A Simple Method for the Conversion of Primary Alcohols into Terminal Olefins

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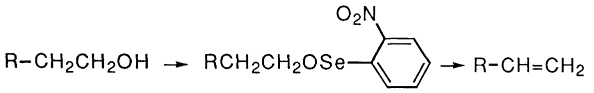
Treatment of benzyl ethers of primary alcohols with *n*-butyllithium (*n*-BuLi) afforded terminal olefins in good yield.

Conversions of primary alcohols into terminal olefins are frequently used in organic synthesis. Although various methods have been reported,[1] the sequence most widely used is conversion of primary alcohols into *o*-nitrophenyl selenoxides followed by oxidation developed by Sharpless[2] and Grieco.[3] (eq.1)


(1)

We describe herein a facile conversion of primary alcohols into terminal olefins *via* [2,3]-Wittig type fragmentation of benzyl ethers. (eq.2)

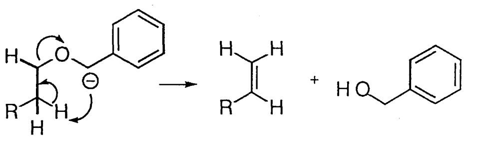
$$RCH_2CH_2OBn \xrightarrow{n\text{-BuLi}} R{-}CH{=}CH_2 \qquad (2)$$

Although the reaction of alkyl benzyl or alkyl allyl ethers with strong bases such as *n*-butyllithium (*n*-BuLi) is known to yield benzyl alcohol derivatives via [1,2]-Wittig rearrangement (eq.3),[4] the elimination reactions shown in eq.2 have not been studied extensively except for the related reaction of some simple ethers.[5,6]

$$ROCH_2Ph \xrightarrow{n\text{-BuLi}} RCH(OH)Ph \qquad (3)$$

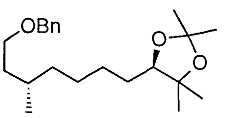
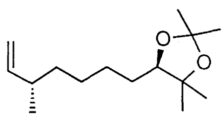
Treatment of benzyloxyethyl derivatives with 3 equivalent of *n*-BuLi in tetrahydrofuran (THF) at -78 °C afforded terminal olefins in good yield (see Table 1). The yield of benzyl alcohol derivatives formed by [1,2]-Wittig rearrangement was less than 5%. To complete the elimination reaction, it is essential to warm the reaction mixture to 0 °C (entry 1). Co-occurrence of functional groups such as trityl (Tr), silyl (TBDPS, TBS), tetrahydropyranyl (THP), and methoxymethyl (MOM) ethers or dimethyl acetals did not interfere the olefin formations (entry 2-7). *p*-Methoxybenzyl (MPM) ether instead of benzyl ether also gave an eliminated product, but some of starting material was recovered under the same reaction conditions (entry 8). Benzyl ether was eliminated preferentially in the presence of MPM ether (enry 9). Reaction of allyl ether gave a complex mixture (entry 10). No reaction was observed when toluene was used as a solvent (entry 11).

The formation of olefins can be reasonably explained by the mechanism that the anion generated at the benzylic position abstracts the proton β to the ether oxygen, just like [2,3]-Wittig rearrangement (eq.4).


(4)

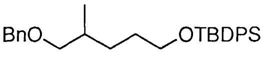
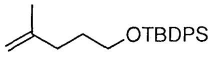
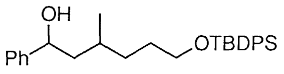
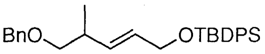
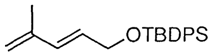
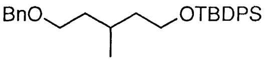
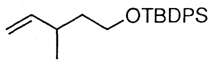
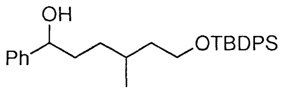
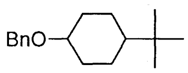
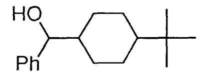
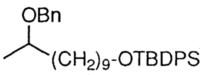
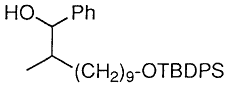
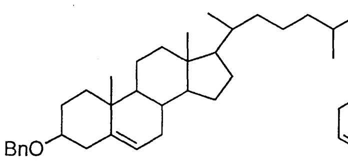
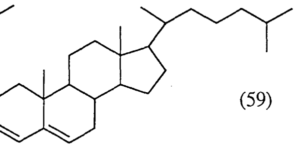
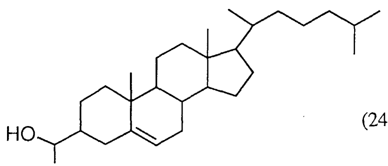
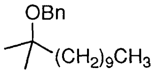
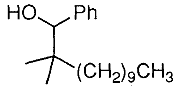
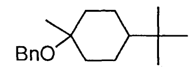
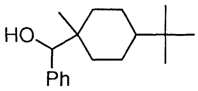
In order to explore the scope and limitation of the olefin formation, the reactions of various alkyl benzyl ethers were examined and the results are summarized in Table 2. Substituents on the β carbon of benzyloxyethyl derivative lower the yield of terminal olefine and increase the ratio of benzyl alcohol produced

Table 1. Reaction of benzylethers with *n*-BuLi

entry	Benzylether	temperature (°C)	Product[a]	yield[b] (%)	recovery of starting material (%)
1	$BnO\text{-}(CH_2)_6\text{-}OTr$	-78[c]	$CH_2{=}CH\text{-}(CH_2)_4\text{-}OTr$	0	87
2	$BnO\text{-}(CH_2)_6\text{-}OTr$	-78~0	$CH_2{=}CH\text{-}(CH_2)_4\text{-}OTr$	73	-
3	$BnO\text{-}(CH_2)_{10}\text{-}OTBDPS$	-78~0	$CH_2{=}CH\text{-}(CH_2)_8\text{-}OTBDPS$	73	-
4	$BnO\text{-}(CH_2)_{10}\text{-}OTHP$	-78~0	$CH_2{=}CH\text{-}(CH_2)_8\text{-}OTHP$	79	-
5	$BnO\text{-}(CH_2)_{10}\text{-}OMOM$	-78~0	$CH_2{=}CH\text{-}(CH_2)_8\text{-}OMOM$	80	-
6	$BnO\text{-}(CH_2)_{10}\text{-}OTBS$	-78~0	$CH_2{=}CH\text{-}(CH_2)_8\text{-}OTBS$	90	-
7		-78~0		83	-
8	$MPMO\text{-}(CH_2)_{10}\text{-}OTBDPS$	-78~0	$CH_2{=}CH\text{-}(CH_2)_8\text{-}OTBDPS$	47	24
9[d]	$BnO\text{-}(CH_2)_6\text{-}OMPM$	-78~0	$CH_2{=}CH\text{-}(CH_2)_4\text{-}OTBDPS$	58	14
10	$AllylO\text{-}(CH_2)_6\text{-}OTBDPS$	-78~0	$CH_2{=}CH\text{-}(CH_2)_4\text{-}OTBDPS$	34	-
11[e]	$BnO\text{-}(CH_2)_6\text{-}OTBDPS$	-78~0	$CH_2{=}CH\text{-}(CH_2)_4\text{-}OTBDPS$	0	54

[a] All the compounds exhibited spectral date consistent with their structures. [b] Isolated yield. [c] The reaction was quenched at -78 °C. [d] 1.5 equivalent of *n*-BuLi was used. [e] Toluene was used as a solvent.

Table 2. Reaction of benzylethers with *n*-BuLi[a]

entry	Benzylether	Elimination product (Yield%)	1,2-Rearrangement product (Yield%)
1		 (64)	 (18)
2		 (14)	—
3		 (79)	 (11)
4		—	 (51)
5		CH$_2$=CH-(CH$_2$)$_9$-OTBDPS (47)	 (36)[b]
6		 (59)	 (24)
7		—	 (61)
8		—	 (20)

[a]All the reaction was performed at -78~0 °C in THF. 3.0 Equivalent of *n*-BuLi was used. [b]syn:anti=1:1.

by [1,2]-Wittig rearrangement (entry 1). γ, δ-Unsaturated benzyl ether gave a complex mixture including a conjugated diene (entry 2). Substituent on the γ carbon did not influence the elimination reaction (entry 3).

So far as reported in the literature, only [1,2]-Wittig rearrangement takes place in the case of benzyl ethers of secondary alcohols.[4] However, as can be seen from entries 5 and 6, in the case of benzyl ethers of secondary alcohols, the elimination reaction took place in some extent together with [1,2]-Wittig rearrangement. Application of the reaction to benzyl ether of tertiary alcohols resulted in the formation of a complex mixture, from which benzyl alcohols were obtained in moderate yield (entry 7, 8).

In conclusion, we developed a simple method for the conversion of primary alcohols into terminal olefins without using a toxic and bad-smelling selenium reagent.

Typical experimental procedure: (Table 1, entry 6) To a solution of 1-benzyloxy-10-(*tert*-butyldimethylsiloxy)-decane (216 mg, 0.57 mmol) in THF (5.0 ml) was added *n*-BuLi (1.09 ml of 1.57 M *n*-hexane solution, 1.71 mmol) at -78 ˚C under argon. After stirring at -78 ˚C for 30 min, the resulting yellow solution was allowed to warm to 0 ˚C and quenched by adding saturated aqueous ammonium chloride solution (1.0 ml). The reaction mixture was extracted with ethyl acetate (50 ml) and the extract was washed with saturated ammonium chloride and brine and dried over sodium sulfate. Evaporation of the solvent gave a residue, which was purified by column chromatography to yield 10-(*tert*-butyl-dimethylsiloxy)-1-decene (138 mg, 90%). ^{13}C NMR (50 MHz, CDCl$_3$): δ 139.09, 114.09, 63.28, 33.84, 32.91, 29.51, 29.42, 29.12, 28.96, 26.00, 25.82, 18.38. ^{1}H NMR (200 MHz, CDCl$_3$): δ 5.87-5.70 (1H, m), 4.94-4.89 (2H, m), 3.60 (2H, t, *J*=6.4 MHz), 2.08-1.98 (2H, m), 1.54-1.30 (12H, m), 0.90 (9H, s), 0.05 (6H, s). FTIR (neat): 3078, 2950, 1641 cm^{-1}.

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References and Notes

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