bu$_3$MnLi	87 (**2**)	46/54
3[b]	Ph	SiMe$_3$ (**1b**)	*n*-Bu$_3$MnLi	81 (**2**)	47/53
4	Ph	CH$_2$Ph (**1c**)	*n*-Bu$_3$MnLi	52 (**2**)	61/39
5[b]	Ph	H (**1d**)	*n*-Bu$_3$MnLi	65 (**2**)	69/31
6	Ph	SiMe$_3$ (**1b**)	Ph$_3$MnLi	78 (**4**)	63/37
7	*n*-C$_6$H$_{13}$	SiMe$_3$ (**3**)	*n*-Bu$_3$MnLi	76 (**5**)	47/53
8[c]	*n*-C$_6$H$_{13}$	SiMe$_3$ (**3**)	Ph$_3$MnLi	87 (**6**)	45/55

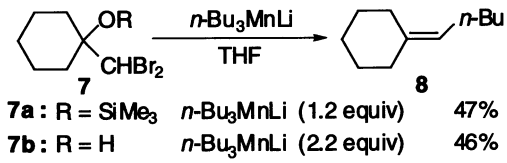
The reactions were performed with dibromoalkane (1.0 mmol) and manganate (1.2 mmol) in THF unless otherwise noted.
[a] Yields are based on dibromoalkane and are isolated yield.
[b] Manganate (2.2 mmol) was used.
[c] The reaction was performed with **3** (0.5 mmol) and Ph$_3$MnLi (1.1 mmol) in THF.

(2) The use of 1.2 equiv. of trialkylmanganate is sufficient. The yield of **2** was not improved by the use of 2.2 equiv. of the manganate (entry 3). (3) The reaction of 1-benzyloxy-2,2-dibromo-1-phenylethane (**1c**) afforded **2** in moderate yield (entry 4). (4) The use of unprotected alcohol **1d** as a substrate afforded **2** in moderate yield (entry 5). (5) Ph$_3$MnLi provided the desired phenylated alkene **4** in good yield (entry 6). (6) The substrate **3** (R^1=*n*-C$_6$H$_{13}$) also provided the corresponding alkenes upon treatment with trialkylmanganates (entries 7 and 8).

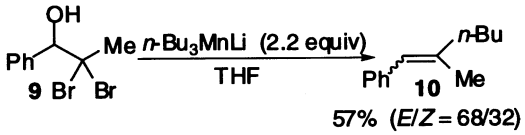
We also investigated the reaction of **7** to examine the feasibility of the synthesis of trisubstituted alkenes. Treatment of **7a** with tributylmanganate afforded pentylidenecyclohexane (**8**) in 47% yield. The reaction of **7b** with 2.2 equiv. of *n*-Bu$_3$MnLi furnished the desired trisubstituted alkene **8** in 46% yield (Scheme 3).

A trisubstituted alkene can be also prepared from dibromo compound **9**. Treatment of **9** with 2.2 equiv. of tributylmanganate provided **10** (*E*/*Z*=68/32) in 57% yield (Scheme 4).

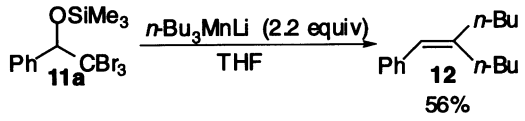
We then turned our attention toward the reaction of tribromoalkanes. Treatment of 1,1,1-tribromo-2-phenyl-2-



Scheme 3.



Scheme 4.



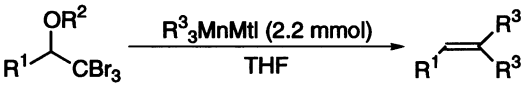
Scheme 5.

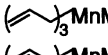
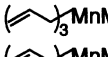
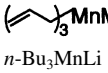
(trimethylsiloxy)ethane (**11a**) with *n*-Bu$_3$MnLi resulted in the incorporation of two butyl groups to afford 2-butyl-1-phenyl-1-hexene (**12**) in 56% yield (Scheme 5).

Table 2 summarizes the double alkylation reaction of various tribromoalkanes with manganates. Several issues regarding the results in Table 2 merit comment.[13] (1) The tribromo compound **11b** with a *t*-butyldimethylsiloxy group also provided **12** in almost same yield (entry 1). (2) The use of benzoate **11c** decreased the yield of the product **12** slightly (entry 2). (3) The reaction of the unprotected alcohol **11d** also provided the desired alkene **12** (entry 3). (4) The reaction of **11a** with 2.2 equiv. of triallylmanganate, which was prepared by mixing allylmagnesium chloride and MnCl$_2$ in a 3:1 ratio, proceeded effectively and 2-allyl-1-phenyl-1,4-pentadiene (**13**) was obtained in 65% yield. However, in the case of magnesium manganate, the use of the unprotected alcohol as a substrate resulted in a considerable decrease of the yield of **13** (entries 4–6). (5) This reaction was applicable for the preparation of an *exo*-methylene compound (entry 7). (6) The reaction of **18** with *n*-Bu$_3$MnLi afforded the diene **19** in moderate yield (entry 8).

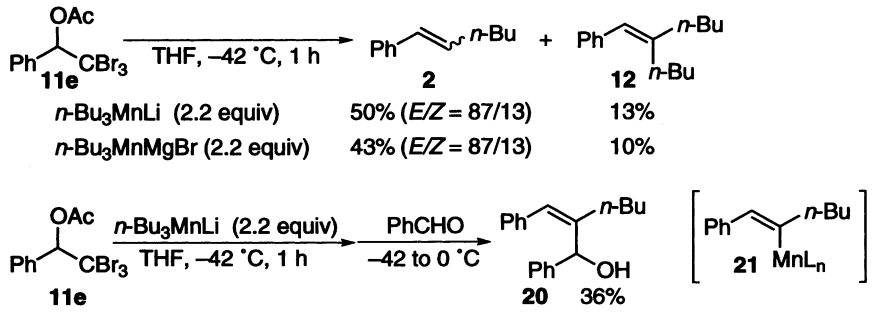
To our surprise, the reaction of acetate **11e** with lithium tributylmanganate provided 1-phenyl-1-hexene (**2**,

Table 2. The reaction of tribromoalkanes with trialkylmanganate

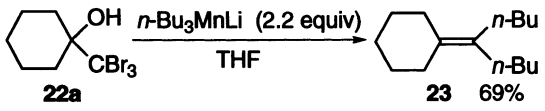


Entry	R^1	R^2	$R^3{}_nMnMtl$	Yield (%)[a]
1	Ph	Si*t*-BuMe$_2$ (**11b**)	*n*-Bu$_3$MnLi	58[b] (**12**)
2	Ph	CH$_2$Ph (**11c**)	*n*-Bu$_3$MnLi	43 (**12**)
3	Ph	H (**11d**)	*n*-Bu$_3$MnLi	44 (**12**)
4	Ph	SiMe$_3$ (**11a**)		65[b] (**13**)
5	Ph	H (**11d**)		24 (**13**)
6	*n*-C$_6$H$_{13}$	SiMe$_3$ (**14**)		43 (**15**)
7	H	Si*t*-BuMe$_2$ (**16**)	*n*-Bu$_3$MnLi	49[b] (**17**)
8	PhCH=CH	SiMe$_3$ (**18**)	*n*-Bu$_3$MnLi	48 (**19**)

The reactions were performed with tribromoalkane (1.0 mmol) and manganate (2.2 mmol) in THF.
[a] Yields are based on tribromoalkane and are isolated yields.
[b] NMR yield.

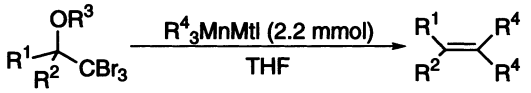


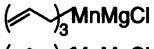
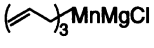
Scheme 6.



Scheme 7.

Table 3. Preparation of tetrasubstituted alkene



Entry	R^1	R^2	R^3	$R^4{}_3MnMtl$	Yield (%)[a]
1	$-(CH_2)_5-$		H (**22a**)	n-Bu_3MnLi	69 (**23**)
2	$-(CH_2)_5-$		H (**22a**)	Ph_3MnLi	53 (**24**)
3	$-(CH_2)_5-$		H (**22a**)	n-$Bu_3MnMgBr$	56 (**23**)
4	$-(CH_2)_5-$		H (**22a**)		59 (**25**)
5	$-(CH_2)_5-$		$SiMe_3$ (**22b**)		13 (**25**)
6	n-Bu	n-Bu	H (**26**)		56 (**27**)
7	n-C_5H_{11}	Me	H (**28**)	n-Bu_3MnLi	62 (**29**)

The reactions were performed with tribromo compound (1.0 mmol) and manganate (2.2 mmol) in THF at 0°C for 1 h.
[a] Yields are based on tribromo compound and are isolated yields.

E/*Z*=87/13) in 50% yield along with the desired trisubstituted alkene **12** in 13% yield. The use of n-$Bu_3MnMgBr$ also afforded **2**, predominately. Moreover, the sequential treatment of **11e** with tributylmanganate and benzaldehyde afforded allylic alcohol **20** in 36% yield. On the basis of these facts, it is obvious that vinyl manganese species **21** is formed in situ (Scheme 6).

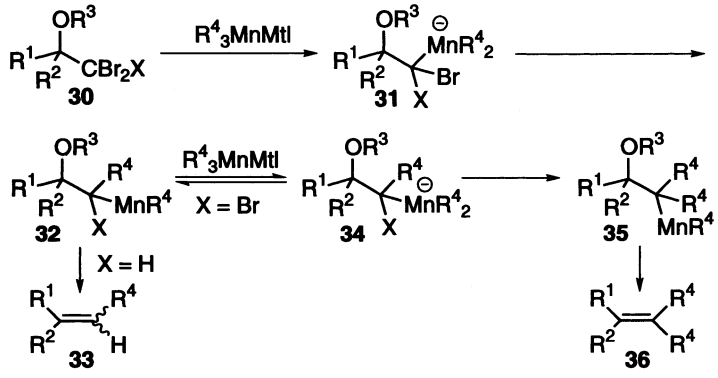
The migration–elimination reaction also proved to be effective to synthesize tetrasubstituted alkenes. Treatment of 1-(tribromomethyl)cyclohexanol (**22a**) with lithium tributylmanganate provided the dibutylated alkene **23** in 69% yield (Scheme 7).

The results of the reaction of various tribromoalkanes with manganates are shown in Table 3. Several characteristics of this reaction are noteworthy.[13] (1) The reaction with Ph_3MnLi provided the product **24** (entry 2). (2) Magnesium manganate (R_3MnMgX) was as effective as lithium trialkylmanganate (R_3MnLi) (entries 3 and 4). (3) The use of trimethylsilyl ether **22b** resulted in a decrease in the yield of the product (entry 5). (4) In the case of **28**, a tetrasubstituted alkene with three different substituents was obtained (entry 7).

We propose the following reaction mechanism for the formation of alkenes (Scheme 8): Initial bromine–manganese exchange to afford **31**, alkyl migration from manganese to adjacent carbon under Br^- elimination producing **32**. When X is hydrogen, elimination of Mn and the alkoxy group at the β-position takes place to give the alkene **33**. Meanwhile, when X is Br, dialkylated alkenes **36** is produced by the following pathway: generation of manganate **34** by the action of another trialkylmanganate, further 1,2-migration of the alkyl group of **34** providing **35**, and elimination of Mn and the alkoxy group.[14]

3. Conclusion

We found that 1,1-di- or 1,1,1-tribromoalkanes bearing a β-alkoxy group provided the alkylated alkenes upon



Scheme 8.

treatment with trialkylmanganates via a migration–elimination sequence. In the reaction of a *gem*-dibromoalkane with tributylmanganate, which we have reported earlier,[12] two regioisomeric alkenes were obtained because of the presence of two types of β-hydrogen atoms. However, the reaction described in this report provided an alkene as a single regioisomer because an alkoxy group was eliminated selectively over β-hydrogen. In the reaction of dibromo compounds, lithium trialkylmanganese was much more effective than the corresponding magnesium ate complex to achieve incorporation of the alkyl group on manganese into the products. In contrast, trialkylmanganates, derived from Grignard reagents, were also applicable in the reaction of tribromoalkanes.

4. Experimental

Melting points were obtained on a Yanako MP-50929 melting point apparatus and are uncorrected. 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. Starting materials

According to literature procedures, 1,1-dibromo-2-(*t*-butyldimethylsiloxy)-2-phenylethane (**1a**),[15] 1-(dibromomethyl)-cyclohexanol (**7b**),[16] and 1-(tribromomethyl)cyclohexanol (**22a**)[16] were prepared. In a similar fashion,[16] 2,2-dibromo-1-phenylethanol (**1d**), 2,2-dibromo-1-phenyl-1-propanol (**9**), 2,2,2-tribromo-1-phenylethanol (**11d**), 5-(tribromomethyl)-5-nonanol (**26**), and 1,1,1-tribromo-2-methyl-2-heptanol (**28**) were prepared.

Spectroscopic data for 2,2-dibromo-1-phenylethanol (**1d**) were identical with those reported in the literature.[17]

4.1.1. 2,2-Dibromo-1-phenyl-1-propanol (9). IR (neat) 3454, 1454, 1377, 1043, 756, 702 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.41 (s, 3H), 3.12 (s, 1H), 5.00 (s, 1H), 7.32–7.40 (m, 3H), 7.49–7.58 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 35.55, 74.78, 83.32, 127.90, 128.83, 129.00, 136.32. Found: C, 36.83; H, 3.47%. Calcd for $C_9H_{10}Br_2O$: C, 36.77; H, 3.43%.

4.1.2. 2,2,2-Tribromo-1-phenylethanol (11d). Mp 76°C; IR (nujol) 3506, 1049, 750, 694 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 3.50 (d, J=3.6 Hz, 1H), 5.17 (d, J=3.6 Hz, 1H), 7.34–7.46 (m, 3H), 7.68–7.74 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 54.50, 85.81, 127.73, 129.52, 129.71, 135.24. Found: C, 26.94; H, 2.01%. Calcd for $C_8H_7Br_3O$: C, 26.78; H, 1.97%.

4.1.3. 5-(Tribromomethyl)-5-nonanol (26). IR (neat) 3558, 2932, 2872, 1466, 1379, 1342, 1285, 1126, 1037, 708 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.96 (t, J=7.2 Hz, 6H), 1.30–1.60 (m, 8H), 1.95–2.16 (m, 4H), 2.40 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 13.86, 23.20, 27.38, 35.56, 66.34, 82.99. Found: C, 30.21; H, 4.83%. Calcd for $C_{10}H_{19}Br_3O$: C, 30.41; H, 4.85%.

4.1.4. 1,1,1-Tribromo-2-methyl-2-heptanol (28). IR (neat) 3548, 3466, 2952, 2926, 2864, 1461, 1377, 1345, 1136, 1089, 1046, 963, 894, 794, 721 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.93 (t, J=6.9 Hz, 3H), 1.24–1.61 (m, 6H), 1.63 (s, 3H), 1.96–2.18 (m, 2H), 2.36 (bs, 1H); ^{13}C NMR ($CDCl_3$) δ 13.90, 21.44, 22.52, 24.59, 32.16, 35.90, 65.66, 82.86. Found: C, 26.48; H, 4.01%. Calcd for $C_8H_{15}Br_3O$: C, 26.19; H, 4.12%.

4.2. Preparation of silyl ether

Method A. Preparation of 1,1-dibromo-2-phenyl-2-(trimethylsiloxy)ethane (**1b**) is representative. Trimethylsilyl chloride (0.60 g, 5.5 mmol), imidazole (0.37 g, 5.5 mmol), and 4-dimethylaminopyridine (12 mg, 0.1 mmol) were added to 2,2-dibromo-1-phenylethanol (**1d**, 1.40 g, 5.0 mmol) in DMF (8 mL). The mixture was stirred for 2 h at room temperature. The reaction was quenched with water and the mixture was extracted with hexane. Purification by silica gel column chromatography afforded 1,1-dibromo-2-phenyl-2-(trimethylsiloxy)ethane (**1b**, 1.57 g, 4.5 mmol) in 89% yield. In a similar fashion, 1,1-dibromo-2-(trimethylsiloxy)-octane (**3**), 1,1,1-tribromo-2-phenyl-2-(trimethylsiloxy)-ethane (**11a**), 1,1,1-tribromo-2-(trimethylsiloxy)octane (**14**), 1,1,1-tribromo-2-(*t*-butyldimethylsiloxy)ethane (**16**), and 4,4,4-tribromo-1-phenyl-3-(trimethylsiloxy)-1-butene (**18**) were prepared.

Method B. Preparation of 1,1,1-tribromo-2-(*t*-butyldimethylsiloxy)-2-phenylethane (**11b**) is representative. *t*-Butyldimethylsilyl trifluoromethanesulfonate (1.90 g, 7.2 mmol) was added to a mixture of 2,2,2-tribromo-1-phenylethanol (**11d**, 2.15 g, 6.0 mmol) and 2,6-lutidine (1.29 g, 12.0 mmol) in dichloromethane (6 mL) at room temperature. The mixture was stirred for 7 h. The reaction was quenched with 1 M HCl. Extraction with hexane, followed by silica gel column purification afforded 1,1,1-tribromo-2-(*t*-butyldimethylsiloxy)-2-phenylethane (**11b**, 2.62 g, 5.6 mmol) in 93% yield. In a similar fashion, 1-dibromomethyl-1-(trimethylsiloxy)cyclohexane (**7a**) and 1-tribromomethyl-1-(trimethylsiloxy)cyclohexane (**22b**) were prepared.

4.2.1. 1,1-Dibromo-2-phenyl-2-(trimethylsiloxy)ethane (1b). IR (neat) 2959, 1454, 1254, 1136, 1094, 964, 878, 843, 756, 702 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.11 (s, 9H), 4.96 (d, J=5.1 Hz, 1H), 5.65 (d, J=5.1 Hz, 1H), 7.31–7.42 (m, 5H); ^{13}C NMR ($CDCl_3$) δ −0.07, 51.37, 79.82, 127.33, 128.23, 128.65, 139.91. Found: C, 37.34; H, 4.50%. Calcd for $C_{11}H_{16}Br_2OSi$: C, 37.52; H, 4.58%.

4.2.2. 1,1-Dibromo-2-(trimethylsiloxy)octane (3). IR (neat) 2957, 2928, 2858, 1252, 1103, 843, 750, 687 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.20 (s, 9H), 0.89 (t, J=6.3 Hz, 3H), 1.18–1.48 (m, 8H), 1.56–1.84 (m, 2H), 3.80–3.87 (m, 1H),

5.60 (d, J=3.3 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 0.33, 13.95, 22.47, 25.22, 29.03, 31.62, 33.68, 51.79, 77.27. Found: C, 36.69; H, 6.78%. Calcd for $C_{11}H_{24}Br_2OSi$: C, 36.68; H, 6.72%.

4.2.3. 1-Dibromomethyl-1-(trimethylsiloxy)cyclohexane (7a). IR (neat) 2932, 2854, 1252, 1174, 1139, 1094, 1072, 896, 840, 753, 687 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.23 (s, 9H), 1.16–1.35 (m, 1H), 1.46–1.62 (m, 5H), 1.68–1.86 (m, 4H), 5.69 (s, 1H); ^{13}C NMR ($CDCl_3$) δ 2.56, 22.28, 25.26, 34.81, 58.40, 78.47. Found: C, 34.73; H, 5.89%. Calcd for $C_{10}H_{20}Br_2OSi$: C, 34.90; H, 5.86%.

4.2.4. 1,1,1-Tribromo-2-phenyl-2-(trimethylsiloxy)-ethane (11a). Mp 43°C; IR (nujol) 1254, 1124, 880, 843, 762, 691, 573 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.11 (s, 9H), 5.08 (s, 1H), 7.30–7.43 (m, 3H), 7.64–7.70 (m, 2H); ^{13}C NMR ($CDCl_3$) δ −0.10, 53.73, 86.32, 127.45, 129.11, 130.02, 137.56. Found: C, 30.44; H, 3.41%. Calcd for $C_{11}H_{15}Br_3OSi$: C, 30.65; H, 3.51%.

4.2.5. 1,1,1-Tribromo-2-(*t*-butyldimethylsiloxy)-2-phenylethane (11b). IR (neat) 2950, 2926, 2882, 2852, 1472, 1463, 1455, 1257, 1198, 1119, 1074, 864, 837, 778, 762, 703, 692 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ −0.22 (s, 3H), 0.20 (s, 3H), 0.94 (S, 9H), 5.07 (s, 1H), 7.32–7.43 (m, 3H), 7.65–7.72 (m, 2H); ^{13}C NMR ($CDCl_3$) δ −5.15, −4.76, 18.15, 25.52, 53.67, 86.46, 127.45, 129.18, 130.10, 137.71. Found: C, 35.53; H, 4.49%. Calcd for $C_{14}H_{21}Br_3OSi$: C, 35.54; H, 4.47%.

4.2.6. 1,1,1-Tribromo-2-(trimethylsiloxy)octane (14). IR (neat) 2959, 2928, 2858, 1458, 1342, 1252, 1142, 1109, 901, 843, 750, 706 cm^{-1}; ^{1}H NMR (CDCl3) δ 0.28 (s, 9H), 0.91 (t, J=6.6 Hz, 3H), 1.23–1.59 (m, 8H), 1.60–1.73 (m, 1H), 2.14–2.25 (m, 1H), 3.92 (dd, J=9.0, 1.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 0.83, 13.91, 22.45, 26.30, 28.99, 31.58, 34.24, 55.21, 85.95. HRMS Found: m/z 187.1526. Calcd for $C_{11}H_{23}Br_3OSi$: (M−CBr_3), 187.1518.

4.2.7. 1,1,1-Tribromo-2-(*t*-butyldimethylsiloxy)ethane (16). IR (neat) 2930, 2856, 1472, 1464, 1258, 1146, 841, 779, 702, 633 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.19 (s, 6H), 0.97 (s, 9H), 4.28 (s, 2H); ^{13}C NMR ($CDCl_3$) δ −5.23, 18.28, 25.62, 45.45, 79.33. Found: C, 24.49; H, 4.23%. Calcd for $C_8H_{17}Br_3OSi$: C, 24.40; H, 4.32%.

4.2.8. 4,4,4-Tribromo-1-phenyl-3-(trimethylsiloxy)-1-butene (18). Mp 69°C; IR (nujol) 1449, 1255, 1122, 1104, 965, 887, 842, 752, 693 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.25 (s, 9H), 4.63 (d, J=6.6 Hz, 1H), 6.38 (dd, J=15.9, 6.6 Hz, 1H), 6.82 (d, J=15.9 Hz, 1H), 7.26–7.39 (m, 3H), 7.42–7.47 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 0.35, 53.15, 85.54, 126.10, 126.95, 128.49, 128.83, 136.00, 136.15. Found: C, 33.98; H, 3.66%. Calcd for $C_{13}H_{17}Br_3OSi$: C, 34.16; H, 3.75%.

4.2.9. 1-Tribromomethyl-1-(trimethylsiloxy)cyclohexane (22b). IR (neat) 2940, 2856, 1250, 1168, 1094, 902, 840, 753, 697 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 0.30 (m, 9H), 1.07–1.24 (m, 1H), 1.41–1.80 (m, 5H), 1.95–2.09 (m, 2H), 2.11–2.22 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 2.81, 22.64, 25.00, 32.31, 65.86, 86.32. HRMS Found: m/z 171.1211. Calcd for $C_9H_{19}OSi$: (M−CBr_3), 171.1205.

4.3. Preparation of benzyl ether[18]

Benzylation of 2,2,2-tribromo-1-phenylethanol (**11d**) is representative. Benzyl 2,2,2-trichoroacetimidate (3.48 g, 13.8 mmol) and 2,2,2-tribromo-1-phenylethanol (**11d**, 2.60 g, 7.3 mmol) were dissolved in CH_2Cl_2 (50 mL). After cooling to 0°C, trimethylsilyl trifluoromethanesulfonate (222 mg, 1.0 mmol) was added slowly and the mixture was stirred for 24 h at room temperature. The solvent was removed in vacuo and diethyl ether was added to the residue. The mixture was poured into 0.5 M NaOH solution and extracted with Et_2O. The combined organic layers were washed with 1 M HCl and with sat. $NaHCO_3$ solution and concentrated in vacuo. Purification by silica gel column chromatography provided 2-benzyloxy-1,1,1-tribromo-2-phenylethane (**11c**) in 40% yield. In a similar fashion, 1-benzyloxy-2,2-dibromo-1-phenylethane (**1c**) was prepared.

4.3.1. 1-Benzyloxy-2,2-dibromo-1-phenylethane (1c). IR (neat) 3026, 1493, 1454, 1071, 1027 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.44 (d, J=11.7 Hz, 1H), 4.64 (d, J=11.7 Hz, 1H), 4.69 (d, J=5.7 Hz, 1H), 5.71 (d, J=5.7 Hz, 1H), 7.32–7.47 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 47.61, 71.60, 84.86, 120.06, 128.15, 128.32, 128.52, 129.21, 136.81, 137.25. HRMS Found: m/z 262.8890. Calcd for $C_8H_7{}^{79}Br^{81}Br$: (M−$PhCH_2O$), 262.8894.

4.3.2. 2-Benzyloxy-1,1,1-tribromo-2-phenylethane (11c). IR (neat) 3058, 3026, 2864, 1492, 1454, 1092, 1070, 1029, 992, 752, 730, 705, 693 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 4.52 (d, J=12.0 Hz, 1H), 4.70 (d, J=12.0 Hz, 1H), 4.83 (s, 1H), 7.28–7.49 (m, 8H), 7.65–7.73 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 48.37, 72.04, 90.77, 127.80, 128.08, 128.23, 128.39, 129.49, 130.52, 134.49, 136.68. HRMS Found: m/z 342.7969. Calcd for $C_8H_6{}^{79}Br^{81}Br_2$: (M−$PhCH_2O$), 342.7979.

4.3.3. Preparation of 2,2,2-tribromo-1-phenylethyl acetate (11e). Acetic anhydride (1.02 g, 10 mmol) and 4-dimethylaminopyridine (12 mg, 0.10 mmol) were added to a mixture of 2,2,2-tribromo-1-phenylethanol (**11d**, 1.79 g, 5.0 mmol) and pyridine (1.58 g, 20 mmol) at room temperature. The mixture was warmed up to 60°C and stirred for 5 h at 60°C. After the mixture had been cooled down to room temperature, toluene (20 mL) was added to the resulting mixture. Then, the mixture was dried over Na_2SO_4 and the solvent was removed in vacuo. Purification by silica gel column chromatography afforded **11e** in 81% yield: mp 144°C; IR (nujol) 1745, 1225, 1039, 928, 766, 712, 692 cm^{-1}; ^{1}H NMR ($CDCl_3$) δ 2.23 (m, 3H), 6.40 (s, 1H), 7.35–7.48 (m, 3H), 7.69–7.76 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 20.78, 45.16, 83.67, 127.87, 129.79, 130.13, 133.87, 168.71. Found: C, 29.88; H, 2.19%. Calcd for $C_{10}H_9Br_3O_2$: C, 29.96; H, 2.26%.

4.4. General procedure for the preparation of alkene

The reaction of 1-(tribromomethyl)cyclohexanol (**22a**) with tributylmanganate is representative. Manganese(II) chloride (277 mg, 2.2 mmol) was sonicated in THF (10 mL) under argon atmosphere for 10 min. Butyllithium (1.6 M hexane solution, 4.1 mL, 6.6 mmol) was added to the suspension of

$MnCl_2$ in THF at 0°C. The mixture turned into a clear brown solution and the solution was stirred for 20 min at 0°C. A solution of 1-(tribromomethyl)cyclohexanol (**22a**, 351 mg, 1.0 mmol) in THF (2 mL) was added at 0°C. The mixture was stirred at 0°C for 1 h. The resulting mixture was poured into water and extracted with hexane (20 mL×3). The combined organic layers were dried over Na_2SO_4 and concentrated in vacuo. The crude product was purified by silica gel column chromatography to provide (1-butylpentylidene)cyclohexane (**23**, 144 mg) in 69% yield: IR (neat) 2926, 2856, 1448, 1377, 1259, 1236, 851 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (t, J=6.6 Hz, 6H), 1.22–1.35 (m, 8H), 1.43–1.64 (m, 6H), 1.98 (t, J=7.2 Hz, 4H), 2.11 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 14.00, 22.87, 27.00, 28.46, 30.39, 31.76, 31.91, 130.05, 133.01. HRMS Found: m/z 208.2192. Calcd for $C_{15}H_{28}$: M, 208.2191.

Spectroscopic data for 1-phenyl-1-hexene (**2**),[19,20] 5-dodecene (**5**),[21] 1-phenyl-1-octene (**6**),[22,23] 2-methyl-1-phenyl-1-hexene (**10**),[24] 2-butyl-1-phenyl-1-hexene (**12**),[25] 2-allyl-1-phenyl-1,4-pentadiene (**13**),[25,26] and 4-(cyclohexylidene)-1,6-heptadiene (**25**)[25] were identical with those reported in literatures.

4.4.1. Pentylidenecyclohexane (8). IR (neat) 2928, 2855, 1670, 1447, 833 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.89 (t, J=6.9 Hz, 3H), 1.23–1.35 (m, 4H), 1.44–1.58 (m, 6H), 1.97 (dt, J=6.9, 6.9 Hz, 2H), 2.02–2.15 (m, 4H), 5.07 (t, J=6.9 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.90, 22.19, 26.65, 26.90, 27.77, 28.57, 28.64, 32.33, 37.12, 121.53, 139.53. Found: C, 86.72; H, 13.32%. Calcd for $C_{11}H_{20}$: C, 86.76; H, 13.24%.

4.4.2. 4-Allyl-1,4-undecadiene (15). IR (neat) 2959, 2926, 2856, 1638, 1458, 1431, 1379, 993, 912 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88 (t, J=6.9 Hz, 3H), 1.19–1.42 (m, 8H), 2.00 (dt, J=6.9, 6.9 Hz, 2H), 2.72 (d, J=6.9 Hz, 2H), 2.77 (d, J=6.9 Hz, 2H), 4.94–5.07 (m, 4H), 5.25 (t, J=7.2 Hz, 1H), 5.66–5.85 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 13.98, 22.54, 27.77, 28.96, 29.77, 31.69, 34.50, 41.25, 115.20, 115.75, 127.47, 135.00, 136.31, 137.24. HRMS Found: m/z 192.1880. Calcd for $C_{14}H_{24}$: M, 192.1878.

4.4.3. 2-Butyl-1-hexene (17). IR (neat) 2930, 2860, 1645, 1466, 1379, 887 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.91 (t, J=7.2 Hz, 6H), 1.24–1.48 (m, 8H), 2.00 (t, J=6.9 Hz, 4H), 4.69 (s, 2H); ^{13}C NMR ($CDCl_3$) δ 13.90, 22.41, 29.95, 35.70, 108.35, 150.54. Found: C, 85.39; H, 14.60%. Calcd for $C_{10}H_{20}$: C, 85.63; H, 14.37%.

4.4.4. (1*E*)-4-Butyl-1-phenyl-1,3-octadiene (19). IR (neat) 3024, 2952, 2924, 2856, 1638, 1596, 1496, 1466, 1459, 1450, 1377, 959, 745, 689 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.88–0.98 (m, 6H), 1.25–1.50 (m, 8H), 2.11 (t, J=7.5 Hz, 2H), 2.26 (t, J=7.5 Hz, 2H), 6.00 (d, J=11.1 Hz, 1H), 6.44 (d, J=15.6 Hz, 1H), 7.02 (dd, J=11.1, 15.6 Hz, 1H), 7.14–7.22 (m, 1H), 7.26–7.32 (m, 2H), 7.35–7.42 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 13.92, 22.48, 22.74, 30.36, 30.61, 31.06, 37.12, 125.00, 125.67, 126.14, 126.92, 128.61, 129.88, 138.31, 145.43. HRMS found: m/z 242.2027. Calcd for $C_{18}H_{26}$: M, 242.2035.

4.4.5. 2-Butyl-1,3-diphenyl-2-propen-1-ol (20). IR (neat) 3368, 2950, 2924, 2856, 1493, 1450, 1021, 918, 749, 731, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.87 (t, J=7.2 Hz, 3H), 1.22–1.62 (m, 4H), 1.80 (bs, 1H), 1.88–2.02 (m, 1H), 2.10–2.23 (m, 1H), 5.88 (s, 1H), 6.61 (s, 1H) 7.20–7.39 (m, 10H); ^{13}C NMR ($CDCl_3$) δ 13.85, 22.60, 30.22, 31.03, 71.53, 125.89, 126.81, 127.09, 128.25, 128.29, 128.43, 128.74, 137.63, 142.50, 143.50. Found: C, 85.38; H, 8.39%. Calcd for $C_{19}H_{22}O$: C, 85.67; H, 8.32%.

4.4.6. (Diphenylmethylidene)cyclohexane (24). Mp 82°C; IR (nujol) 1489, 1441, 1072, 995, 760, 704 cm^{-1}; ^1H NMR ($CDCl_3$) δ 1.53–1.66 (m, 6H), 2.19–2.29 (m, 4H), 7.10–7.15 (m, 4H), 7.16–7.21 (m, 2H), 7.22–7.30 (m, 4H); ^{13}C NMR ($CDCl_3$) δ 26.71, 28.58, 32.32, 126.09, 127.95, 129.88, 134.62, 139.27, 143.24. HRMS found: m/z 248.1562. Calcd for $C_{19}H_{20}$: M, 248.1565.

4.4.7. 4-Allyl-5-butyl-1,4-nonadiene (27). IR (neat) 2959, 2930, 2860, 1636, 1466, 1429, 1379, 993, 910 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.90 (t, J=6.9 Hz, 6H), 1.22–1.40 (m, 8H), 2.00 (t, J=7.5 Hz, 4H), 2.75 (d, J=6.0 Hz, 4H), 4.93–5.03 (m, 4H), 5.74 (ddt, J=10.2, 16.8, 6.3 Hz, 2H); ^{13}C NMR ($CDCl_3$) δ 13.97, 22.97, 31.32, 31.60, 35.76, 114.69, 127.44, 137.19, 137.25. HRMS found: m/z 220.2182. Calcd for $C_{16}H_{28}$: M, 220.2191.

4.4.8. 5-Butyl-6-methyl-5-undecene (29). IR (neat) 2952, 2920, 2854, 1466, 1458, 1377 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.82–0.96 (m, 9H), 1.17–1.42 (m, 14H), 1.61 (s, 3H), 1.92–2.03 (m, 6H); ^{13}C NMR ($CDCl_3$) δ 13.99, 17.78, 22.58, 22.90, 23.00, 28.30, 30.99, 31.49, 31.71, 31.95, 32.00, 34.11, 128.58, 133.38. HRMS found: m/z 224.2500. Calcd for $C_{16}H_{32}$: M, 224.2504.

Acknowledgements

Financial support by Grant-in-Aids for Scientific Research on (Nos. 10208208 and 12305058) from the Ministry of Education, Culture, Sports, Science, and Technology, Japan, is acknowledged. H. K. thanks the JSPS Research Fellowship for Young Scientists.

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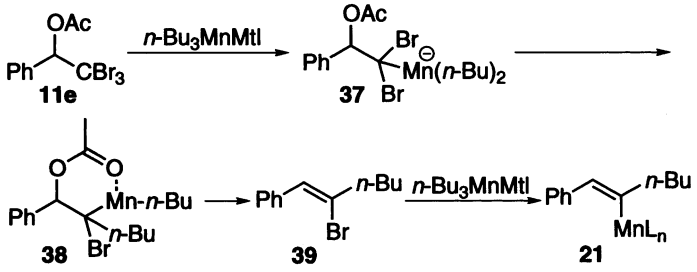

Scheme 9.

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13. In spite of extensive attempts to optimize the reaction conditions, the yield remained moderate. In the reaction of 5-(tribromomethyl)-5-nonanol with tributylmanganate, no trace of the starting material was recovered. 5-Nonanone and 5-butyl-5-nonanol were formed as byproducts. These products would be formed as follows: The reaction of a hydroxy group with manganate afforded the manganese alkoxide and the subsequent elimination of a tribromomethyl group provided the ketone. The reaction of the resulting ketone with tributylmanganate yielded 5-butyl-5-nonanol. In the reaction of silyl ethers, silyl enol ethers were obtained as byproducts through dehydrobromination.
14. The formation of **21** might be explained as follows. Bromine–manganese exchange and 1,2-migration of butyl group provides manganese species **38**. Sequential elimination of Mn and acetoxy group affords intermediary bromoalkene **39**. Then, bromoalkene **39** is converted into alkenylmanganese species **21** through halogen–metal exchange under the reaction condition (Scheme 9). The chelation of the carbonyl oxygen atom of the acetoxy group to manganese would facilitate the elimination of the acetoxy group to provide **39**.
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