Synthetic Methods and Reactions; 68[1]. Nafion-H-Catalyzed Hydration and Methanolysis of Epoxides

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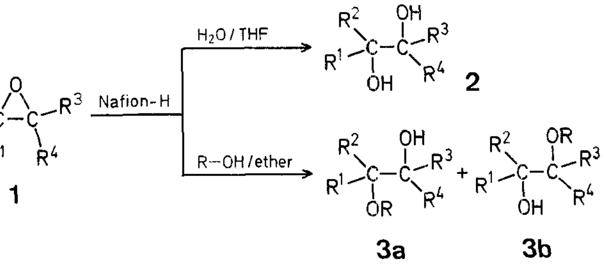
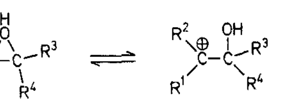
Acid-catalyzed ring-opening reactions of 1,2-epoxides are abundant[2,3,4], including polymerization, as well as those related to biological systems[5,6]. In most of the described epoxide openings, higher temperatures were required, and frequently extensive polymerization also occurred. More recently, displacement reactions, including those of epoxides effected by dehydrated alumina surfaces have been reported[7]. However, the preparation and handling of the catalyst is somewhat inconvenient, and reactions were of limited scope.

We report now that Nafion-H perfluorinated resinsulfonic acid catalyst, is able to catalyze epoxide ring-opening reactions, combining the high acidity required with the advantages of a solid catalyst. It provides a very simple work-up and product isolation upon completion of the reactions. The catalyst can be readily regenerated for further use without loss of activity. The method allows the reactions to be carried out under mild conditions, without heating of the reaction mixtures. Generally high yields are obtained.



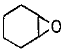
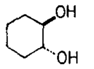
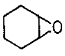
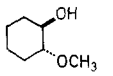
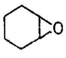
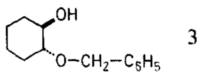
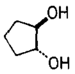
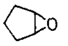
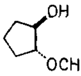
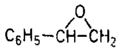
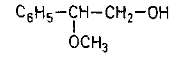
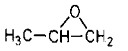
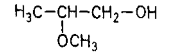
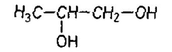
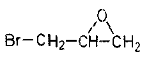
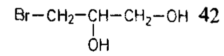
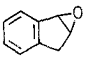
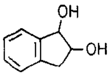
The nucleophilic ring-opening reactions are considerably accelerated by the solid acid catalyst due to the reversible formation of the reactive conjugated acids of the epoxides, i.e. the epoxonium ions.



The influence of the electronic character of the R-group further determines the products formed in the ring-opening reaction. The initial epoxonium ion formed is in equilibrium with a secondary β-hydroxy carbenium ion, which is significantly stabilized when benzylic in nature. Thus, the only product formed from styrene oxide is 2-phenyl-2-methoxyethanol. In the case of propylene oxide, a mixture of the primary and secondary alcohols was obtained, although the reaction tends to favor a S_N1 type pathway formation of the secondary alcohols (*sec*-R—OH/*prim*-R—OH = 88:12). The use of catalytic amounts of sulfuric acid or boron trifluoride in similar reactions, likewise, causes formation of such mixtures[8,9,10].

The Nafion-H catalyzed hydration and methanolysis of cyclohexene oxide and cyclopentene oxide gives only *trans* isomers. Since the fusion of the epoxide and cyclohexane (cyclopentene) rings can only be *cis*, the formation of *trans* products from the epoxide opening reactions signifies inversion. This is in accordance with the previous observation[7,11,12]. Moreover, studies of

Table. Nafion-H Catalyzed Hydration and Alcoholysis of Epoxides[a,b]

Epoxide	Nucleophile/ Solvent	Reaction time [h]	Products[c]	Yield[d] [%]	m.p. or b.p./torr [°C]		Results reported in Literature		
					found	reported	Yield [%]	Reaction conditions	Ref.
	H_2O/THF	2		73	101–104°/760	102.5–104.5°[14]	—	$H^{\oplus}/H_2O$	[11]
	CH_3OH/ether	2		74	81–83°/12	72.5–73.2°/10[15]	66	25 °C/1 h	[7]
	$C_6H_5-CH_2-OH$	3		37	122–124°/5	100–112°/0.3[20]	40	25°/1 h	[7]
	H_2O/THF	2		80	92–93°/2	93°/2[16]	—	$H^{\oplus}/H_2O$	[11]
	CH_3OH	2		77	81–83°/10	175°/760[17]	—	$H^{\oplus}/CH_3OH$	[11]
 $C_6H_5-\overbrace{CH-CH_2}^{O}$	CH_3OH/ether	2	 $C_6H_5-\underset{OCH_3}{CH}-CH_2-OH$	81	115°/9	134°/30 or 79°/2[18]	42	H_2SO_4 (conc), reflux, 15 min	[18]
 $H_3C-\overbrace{CH-CH_2}^{O}$	CH_3OH/ether	2	 $H_3C-\underset{OCH_3}{CH}-CH_2-OH$	66 88	126–129°/760	129–130°/760[10]	69	H_2SO_4, reflux, 16 h	[10]
			 $H_3C-\underset{OH}{CH}-CH_2-OH$	*12*	*118–120°/760*	*119°/760*[10]			
 $Br-CH_2-\overbrace{CH-CH_2}^{O}$	H_2O/THF	4	 $Br-CH_2-\underset{OH}{CH}-CH_2-OH$	42	80°/0.03	90°/0.8[19]			
	H_2O/THF	2		81	92–93°			$H^{\oplus}/H_2O$	[11]

[a] Reactions were carried out at 20 °C, with the only exception at 0 °C, when benzyl alcohol was used as a nucleophile.
[b] Catalytic amount of Nafion-H (1 g) was used in all reactions.
[c] Product purity was found to be ≥97% by I.R. and ^{1}H-N.M.R. analysis.
[d] Yield of isolated product.

the hydration of epibromohydrin indicated no products derived from neighboring-group participation[13].

In view of the high yields and mild reaction conditions, the presently described new hydration and methanolysis of epoxides should find use in organic synthesis.

Nafion-H Catalyst:

Nafion-K[21] (DuPont) resin (50 g) is stirred in boiling deionized water (150 ml) for 1 h. After decanting the water, the resin is stirred in 25% nitric acid (200 ml) at room temperature for 2 h. The nitric acid is decanted and replaced by a fresh portion of nitric acid. This step is repeated 3 times. Subsequently, the mixture, stirred in nitric acid, is allowed to stand overnight. The solid acid catalyst (Nafion-H) is filtered and dried at 105 °C for two days until a constant weight is achieved.

Regeneration of Catalyst:

After filtration, the catalyst is washed successively with acetone and deionized water, then dried overnight at 105 °C. Repeating the reaction of epoxides with the regenerated catalyst gave identical results with those using freshly activated catalyst.

***trans*-1,2-Cyclohexanediol; Typical Procedure:**

Over a period of 20 min, a solution of cyclohexene oxide (1.96 g, 20 mmol) in dry tetrahydrofuran (10 ml) is slowly added to a stirred mixture of Nafion-H (1 g) and deionized water (1 g). After keeping the reaction mixture for 2 h at room temperature, it is filtered and the solvent evaporated. The pure diol is obtained by recrystallization from toluene; yield: 1.8 g (78%); m.p. 101–104.5 °C [correct microanalysis].

Methanolysis of Propylene Oxide; Typical Procedure:

A solution of propylene oxide (1.16 g, 20 mmol) in dry ether (10 ml) is slowly added to a stirred mixture of Nafion-H (1 g) and anhydrous methanol (1.12 g, 35 mmol) over a period of 30 min. After keeping the reaction mixture for 2 h at room temperature, it is filtered, the solvent evaporated, and the residue fractionally distilled to give two products.

1-Methoxy-2-propanol; yield: 1.13 g (70%); b.p. 118–120 °C/760 torr.

2-Methoxy-1-propanol; yield: 0.15 g (9.5%); b.p. 126–129 °C/760 torr.

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