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ELECTROCHEMICAL PROCEDURE DIRECTED TO THE SELECTIVE RING OPENING OF EPOXIDES TO ALLYLIC ALCOHOLS

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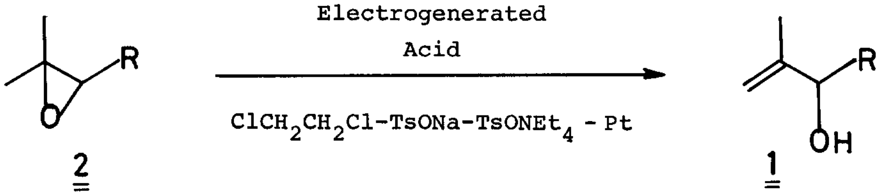
Summary: A transformation of epoxides 2 into allylic alcohols 1 was achieved by an electrogenerated acid-catalysis in a $ClCH_2CH_2Cl$ - TsONa - $TsONEt_4$ - Pt system.

Allylic alcohols 1 are useful synthetic intermediates for terpenoids. Many attempts on the transformation of 2 into 1 have been made by a base-catalyzed 1,2-elimination with $LiNR_2$,[1] and t-BuOK,[2] and by specially deviced Lewis acid-type catalysts with aluminium (DATMP),[3] boron (9-BBNOTf),[4] silicon (TMSOTf),[5] and titanium $[Ti(O\text{-}i\text{-}Pr)_4]$.[6] The use of Al_2O_3,[6,7] Li_3PO_4,[8] and H_2SO_4[9] has also been proposed although the yield of 1 is not necessarily satisfactory. Meanwhile, the conventional acid-catalyzed reaction of 2 mostly leads to the predominant formation of ketones 3 rather than 1. We have deviced an electrochemical method specifically directed to the selective transformation (2 → 1) in a $ClCH_2CH_2Cl$-TsONa-$TsONEt_4$-Pt system.



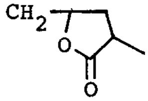
2 1

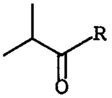
A typical electrolysis procedure is as follows; A solution of TsONa (0.5 mmol), $TsONEt_4$ (0.6 mmol) in a distilled $ClCH_2CH_2Cl$ (DCE) (40 ml) was electrolyzed using Pt foil electrodes (1.5 x 2 cm^2) (2.7 mA/cm^2, for 2 h, 0.3 F/mol). Then 2a (524 mg, 2 mmol) was added to the electrolyzed solution and was allowed to react at room temperature for 1 h, and electrolyzed again (1 h, 0.15 F/mol) and stirred for additional 4 h, affording 1a (74%) and ketone 3a (7%) along with recovered 2a (13%). On the other hand, the reaction of 2a with TsOH gave 1a (53%) and 3a (47%), while BF_3 etherate led to exclusive formation of 3a (77%). Trisubstituted epoxides 2a - 2f provided 1a - 1f in reasonable yields. Epoxide of pulegone gave the allylic alcohols 4, a precursor of menthofuran, in 78% yield.

Electrolyte intensively affects the reaction pathway. The use of tosylate ion in DCE is essential for the selective transformation (2 → 1). Thus, a DCE-TsONa-$TsONEt_4$-Pt system exclusively leads to the desired alcohol 1a (74%), while a DCE-$TsONEt_4$-Pt (65%). However, perchlorates and $LiBF_4$ in DCE promoted the preferencial formation of 3a rather than 1a;

[1a and 3a (%): 2% and 91% (LiClO$_4$), 6% and 90% (NaClO$_4$), 3% and 87% (Et$_4$NClO$_4$), 28% and 50% (LiBF$_4$)]. The use of Et$_4$NBr resulted in a recovery of 2a. In contrast to the facile conversion (2 → 1) with TsONa in DCE, the reaction proceeded slowly and gave moderate yields of 1a in THF-DCE (48%), AcOEt-DCE (50%), and MeCN (53%), while the use of MeOH resulted in a recovery of 2a.

The ring opening of epoxides 2 would be initiated by the electrogenerated acid-catalyst.[10] The incipient carbenium ion would be bonded or tightly ion-paired with tosylate anion in non-polar solvent like DCE and subsequently converted to 1 *via* elimination as shown in 5. In fact, the tosylate (8%) from 2a was isolated in the low temperature reaction (5 °C). Therefore, in contrast to the successful transformation of acyclic epoxides, epoxides of cyclic olefins such as limonene (products 6a - 6c) and α-pinene (products 7 and 8) yielded scarcely the desired alcohols 1 because of the unfavorable conformation of 5 for the elimination.[11]

1 R:	a	$(CH_2)_2CH(Me)CH_2CH_2OCH_2Ph$	(74%)
	b	CH_2OPh	(83%)
	c	$(CH_2)_2C(Me)(OAc)C\equiv CH$	(70%)
	d	$(CH_2)_2C(Me)=CHCH_2OAc$	(73%)
	e	$(CH_2)_2C(Me)=CHCH_2SO_2Ph$	(81%)
	f		(81%)



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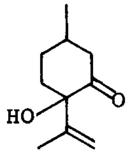
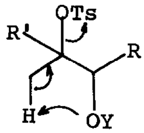
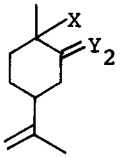
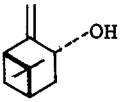


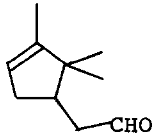
4 (78%)







7 (18%)



8 (45%)

5 Y= Na, Et$_4$N

6a	X=OH,	Y=H,	OTs	(17%)
b	Cl	H,	OH	(49%)
c	H	O,	O	(32%)

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