## OXIDATIVE CLEAVAGE OF B,Y- UNSATURATED ETHER

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(Received in Japan 2 June 1970; received in UK for publication 9 June 1970)

The hydrolytic cleavage of allyl ether has hitherto been performed by two suscessive steps, i.e., allyl ether is first isomerized<sup>1)</sup> to the corresponding propenyl ether, which is then hydrolyzed<sup>2)3)</sup>.

The communication describes a single step procedure of the oxidative cleavages of allyl and propargyl ethers by selenium dioxide.

Aryl allyl ether and alkyl allyl ether are readily splitted to produce phenolic and alcoholic products, respectively. The allyl ether group is converted into acrolein.

$$R-O-CH_2 CH=CH_2 \xrightarrow{SeO_2} R-OH + CH_2 = CHCHO$$
(1)  
in AcOH

A mixture of an allyl ether (0.1 mole), SeO<sub>2</sub> (0.11 mole) and acetic acid (0.15 mole) in dioxane (50 ml, solvent) was heated under reflux for 1 hr. The reaction mixture was then filtered in order to remove insoluble material. Evaporation of the filtrate gave the hydroxyl product of eq. (1). The results are illustrated in Table 1.

Usually, selenium dioxide is known to oxidize phenolic compounds<sup>4</sup>. Under the present reaction conditions, however, no oxidation of the phenolic product takes place. These findings impley that the allyl etherification of phenol is conveniently employed for the purpose of a tentative protection of phenolic hydroxyl group.

After the reaction upon aryl allyl ether, the corresponding phenolic compound is generated by this procedure.

R in eq. (1)	Yield of ROH	(%) <sup>b)</sup>
С, Н, –	57	
2-Me,C6H4-	41	
3-CF3 C6 H4 -	44	
3-Me,4-Cl-C <sub>6</sub> H <sub>3</sub> -	54	
2-NQ2,4-C1-C6H3-	52	
2-MeO, 5-CHO-C <sub>6</sub> H <sub>3</sub> -	50	
2-Me0,4-COOMe,5-NO <sub>2</sub> -C <sub>6</sub> H <sub>2</sub> -	51	
	38	
C <sub>6</sub> H <sub>5</sub> CH <sub>2</sub> -	50	

Table 1. Oxidative Cleavage of Allyl Ethers. a)

a) The reaction conditions are given in the text.

b) When the recovery is deducted from the starting material, the yield of ROH increase to nearly quantitative.

This procedure is applied to other  $\beta$ , Y-unsaturated ethers. For example, methyl cinnamyl ether was cleavaged to cinnamyl aldehyde (66 % yield, isolated as phenyl semicarbazone) and methanol.

The oxidative cleavage may be explained by the following scheme which contains the corresponding hemiacetal of acrolein (2) as an intermediate.

$$R-O-CH_2-CH=CH_2 \xrightarrow{SeO_2} R-O-CHCH=CH_2 \xrightarrow{R-OH} R-OH + CH_2 = CHCHO (2)$$
in AcOH OH

The similar reaction took place in propargyl ether, too. 3-Methyl-4chlorophenyl phenylpropargyl ether was cleaved to phenylpropargylaldehyde (35 % yield)<sup>5)6)</sup> and 4-chloro-m-cresole. Generation of phenolic compound from aryl propargyl ether is even more efficient as is shown in Table 2.

Table 2. Oxidative Cleavage of Aryl Propargyl Ethers. a)

SeO<sub>2</sub>

$Ar - O - CH_2 C = CH \longrightarrow AcOH$	Ar-OH + CH=C-CHO	
Ar	Yield of Ar-OH (%) b)	
C <sub>6</sub> H <sub>5</sub> -	79	
3-CF3 -C6 H4 -	62	
3-Me,4-Cl-C <sub>6</sub> H <sub>3</sub> -	66	
2-MeO,4-CHO-C <sub>6</sub> H <sub>3</sub> -	72	

a) The reaction conditions are the same as that for allyl ethers.

b) When the recovery is deducted from the starting material, the yields of ROH increase to nearly quantitative.

The authors wish to thank Professor T. Saegusa, Kyoto University for his helpful discussion.

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