Pergamon

Tetrahedron Letters 40 (1999) 6613–6616

TETRAHEDRON
LETTERS

Transformation of tetrahydropyranyl ether of allylic alcohol into 7-octene-1,5-diol by means of trialkylmanganate

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Received 24 May 1999; revised 1 July 1999; accepted 2 July 1999

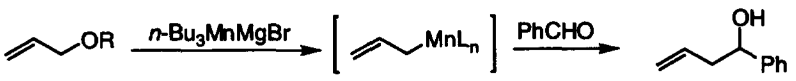
Abstract

Treatment of tetrahydropyranyl (or tetrahydrofuranyl) ether of allylic alcohol with tributylmanganate provided 7-octene-1,5-diol (or 6-hepten-1,4-diol) in good yields. The reaction of propargylic tetrahydropyranyl ether with tributylmanganate is also described. © 1999 Elsevier Science Ltd. All rights reserved.

Keywords: manganese; manganese compounds; allylation; acetals; diols.

Allylmetallic compounds have been widely used for selective carbon–carbon bond formation during the last three decades.[1] Among them, allylchromium[2] has been extensively studied for stereoselective synthesis of homoallylic alcohols. In contrast, there are only a few examples of the synthetic use of the allylic manganese species.[3] Here we wish to report an alternative method for the preparation of an allylic manganese compound from allylic ether and its application to the conversion of the tetrahydropyranyl ether of allylic alcohol into 7-octene-1,5-diol.

Treatment of the diallyl ether or allyl octyl ether with tributylmanganate,[4] derived from $MnCl_2$ and three equivalents of butylmagnesium bromide, followed by an addition of benzaldehyde afforded 1-phenyl-3-buten-1-ol in 50 or 49% yield, respectively (Scheme 1).



R = CH_2=$CHCH_2$- or n-C_8H_{17}

Scheme 1.

Then, the tetrahydropyranyl ether of allylic alcohol **1a** was chosen as a substrate instead of allyl ethers. Tributylmanganate (1.0 mmol)[5] was added to a solution of **1a** (0.14 g, 1.0 mmol) in THF (12 mL) at 0°C

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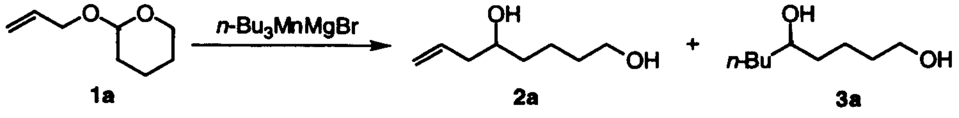
PII: S0040-4039(99)01319-2

and the resulting mixture was stirred for 12 h at 25°C (Scheme 2). Extractive work up followed by silica-gel column purification provided 7-octene-1,5-diol (**2a**,[6] 78 mg) in 55% yield along with nonane-1,5-diol (**3a**, 5 mg, 3%). An addition of 3 molar equivalents of HMPA increased the yield of **2a** up to 84%.



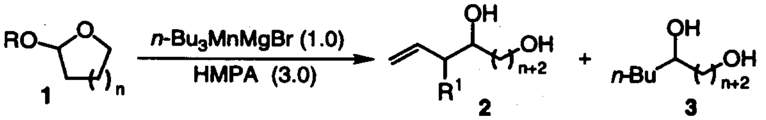
Scheme 2.

The reaction of the representative allylic tetrahydropyranyl ethers and tetrahydrofuranyl ethers were examined under the same reaction conditions. The results are shown in Table 1. Several comments are worth noting: (1) crotyl THP ether **1c** provided the same product **2b** (6-methyl-7-octen-1,5-diol) as 1-methyl-2-propenyl THP ether **1b**. No trace of an isomeric product, 7-nonene-1,5-diol, could be detected in the reaction mixture. On the other hand, cinnamyl THP ether **1d** and its isomer **1e** gave a trace of 8-phenyl-7-octen-1,5-diol in <3% yield in addition to 6-phenyl-7-octen-1,5-diol (**2d**); (2) the yield of **2b** was much higher in the case of the reaction of **1b** compared to the reaction of **1c** as the starting material. An attack of manganate on an alkenic moiety might be impeded by the methyl substituent in the case of **1c**; and (3) whereas the reaction of THP ethers with tributylmanganate afforded a butylated byproduct (nonane-1,5-diol) in only <4% yield, the reaction of THF ethers gave slightly more of the butylated byproduct (octane-1,4-diol) in 8–14% yield.

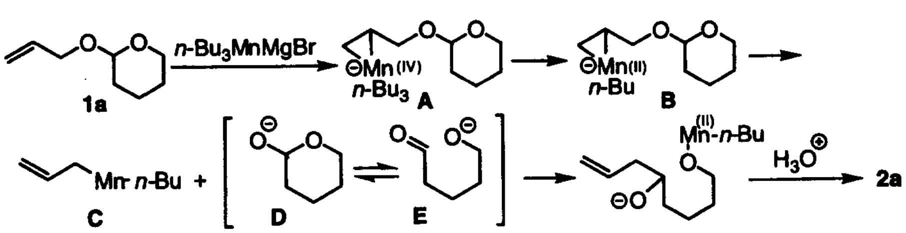
We were tempted to assume the following reaction mechanism. Oxidative addition of manganate (Mn(II)) to the olefinic bond of **1a** would give manganese–olefin complex (Mn(IV)) **A** which could be transformed into Mn(II) species **B** by reductive elimination under departure of *n*-Bu–*n*-Bu (Scheme 3).[7] Elimination of magnesium oxide from **B** would provide allylmanganese **C** and magnesium salt of γ-lactol **D** which is equilibrated with aldehyde **E**. Recombination[8] of allylmanganese **C** and aldehyde **E** could afford 7-octene-1,5-diol (**2a**).

The reaction proved to proceed in the presence of a catalytic amount of $MnCl_2$. For instance, an addition of **1a** (1.0 mmol) to a solution of butylmagnesium bromide (3.0 mmol) in THF containing

Table 1
Reaction of allylic THP (THF) ether with tributylmanganate

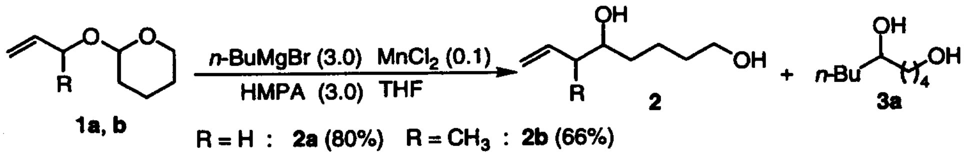


Entry	Substrate 1	R	n	Product / Yield (%) 2		3	
1	**1a**:	CH_2=$CHCH_2$-	2	**2a**: $R^1 = H$	84	**3a**:	3
2	**1b**:	CH_2=$CHCH(CH_3)$-	2	**2b**: $R^1 = CH_3$	72	**3a**:	4
3	**1c**:	CH_3CH=$CHCH_2$-	2	**2b**: $R^1 = CH_3$	14	**3a**:	2
4	**1d**:	PhCH=$CHCH_2$-	2	**2d**: R^1 = Ph	35	**3a**:	3
5	**1e**: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



Scheme 3.

HMPA (3.0 mmol) and $MnCl_2$ catalyst (0.1 mmol) gave **2a** in 80% yield after 12 h at 25°C (Scheme 4). 1-Methyl-2-propenyl THP ether **1b** also provided the corresponding 1,5-diol **2b** in 66% yield, respectively. A byproduct, nonane-1,5-diol **3a**, was obtained in 3–8% yield in these reactions along with the desired allylated products.

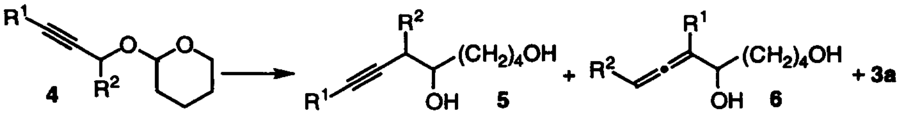


Scheme 4.

Treatment of propargylic acetal **4a** and **4b**, generated from primary propargylic alcohol, with n-$Bu_3MnMgBr$ afforded a mixture of homopropargylic alcohol **5** and allenylated product **6** in addition to butylated product **3a**. The product distribution heavily depended on the nature of the starting material. The acetals, **4c**, **4d**, and **4e**, which are derived from secondary propargylic alcohols, gave only homopropargylic alcohols **5** without contamination by **6** (Table 2). A catalytic reaction also proceeded smoothly in the case of the reaction of these propargylic acetals as in the case of allylic acetals. For instance, an addition of **4c** (1.0 mmol) or THF ether of 4-trimethylsilyl-3-butyn-2-ol (1.0 mmol) to a THF solution of butylmagnesium bromide (3.0 mmol) in the presence of $MnCl_2$ (12 mg, 0.1 mmol) provided homopropargylic alcohol **5c** or 5-methyl-7-trimethylsilyl-6-heptyn-1,4-diol in 76 or 76% yield, respectively, along with **3a** (3%) or **3b** (13%).

Table 2

Reaction of propargylic THP ether with tributylmanganate



4a	$R^1 = Me_3Si$	$R^2 = H$	46%	28%	16%
4b	$R^1 = n\text{-}C_6H_{13}$	$R^2 = H$	30%	14%	5%
4c	$R^1 = Me_3Si$	$R^2 = CH_3$	50%	—	3%
4d	$R^1 = n\text{-}C_6H_{13}$	$R^2 = CH_3$	61%	—	12%
4e	$R^1 = n\text{-}C_6H_{13}$	$R^2 = CH_2{=}CH\text{-}$	63%	—	6%

Acknowledgements

This work was supported by a Grant-in-Aid for Scientific Research (B) (No. 09450341) from the Ministry of Education, Science, Sports and Culture, Government of Japan.

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5. Triethylmanganate ($Et_3MnMgBr$) was also effective as tributylmanganate. However, trimethylmanganate derived from $MnCl_2$ and MeMgI was not effective for the transformation. For instance, treatment of **1f** with Me_3MnMgI gave a methylated product (1,4-pentanediol) in only 13% in addition to unidentified complex products. The use of *n*-Bu_3MnLi derived from *n*-BuLi instead of *n*-BuMgBr afforded **2a** in only 31% yield along with **3a** (7%).
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7. Hexadecane could be detected in only 20% yield in the reaction of **1a** with *n*-$(Octyl)_3MnMgBr$. Thus, stepwise elimination of the butyl radicals, which would collapse to butane and butene, could be an alternative route to **B**.
8. The intermolecular version of the reaction was confirmed by the following experimental result: Treatment of a mixture of **1a** (0.5 mmol) and **1g** (0.5 mmol) with tributylmanganate (1.0 mmol) provided cross-coupling products **2b** and **2f** in addition to the intramolecular addition products **2a** and **2g**. The ratio of these compounds was **2a**:**2b**:**2f**:**2g**=42:24:14:20.