Novel Synthesis of Enol Ethers from β-Alkoxy Alcohols through *t*-BuOK-Promoted Elimination Reaction

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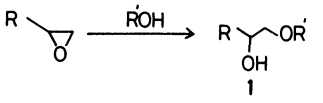
Synopsis. A new synthesis of enol ethers from β-alkoxy alcohols was achieved through a *t*-BuOK-promoted elimination reaction.

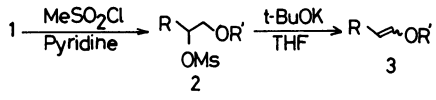
It was not until recently that enol ethers proved to be synthetically useful intermediates and accordingly so much attention has not been paid for their efficient synthetic methods.[1] Previously, we have demonstrated a new route via *t*-BuOK-promoted elimination of a phenylsulfinyl or phenylsulfonyl group from α-methoxy sulfoxides or sulfones.[2] Here we wish to describe another route starting from β-substituted alcohols.

We have already disclosed the practical ring opening of epoxides by alcohols with the aid of organotin phosphate condensate catalysts (Eq. 1).[3] The reaction



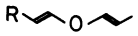
1 (1)

proceeds under neutral conditions with an excellent regioselectivity so that a wide variety of the β-alkoxy alcohols **1** are now accessible. In the development of synthetic applications of these compounds, we have achieved an effective route to enol ethers which has recourse to a *t*-BuOK-promoted elimination reaction of the corresponding mesylates **2** (Eq. 2).



2 3 (2)

Treatment of **1**[4] with methanesulfonyl chloride in pyridine at room temperature delivered **2** in quantitative yields. β-Alkoxy mesylates thus obtained were exposed to five equiv of *t*-BuOK in THF at room temperature or under reflux. The reaction proceeded smoothly to give various types of enol ethers **3** in good yields. The results are summarized in Table 1. It should be noted that the allyloxy derivative suffered from substantial contamination of 1-propenyl ether **4** under analogous reaction conditions due to the base-catalyzed isomerization of the allyl ether. The difficulty, however, was overcome by decreasing the amount of employed *t*-BuOK (1 equiv) along with employment of one equiv of 18-crown-6. As a whole, the present procedure has established a new method for transformation of epoxides to enol ethers.



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Experimental

Preparation of β-Alkoxy Mesylates 2 (Typical Procedure). A pyridine solution (10 cm³) of 2-hydroxypropyl octyl ether[3] (1.24 g, 6.60 mmol) and methanesulfonyl chloride (903 mg, 7.90 mmol) was stirred at room temperature for 12 h. The reaction mixture was extracted with ether-water and the ethereal layer was washed with water repeatedly. Drying ($MgSO_4$), evaporation, and column chromatography (silica gel, 50:1 hexane-ethyl acetate) gave 2-(methylsulfonyloxy)-propyl octyl ether (1.58 g, 90%): ^{1}H NMR (CCl_4) δ=0.87 (br t, 3H), 1.07—1.77 (m, 15H), 2.88 (s, 3H), 3.20—3.53 (m, 4H), and 4.47—4.97 (m, 1H).

Synthesis of Enol Ethers 3 (Typical Procedure). A THF solution (10 cm³) of 2-(methylsulfonyloxy)propyl octyl ether (266 mg, 1 mmol) and *t*-BuOK (561 mg, 5 mmol) was heated at reflux for 2 h. The reaction mixture was extracted with ether-water. The organic layer was dried ($MgSO_4$) and evaporated. The residual oil was distilled (120 °C/4660 Pa, Kugelrohr bath temperature) to give 1-octyloxy-1-propene (128 mg, 75%, *E*/*Z*= 62:38): ^{1}H NMR ($CDCl_3$) δ=0.89 (t, 3H, *J*=7.1 Hz), 1.14—1.44 (m, 12H), 1.54 (dd, 1.86H, *J*=6.7 and 1.7 Hz), 1.57 (dd, 1.14H, *J*=6.7 and 1.7 Hz), 3.47—3.77 (m, 2H), 4.34 (dq, 0.38H, *J*=6.4 and 6.7 Hz), 4.73 (dq, 0.62H, *J*=12.6 and 6.7 Hz), 5.89 (dq, 0.38H, *J*=6.4 and 1.7 Hz), and 6.18 (dq, 0.62H, *J*=12.6 and 1.7 Hz); MS *m*/*z* 170 (M^+) and

Table 1. Conversion of the Mesylates **2** into Enol Ethers **3**[a]

R	R′	Reaction		Product	
		Temp	Time/h	Yield/%	E:Z[b]
CH_3	C_8H_{17}	Reflux	2	75[c]	62:38
	$PhCH_2$	Reflux	12	74[c]	63:37
C_6H_{13}	CH_3	Reflux	1	74[d]	79:21
	$PhCH_2$	Rt	1	70[d]	71:29
$C_{10}H_{21}$	CH_3	Reflux	1	75[d]	67:33
	$PhCH_2$	Reflux	1	68[d]	63:37
	CH_2=$CHCH_2$	Rt	12[e]	66[d]	73:27
$(CH_3)_2C$=$CH(CH_2)_2$	$PhCH_2$	Reflux	2	69[d]	71:29

a) Five equiv of *t*-BuOK was employed unless otherwise noted. b) Determined on the basis of ^{1}H NMR spectra. c) Purified by means of distillation. d) Purified by means of column chromatography on silica gel. e) Each one equiv of *t*-BuOK and 18-crown-6 was added.

171 (M^++1). Found: C, 77.44; H, 13.09. Calcd for $C_{11}H_{22}O$: C, 77.58; H, 13.02.

1-Benzyloxy-1-propene (E/Z=63:37): ^1H NMR ($CDCl_3$) δ=1.44—1.71 (m, 3H), 4.31-5.01 (m, 3H), 5.98 (dt, 0.37H, J=7.1 and 1.4 Hz), 6.28 (dt, 0.63H, J=12.8 and 1.6 Hz), and 7.27 (br s, 5H); MS m/z 148 (M^+). Found: C, 81.35; H, 8.01. Calcd for $C_{10}H_{12}O$: C, 81.04; H, 8.16.

1-Methoxy-1-octene (E/Z=79:21): ^1H NMR ($CDCl_3$) δ= 0.89 (t, 3H, J=7.1 Hz), 1.07—1.46 (m, 8H), 1.71—2.09 (m, 2H), 3.46 (s, 2.37H), 3.54 (s, 0.63H), 4.31 (dt, 0.21H, J=7.1 and 6.3 Hz), 4.70 (dt, 0.79H, J=12.6 and 7.1 Hz), 5.80 (dt, 0.21H, J=6.3 and 1.4 Hz), and 6.23 (dt, 0.79H, 12.6 and 1.3 Hz); MS m/z 142 (M^+). Found: C, 75.85; H, 12.98. Calcd for $C_9H_{18}O$: C, 76.00; H, 12.75.

1-Benzyloxy-1-octene (E/Z=71:29): ^1H NMR ($CDCl_3$) δ=0.86 (t, 3H, J=7.1 Hz), 1.00—1.45 (m, 8H), 1.63—2.26 (m, 2H), 4.20—4.97 (m, 3H), 5.94 (dt, 0.29H, J=6.3 and 1.6 Hz), 6.27 (dt, 0.71H, J=12.6 and 1.2 Hz), and 7.30 (br s, 5H); MS m/z 218 (M^+). Found: C, 81.53; H, 10.65. Calcd for $C_{14}H_{22}O$: C, 81.50; H, 10.75.

1-Methoxy-1-dodecene (E/Z=67:33): ^1H NMR ($CDCl_3$) δ=0.87 (t, 3H, J=7.1 Hz), 1.01—1.54 (m, 16H), 1.69—2.17 (m, 2H), 3.46 (s, 2.0H), 3.54 (s, 1.0H), 4.31 (dt, 0.33H, J=7.4 and 6.9 Hz), 4.70 (dt, 0.67H, J=12.6 and 7.1 Hz), 5.83 (dt, 0.33H, J=6.9 and 1.7 Hz), and 6.23 (dt, 0.67H, J=12.6 and 1.5H); MS m/z 198 (M^+). Found: C, 78.46; H, 13.50. Calcd for $C_{13}H_{26}O$: C, 78.72; H, 13.21.

1-Benzyloxy-1-dodecene (E/Z=63:37): ^1H NMR ($CDCl_3$) δ=0.87 (t, 3H, J=6.3 Hz), 1.09—1.40 (m, 16H), 1.75—2.20 (m, 2H), 4.20—5.00 (m, 3H), 5.94 (dt, 0.37H, J=6.3 and 1.4 Hz), 6.27 (dt, 0.63H, J=12.6 and 1.4 Hz), and 7.31 (br s, 5H); MS m/z 274 (M^+). Found: C, 83.00; H, 11.22. Calcd for $C_{19}H_{30}O$: C, 83.15, H, 11.02.

1-Allyloxy-1-dodecene (E/Z=73:27): ^1H NMR ($CDCl_3$) δ=0.88 (t, 3H, J=7.1 Hz), 1.14—1.43 (m, 16H), 1.74—2.17 (m, 2H), 4.19 (m, 2H), 4.34 (dt, 0.27H, J=7.1 and 6.6 Hz), 4.79 (dt, 0.73H, J=12.6 and 7.4 Hz), 5.06—5.41 (m, 2H), 5.67—6.07 (m, 1.27H), and 6.17 (dt, 0.73H, J=12.6 and 1.3 Hz); MS m/z 224 (M^+). Found: C, 80.51; H, 12.44. Calcd for $C_{15}H_{28}O$: C, 80.29; H, 12.58.

1-Benzyloxy-6-methyl-1,5-heptadiene (EE/ZE=71:29): ^1H NMR ($CDCl_3$) δ=1.58 (s, 3H), 1.67 (s, 3H), 1.81—2.23 (m, 4H), 4.26—5.23 (m, 4H), 5.95 (dt, 0.29H, J=6.1 and 1.4 Hz), 6.30 (dt, 0.71H, J=13.0 and 1.1 Hz), and 7.27 (br s, 5H); MS m/z 216 (M^+). Found: C, 83.54; H, 9.22. Calcd for $C_{15}H_{20}O$: C, 83.29; H, 9.32.

References

1) For the most recent studies on this subject: J.-M. Vatele, *Tetrahedron Lett.*, **25**, 5997 (1984); G. M. McGarvey, M. Kimura, and A. Kucerovy, *ibid.*, **26**, 1419 (1985).

2) T. Mandai, K. Hara, T. Nakajima, M. Kawada, and J. Otera, *Tetrahedron Lett.*, **24**, 4993 (1983).

3) J. Otera, Y. Yoshinaga, and K. Hirakawa, *Tetrahedron Lett.*, **26**, 3219 (1985).

4) In the case where the regioisomer is contaminated, **1** can be separated easily by means of column chromatography.