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Invited review

Use of organomanganese reagents in organic synthesis

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Abstract

Three types of reactions with organomanganate have been examined. The first topic is a reaction of *gem*-dibromo compounds such as *gem*-dibromocyclopropane and dibromomethyltrialkylsilane with trialkylmanganates(II). The reaction was initiated by bromine–manganese exchange. The second reaction is a radical cyclization of iodophenyl allyl ether and 2-iodoethanal acetal by means of trialkylmanganate(II). The third topic is an addition of allylmanganate to a carbon–carbon triple bond. A catalytic version of these reactions is also disclosed. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Organomanganese reagents; Bromine–manganese exchange; Radical cyclization; Addition reaction

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1. Introduction

Organomanganese reagents are among the less expensive organotransition metal compounds due to the low cost of manganese metal. However, contrary to organocopper reagents which have been extensively studied in organic synthesis, organomanganese compounds have been almost ignored until 1976. Then, Professors J.F. Normant and G. Cahiez started studies on the preparation of organomanganese reagents and subsequent synthetic applications of these compounds [1]. They introduced the procedure for preparation of three types of organomanganese reagents, organomanganese halide (RMnX), dialkylmanganese (R_2Mn), and organomanganate (R_3MnMtl). Among them, trialkylmanganate is the most stable reagent and it is stable at room temperature (r.t.). Meanwhile, dialkylmanganese such as n-Bu_2Mn is unstable and decomposes at − 30°C. The stability of RMnX is between dialkylmanganese and trialkylmanganate. Taking account of the stability and reactivity, we chose trialkylmanganate and examined several reactions.

2. Results and discussion

2.1. Reaction of gem-dibromo compounds with trialkylmanganate(II)

2.1.1. Dialkylation of gem-dibromocyclopropanes with trialkylmanganate and manganese(II) chloride-catalyzed reaction with alkylmagnesium bromide

Cyclopropane derivatives are versatile synthetic intermediates. Double alkylation of *gem*-dihalocyclopropanes, which can be easily prepared by the addition of dihalocarbene to olefins, provides us with an effective route to a variety of functionalized cyclopropane derivatives. The transformation of *gem*-dihalocyclopropanes into 1-alkyl-1-butylcyclopropanes has been reported to proceed by subsequent treatment with dibutylcuprate [2] or tributylzincate [3,4] and several electrophiles. Here we describe that the reaction of *gem*-dibromocyclopropanes with trialkylmanganate followed by treatment with electrophiles provides dialkylated cyclopropanes as in the case of the reaction with cuprates or zincates and also that the reaction of *gem*-dibromocyclopropanes with alkylmagnesium halides takes place in the presence of a catalytic amount of manganese(II) chloride [5].

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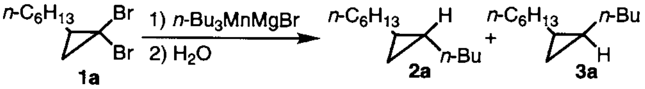


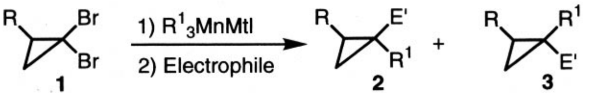
Scheme 1.

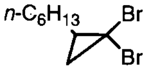
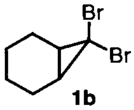
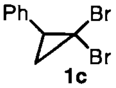
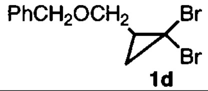
Treatment of dibromocyclopropane **1a** with tributylmanganate provided butylated cyclopropane **2a** and **3a** as a stereoisomeric mixture after aqueous workup (Scheme 1).

Various *gem*-dibromocyclopropanes were allowed to react first with trialkylmanganate, triallylmanganate or tris(phenyldimethylsilyl)manganate [6] and then with a variety of electrophiles. The results are summarized in Table 1. Among the solvent systems examined (THF, ether, DME), THF gave the best results. Several observations are worth noting as follows:

1. In contrast to the reaction with cuprate or zincate which has been performed at −48 or −85°C, the reaction with manganate could be performed conveniently at 0°C. The reaction of **1a** with n-Bu$_3$MnLi at −78°C for 30 min provided 1-bromo-2-hexylcyclopropane (*cis*/*trans* = 1/2) in 65% yield in addition to an isomeric mixture of 1-butyl-2-hexylcyclopropane (**2a**/**3a** = 76/24, 30% yield). The formation of monobromide could be ascribed to the quenching an intermediary manganate **4** with H$_2$O before being converted to **5**. Moreover, treatment of **1a** with n-Bu$_3$MnMgBr at −78°C for 30 min resulted in almost complete recovery of **1a**.
2. n-Bu$_3$MnMgBr, derived from MnCl$_2$ and three equivalents of butylmagnesium bromide, afforded better yields of butylated cyclopropanes **2** and **3** than n-Bu$_3$MnLi generated from butyllithium (see Table 1—entries 2 vs. 3, 12 vs. 13).
3. Triphenylmanganate Ph$_3$MnMgBr or Ph$_3$MnLi gave phenylated cyclopropane in 34 or 30% yield, respectively, upon treatment of **1a**.
4. (CH$_2$=CH)$_3$MnMgBr and (Me$_3$Si–C≡C)$_3$MnMgBr gave a minimal amount of the corresponding alkenyl- or alkynylcyclopropanes ($<5\%$). Manganates having secondary and tertiary alkyl ligands such as i-Pr$_3$MnMgBr and t-Bu$_3$MnMgCl gave 1-bromo-2-hexylcyclopropane in 50–55% yield along with an unidentified complex mixture which did not contain the desired i-propylcyclopropane or t-butylcyclopropane.

Table 1
Stereoselective dialkylation of *gem*-dibromocyclopropanes[a]



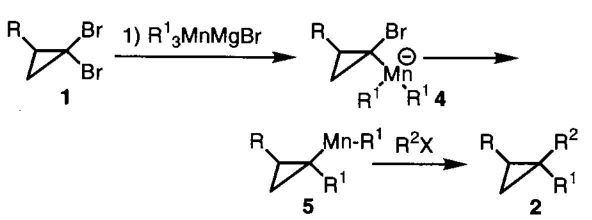
Entry	Substrate **1**	R$^1_3$MnMtl	Electrophile	Yield (%)	Isometric ratio of **2**/**3**
1	 **1a**	Me$_3$MnLi	H$_2$O	65	82/18
2		n-Bu$_3$MnLi	EtOH[b]	53	68/32
3		n-Bu$_3$MnMgBr	H$_2$O	89	71/29
4		n-Bu$_3$MnMgBr	CH$_2$=CHCH$_2$Br	77	89/11
5		n-Bu$_3$MnMgBr	MeI	65	94/6
6		n-Bu$_3$MnMgBr	PhCOCl	72	83/17
7		n-Bu$_3$MnMgBr	I$_2$	54	72/28
8		n-Bu$_3$MnMgBr	CH$_2$=CHBr[c]	58	99/1
9		n-Hex$_3$MnMgBr	H$_2$O	61	86/14
10		n-Hex$_3$MnMgBr	CH$_2$=CHCH$_2$Br	69	88/12
11		(PhMe$_2$Si)$_3$MnLi	H$_2$O	84	58/42
12	 **1b**	n-Bu$_3$MnLi	H$_2$O	56	87/13
13		n-Bu$_3$MnMgBr	H$_2$O	82	97/3
14		n-Bu$_3$MnMgBr	CH$_2$=CHCH$_2$Br	88	97/3
15	 **1c**	n-Bu$_3$MnMgBr[d]	H$_2$O	78	87/13
16		n-Bu$_3$MnMgBr[d]	CH$_2$=CHCH$_2$Br	50	92/8
17	 **1d**	n-Bu$_3$MnMgBr	H$_2$O	75	88/12
18		n-Bu$_3$MnMgBr	CH$_2$=CHCH$_2$Br	66	88/12

[a] The reactions were performed at 0°C unless otherwise stated.

[b] Quenching the reaction with EtOH or H$_2$O gave the same results (yield and isomeric ratio of **2**/**3**).

[c] Pd(PPh$_3$)$_4$ (10 mol%) was added.

[d] The reaction was performed at −48°C.



Scheme 2.

5. The intermediary cyclopropylmanganese reagents **5** could be trapped by acid chloride [7], iodine, and vinyl bromide (in the presence of $Pd(PPh_3)_4$ (10 mol%)) [8] as well as methyl iodide and allyl bromide.
6. 1,1-Dichlorocyclopropane such as 9,9-dibromobicyclo[6.1.0]nonane was found to be unreactive.

We are tempted to assume a similar reaction mechanism to the reaction with cuprate and zincates:

1. the initial halogen–manganese exchange at the less hindered bromine to afford **4**,
2. alkyl migration under Br^- elimination producing **5** (inversion on the cyclopropane carbon),
3. the second alkylation by R^2X with retention of the configuration. The stereoselective formation of **2** might be attributed to the bulkiness of the manganese reagents which attack the less hindered halogen selectively (Scheme 2).

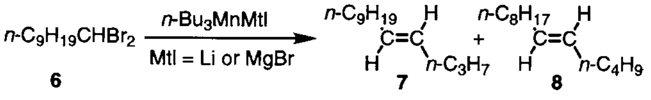
Moreover, the reaction proceeded in the presence of a catalytic amount of manganese(II) chloride. For instance, an addition of a solution of dibromocyclopropane **1a** (1.0 mmol) to a THF solution of butylmagnesium bromide (3.0 mmol) and manganese(II) chloride (12 mg, 10 mol%) at 0°C gave 1-butyl-2-hexylcyclopropane **2a** and **3a** in 75% combined yield after aqueous workup. In contrast, the reaction of **1a** with butylmagnesium bromide without manganese provided 1,2-nonadiene in 95% yield. The representative results of the catalytic reactions are shown in Table 2.

2.1.2. Manganese-catalyzed reaction of gem-dibromoalkanes with Grignard reagents—selective synthesis of alkenylsilanes [9]

Treatment of *gem*-dibromoalkanes with trialkylmanganate afforded alkenes [10]. A solution of 1,1-dibromodecane **6** in THF was added to a solution of tributylmanganate at 0°C. After being stirred for 1 h at 0°C and then 25°C for another 1 h, extractive workup followed by silica gel column chromatography gave a mixture of 4-tetradecene **7** ($E/Z = 92/8$) and 5-tetradecene **8** ($E/Z = 92/8$) in 95% combined yield (Scheme 3). The reaction proved to proceed in the presence of a catalytic amount of manganese(II) chloride.

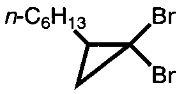
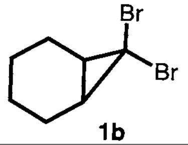
The reaction was applied to the preparation of alkenylsilanes [11] and the representative results are shown in Table 3 and Scheme 4. Several comments are worth noting as follows:

1. Stoichiometric reaction and catalytic reaction were equally effective for the formation of 1-trialkylsilyl-1-alkenes.
2. (*E*)-Alkenylsilanes were obtained exclusively and no trace of the *Z*-isomer could be detected in the reaction mixture.



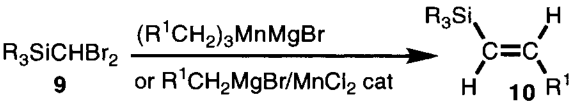
Scheme 3.

Table 2
Manganese(II) chloride-catalyzed reaction of *gem*-dibromocyclopropanes[a]

Entry	Substrate **1** (1.0 mmol)	RMtl (3.0 mmol)	Electrophile (3.0 mmol)	Yield (%)	Isomeric ratio of **2**/**3**
1	 **1a**	*n*-BuLi	H_2O	68	66/34
2		*n*-BuMgBr	H_2O	75	79/21
3		n-BuMgBr	$CH_2{=}CHCH_2Br$	57	81/19
4		$CH_2{=}CHCH_2MgBr$	H_2O	79	58/42
5		$CH_2{=}CHCH_2MgBr$	$CH_2{=}CHCH_2Br$	47	–
6	 **1b**	$PhMe_2SiLi$	EtOH	43	79/21
7		*n*-BuLi	H_2O	62	85/15
8		*n*-BuMgBr	EtOH	51	93/7

[a] The reactions were performed in the presence of 0.1 mmol of $MnCl_2$.

Table 3
Preparation of (*E*)-1-trialkylsilyl-1-alkene[a]

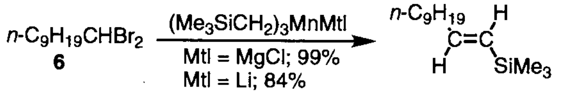


Entry		Substrate	Reagent	Yield (%)
1	**9a**	$Ph_2MeSiCHBr_2$[b]	Me_3MnMgI	89
2	**9a**	$Ph_2MeSiCHBr_2$[b]	$Et_3MnMgBr$	76
3	**9a**	$Ph_2MeSiCHBr_2$[b]	*n*-Bu_3MnLi	95
4	**9a**	$Ph_2MeSiCHBr_2$[b]	$(PhCH_2)_3MnMgBr$	88
5	**9b**	*t*-$BuMe_2SiCHBr_2$	$(Me_3SiCH_2)_3MnMgCl$	57
6	**9b**	*t*-$BuMe_2SiCHBr_2$	*n*-$Bu_3MnMgBr$	72
7	**9b**	*t*-$BuMe_2SiCHBr_2$	*n*-Bu_3MnLi	96
8	**9c**	*i*-$Pr_3SiCHBr_2$	$Et_3MnMgBr$	79
9	**9a**	$Ph_2MeSiCHBr_2$[b]	*n*-$C_4H_9MgBr/MnCl_2$	67
10	**9a**	$Ph_2MeSiCHBr_2$[b]	*n*-$C_{16}H_{33}MgBr/MnCl_2$	62
11	**9b**	*t*-$BuMe_2SiCHBr_2$	*n*-$C_4H_9MgBr/MnCl_2$	87
12	**9c**	*i*-$Pr_3SiCHBr_2$	$EtMgBr/MnCl_2$	88
13	**9c**	*i*-$Pr_3SiCHBr_2$	$MeMgI/MnCl_2$	75
14	**9d**	$Me_3SiCHBr_2$	*n*-$C_8H_{17}MgBr/MnCl_2$	76
15	**9e**	(*c*-$C_6H_{11})_2MeSiCHBr_2$[c]	*n*-$C_4H_9MgBr/MnCl_2$	95

[a] Stoichiometric reactions were performed with $R_3SiCHBr_2$ (1.0 mmol) and manganate (1.2 mmol) at 0°C unless otherwise noted. In the catalytic reactions, Grignard reagent (3.0 mmol), $R_3SiCHBr_2$ (1.0 mmol) and $MnCl_2$ (5 mol%) were employed.

[b] The reactions were performed at 25°C.

[c] *c*-C_6H_{11} = cyclohexyl.



Scheme 4.

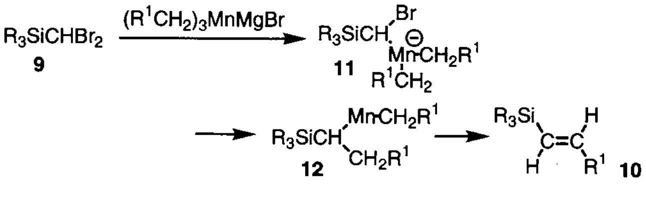
3. Among various manganese salts examined, $MnCl_2$, $Mn(acac)_3$, and $Mn_2(CO)_{10}$ proved to be good catalysts. For instance, treatment of *i*-$Pr_3SiCHBr_2$ with ethylmagnesium bromide in the presence of these catalysts gave (*E*)-1-triisopropylsilyl-1-propene in 88, 74, or 85% yield, respectively.
4. Diiodide (*t*-$BuMe_2SiCHI_2$) was as reactive as dibromide **9b** and afforded the 1-*t*-butyldimethylsilyl-1-pentene in 88% yield upon treatment with *n*-Bu_3MnLi. Dichloride (*t*-$BuMe_2SiCHCl_2$) was less reactive than **9b**, and the reaction with *n*-Bu_3MnLi gave the same alkenylsilane in 57% yield after prolonged reaction time (25°C, 21 h).
5. The reaction of 1,1-dibromodecane **6** with tris(trimethylsilylmethyl)manganate gave 1-trimethylsilyl-1-undecene exclusively and no isomeric allylic silane (1-trimethylsilyl-2-undecene) could be detected (Scheme 4). The hydrogen on the carbon-bearing trimethylsilyl group was eliminated selectively.

We are tempted to assume the following reaction mechanism for the stoichiometric reaction:

1. initial halogen–manganese exchange to give **11**,
2. alkyl migration under Br^- elimination providing **12**, and
3. elimination of Mn and hydrogen at the β-position to afford **10** (Scheme 5).

Meanwhile, the reaction mechanism for catalytic pathway could be as shown in Fig. 1. Low-valent manganese species Mn(0), generated from *n*-BuMnH [12], would insert into one of the carbon–bromine bonds to give $R_3SiCH(Br)MnBr$. An attack of two equivalents of *n*-BuMgBr on $R_3SiCH(Br)MnBr_2$ regenerates **11** [13].

The facility of Mn–H elimination depended on the nature of substituents on silicon. In the case of trialkylsilyldibromomethane such as **9b**, **9c**, **9d**, and **9e**, elimination took place easily at 0°C for 2 h. On the other hand, the elimination from $Ph_2MeSiCH(MnEt)Et$, derived from the reaction of **9a** with triethylmanganate, was slow and diphenylmethylpropylsilane was obtained in 17% yield along with alkenylsilane (47%). Thus, the reaction temperature was raised and the reaction mixture of **9a** was stirred at 25°C for 2 h to suppress the formation of diphenylmethylpropylsilane (< 5%).



Scheme 5.

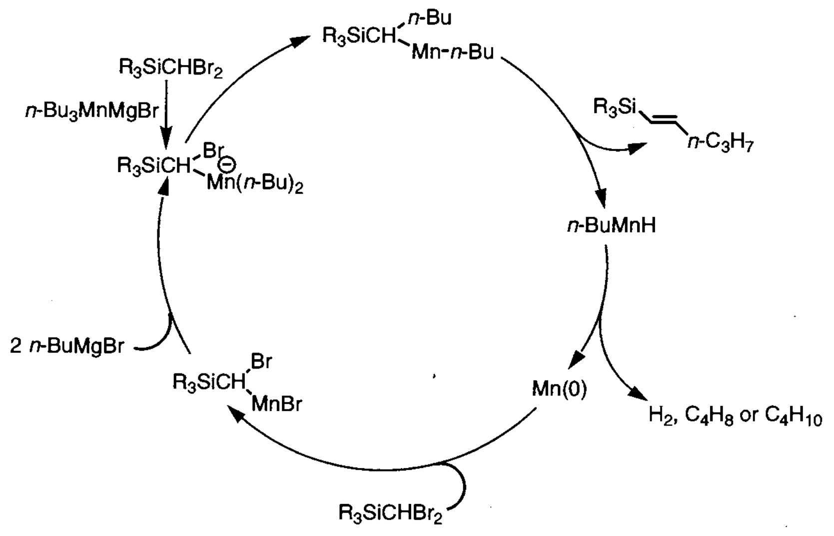
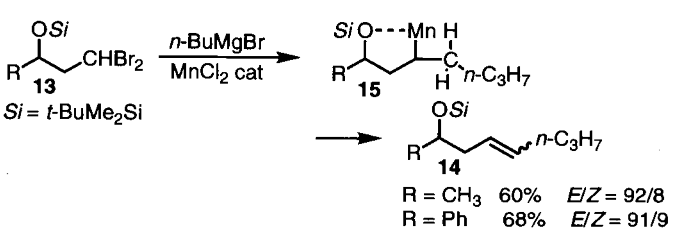


Fig. 1. Reaction mechanism showing the catalytic pathway for the manganese-catalyzed reaction of *gem*-dibromoalkanes with Grignard reagents.

In the reaction of 1,1-dibromodecane with butylmagnesium, two regioisomeric alkenes were produced as shown in Scheme 3 because of the presence of two types of β-hydrogens. The reaction is not useful for synthetic purposes. However, treatment of dibromoalkane **13**, generated from epoxide and *t*-butyldimethylsilyldibromomethyllithium [14], with butylmagnesium bromide in the presence of $MnCl_2$ catalyst gave alkene **14** as a single regioisomer. The coordination of oxygen of the siloxy group to manganese would cause formation of five-membered ring intermediate **15** in which only one hydrogen is available for *syn*-elimination of Mn–H (Scheme 6).

β-Siloxydibromo compound such as **16**, derived from the reaction of benzaldehyde with *t*-butyldimethylsilyldibromomethyllithium, gave alkene **17** via the elimination of Mn-OSiMe$_2$-*t*-Bu instead of elimination of the Mn–H unit (Scheme 7).

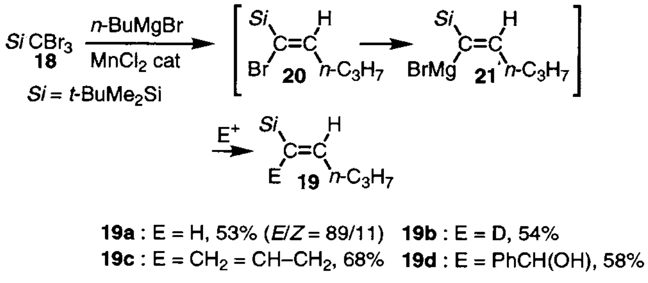


Scheme 6.

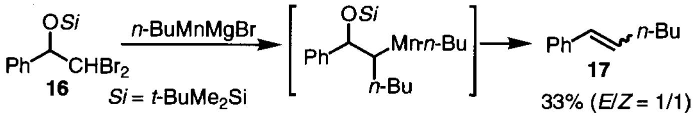
Tribromomethyltrialkylsilane, *t*-BuMe$_2$SiCBr$_3$ (**18**) afforded alkenylsilane **19** upon treatment with *n*-BuMgBr under $MnCl_2$ catalysis. Addition of an electrophile such as D_2O, allylbromide, or benzaldehyde provided the corresponding adducts in good yields. The results supported that an intermediary bromoalkene **20** was converted into the alkenylmagnesium species **21** through metal–halogen exchange under the reaction conditions (Scheme 8).

2.1.3. Reaction of t-butyldibromoacetate or N,N-diethyldibromoacetamide with trialkylmanganate providing an alkylated manganese enolate

A multiple-component coupling reaction in one-pot [15] promoted by various organometallics represents an extremely powerful means to produce complex organic



Scheme 8.



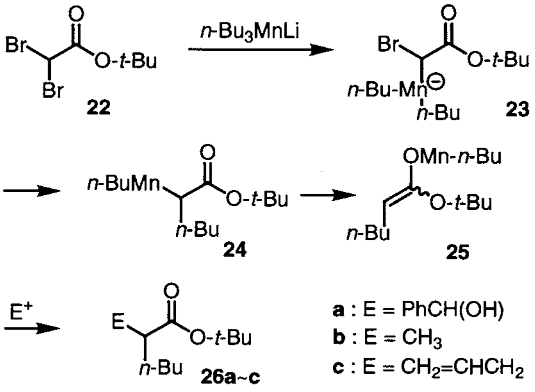
Scheme 7.

molecules. Our interest in utilizing organomanganese reagents for selective organic transformations prompted us to explore employment of trialkylmanganate for a consecutive carbon–carbon bond formation.

We have already described above that the treatment of *gem*-dibromocyclopropanes with trialkylmanganate followed by addition of an electrophile provided dialkylated cyclopropanes. The reaction proceeds as follows:

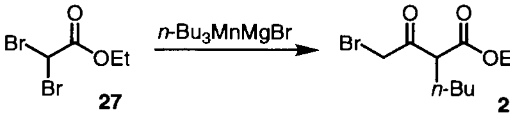
1. the initial halogen–manganese exchange,
2. alkyl migration under Br^- elimination,
3. second alkylation with an electrophile such as iodomethane (Scheme 2).

It then occurred to us that, if both steps of the halogen–manganese exchange and alkyl migration [16] should proceed well, the reaction of dibromoacetate with tributylmanganate would provide an expeditious route to butylated manganese enolate **25** (Scheme 9) [17]. We have indeed found that treatment of *t*-butyldibromoacetate **22** with tributylmanganate followed by addition of an electrophile such as benzaldehyde afforded a three-component coupling aldol-type adduct **26a** (*syn*/*anti* = 77/23) in 46% yield. An addition of iodomethane or 3-bromopropene instead of benzaldehyde afforded the corresponding adduct **26b** or **26c** in 42 or 69% yield, respectively [18].



Scheme 9.

Treatment of ethyl dibromoacetate **27** with tributylmanganate provided acetoacetate derivative **28** in 32% yield along with an unidentified complex mixture (Scheme 10).



Scheme 10.

The use of *N*,*N*-diethyldibromoacetamide **29a** in place of *t*-butyldibromoacetate **22** improved the yield of the corresponding adducts. The representative results are shown in Table 4 (entries 1–10). Several comments are worth noting as follows:

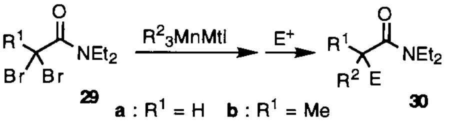
1. Manganate reagents, derived from $MnCl_2$ and a Grignard reagent such as *n*-BuMgBr, EtMgBr, and PhMgBr, proved to be as equally effective as lithium tributylmanganate. This result is in sharp contrast to the reaction of *t*-butyldibromoacetate **22** with tributylmanganate, generated from $MnCl_2$ and butylmagnesium bromide, which results in formation of a small amount of butylated product **26** (E = H) (< 5% yield) along with a complex mixture. Treatment of **22** with triethylmanganate or triphenylmanganate, derived from $MnCl_2$ and EtMgBr or PhMgBr, gave the corresponding ethylated product or phenylated product in only 15 or 17% yield along with an unidentified complex mixture, respectively, after quenching the reaction mixture with water.
2. No products arising from attack of the α-bromoenolate, $BrCH{=}C(OMn^-Bu_2)NEt_2$ (**31**), on the electrophile such as iodomethane or benzaldehyde could be detected. This indicated that the migration of the alkyl group on manganese to the adjacent carbon providing **24** occurred at a rate which was much faster than the rate of conversion of $BrCH(Mn^-Bu_2)CONEt_2$ (**23**) into the α-bromoenolate **31**.
3. Not only *N*,*N*-diethyldibromoacetamide (**29a**) but also *N*,*N*-diethyldibromopropionamide (**29b**) reacted with trialkylmanganate easily to give the expected adducts (entries 11–13 in Table 4).

The reaction proceeded in the presence of a catalytic amount of $MnCl_2$. For instance, treatment of **29a** (1.0 mmol) with butylmagnesium bromide (3.0 mmol) in the presence of $MnCl_2$ (0.1 mmol) followed by an addition of 3-bromopropene (3.0 mmol) provided **30b** in 61% yield. The results are also summarized in Table 4 (entries 14–19). Unfortunately, the use of **29b** (R^1 = Me) as a starting material in this catalytic process resulted in a formation of diethyl-2-bromopropionamide and no butylated amide was observed. The reaction was applied to one-pot synthesis of α,β-unsaturated amide [19]. Treatment of **29a** with $(PhMe_2Si)_3MnLi$, derived from $PhMe_2SiLi$ [20] and $MnCl_2$, followed by addition of an aldehyde provided unsaturated amide **32** in good yield as shown in Scheme 11.

Treatment of dibromo β-lactam **33** [21,22] with tributylmanganate gave butylated lactam **34a** (*trans*/*cis* = 26/74) in 62% yield [23]. An addition of benzaldehyde or 3-bromopropene before quenching with water afforded **34b** or **34c** in 48% (isomeric ratio = 67/33) or 46% yield, respectively (Scheme 12).

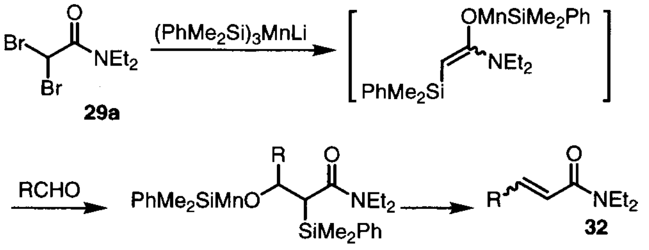
The reaction of *N*,*N*-diethyldichloroacetamide **35** with tributylmanganate (n-Bu_3MnLi) provided *N*,*N*-diethyl-2-chlorohexanamide **36a** in 34% yield after

Table 4
Reaction of dibromoamide with trialkylmanganate



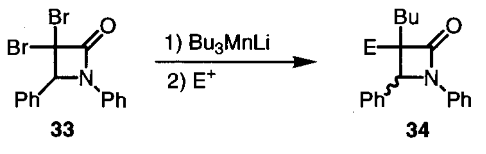
Entry	Amide **29**	R$^2_3$MnMtl or R^{2}MgX	Electrophile	Yield (%)
1	**29a**: R^1 = H	n-Bu$_3$MnLi	D_2O	**30a** 82
2	**29a**	n-Bu$_3$MnLi	$CH_2{=}CHCH_2Br$	**30b** 76
3	**29a**	n-Bu$_3$MnLi	PhCHO	**30c** 72[a]
4	**29a**	n-Bu$_3$MnLi	n-$C_6H_{13}CHO$	**30d** 77[b]
5	**29a**	n-Bu$_3$MnLi	CH_3I	**30e** 70
6	**29a**	n-Bu$_3$MnMgBr	H_2O	**30f** 80
7	**29a**	n-Bu$_3$MnMgBr	PhCHO	**30c** 84[c]
8	**29a**	Et$_3$MnMgBr	PhCHO	**30g** 95[d]
9	**29a**	Ph$_3$MnMgBr	H_2O	**30h** 83
10	**29a**	Ph$_3$MnMgBr	PhCHO	**30I** 73[e]
11	**29b**: R^1 = Me	n-Bu$_3$MnLi	H_2O	**30j** 89
12	**29b**	n-Bu$_3$MnLi	$CH_2{=}CHCH_2Br$	**30k** 51
13	**29b**	n-Bu$_3$MnLi	PhCHO	**30l** 90[f]
14	**29a**	n-BuMgBr	$CH_2{=}CHCH_2Br$	**30b** 61
15	**29a**	n-BuMgBr	PhCHO	**30c** 95[g]
16	**29a**	EtMgBr	H_2O	**30m** 74
17	**29a**	EtMgBr	PhCHO	**30g** 80[h]
18	**29a**	PhMgBr	H_2O	**30h** 67
19	**29a**	PhMgBr	PhCHO	**30i** 60[i]

[a] *syn*/*anti* = 65/35.
[b] *syn*/*anti* = 69/31.
[c] *syn*/*anti* = 49/51.
[d] *syn*/*anti* = 49/51.
[e] *syn*/*anti* = 49/51.
[f] Isomeric ratio = 36/61.
[g] *syn*/*anti* = 45/55.
[h] *syn*/*anti* = 47/53.
[i] *syn*/*anti* = 51/49.



32a : R^1 = Ph 60% (*Z*/*E* = 64/36)
32b : R^1 = n-C_6H_{13} 61% (*Z*/*E* = 69/31)

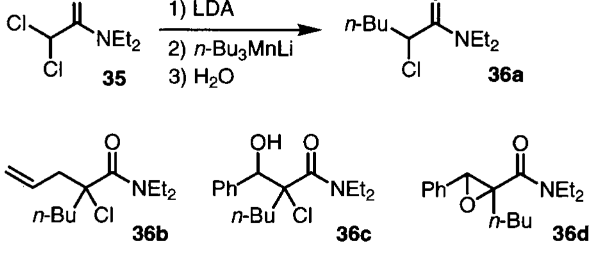
Scheme 11.



a : E = H **b** : E = PhCH(OH) **c** : E = $CH_2{=}CHCH_2$

Scheme 12.

quenching the reaction mixture with 1 M HCl. Thus, deprotonation of the α-proton with tributylmanganate took place in preference to the chlorine–manganese exchange in this case. Treatment of **35** with lithium diisopropylamide followed by tributylmanganate improved the yield of **36a** up to 69% yield. Quenching the reaction mixture with 3-bromopropene or benzaldehyde gave allylated product **36b** or a mixture of **36c** and **36d** (**36c**/**36d** = 62/38) in 63 or 55% combined yield (Scheme 13).



Scheme 13.

2.2. Radical cyclization of allyl 2-iodophenyl ether, N,N-diallyl-2-iodoaniline, and 2-iodoethanal acetal by means of trialkylmanganate(II)

Very recently, a synthesis of substituted indolines via anionic cyclization has been reported [24]. In addition, several procedures mediated by free radical [25], transition metal species [26], and samarium(II) iodide [27] have also been published on the construction of the heteroatom ring of these molecules. Herein we disclose an effective method for the preparation of indoline, dihydrobenzofuran, and 2-alkoxytetrahydrofuran derivatives by means of tributylmanganate(II) [28].

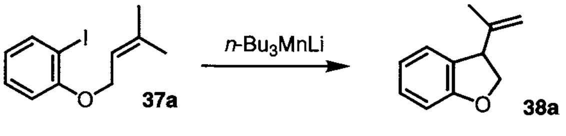
2.2.1. Trialkylmanganate(II)-induced cyclization of allyl 2-iodophenyl ether and N,N-diallyl-2-iodoaniline

Treatment of 2-iodophenyl prenyl ether (**37a**) with tributylmanganate(II), generated from $MnCl_2$ and three molar amounts of butyllithium, in THF afforded 3-isopropenyl-2,3-dihydrobenzofuran (**38a**) in 88% yield (Scheme 14). The use of tributylmanganate(II) (n-$Bu_3MnMgBr$), derived from $MnCl_2$ and three molar amounts of butylmagnesium bromide, instead of n-Bu_3MnLi also provided **38a** in 87% yield. In contrast, n-Bu_2Mn, n-BuMnCl, Me_3MnLi, or n-Bu_2CuLi could not give any cyclized product.

Treatment of **37a** with n-Bu_2Mn and n-BuMnCl resulted in recovery of the starting ether **37a**. The reaction of **37a** with Me_3MnLi provided phenyl prenyl ether quantitatively. Treatment of **37a** with Me_3MnLi followed by an addition of D_2O provided 2-deuteriophenyl prenyl ether in 93% yield ($>98\%d$). n-Bu_2CuLi afforded the starting material **37a** (60%) and phenyl prenyl ether (35%). In addition, treatment of **37a** with n-BuLi gave phenyl prenyl ether exclusively after aqueous workup.

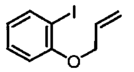
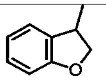
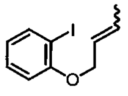
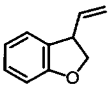
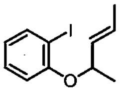
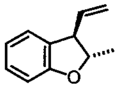
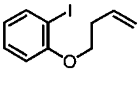
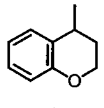
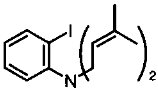
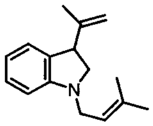
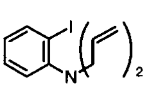
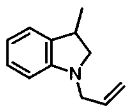
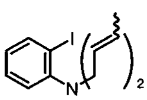
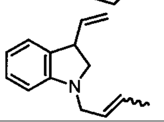
Representative examples are shown in Table 5. Not only 2-iodophenol derivatives **37** but also 2-iodoaniline derivatives **39** reacted in the same way to provide the corresponding indoline derivatives **40** upon treatment with tributylmanganate(II). The following comments are worth noting:

1. Tributylmanganese magnesium bromide, n-$Bu_3MnMgBr$, was equally as effective as n-Bu_3MnLi.
2. The corresponding bromo compound such as 2-bromophenyl prenyl ether afforded phenyl prenyl ether (30%), 3-isopropenyl-2,3-benzofuran (**38a**, 10%) along with the starting material (52%) upon treatment with tributylmanganate(II).



Scheme 14.

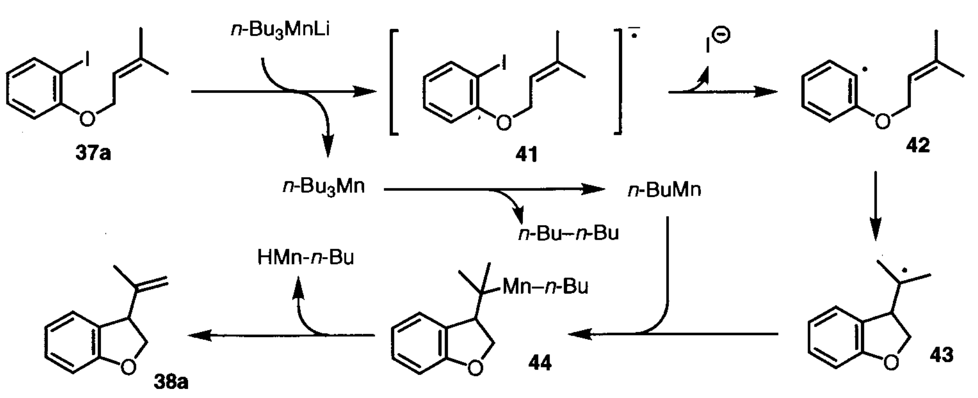
Table 5
Tributylmanganate-induced cyclization of allyl 2-iodophenyl ethers and N,N-diallyl-2-iodoaniline[a]

Entry	Substrate		Product		Yield (%)
1		**37b**		**38b**	40
2		**37c**		**38c**	63
3		**37d**		**38d**	70[b]
4		**37e**		**38e**	30
5		**39a**		**40a**	92 (90)[c]
6		**39b**		**40b**	72 (72)[c]
7		**39c**		**40c**	74

[a] n-Bu_3MnLi (1.5 mmol) and substrate (1.0 mmol) were employed.
[b] *cis/trans* = 15/85.
[c] n-$Bu_3MnMgBr$ was used instead of n-Bu_3MnLi.

3. The addition of a THF solution of n-Bu_2Mn to 2-lithiophenyl prenyl ether, generated from **37a** and n-BuLi in THF gave a complex mixture that did not contain the cyclized product **38a**.
4. The reaction of 2-iodophenyl homoallyl ether **37e** with tributylmanganate(II) provided chroman derivative **38e** in only 30% yield.
5. The relative stereochemistry between the substituents attached to C(2) and C(3) of compound **38d** was *trans/cis* = 85/15. This isomeric ratio was the same as that of the radical cyclization product, 3-ethyl-2-methyl-2,3-dihydrobenzofuran (*trans/cis* = 87/13), which was generated by the reaction of **37d** with n-Bu_3SnH.
6. Whereas products (**38b**, **38e**, and **40b**) having methyl group were obtained in the case of the substrates which have terminal olefinic group, alkenes (**38a**, **38c**, **38d**, **40a**, and **40c**) were produced from the iodophenyl ethers and iodoanilines having internal olefinic moiety.

Based on these facts, we are tempted to assume the following reaction mechanism (Scheme 15). Single elec-



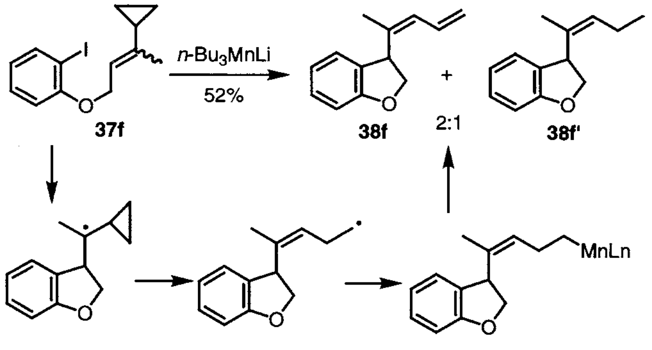
Scheme 15.

tron transfer from tributylmanganate(II) to 2-iodophenol derivative **37a** would give an anion radical **41** which generates phenyl radical **42** under departure of the iodide anion. *Exo*-mode radical cyclization should afford tertiary carbon radical **43** which recombines with *n*-BuMn [29] to give the dialkylmanganese(II) compound **44**. Dehydromanganation would provide the final product **38a** [30,31].

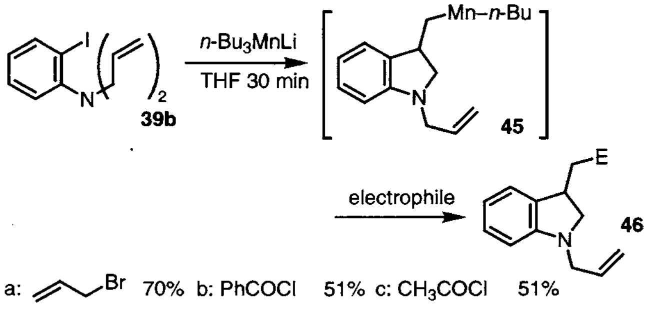
The intermediacy of the radical species was confirmed by the following experiment. Treatment of allylic ether **37f** having a cyclopropane ring on the alkenyl carbon with tributylmanganate(II) provided a mixture of dienyl-substituted dihydrobenzofuran derivative **38f** and alkenyl-substituted compound **38f′** (**38f**:**38f′** = 2:1) in 52% combined yield (Scheme 16). No trace of the product having the cyclopropane ring could be observed in the reaction mixture. One election transfer from tributylmanganate to **37f** provides a phenyl radical. The radical cyclizes to give cyclopropylmethyl radical which collapses to yield a homoallyl radical under cyclopropane ring cleavage [32]. Recombination with manganese species affords an alkylmanganese compound. Finally, β-elimination or protonation would give dihydrobenzofuran derivative **38f** or **38f′**.

The intermediary manganese species could be trapped by various electrophiles [33]. An addition of tributylmanganate(II) to *N*,*N*-diallylaniline derivative **39b**, followed by treatment with allyl bromide, provided the corresponding allylated product **46a** (E = $CH_2CH{=}CH_2$) in 70% yield. Trapping the reaction by acid chlorides such as acetyl chloride and benzoyl chloride afforded methyl ketone and phenyl ketone, respectively (Scheme 17).

Unexpectedly, the reaction proved to proceed in the presence of a catalytic amount of manganese(II) chloride. For instance, treatment of **37a** (1.0 mmol) or **39a** (1.0 mmol) with excess *n*-BuMgBr (4.0 mmol) in the presence of a catalytic amount of $MnCl_2$ (0.2 mmol) in THF at 25°C for 12 h provided **38a** or **40a** in 70 or 81% yield, respectively [34]. The reactions were performed in a flask equipped with a balloon filled with argon. Atmospheric oxygen could diffuse into the balloon to equilibrate the partial pressures, and the concentration of oxygen reached 10% (v/v) after 12 h. The catalytic reaction also proceeded in the atmosphere. Stirring a mixture of **39a** (1.0 mmol) and *n*-BuMgBr (4.0 mmol) in the presence of a catalytic amount of $MnCl_2$ (0.1 mmol) or $MnCl_2$ (0.3 mmol) in the atmosphere afforded **40a** in 60 or 80% yield, respectively, along with the recovered starting material **39a** in 30 or 14% yield. The reaction in a flask under argon balloon gave a better yield of **39a** than the reaction in the atmosphere. Thus, slow injection of oxygen might be essential for the catalytic reaction. The role of oxygen is not clear at this stage. However, we are tempted to



Scheme 16.



Scheme 17.

assume following explanation. Zero-valent manganese could not react with iodoaniline, thus, Mn(0) must be reoxidized to Mn(II) species ($MnCl_2$ or MnI_2) by oxygen to complete a catalytic cycle. The presence of oxygen was essential for the catalytic reaction. Without oxygen, the cyclization reaction did not complete under $MnCl_2$ catalysis.

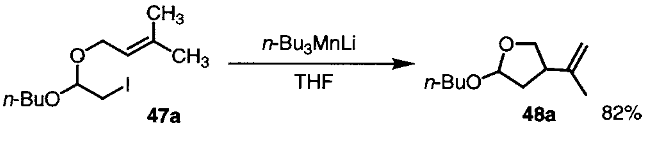
2.2.2. Trialkylmanganate(II)-induced cyclization of 2-iodoethanal acetal

Carbon–carbon bond formation via radical reactions is one of the most important synthetic steps in the construction of organic molecules [35]. In Section 2.2.1, we have shown that intramolecular radical cyclization of aryl iodide having alkenyl group has been carried out by using tributylmanganate(II). Further exploitation of this method and development of an intramolecular radical reaction of alkyl iodide carrying alkene moiety in the molecule will be discussed here.

The radical cyclization reaction of unsaturated 2-iodoethanal acetals **47a** was examined. A solution of 2-iodoethanal acetal **47a** in THF was added to a solution of *n*-Bu_3MnLi in THF at 0°C. The resulting mixture was stirred for 1 h at 0°C to afford the THF derivative **48a** in 82% yield (Scheme 18).

The representative results are summarized in Table 6. These 2-iodoethanal acetals **47** were prepared by the reactions of allylic or 2-propynylic alcohols with butyl vinyl ether or silyl enol ether in the presence of *N*-iodosuccinimide in dichloromethane [36]. Several comments are worth noting as follows:

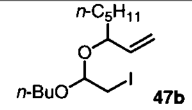
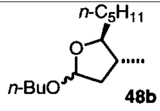
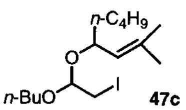
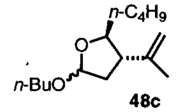
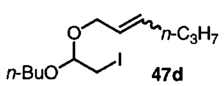
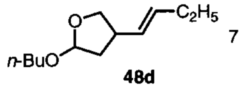
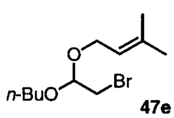
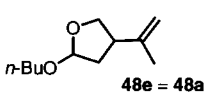
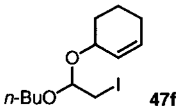
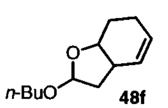
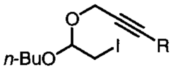
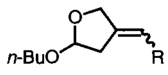
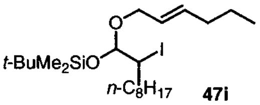
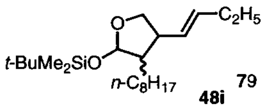
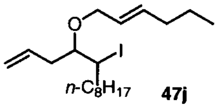
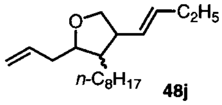
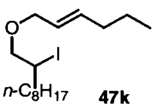
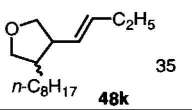
1. The use of the iodide derivative was essential to obtain the cyclization product in high yield. Whereas 2-iodoethanal mixed acetal **47a** provided **48a** in 82% yield, the corresponding 2-bromoethanal acetal **47e** gave **48a** in only 41% yield.
2. The carbon–carbon triple bonds were as effective as olefinic linkage to trap an radical intramolecularly (entry 6).
3. The use of tributylmanganate(II) (*n*-$Bu_3MnMgBr$), derived from $MnCl_2$ and three molar amounts of butylmagnesium bromide, instead of *n*-Bu_3MnLi gave **48a** in 42% yield.
4. 2-Iodoethanal silyl acetal **47i** derived from silyl enol ether also provided the corresponding 2-siloxy-tetrahydrofuran **48i** in good yield.



47a **48a** 82%

Scheme 18.

Table 6
Radical cyclization of iodoacetals by means of tributylmanganate (*n*-Bu_3MnLi)

Entry	Substrate	Product	(%)
1	 **47b**	 **48b**	68
2	 **47c**	 **48c**	70
3	 **47d**	 **48d**	73
4	 **47e**	 **48e = 48a**	41
5	 **47f**	 **48f**	48
6	 **47g** R = SiMe$_3$ **47h** R = Ph	 **48g** **48h**	83 65
7	 **47i**	 **48i**	79
8	 **47j**	 **48j**	77
9	 **47k**	 **48k**	35

5. Whereas the relative stereochemistry of the anomeric carbon is not controlled, a high diastereocontrol is observed between C(4) and C(5) giving the *trans*-product in over 98% stereoselectivity [37]. Thus, treatment of **47b** or **47c** with *n*-Bu_3MnLi gave **48b** or **48c** as a mixture of two stereoisomers which could be converted into single isomeric *trans*-lactone **54b** or **54c** by oxidation (vide infra). The reaction of **47f** with *n*-Bu_3MnLi gave the cyclized product **48f** as a stereoisomeric mixture which was contaminated by the corresponding saturated compound. However, a single stereoisomer was obtained concerning to the ring-junction. The *cis*-stereochemistry of the

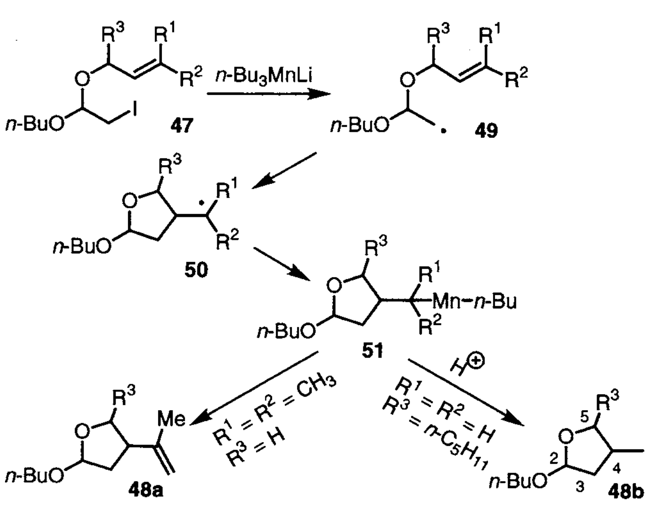
ring-junction of **48f** was confirmed by hydrogenation (H_2, PtO_2) and oxidation (Jones oxidation) to the known lactone. In contrast, the lactone **54i**, derived from **48i**, consisted of two stereoisomers (*cis*/*trans* = 1/1) and therefore the relative stereochemistry between C(3) and C(4) of **48i** was *cis*/*trans* = 1/1.

6. (*E*)-Alkenes were produced selectively ($E/Z = >95/5$) in the cyclization of 2-alkenyl ethers (**47d**, **47i**, **47j** and **47k**) irrespective of the geometry of the starting olefins.
7. 2-Alkenyl-2-iodoalkyl ethers (**47j** and **47k**) as well as 2-iodoalkanal acetals afforded THF derivatives in good yields upon treatment with *n*-Bu_3MnLi.
8. Not only primary alkyl iodides but also secondary iodides (**47i**, **47j**, and **47k**) proved to cyclize effectively to give the desired products.

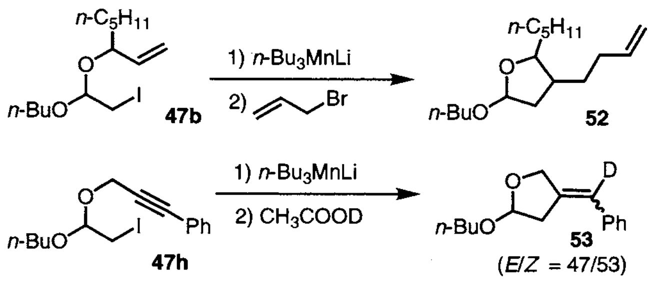
We are tempted to assume the following reaction mechanism for the stoichiometric reaction [38]. Single electron transfer from tributylmanganate(II) to the 2-iodoethanal acetal **47** would give a 2,2-dialkoxyethyl radical **49** under departure of iodide anion. 5-*Exo*-mode cyclization could afford a carbon radical **50** which recombines with *n*-BuMn to give alkylmanganese compound **51**. Protonation or dehydromanganation of **51** would provide the final product **48a** or **48b** (Scheme 19).

The intermediary manganese species could be trapped by various electrophiles. For instance, the addition of tributylmanganate(II) to **47b** followed by treatment with allyl bromide gave an allylated product **52** in 38% yield. Quenching the reaction mixture, derived from **47h** and *n*-Bu_3MnLi, with CH_3COOD provided a deuterated product **53** (**48h**-*d* 85%D) (Scheme 20).

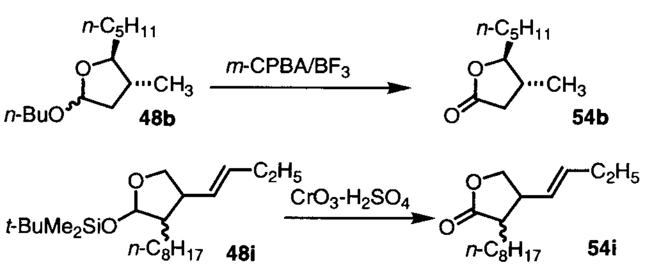
The cyclized products were easily transformed into γ-butyrolactones. For instance, treatment of **48b** or **48i** with $mCPBA/BF_3{\cdot}Et_2O$ [39] or $CrO_3{\cdot}H_2SO_4$ [40] provided lactone **54b** or **54i** (*cis*/*trans* = 1/1) in 70 or 99% yield, respectively (Scheme 21).



Scheme 19.

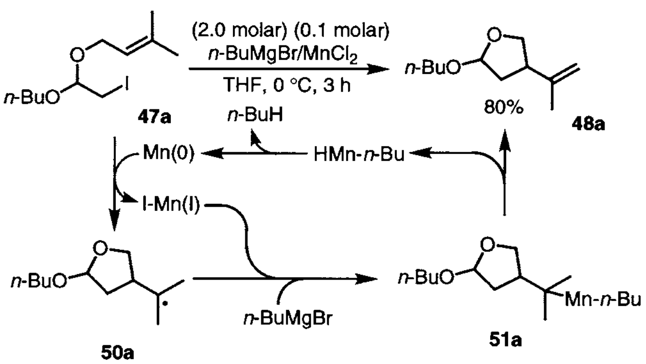


Scheme 20.



Scheme 21.

The catalytic reaction (0.1 molar amount of $MnCl_2$) using *n*-BuMgBr could also be applied to iodo acetal **47** to give **48**, in case of which the presence of oxygen was not necessary in contrast to the catalytic reaction of **37a**, in which the presence of oxygen was essential. The catalytic reaction of **47** completed in 3 h at 0°C under argon atmosphere in a sealed system. For instance, treatment of **47a** or **47d** (1.0 mmol) with *n*-BuMgBr (2.0 mmol) in the presence of $MnCl_2$ (0.1 mmol) at 0°C for 3 h afforded **48a** or **48d** in 80 or 78% yield, respectively. Thus, the mechanism for the catalytic reaction might be as follows. The reaction between **47a** and tributylmanganate, derived from *n*-BuMgBr and $MnCl_2$, would provide **48a** and *n*-BuMn–H which decomposes to Mn(0). Then, single electron transfer from this zero-valent manganese to **47a** would afford alkyl radical **49a** and manganese(I) species. Radical cyclization of **49a** into **50a** followed by recombination with manganese(I) could give **51a** (Scheme 22).



Scheme 22.

In conclusion:

1. Treatment of allyl 2-iodophenyl ether or *N*,*N*-diallyl-2-iodoaniline with tributylmanganate(II) provided the corresponding dihydrobenzofuran or indoline derivative in good yield.
2. The reaction of 2-iodoethanal acetals with tributylmanganate(II) proceeded effectively to give THF derivatives.
3. Whereas the latter reaction took place in the presence of a catalytic amount of $MnCl_2$ without oxygen, the former reaction required the coexistence of oxygen under catalytic process.
4. The radical cyclization mechanism was postulated for these reaction.

2.3. Silylmanganation and allylmanganation of acetylenic compounds

2.3.1. Disilylation of acetylenes with Si–Mn reagents

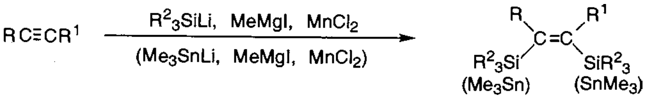
Palladium(0) catalyzed reaction of acetylenes with disilanes such as $HMe_2SiSiMe_2H$, $FMe_2SiSiMe_2F$, and $(MeO)Me_2SiSiMe_2(OMe)$ produces the corresponding disilylated olefins in good yields [41]. In contrast, hexamethyldisilane gives $< 10\%$ yield of doubly silylated products.

We examined the reaction of the Si–Mn reagent with acetylenes [42] and observed the rather unexpected formation of disilylated products [43]. (Trimethylsilyl)lithium [44] was treated with methylmagnesium iodide and anhydrous manganese(II) chloride. Addition of 1-alkyne to the resulting reagent provided an *E*,*Z* mixture of 1,2-bis(trimethylsilyl)-1-alkene. The reaction proceeded smoothly with silylacetylenes as well as terminal acetylenes to give tri- and tetrasilylated ethenes.

Although the role of MeMgI is not clear, its presence is essential for the formation of disilylated products. Without MeMgI, monosilylated products were obtained predominantly after aqueous workup. For instance, treatment of 4-(benzyloxy)-1-butyne with $3Me_3SiLi–Li_2MnCl_4$ gave a mixture of 4-(benzyloxy)-2-(trimethylsilyl)-1-butene, 4-(benzyloxy)-1-(trimethylsilyl)-1-butene, and disilylated product in 1:1:1 ratio (65% combined yield). The reaction has been extended to distannylation of acetylenes [45]. The representative results are shown in Table 7.

Table 7

Disilylation or distannylation of acetylenes with Si–Mn or Sn–Mn reagent

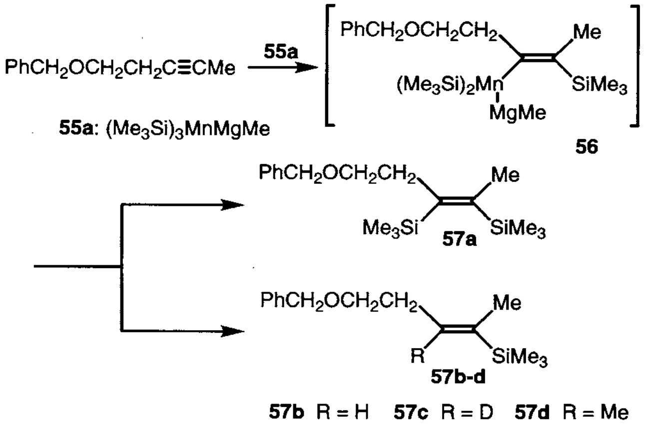


Acetylene RC–CR	Reagent R^2_3SiLi	Product Yield (%)	*Z*/*E*
$HC{\equiv}CSiMe_3$	Me_3SiLi	72	–
n-$C_6H_{13}C{\equiv}CH$	Me_3SiLi	66	33/67
$PhC{\equiv}CH$	Me_3SiLi	65	50/50
n-$C_6H_{13}C{\equiv}CSiMe_3$	Me_3SiLi	80	–
$PhCH_2OCH_2CH_2C{\equiv}CH$	Me_3SiLi	55	50/50
$PhCH_2OCH_2CH_2C{\equiv}CH$	$PhMe_2SiLi$	51	42/58
$PhCH_2OCH_2CH_2C{\equiv}CD$	$PhMe_2SiLi$	55	42/58[a]
$PhCH_2OCH_2CH_2C{\equiv}CSiMe_3$	Me_3SiLi	59	–
$THPOCH_2CH_2C{\equiv}CH$	Me_3SiLi	63	65/35
$THPOCH_2CH_2C{\equiv}CH$	$PhMe_2SiLi$	70	65/35
$THPOCH_2CH_2C{\equiv}CSiMe_3$	Me_3SiLi	83	–
$HOCH_2CH_2C{\equiv}CSiMe_3$	Me_3SiLi[b]	58	–
n-$C_{10}H_{21}C{\equiv}CH$	Me_3SiLi[c]	56	100/0
n-$C_{10}H_{21}C{\equiv}CD$	Me_3SiLi	55	100/0
$THPOCH_2CH_2C{\equiv}CH$	Me_3SiLi	54	100/0
$THPOCH_2CH_2C{\equiv}CH$	Bu_3SnLi[c]	48	90/10
$PhCH_2OCH_2CH_2C{\equiv}CH$	Me_3SiLi	52	90/10

[a] Deuterium was retained completely, thus reagents did not cause the acetylenic proton–metal exchange.

[b] Three millimoles of manganese reagent and 1.0 mmol of substrate were employed.

[c] Prepared from $SnCl_2$ and three equivalents of alkyllithium.



Scheme 23.

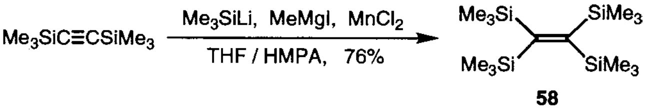
Treatment of 5-(benzyloxy)-2-pentyne with the reagent which is assumed to be $(Me_3Si)_3MnMgMe$ (**55a**) [46] gave 2,3-bis(trimethylsilyl)-2-alkene (**57a**) in 78% yield. Meanwhile, the addition of H_2O (or D_2O, MeI) to the reaction mixture after stirring at 0°C for 20 min without warming up to r.t. gave monosilylated product **57b** (71%) (or **57c** (71%), **57d** (70%)) along with the disilylated one **57a** (13–20%) (Scheme 23) [47]. Thus, the formation of disilylated alkenes may be explained as follows: (1) addition of the reagent **55a** to the triple bond in a *cis* fashion giving silylated alkenylmanganese **56** and (2) reductive elimination of manganese affording disilylated olefin. The *cis* addition of the Si–Mn component was confirmed by the following experiment. A monosilylated alkene, 5-(benzyloxy)-2-(dimethylphenylsilyl)-2-pentene was prepared from $(PhMe_2Si)_3MnMgMe$ (**55b**) and 5-(benzyloxy)-2-pentyne in the same way as **57b**. Protodesilylation with Bu_4NF [48] gave 5-(benzyloxy)-2-pentene. The ^1H-NMR spectrum proved that the olefin had *Z* configuration (> 95%, $J = 11$ Hz). Similar desilylation of **57b** failed.

The reaction can be successfully applied to the synthesis of highly strained tetrakis(trimethylsilyl)ethene **58**, which is not readily available by known methods (Scheme 24) [49].

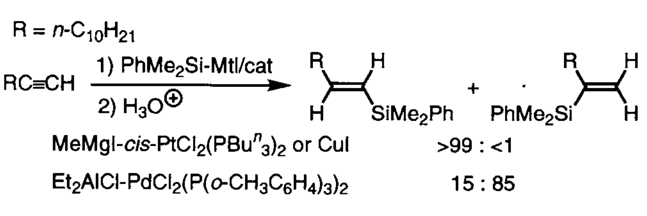
2.3.2. Manganese-catalyzed silylmagnesiation of acetylenes

In section Section 2.3.1, disilylation of acetylenes with $(PhMe_2Si)_3MnMgMe$ was described. Here we wish to disclose a $MnCl_2$-catalyzed reaction of acetylenes with $PhMe_2SiMgMe$ [50]. We have reported on the simultaneous *cis* addition of a silyl group and a metal to acetylenes with regioselectivity using $PhMe_2SiLi$ and metal compounds, such as MeMgI, Et_2AlCl, $ZnBr_2$, and Et_3B, in the presence of a transition-metal catalyst [51,52]. Platinum- or copper-catalyzed silylmagnesiation ($PhMe_2SiMgMe$) of 1-dodecyne, followed by aqueous quenching, provided (*E*)-1-dimethylphenylsilyl-1-dodecene exclusively, which has the same regiochemistry as those products prepared from stoichiometric silylcupration [53] or silyltitanation [54]. On the other hand, palladium-catalyzed silylalumination ($PhMe_2SiAlEt_2$) afforded the regioisomer, 2-dimethylphenylsilyl-1-dodecene, with high regioselectivity (Scheme 25).

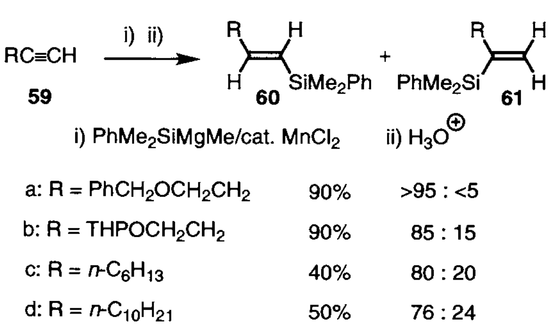
The treatment of 4-benzyloxy-1-butyne (**59a**, 1.0 mmol) with $PhMe_2SiMgMe$, prepared from $PhMe_2SiLi$ (1.6 mmol) [20] and MeMgI (1.6 mmol) in situ, in the presence of a catalytic amount of $MnCl_2$ (0.08 mmol) at 0°C, gave a mixture of monosilylated products, **60a** and **61a**, in 90% combined yield after an aqueous workup [55]. The reaction proceeded with high regio- and stereoselectivities. (*E*)-4-Benzyloxy-1-dimethylphenylsilyl-1-butene (**60a**) was obtained as the major product, and only a small amount of the regioisomer, 4-benzyloxy-2-dimethylphenylsilyl-1-butene (**61a**), was detected in the reaction mixture (**60a**/**61a** = > 95/5) (Scheme 26). The stereoisomer, (*Z*)-4-benzyloxy-1-dimethylphenylsilyl-1-butene, could not be observed in the reaction mixture. The use of tetrahydropyranyl ether of 3-butyn-1-ol (**59b**) in place of **59a** provided a regioisomeric mixture of **60b** and **61b** in 90% combined yield (**60b**/**61b** = 85/15). The oxygen atom of 3-butynyl ether played a critical role in the case of terminal acetylenes, since the yield dropped to 40 and 50% in the manganese-catalyzed reaction of 1-octyne (**59c**) and 1-dodecyne (**59d**).



Scheme 24.



Scheme 25.



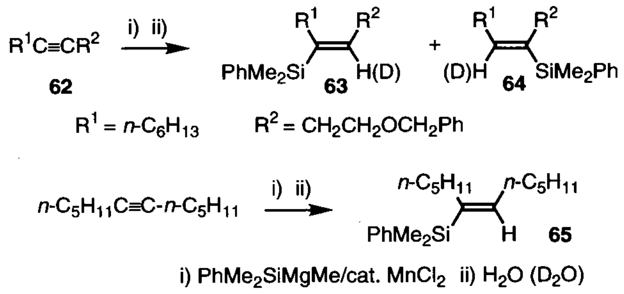
i) $PhMe_2SiMgMe$/cat. $MnCl_2$ ii) $H_3O^{\oplus}$

a: R = $PhCH_2OCH_2CH_2$	90%	>95 : <5
b: R = $THPOCH_2CH_2$	90%	85 : 15
c: R = $n\text{-}C_6H_{13}$	40%	80 : 20
d: R = $n\text{-}C_{10}H_{21}$	50%	76 : 24

Scheme 26.

(Dimethylphenylsilyl)magnesium reagent was added effectively to internal acetylenes as well as to terminal acetylenes to provide alkenylsilanes. The reaction proceeded with high regio- and stereoselectivities. For instance, a treatment of 1-benzyloxy-3-decyne (**62**) with $PhMe_2SiMgMe$ in the presence of a catalytic amount of $MnCl_2$ at 25°C for 2 h afforded a mixture of (*E*)-1-benzyloxy-4-dimethylphenylsilyl-3-decene (**63**) and its regioisomer **64** in 95% combined yield (**63**/**64** = 73/27). Quenching the reaction mixture with D_2O gave the corresponding mixture of (*E*)-alkenylsilane and regioisomer (**63**-*d*/**64**-*d* = 70/30, 95% combined yield). 6-Dodecyne provided (*E*)-6-dimethylphenylsilyl-6-dodecene (**65**) as a single product in 95% yield. The yield was much higher than that of the reaction between 1-dodecyne and $PhMe_2SiMgMe$ (Scheme 27).

The intermediary alkenylmagnesium compound could be trapped by various electrophiles. The addition of allyl bromide provided allylated products **66** and **67** (**66**/**67** = 80/20) in 68% yield. The addition of benzaldehyde afforded 4-[(2-benzyloxy)ethyl]-3-hexyl-2,2-dime-

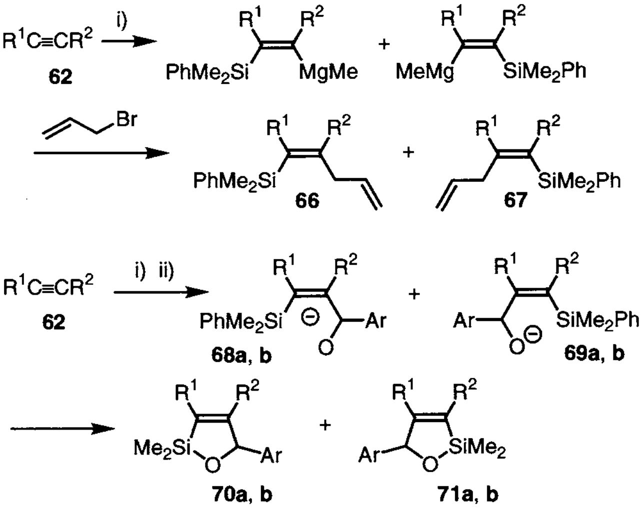


Scheme 27.

thyl-5-phenyl-1-oxa-2-silacyclopent-3-ene **70a** and regioisomer **71a** (**70a**/**71a** = 8/2) in 65% yield. *p*-Methoxybenzaldehyde also gave the corresponding silyl ether, **70b** and **71b** (**70b**/**71b** = 7/3), in 70% yield (Scheme 28). The use of butyraldehyde in place of aromatic aldehydes provided a complex mixture containing the corresponding oxasilacyclopentene derivative in only < 20% yield. The formation of silyl ether, **70** and **71**, might be explained by an internal attack of oxides **68** and **69** on silicon under cleavage of silicon–phenyl bond [48,56]. In these reactions, (*E*)-1-benzyloxy-4-dimethylphenylsilyl-3-decene (**63**), (*E*)-1-benzyloxy-3-dimethylphenylsilyl-3-decene (**64**), and 1-benzyloxy-3,4-bis(dimethylphenylsilyl)-3-decene were obtained as by-products (10–15% combined yield).

2.3.3. Stoichiometric reaction of acetylenic compounds with triallyl- and tetraallylmanganate

Allylic organometallic compounds have been studied extensively and widely used for highly stereoselective synthesis of homoallylic alcohols [57]. In contrast, only a few reports regarding the addition of allylic metals to triple bonds are found in the literature [58], although allylmetalation of the carbon–carbon triple bond by allylmetals is useful for the synthesis of 1,4-dienes that widely exist in naturally occurring compounds. An allyl Grignard reagent adds to propargylic alcohols or homopropargylic alcohols by an *anti* addition process to give both regioisomers in the absence [59] or in the presence of a CuI catalyst [60]. Allylzincation of terminal alkynes is generally complicated by competitive zincation of alkynes and double allylzincation [61,62]. Bis-addition is sometimes observed and becomes the main reaction if the alkyne is metalated with an organomagnesium or organolithium reagent prior to the addition of allylzinc halides. Here we report the preparation of tetraallylmanganate and triallylmanganate and their reaction with acetylenes.



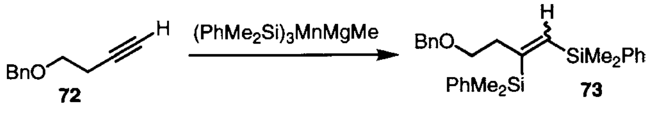
R^1 = n-C_6H_{13} R^2 = $CH_2CH_2OCH_2Ph$

i) $PhMe_2SiMgMe$/cat. $MnCl_2$ ii) a: PhCHO, b: *p*-$MeOC_6H_4CHO$

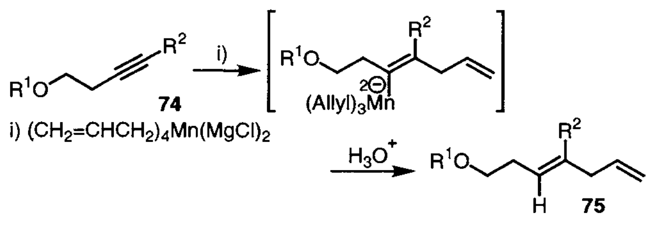
Scheme 28.

We have already described on the preparation of tris(trialkylsilyl)manganate $(R_3Si)_3MnMgMe$ and its reaction with acetylenes in Section 2.3.1. For instance, the treatment of 4-benzyloxy-1-butyne (**72**) with $(PhMe_2Si)_3MnMgMe$, derived from three equivalents of $PhMe_2SiMgMe$ and one equivalent of $MnCl_2$, afforded a disilylated product, 4-benzyloxy-1,2-bis(dimethylphenylsilyl)-1-butene (73) in 51% yield as a stereoisomeric mixture (*Z*/*E* = 42/58) (Scheme 29). The use of Me_3MnMgI or $Et_3MnMgBr$ in place of $(PhMe_2Si)_3MnMgMe$ resulted in formation of complex mixtures and only small amounts of the desired dimethylated or diethylated products could be obtained (< 10% yield). Fortunately, we have found that triallylmanganate or tetraallylmanganate added to the triple bond of propargylic alcohols or homopropargylic alcohol and its derivatives to give monoallylated products or diallylated products.

We prepared several stoichiometric reagents such as allylmanganese chloride [(allyl)MnCl] [63], diallylmanganese [$(allyl)_2Mn$], triallylmanganate [$(allyl)_3MnMgCl$], and tetraallylmanganate [$(allyl)_4Mn(MgCl)_2$] [64] and examined the reaction of these reagents with the methyl ether of 3-decyn-1-ol (**74a**). Among them, tetraallylmanganate, derived from four equivalents of allylmagnesium chloride and one equivalent of manganese(II) chloride, proved to be the best reagent in terms of the yield of the allylated product. Thus, treatment of **74a** with tetraallylmanganate at 0°C for 1 h and 25°C for 12 h gave (*E*)-4-hexyl-7-methoxy-1,4-heptadiene (**75a**) in 80% yield after aqueous workup (Scheme 30). The reaction of **74a** with triallylman-



Scheme 29.



a : R^1 = Me, R^2 = *n*-C_6H_{13} b : R^1 = H, R^2 = *n*-C_6H_{13}

c : R^1 = $PhCH_2$, R^2 = *n*-C_6H_{13} d : R^1 = THP, R^2 = *n*-C_6H_{13}

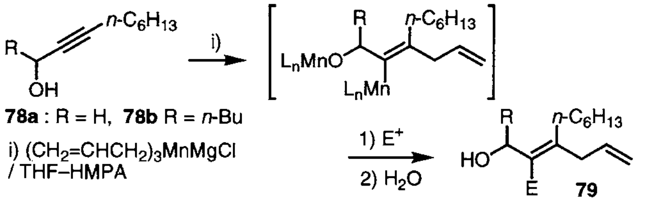
Scheme 30.

ganate at 0°C for 1 h and 25°C for 12 h gave (*E*)-4-hexyl-7-methoxy-1,4-heptadiene (**75a**) in 80% yield after aqueous workup (Scheme 30). The reaction of **74a** with triallylmanganate provided **75a** in only 35–40% yield accompanied by unidentified complex side products and the starting ether **74a** was recovered completely in the reaction with diallylmanganese or allylmanganese chloride. 3-Decyn-1-ol (74b), benzyl ether of 3-decyn-1-ol (**74c**) and tetrahydropyranyl ether of 3-decyn-1-ol (**74d**) also provided the corresponding allylated products **75b**, **75c**, **75d** in 60, 30, and 40% yields, respectively, upon treatment with tetraallylmanganate. The reaction was clearly oxygen-assisted since 6-dodecyne was completely recovered even after heating the mixture at reflux in THF for 10 h.

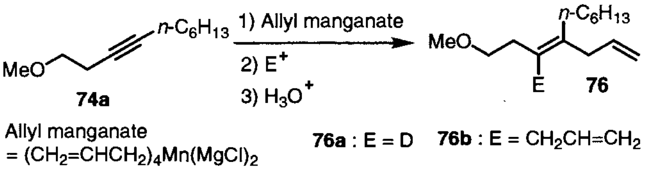
The intermediary alkenylmanganate could be trapped by electrophiles. An addition of deuterium oxide or allyl bromide afforded the corresponding adducts **76a** or **76b** in 70 or 65% yield, respectively (Scheme 31). An attempt to trap the intermediary alkenylmanganese species by benzaldehyde resulted in formation of a complex mixture. The reaction proceeded with high regio- and stereoselectivities. The *syn*-addition of an allyl–manganese component was confirmed by comparison of **76b** with an authentic sample of the *trans*-diallylated product, (4*Z*)-4-hexyl-5-(2-methoxyethyl)-1,4,7-octatriene (**77**) derived from 3-decyn-1-ol according to the reported procedure (Scheme 32) [59].

The use of propargylic alcohol alkyl ether (n-$C_6H_{13}C{\equiv}C{-}CH_2OMe$) instead of homopropargylic ether afforded a complex mixture containing an allenyl product, [n-$C_6H_{13}(CH_2{=}CHCH_2)C{=}C{=}CH_2$], generated by S_N2 displacement of methoxide by the allyl anion. However, the reaction of propargylic alcohol, 2-nonyn-1-ol (**78a**) with triallylmanganate in THF gave allylated product **79a** in 55% yield. The presence of HMPA increased the yield of **79a** up to 90%. In the absence of HMPA, displacement of the metaloxy (OMtl) group by the allylic anion proceeded to give an allenyl compound as by-product. The addition of HMPA could suppress the formation of the allenic product. The use of triallylmanganate was also essential for the successful reaction in this case, and the yield of **79a** dropped to 30–40% upon treatment with tetraallylmanganate because of the formation of an allenyl product. The intermediary alkenylmanganese compound could be trapped by various electrophiles. The addition of D_2O, allyl bromide, iodine, and benzoyl chloride provided the corresponding adducts **79b–e** in 90, 65, 50, and 50%, respectively. Trapping with benzaldehyde or iodomethane was not successful and **79a** was obtained as the main product. Secondary propargylic alcohol such as 6-tridecyn-5-ol (**78b**) was less reactive than primary propargylic alcohol **78a** and afforded 4-hexyl-1,4-decadien-6-ol (**79f**) in only 45% yield. The *syn*-addition of the reaction was confirmed by comparison of **79c** with an authentic sample of the *trans*-diallylated product, (4*Z*)-4-hexyl-5-hydroxymethyl-1,4,7-octatriene (**80**) which was prepared from **78a** with allylmagnesium bromide as **77** (Scheme 33).

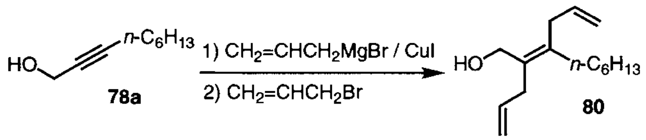
Other allylic Grignard reagents were studied on the reaction with **78a**. The tricrotylmanganate reagent provided 3-hexyl-2,5-heptadien-1-ol (**81a**) exclusively in 90% yield upon treatment with **78a** in THF–HMPA (Scheme 34). The regioisomeric product, 3-hexyl-4-methyl-2,5-hexadien-1-ol could not be detected in the



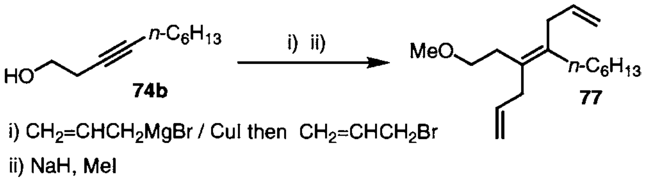
79a : R = H, E = H **79b** : R = H, E = D **79c** : R = H, E = $CH_2CH{=}CH_2$
79d : R = H, E = I **79e** : R = H, E = C(O)Ph **79f** : R = n-Bu, E = H



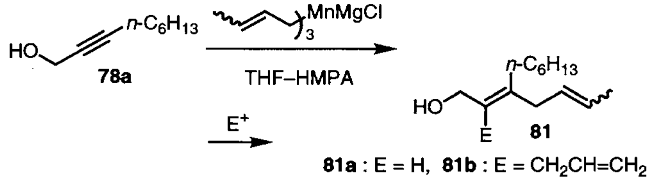
Scheme 31.



Scheme 33.



Scheme 32.



Scheme 34.

reaction mixture. An addition of allyl bromide gave the corresponding allylated product **81b** in 65% yield. Triprenylmanganate did not react with **78a** and the starting alcohol **78a** was recovered unchanged.

A diallylation product was obtained after standing the reaction mixture overnight at 25°C in a flask equipped with a balloon filled with argon. Atmospheric oxygen could diffuse into the balloon to equilibrate the partial pressure and the concentration of oxygen reached 10% (v/v) after 12 h. Thus, treatment of **74a** with tetraallylmanganate in a flask equipped with a balloon filled with argon for 12 h afforded (4*E*)-4-hexyl-5-(2-methoxyethyl)-1,4,7-octatriene (**76b**) in 75% yield. The addition of iodobenzene was also effective for the formation of the diallylated product. An addition of iodobenzene to the reaction mixture, derived from **74a** and tetraallylmanganate under argon atmosphere, gave **76b** in 80% yield (Scheme 35).

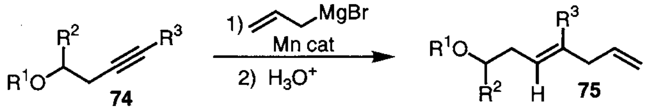
We can summarize the stoichiometric reactions as follows:

1. Tetraallylmanganate is the choice for the allylmanganation of homopropargylic alcohols and their ethers.
2. The use of triallylmanganate and HMPA as a cosolvent is recommendable for the allylmanganation of propargylic alcohols.
3. Oxidative conditions (O_2 or PhI) are necessary to obtain diallylation products.

2.3.4. Allylmagnesation and diallylation of acetylenic compounds catalyzed by manganese salts

We report here that allylmagnesium bromide adds to the triple bond of the alkyl ethers of homopropargylic alcohols to give monoallylated products with high regio- and stereoselectivities in the presence of a catalytic amount of a manganese salt such as MnI_2, $Mn(acac)_3$, or $Mn_2(CO)_{10}$. The formation of diallylation products under an oxygen atmosphere is also disclosed.

Treatment of an ethereal solution of homopropargylic alcohol methyl ether (**74a**, 1.0 mmol) with allylmagnesium bromide (1.5 mmol) in the presence of a MnI_2 catalyst (3 mol %) at 25°C for 3 h provided monoallylated product **75a** in 83% yield (Scheme 36). Other manganese catalysts such as $Mn(acac)_3$, $MeC_5H_4Mn(CO)_3$, and $Mn_2(CO)_{10}$ were also effective for the reaction. The yields of **75a** with these catalysts were 93, 89, and 80%, respectively, under the same reaction conditions [65]. Benzyl ether of 3-decyn-1-ol (**74c**), THP ether of 3-decyn-1-ol (**74d**), methyl ether of 5-nonyn-3-ol (**74e**), or methyl ether of 4-phenyl-3-butyn-1-ol (**74f**) also gave the corresponding allylated product **75c–f** in 77, 74, 72, or 74% yield, respectively, upon treatment with allylmagnesium bromide in the presence of $Mn(acac)_3$ (3 mol %) in toluene at 25°C for 3 h. 3-Decyn-1-ol (**74b**) and 2-nonyn-1-ol (**78a**) pro vided only small amounts of the corresponding allylated products **75a** and **79a** (< 5% yield) upon treatment with allylmagnesium bromide in the presence of MnI_2 (3 mol%) in ether at 25°C for 3 h. After heating at reflex for 10 h, **75a** was obtained in 48% yield, but **79a** was obtained in only < 5% yield. Other metallic catalysts such as $PdCl_2(CH_3CN)_2$, $NiCl_2(PPh_3)_2$, $CrCl_3$, and $RuCl_3$ were ineffective, and the starting acetylenic compound **74a** was recovered unchanged.

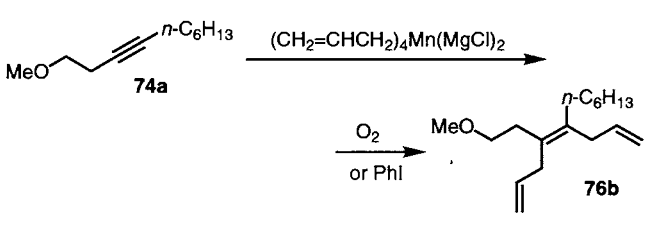


a : R^1 = Me, R^2 = H, R^3 = n-C_6H_{13}
b : R^1 = R^2 = H, R^3 = n-C_6H_{13}
c : R^1 = $PhCH_2$, R^2 = H, R^3 = n-C_6H_{13}
d : R^1 = THP, R^2 = H, R^3 = n-C_6H_{13}
e : R^1 = Me, R^2 = Et, R^3 = n-C_3H_7
f : R^1 = Me, R^2 = H, R^3 = Ph

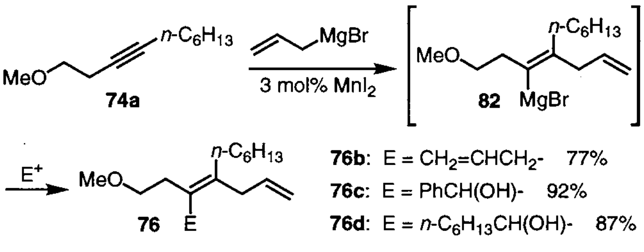
Scheme 36.

The intermediary alkenylmagnesium compound **82** could be trapped by electrophiles such as allyl bromide, PhCHO, or n-$C_6H_{13}CHO$ (Scheme 37). The *syn* addition of an allyl–metal component was confirmed by comparison of **76b** with the sample derived from the stoichiometric reaction described in Schemes 31 and 32.

The reaction was clearly oxygen-assisted as in the case of the stoichiometric reaction since the yield dropped to 42% in the case of benzyl ether of 4-hexyn-1-ol, and 6-dodecyne was completely recovered even after heating the mixture at reflux in ether for 10 h. The



Scheme 35.



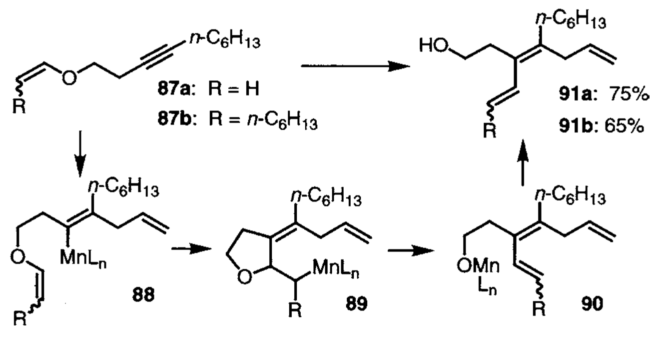
76b: E = CH_2=$CHCH_2$- 77%
76c: E = PhCH(OH)- 92%
76d: E = n-C_6H_{13}CH(OH)- 87%

Scheme 37.

use of propargylic alcohol alkyl ether **83** instead of homopropargylic substrate afforded allenyl product **84** which was generated by S_N2 type displacement of the alkoxy group by the allylic anion (Scheme 38) [66]. Treatment of allyl propargyl ether **85** with allylmagnesium bromide under the same reaction conditions gave furan derivative **86** in only 27% yield in addition to allenic product **84** (15%) (Scheme 39).

Next, the reaction of homopropargylic ether having an olefinic moiety was examined. An addition of allylmagnesium bromide to a THF solution of homopropargyl alkenyl ether **87a** and **87b** (*Z*/*E* = 90/10) in the presence of a catalytic amount of $Mn(acac)_3$ afforded tetrasubstituted alkene **91a** (75%) and **91b** (*Z*/*E* = 10/90, 65%) with high stereoselectivity. The formation of **91b** as a mixture of *Z*/*E* = 10/90 starting from **87b** (*Z*/*E* = 90/10) might suggest that both intramolecular carbomanganation and deoxymanganation proceed in *syn* fashion. We are tempted to assume the following reaction mechanism:

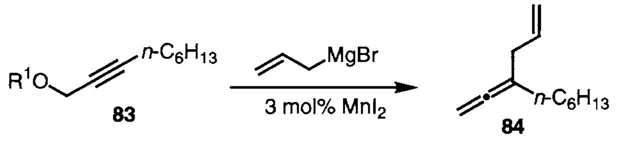
1. allylmanganation of **87** gives alkenylmanganese intermediate **88**,
2. intramolecular carbomanganation provides furan derivative **89**, and
3. deoxymanganation followed by transmetallation and aqueous workup affords tetrasubstituted alkene **91** (Scheme 40).



Scheme 40.

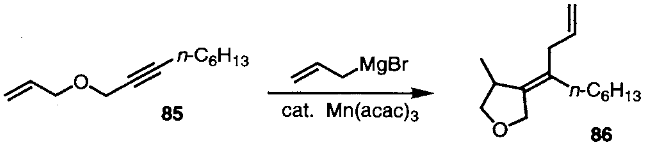
Diallylation products could be formed along with the monoallylated product in the presence of oxygen. The nature of the manganese catalysts and the solvent have played a critical role in the successful formation of diallylation products. The manganese salt $MeC_5H_4Mn(CO)_3$ was our choice. Thus, treatment of a THF solution of **74a** (1.0 mmol) with allylmagnesium bromide (4.0 mmol) in the presence of $MeC_5H_4Mn(CO)_3$ (10 mol%) under argon atmosphere for 2 h at 25°C followed by exposure of the reaction mixture to air for 12 h gave diallylated product **92a** = **76b** in 80% yield without contamination of monoallylated product **75a** (Scheme 41). Starting from **74c–e**, the corresponding diallylated product **92c–e** were obtained in 78, 35, and 78% yields, respectively under the same reaction conditions. The use of $Mn(acac)_3$ instead of $MeC_5H_4Mn(CO)_3$ decreased the yield of diallylated product **92a** to 66% and the MnI_2-catalyzed reaction afforded a mixture of **75a** (42%) and **92a** (22%). We are tempted to assume that reductive elimination from alkenylmanganese intermediate **93** affords the diallylated product in the presence of air. Oxygen would facilitate the reductive elimination but the role of oxygen and precise mechanism of the reaction are not clear at this stage. (Scheme 42).

We can summarize the allylmagnesation and diallylation of acetylenic compounds catalyzed by manganese salts as follows:

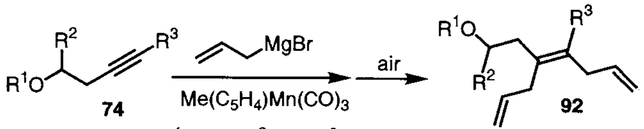


a : $R^1 = Me_2C{=}CHCH_2$: 56%
b : $R^1 = Me$: 56%

Scheme 38.

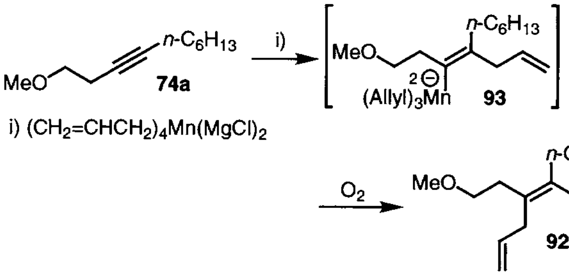


Scheme 39.



a : $R^1 = Me$, $R^2 = H$, $R^3 = n\text{-}C_6H_{13}$
c : $R^1 = PhCH_2$, $R^2 = H$, $R^3 = n\text{-}C_6H_{13}$
d : $R^1 = THP$, $R^2 = H$, $R^3 = n\text{-}C_6H_{13}$
e : $R^1 = Me$, $R^2 = Et$, $R^3 = n\text{-}C_3H_7$

Scheme 41.



i) $(CH_2{=}CHCH_2)_4Mn(MgCl)_2$

Scheme 42.

1. Treatment of homopropargylic alcohol methyl ether with allylmagnesium bromide in the presence of a manganese salt catalyst provided the monoallylated product in good yields with high regio- and stereoselectivities.
2. The intermediary alkenylmagnesium compound was trapped by various electrophiles such as carbonyl compounds and allyl bromide.
3. The $MeC_5H_4Mn(CO)_3$ catalyzed reaction with excess allylmagnesium bromide in the presence of oxygen gave the diallylated product exclusively.

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