Pergamon

Tetrahedron 56 (2000) 2131–2137

TETRAHEDRON

Reaction of *gem*-Dibromocyclopropanes or Iodobenzofuran with Trialkylmanganate

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Accepted 7 December 1999

Abstract—Treatment of *gem*-dibromocyclopropanes with trialkylmanganate, derived from manganese(II) chloride and three equivalents of Grignard reagent or alkyllithium, followed by an addition of electrophiles provided dialkylated cyclopropanes in good yields. It was found that the reaction of *gem*-dibromocyclopropanes with alkylmagnesium halide proceeded in the presence of a catalytic amount of manganese(II) chloride. The use of iodobenzofuran in place of *gem*-dibromocyclopropane gave a ring opening product, 2-alkenylphenol.

Introduction

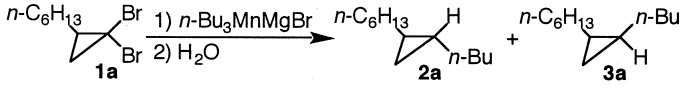
Organomanganese reagents are among the less expensive organo transition metal compounds due to the low cost of manganese metal. However, contrary to organocopper reagents, which have been extensively studied in organic synthesis, organomanganese compounds have been almost ignored until 1976. Then, Professors 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. 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.

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 successive treatment with dibutylcuprate[2] or tributylzincate[3,4] and several electrophiles. In this paper 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.

Treatment of *gem*-dibromocyclopropane **1a** with tributylmanganate, generated from $MnCl_2$ and three equivalents of butylmagnesium bromide gave a mixture of *trans*-1-butyl-2-hexylcyclopropane (**2a**) and *cis*-isomer **3a** in 89% combined yield (**2a/3a**=71/29) (Scheme 1).

Various *gem*-dibromocyclopropanes were allowed to react first with trialkylmanganate, triallylmanganate or tris(dimethylphenylsilyl)manganate[5] 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 comments are worth



Scheme 1.

Keywords: *gem*-dibromocyclopropanes; manganese(II) chloride; 2-alkenylphenol.

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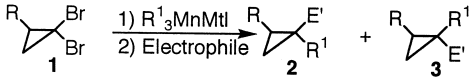
0040–4020/00/$ - see front matter
PII: S0040-4020(99)01095-9

Table 1. Stereoselective dialkylation of *gem*-dibromocyclopropanes (the reactions were performed at 0°C unless otherwise stated)

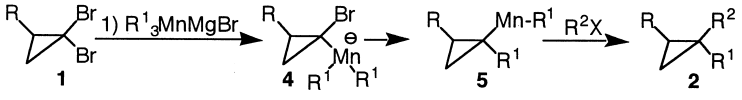


Entry	Substrate **1**	$R^1{}_3MnMtl$	Electrophile	Yield (%)	Isomeric ratio of **2/3**
1		*n*-Bu_3MnLi	EtOH[a]	53	68/32
2		*n*-$Bu_3MnMgBr$	H_2O	89	71/29
3		*n*-$Bu_3MnMgBr$	CH_2=$CHCH_2Br$	77	89/11
4		*n*-$Bu_3MnMgBr$	MeI	65	94/6
5	*n*-C_6H_{13} **1a**	*n*-$Bu_3MnMgBr$	PhCOCl	72	83/17
6		*n*-$Bu_3MnMgBr$	I_2	54	72/28
7		*n*-$Bu_3MnMgBr$	CH_2=$CHBr$[b]	58	99/1
8		*n*-$Bu_3MnMgBr$	H_2O	61	86/14
9		*n*-$Bu_3MnMgBr$	CH_2=$CHCH_2Br$	69	88/12
10		$(PhMe_2Si)_3MnLi$	H_2O	84	58/42
11	**1b**	*n*-Bu_3MnLi	H_2O	56	87/13
12		*n*-$Bu_3MnMgBr$	H_2O	82	97/3
13		*n*-$Bu_3MnMgBr$	CH_2=$CHCH_2Br$	88	97/3
14	**1c**	*n*-$Bu_3MnMgBr$	H_2O	64	87/13
15		*n*-$Bu_3MnMgBr$	PhCOCl	75	84/16
16		$(CH_2$=$CHCH_2)_3MnMgBr$	H_2O	64	83/17
17	Ph **1d**	*n*-$Bu_3MnMgBr$[c]	H_2O	78	87/13
18		*n*-$Bu_3MnMgBr$[c]	CH_2=$CHCH_2Br$	50	92/8
19	$PhCH_2OCH_2$ **1e**	*n*-$Bu_3MnMgBr$	H_2O	75	88/12
20		*n*-$Bu_3MnMgBr$	CH_2=$CHCH_2Br$	66	88/12
21	Me, Me, Me **1f**	$(PhMe_2Si)_3MnLi$	H_2O	62	–

[a] Quenching the reaction with EtOH or H_2O gave the same results (yield and isomeric ratio of **2/3**).
[b] $Pd(PPh_3)_4$ (10 mol%) was added.
[c] The reaction was performed at −48°C.

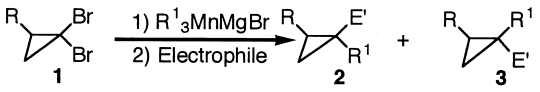
noting. (1) In contrast to the reaction with cuprate or zincate which has been performed at −48 or −85°C, the reaction with manganate could be performed conveniently at 0°C. The reaction of **1a** with *n*-Bu_3MnLi at −78°C for 30 min provided 1-bromo-2-hexylcyclopropane[6] (*cis/trans*=1/2) in 65% yield in addition to an isomeric mixture of 1-butyl-2-hexylcyclopropane (**2a/3a**=76/24, 30% yield). Moreover, treatment of **1a** with *n*-$Bu_3MnMgBr$ at −78°C for 30 min resulted in almost complete recovery of **1a**. (2) Tributylmanganesemagnesium bromide, derived from $MnCl_2$ and three equivalents of butylmagnesium bromide, afforded better yields of butylated cyclopropanes **2** and **3** than tributylmanganeselithium generated from butyllithium (Entry 1 vs. 2, 11 vs. 12). (3) Triphenylmanganate Ph_3Mn-$MgBr$ or Ph_3MnLi gave phenylated cyclopropane in 34% or 30% yield, respectively, upon treatment of **1a**. (4) $(CH_2$=$CH)_3MnMgBr$ and $(Me_3Si$–C≡C$)_3MnMgBr$ gave a minimal amount of the corresponding alkenyl- or alkynylcyclopropanes (<5%). Manganates having secondary and tertiary alkyl ligands such as *i*-$Pr_3MnMgBr$ and *t*-$Bu_3MnMgCl$ gave 1-bromo-2-hexylcyclopropane in 50–55% yield along with an unidentified complex mixture which did not contain the desired isopropylcyclopropane or *tert*-butylcyclopropane. (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-dichlorobicyclo[6.1.0]nonane was found to be unreactive.

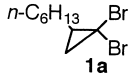
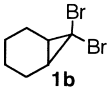
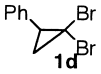
We are tempted to assume a similar reaction mechanism to the reaction with cuprate and zincates: (1) the initial halogen–manganese exchange at the less hindered bromine to afford **4**; (2) alkyl migration under Br^- elimination producing **5** (inversion on the cyclopropane carbon); (3) the second alkylation 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).



Scheme 2.

Table 2. Manganese(II) chloride-catalyzed reaction of *gem*-dibromocyclopropanes (the reactions were performed in the presence of 0.1 mmol of $MnCl_2$)



Entry	Substrate **1** (1.0 mmol)	RMtl (3.0 mmol)	Electrophile (3.0 mmol)	Yield (%)	Isomeric ratio of **2/3**
1		*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		$PhMe_2SiLi$	EtOH	43	79/21
7		*n*-BuLi	H_2O	62	85/15
8		*n*-BuMgBr	EtOH	51	93/7
9		*n*-BuMgBr	H_2O	51	77/23

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** to a THF solution of butylmagnesium bromide and manganese(II) chloride (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.

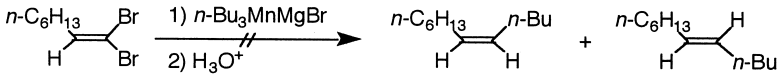
Ring opening of iodobenzofuran with trialkylmanganate

The reaction of 1,1-dibromo-1-octene with tributylmanganate took place very easily even at −78°C. However, the expected product based on 1,2-migration reaction could not be detected and unidentified complex mixture was obtained (Scheme 3).

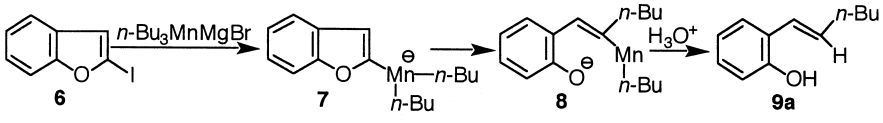
Then, we turned our attention to heteroatom substituted alkenyl halides such as 2-iodobenzofuran,[9,10] 2,6-dibromopyridine,[11] and 2-iodobenzothiophene. Among them, 2-iodobenzofuran proved to be a good substrate and afforded the desired ring-opening product upon treatment with trialkylmanganate. Thus, an addition of tributylmanganate to a solution of 2-iodobenzofuran (**6**) in THF followed by heating a mixture at 50°C for 2.5 h gave 2-[(*E*)-1-hexenyl]-phenol (**9a**) in 49% yield. Quenching the reaction mixture with D_2O provided 2-[(*E*)-2-deuterio-1-hexenyl]phenol. (*E*)-Alkene was obtained exclusively (Scheme 4).

The reaction might proceed as follows: (1) iodine–manganese exchange to provide a manganate **7**; (2) migration of butyl group from manganese to an adjacent carbon under cleavage of C–O bond producing **8**; and (3) protonation of alkenylmanganese species upon aqueous workup.

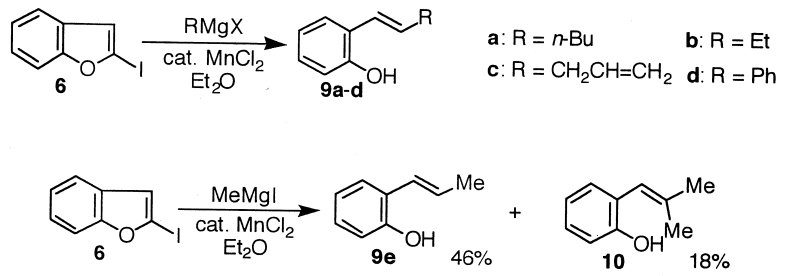
The reaction also proceeded in a catalytic manner. For instance, treatment of **6** with butylmagnesium bromide in THF in the presence of a catalytic amount of $MnCl_2$ (10 mol%) at 25°C for 10 h gave 2-alkenylphenol **9a** in 21% yield. The change of the solvent from THF to ether dramatically increased the yield up to 85% after 1 h at 25°C. Various Grignard reagents were examined in the $MnCl_2$-catalyzed ring-opening reaction of **6**. Ethylmagnesium bromide or allylmagnesium bromide gave the corresponding (*E*)-2-alkenylphenol **9b** or **9c** in 88% or 46% yield, respectively after stirring the reaction mixture for 1 or 1.5 h at 25°C. In contrast, the reaction with phenylmagnesium bromide or methylmagnesium iodide proceeded very slowly at 25°C and afforded the corresponding ring-opened product **9d** or **9e** in 62 or 46% yield, respectively after heating the reaction mixture at reflux for 16 or 28 h. In the case of methylmagnesium iodide, dimethylated product, 2-(2-methyl-1-propenyl)-phenol (**10**) was obtained in 18% yield in addition to the desired **9e** (Scheme 5).



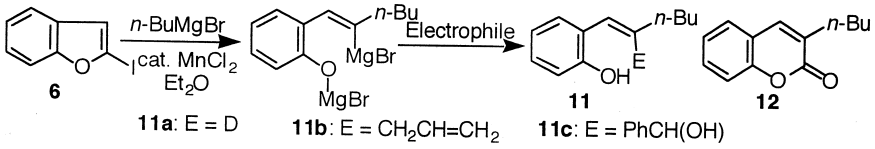
Scheme 3.



Scheme 4.



Scheme 5.



Scheme 6.

The intermediary alkenylmagnesium in the $MnCl_2$-catalyzed reaction of **6** could be trapped by various electrophiles. An addition of D_2O, allyl bromide or benzaldehyde gave the corresponding adducts (**11a**, **11b** or **11c**) in 77, 63 or 86%, respectively. Furthermore, quenching the reaction mixture with CO_2 produced 3-butyl-2H-benzopyran-2-one **12** in 53% yield.[12] (Scheme 6).

Financial support by grant-in-aid for Scientific Research on Priority Area (B) (No. 10208208) and grant-in-aid for Scientific Research (No. 09450341) from the Ministry of Education, Science, Sports and Culture, Japan, is acknowledged. We also thank Prof. Tamejiro Hiyama for helpful discussions.

Experimental

Distillation of the products was performed using Kugelrohr (Büchi); the boiling points are indicated by the air-bath temperature values without any correction. The NMR spectra (^1H and ^{13}C) were recorded on a Varian GEMINI 300 spectrometer in $CDCl_3$; tetramethylsilane (TMS) was used as an internal standard. The IR spectra were determined on a JASCO IR-810 spectrometer. The analyses were carried out at the Elemental Analysis Center of Kyoto University.

General procedure for the reaction of *gem*-dibromocyclopropane with trialkylmanganate

The reaction of 1,1-dibromo-2-hexylcyclopropane (**1a**) with tributylmanganate is representative (Entry 2, Table 1). Manganese(II) chloride (151 mg, 1.2 mmol) was sonicated in tetrahydrofuran (THF, 10 ml) under argon atmosphere for 20 min. Butylmagnesium bromide (1.0 M ether solution, 3.6 ml, 3.6 mmol) was added to the suspension of $MnCl_2$ in THF at 0°C. The mixture turned into a clear brown solution and then was stirred for 20 min at 0°C. A solution of dibromocyclopropane **1a** (0.28 g, 1.0 mmol) in THF (2 ml) was added at 0°C and the whole was stirred at 0°C for 1 h and then at 25°C for 20 min. The mixture was poured into 1 M HCl and extracted with hexane (3×20 ml). Purification of the products by silica-gel column chromatography gave a mixture of **2a** and **3a** (162 mg) in 89% combined yield (**2a/3a**=71/29).

Physical data for **2a**, **3a**, 7-butylnorcarane, 9-butylbicyclo-[6.1.0]nonane, 1-butyl-2-phenylcyclopropane and 1-butyl-2-[(phenylmethoxy)methyl]cyclopropane were identical with those reported in literature.[2,3,13]

1,2-Dihexycyclopropane (2/3=86/14). IR (neat) 3056, 2986, 2952, 2920, 2850, 1467, 1458, 1378, 1020, 721 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.28–−0.23 (m, 0.14H), 0.11 (t, J=6.6 Hz, 1.72H), 0.28–0.40 (m, 1.72H), 0.49–0.57 (m, 0.14H), 0.58–0.68 (m, 0.28H), 0.86 (t, J=6.9 Hz, 6H), 1.01–1.40 (m, 20H); ^{13}C NMR ($CDCl_3$) δ 10.78, 11.64, 14.00, 15.67, 18.68, 22.60, 28.55, 29.13, 29.28, 29.58, 30.11, 31.88, 34.31. Found: C, 85.34; H, 14.15%. Calcd for $C_{15}H_{30}$: C, 85.63; H, 14.37%.

9-Allylbicyclo[6.1.0]nonane (2/3=83/17). IR (neat) 3350, 2974, 2918, 2848, 2684, 1640, 1466, 1446, 1354, 1300, 1277, 1150, 1025, 993, 961, 908, 736 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.12–0.22 (m, 0.83H), 0.32–0.44 (m, 1.66H), 0.60–0.69 (m, 0.17H), 0.70–0.83 (m, 0.17H), 0.84–1.02 (m, 1.83H), 1.03–1.16 (m, 0.34H), 1.25–1.42 (m, 4H), 1.44–1.82 (m, 4H), 1.93–2.10 (m, 4H), 4.89–5.12 (m, 2H), 5.84–5.98 (m, 0.17H), 5.87 (ddt, J=17.1, 10.2, 6.0 Hz, 0.83H); ^{13}C NMR ($CDCl_3$) δ 17.71, 21.51, 22.33, 22.60, 26.45, 26.52, 26.70, 29.59, 29.71, 37.69, 113.86, 138.65. Found: C, 87.68; H, 12.52%. Calcd for $C_{12}H_{20}$: C, 87.73; H, 12.27%.

3-Dimethylphenylsilyl-1,1,2,2-tetramethylcyclopropane. IR (neat) 3066, 3046, 2936, 2866, 1470, 1455, 1428, 1378, 1248, 1139, 1111, 914, 880, 833, 811, 779, 726, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.54 (s, 1H), 0.29 (s, 6H), 1.09 (s, 6H), 1.17 (s, 6H), 7.30–7.39 (m, 3H), 7.50–7.57 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 0.04, 20.64, 24.34, 25.10, 25.34, 127.71, 128.57, 133.69, 141.58. Found: C, 77.30; H, 10.66%. Calcd for $C_{15}H_{24}Si$: C, 77.51; H, 10.41%.

General procedure for the reaction of *gem*-dibromocyclopropane with trialkylmanganate followed by addition of electrophile

Preparation of 1-butyl-2-hexyl-1-iodocyclopropane is representative (Entry 6, Table 1). A solution of **1a** (0.28 g, 1.0 mmol) in THF (2 ml) was added to a solution of tributylmanganate generated from $MnCl_2$ (151 mg, 1.2 mmol) and butylmagnesium bromide (3.6 mmol). The resulting mixture was stirred at 0°C for 1 h and then at 25°C for 20 min. The mixture was cooled to −78°C and iodine (0.46 g, 3.6 mmol) was added. The whole was warmed to room temperature over 1 h and stirred for another 30 min. The mixture was poured into aq. $Na_2S_2O_3$ and extracted with hexane (3×20 ml). Purification by silica-gel column chromatography gave a mixture of *cis*- and *trans*-1-butyl-2-hexyl-1-iodocyclopropane (*cis*/*trans*=72/28): Bp 130–140°C (bath temp, 0.5 Torr); IR (neat) 3058, 2954, 2924, 2852, 1466, 1379, 1294, 1261, 1211, 1164, 1116, 1031, 942, 914, 800, 724 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.05–0.10 (m, 0.72H), 0.32 (t, J=6.3 Hz, 0.28H), 0.68 (t, J=6.0 Hz, 0.72H), 0.80–0.98 (m, 6H), 1.02–1.75 (m, 17.28H); ^{13}C NMR ($CDCl_3$) δ 13.98, 14.01, 21.81, 22.00, 22.51, 22.56, 22.80, 23.67, 24.02, 24.67, 28.63, 28.70, 29.01, 29.17, 30.17, 31.68, 31.77, 32.50, 36.95, 39.15, 46.00. Found: C, 50.79; H, 8.40%. Calcd for $C_{13}H_{25}I$: C, 50.66; H, 8.17%.

Physical data for 1-butyl-1-methyl-2-hexylcyclopropane and 1-benzoyl-1-butyl-2-hexylcyclopropane were identical with those reported in literature.[3,13]

1-Allyl-1-butyl-2-hexylcyclopropane (2/3=89/11). IR (neat) 3072, 3050, 2954, 2920, 2852, 1640, 1467, 1459, 1415, 1379, 1020, 993, 909, 723 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.14 (dd, J=5.1, 4.5 Hz, 0.11H), −0.09 (dd, J=5.4, 4.5 Hz, 0.89H), 0.30–0.39 (m, 1H), 0.43–0.55 (m, 1H), 0.80–0.90 (m, 6H), 1.11–1.44 (m, 16H), 1.76 (dd, J=15.0, 6.6 Hz, 0.11H), 1.92 (dd, J=15.0, 6.6 Hz, 0.89H), 2.01–2.16 (m, 1H), 4.93–5.02 (m, 0.22H), 4.98 (d, J=10.2 Hz, 0.89H), 5.02 (d, J=17.1 Hz, 0.89H), 5.69–5.83 (m, 0.11H), 5.81 (ddt, J=17.1, 10.2, 6.9 Hz, 0.89H); ^{13}C NMR ($CDCl_3$) δ 14.00, 14.06, 18.00, 22.59, 22.86, 22.98, 24.06, 28.50, 29.22, 29.38, 30.07, 31.84, 35.16, 37.44, 115.34, 115.45, 137.75. Found: C, 86.03; H, 13.70%. Calcd for $C_{16}H_{30}$: C, 86.41; H, 13.59%.

1-Butyl-2-hexyl-1-vinylcyclopropane (2/3=99/1). IR (neat) 3080, 3058, 2954, 2920, 2852, 1634, 1460, 1378, 1261, 1026, 993, 908, 894, 723 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.33–0.40 (m, 1H), 0.52–0.58 (m, 1H), 0.62–0.75 (m, 1H), 0.86 (t, J=6.9 Hz, 6H), 1.14–1.48 (m, 16H), 4.93 (dd, J=17.1, 1.8 Hz, 1H), 5.01 (dd, J=10.5, 1.8 Hz, 1H), 5.69 (dd, J=17.1, 10.5 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.01, 18.15, 22.58, 22.90, 26.54, 27.43, 29.03, 29.10, 29.13, 29.75, 31.81, 37.99, 113.32, 140.33. Found: C, 86.21; H, 13.54%. Calcd for $C_{15}H_{28}$: C, 86.46; H, 13.54%.

1-Allyl-1,2-dihexylcyclopropane (2/3=88/12). IR (neat) 3072, 3050, 2954, 2920, 2850, 1640, 1460, 1415, 1379, 1018, 993, 909, 721 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.14 (dd, J=5.4, 5.4 Hz, 0.12H), −0.09 (dd, J=5.4, 5.4 Hz, 0.88H), 0.31–0.40 (m, 1H), 0.43–0.54 (m, 1H), 0.81–0.99 (m, 6H), 1.14–1.42 (m, 20H), 1.76 (dd, J=14.7, 6.6 Hz, 0.12H), 1.90 (dd, J=14.7, 6.6 Hz, 0.88H), 2.00–2.16 (m, 1H), 4.92–5.06 (m, 2H), 5.68–5.88 (m, 1H); ^{13}C NMR ($CDCl_3$) δ 13.91, 17.68, 18.01, 22.55, 23.05, 23.77, 24.11, 26.65, 29.19, 29.37, 29.48, 29.68, 30.06, 30.71, 31.83, 35.24, 37.80, 115.33, 115.49, 137.18, 137.80. Found: C, 86.04; H, 13.76%. Calcd for $C_{18}H_{34}$: C, 86.32; H, 13.68%.

7-Allyl-7-butylnorcarane (2/3=97/3). IR (neat) 3072, 2924, 2854, 1639, 1467, 1449, 1377, 991, 909 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.56–0.66 (m, 2H), 0.86 (t, J=6.9 Hz, 2.91H), 0.91 (t, J=7.2 Hz, 0.09H), 1.06–1.46 (m, 12H), 1.79–1.93 (m, 2.06H), 2.09 (d, J=6.6 Hz, 1.94 H), 4.97 (d, J=10.2 Hz, 0.03H), 4.98 (d, J=17.1 Hz, 0.03H), 5.03 (d, J=10.2 Hz, 0.97H), 5.08 (d, J=17.1 Hz, 0.97H), 5.83 (ddt, J=17.1, 10.2, 6.6 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 14.02, 18.54, 19.11, 22.15, 22.84, 24.46, 28.26, 30.85, 38.95, 115.36, 137.32.

9-Benzoyl-9-butylbicyclo[6.1.0]nonane (2/3=84/16). IR (neat) 3056, 3022, 2954, 2920, 2852, 1672, 1598, 1581, 1467, 1449, 1349, 1280, 1250, 1210, 1196, 1174, 1073, 1053, 1020, 976, 960, 935, 806, 782, 741, 715, 691 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.76 (t, J=6.9 Hz, 2.52H), 0.86 (t, J=7.2 Hz, 0.48H), 0.90–1.08 (m, 4H), 1.10–1.42 (m, 8H), 1.48–1.69 (m, 6H), 1.97–2.06 (m, 2H), 7.39–7.55 (m, 3H), 7.94–8.00 (m, 2H); ^{13}C NMR ($CDCl_3$) major product δ 13.76, 22.33, 24.43, 26.22, 28.47, 29.55, 29.65, 35.87, 39.95, 128.37, 129.57, 132.55, 137.32, 200.61. Found: C, 84.28; H, 10.01%. Calcd for $C_{20}H_{28}O$: C, 84.45; H, 9.92%.

1-Allyl-1-butyl-2-phenylcyclopropane (2/3=92/8). IR (neat) 3058, 3022, 2992, 2952, 2922, 2854, 1639, 1605, 1498, 1457, 1440, 1416, 1378, 1085, 1070, 1028, 996, 910, 775, 728, 696 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.69–0.80 (m, 1.24 H), 0.81–0.87 (m, 0.08H), 0.87–0.96 (m, 3.68H), 1.10–1.66 (m, 6.92H), 1.87–1.99 (m, 2H), 2.34 (dd, J=14.1, 7.5 Hz, 0.08H), 4.89 (d, J=17.4 Hz, 0.92H), 4.91 (d, J=10.2 Hz, 0.92H), 5.07 (d, J=9.9 Hz, 0.08H), 5.08 (d, J=16.8 Hz, 0.08H), 5.67 (ddt, J=17.4, 10.2, 6.9 Hz, 0.92H), 5.91 (ddt, J=16.8, 9.9, 7.2 Hz, 0.08H), 7.12–7.26 (m, 3H), 7.27–7.35 (m, 2H); ^{13}C NMR ($CDCl_3$) δ 13.87, 14.01, 16.06, 16.37, 22.67, 22.87, 26.67, 28.40, 28.50, 28.69, 28.85, 30.10, 35.18, 37.18, 41.70, 115.61, 116.21, 125.57, 125.68, 127.86, 127.96, 129.09, 136.58, 136.92, 139.79. Found: C, 89.59; H, 10.62%. Calcd for $C_{16}H_{22}$: C, 89.66; H, 10.34%.

1-Allyl-1-butyl-2-[(phenylmethoxy)methyl]cyclopropane (2/3=88/12). IR (neat) 3060, 3026, 2988, 2952, 2922, 2852, 1640, 1497, 1455, 1415, 1380, 1363, 1204, 1165, 1093, 1076, 1028, 995, 910, 733, 696 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.13 (dd, J=5.1, 5.1 Hz, 0.12H), 0.18 (dd, J=5.1, 5.1 Hz, 0.88H), 0.50–0.59 (m, 1H), 0.87 (t, J=6.9 Hz, 3H), 0.92–1.03 (m, 1H), 1.15–1.39 (m, 6H), 1.98–2.16 (m, 2H), 3.41–3.60 (m, 2H), 4.51 (d, J=12.0 Hz, 1H), 4.55 (d, J=12.0 Hz, 1H), 4.98–5.09 (m, 2H), 5.74–5.93 (m, 1H), 7.27–7.37 (m, 5H); ^{13}C NMR ($CDCl_3$) major product δ 13.95, 16.43, 22.75, 23.17, 23.53, 28.33, 35.40, 37.05, 70.74, 72.59, 115.67, 127.57, 127.78,

128.44, 137.31. Found: C, 83.69; H, 10.34%. Calcd for $C_{18}H_{26}O$: C, 83.67; H, 10.14%.

General procedure for manganese(II) chloride-catalyzed reaction of *gem*-dibromocyclopropane

A solution of dibromocyclopropane **1a** (0.28 g, 1.0 mmol) in THF (2 ml) was added to a THF solution of butylmagnesium bromide (3.0 mmol) and manganese(II) chloride (12 mg, 10 mol%) at −78°C. The mixture was stirred for 30 min at 0°C. Extractive workup (AcOEt, brine) followed by silica-gel column purification provided a mixture of **2a** and **3a** (**2a/3a**=79/21, 136 mg) in 75% combined yield.

1-Allyl-2-hexylcyclopropane (2/3=58/42). IR (neat) 3058, 2990, 2954, 2920, 2850, 1641, 1459, 1438, 1379, 1022, 992, 909, 719 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.30–−0.23 (m, 0.42H), 0.14–0.23 (m, 1.16H), 0.36–0.50 (m, 1.16H), 0.56–0.65 (m, 0.42H), 0.67–0.80 (m, 0.84H), 0.86 (t, J=6.9 Hz, 3H), 1.13–1.44 (m, 10H), 1.87–2.15 (m, 2H), 4.93 (d, J=9.9 Hz, 0.58H), 4.95 (d, J=10.2 Hz, 0.42H), 5.02 (d, J=17.1 Hz, 0.58H), 5.07 (d, J=17.1 Hz, 0.42H), 5.85 (ddt, J=17.1, 9.9, 6.6 Hz, 0.58H), 5.90 (ddt, J=17.1, 10.2, 6.9 Hz, 0.42H); ^{13}C NMR ($CDCl_3$) δ 10.56, 11.37, 13.99, 14.65, 15.71, 17.61, 18.40, 22.59, 28.62, 29.08, 29.24, 29.47, 30.03, 31.85, 32.75, 34.09, 38.09, 114.05, 114.20, 138.40, 139.06. Found: C, 86.43; H, 13.61%. Calcd for $C_{12}H_{22}$: C, 86.67; H, 13.33%.

1,1-Diallyl-2-hexylcyclopropane. ^1H NMR ($CDCl_3$) δ −0.04 (dd, J=4.5, 4.5 Hz, 1H), 0.43 (dd, J=8.7, 4.5 Hz, 1H), 0.53–0.63 (m, 1H), 0.86 (t, J=6.9 Hz, 3H), 1.14–1.62 (m, 10H), 0.80 (dd, J=13.8, 6.6 Hz, 1H), 0.94 (dd, J=13.8, 6.6 Hz, 1H), 2.00–2.15 (m, 2H), 4.92–5.06 (m, 4H), 5.66–5.87 (m, 2H). HRMS calcd for $C_{15}H_{26}$ 206.2035, found 206.2036.

1-Dimethylphenylsilyl-2-hexylcyclopropane (2/3=79/21). IR (neat) 3064, 3048, 2952, 2920, 2850, 1458, 1428, 1248, 1113, 1037, 943, 861, 831, 812, 770, 727, 698 cm^{-1}; ^1H NMR ($CDCl_3$) δ −0.54–−0.45 (m, 0.79H), −0.26–−0.15 (m, 0.21H), 0.14 (s, 2.37H), 0.16 (s, 2.37H), 0.24 (s, 0.63H), 0.27 (s, 0.63H), 0.31–0.44 (m, 2H), 0.58–0.68 (m, 1H), 0.82–0.91 (m, 3H), 1.10–1.42 (m, 10H), 7.30–7.36 (m, 3H), 7.50–7.59 (m, 2H); ^{13}C NMR ($CDCl_3$) δ −4.04, −3.78, 3.12, 8.91, 14.01, 15.66, 22.57, 29.10, 29.74, 31.86, 35.84, 127.70, 128.84, 133.86, 139.68. Found: C, 78.20; H, 10.92%. Calcd for $C_{17}H_{28}Si$: C, 78.38; H, 10.83%.

The reaction of 2-iodobenzofuran with tributylmanganate

A THF (2 ml) solution of 2-iodobenzofuran (**6**, 0.24 g, 1.0 mmol)[14] was added at 0°C to a solution of tributylmanganate generated from $MnCl_2$ (163 mg, 1.3 mmol) and butylmagnesium bromide (3.9 mmol). The resulting mixture was stirred at 0°C for 30 min and then at 50°C for 2.5 h. The mixture was poured into 1 M HCl and extracted with ethyl acetate (20 ml×3). The combined organic layer was dried over Na_2SO_4 and concentrated in vacuo. The crude products were purified by silica-gel column chromatography (hexane/ethyl acetate=5/1) to give 2-[(*E*)-1-hexenyl]phenol (**9a**): IR (neat) 3032, 2954, 2924, 2854, 1606, 1586, 1499, 1486, 1455, 1378, 1330, 1294, 1239, 1177, 1089, 971, 848, 800, 748 cm^{-1}; ^1H NMR ($CDCl_3$) δ 0.93 (t, J=6.9 Hz, 3H), 1.31–1.53 (m, 4H), 4.24 (dt, J=6.9, 6.9 Hz, 2H), 4.94 (s, 1H), 6.19 (dt, J=15.9, 6.9 Hz, 1H), 6.55 (d, J=15.9 Hz, 1H), 6.79 (dd, J=7.8, 1.2 Hz, 1H), 6.88 (ddd, J=7.8, 7.8, 1.2 Hz, 1H), 7.10 (ddd, J=7.8, 7.8, 1.8 Hz, 1H), 7.31 (dd, J=7.8, 1.8 Hz, 1H); ^{13}C NMR ($CDCl_3$) δ 13.83, 22.17, 31.42, 33.04, 115.70, 120.91, 123.63, 125.10, 127.43, 128.02, 133.84, 152.48. Found: C, 81.50; H, 8.94%. Calcd for $C_{12}H_{16}O$: C, 81.77; H, 9.15%.

General procedure for the reaction of 2-iodobenzofuran with Grignard reagent in the presence of a catalytic amount of $MnCl_2$

Preparation of **9b** is representative. Ethylmagnesium bromide (0.93 M, ether solution, 3.2 ml, 3.0 mmol) was added to a suspension of $MnCl_2$ (12 mg, 10 mol%) in Et_2O (10 ml) at 0°C under argon atmosphere. After being stirred for 20 min at 0°C, a solution of **6** (0.24 g, 1.0 mmol) in Et_2O (2 ml) was added. The mixture was stirred for 30 min at 0°C then for 1 h for 25°C. Extractive workup followed by silica-gel column purification provided **9b**. Physical data for **9b** were identical with those reported in literature.[15]

General procedure for the trapping of an intermediary alkenylmagnesium

Preparation of **11b** is representative. A solution of **6** (0.24 g, 1.0 mmol) in Et_2O (2 ml) was added to a Et_2O solution of butylmagnesium bromide (3.0 mmol) and $MnCl_2$ (12 mg, 10 mol%) at 0°C under argon atmosphere. The resulting mixture was stirred for 30 min at 0°C and then for 1 h at 25°C. The mixture was cooled to 0°C and allyl bromide (8.0 mmol) was added. After being stirred for 30 min at 0°C, the whole mixture was stirred for 1 h at 25°C. Extractive workup followed by silica-gel column purification provided **11b** in 63% yield.

3-Butyl-2*H*-benzopyran-2-one.[16] A suspension of manganese(II) chloride (12 mg, 10 mol%) in Et_2O was sonicated for 10 min under argon atmosphere. Butylmagnesium bromide (0.91 M, Et_2O solution, 3.3 ml, 3.0 mmol) was added to the resulting suspension of $MnCl_2$ at 0°C. The mixture was stirred for 20 min. A Et_2O solution of **6** (1.0 mmol) was added and stirred for 30 min at 0°C. The whole mixture was warmed to 25°C and stirred for 1 h. The mixture was cooled to −78°C and a piece of dry ice was added at −78°C. The reaction mixture was warmed to 25°C over 30 min. Usual workup and purification by silica-gel column chromatography afforded 3-butyl-2*H*-benzopyran-2-one in 53% yield.

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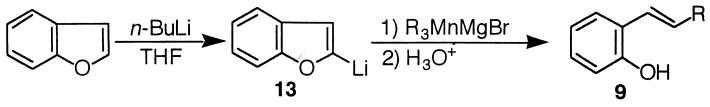

Scheme 7.

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