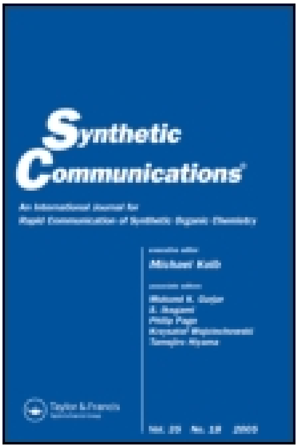

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Highly Regioselective Ring Opening of Epoxides with Polymer Supported Phenoxide and Naphthoxide Anions

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Highly Regioselective Ring Opening of Epoxides with Polymer Supported Phenoxide and Naphthoxide Anions

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ABSTRACT

Amberlite IRA-400 supported phenoxide and naphthoxide anions are easily prepared. These polymer supported reagents that are highly air stable are used for the regioselective ring opening reactions of different epoxides to give aryl ether alcohols in high yields under mild reaction conditions.

Key Words: Functionalized polymer; Polymer supported phenoxides; Polymer supported naphthoxide; Aryl-ether alcohols; Epoxide.

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1. INTRODUCTION

Polymeric reagents have proven useful for many chemical transformations in organic synthesis.[1] Among the advantages of polymer supported reagents are easy work-up, reuse of the supported reagent after regeneration, and clean reaction condition.

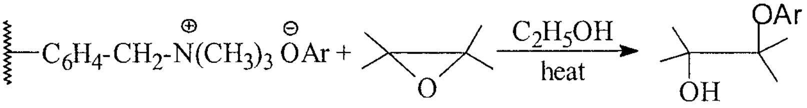
The ring opening reaction of epoxides by nucleophiles is an interesting approach in organic synthesis.[2] and it has been performed by a variety of nucleophiles generally with the use of metal containing catalyst systems, Ref.[3] or very recently reported, by the use of a polymeric phase transfer catalyst.[4–6]

There are a few reports in the literatures on the ring opening of epoxides with phenols and naphthols.[7] The reactions usually occur in the presence of tertiary amines or under alkaline conditions in aqueous media at high temperature. The use of micellar media for the reaction of epoxides with phenoxide anion catalyzed by ceric triflate catalyst has been reported very recently.[8]

As far as we know, there has been no report in the literature on the use of polymer supported phenoxide and naphthoxide anions for the ring opening of epoxides. Here, we report a very simple and efficient method for the regioselective ring opening of epoxides with Amberlite IRA-400 (ArO^-, Ar=Ph, naphthyl) in high yields under nonaqueous condition avoiding the use of any catalyst and bases (Sch. 1).

2. RESULTS AND DISCUSSION

The Amberlite IRA-400 phenoxide or naphthoxide anion resin was easily prepared by the reaction of Amberlite IRA-400 (Cl^- form) with aqueous sodium salt of different substituted phenols or naphthol. Unlike the ordinary phenoxides or naphthoxides that are air sensitive and should be prepared just prior to their use, these polymer supported counterparts are highly air stable and can be kept for months without any oxidation. The polymer supported anions were used for the regioselective ring opening of different epoxides. The effects of solvent and molar ratio of the polymer on the ring opening reaction of epoxides were investigated. The reactions were carried



Scheme 1.

out in benzene, acetonitrile, dichloromethane, and ethanol. The experimental results showed that ethanol was the most suitable solvent. The optimum molar ratio of polymer supported phenoxide or naphthoxide to the epoxide was found to be 3 : 1. The used polymeric reagents can be regenerated and used several times without any decrease in their reactivity. In addition, the use of polymer supported phenoxides carrying electron-withdrawing group can also be performed without difficulty.

Except for the reaction of styrene oxide, which produced some of the other regio-isomer (Table 1, entry 1) as a side product, the reaction of other epoxides were found to be highly regioselective and only one isomer was obtained (Table 1). In the case of cyclohexene oxide, trans-product was produced. Obviously, in these reactions, the attack appears to be largely at the primary carbon atom of the epoxide ring and this is probably dictated by steric and electronic factors. The results obtained for the ring opening of different substituted epoxides with the polymer supported phenoxide and naphthoxide ions are shown in Tables 1 and 2.

The advantages of using these air stable polymer supported phenoxides or naphthoxide for the ring opening of epoxides over other methods reported in the literature are nonaqueous and neutral reaction conditions, no catalyst used, easy reaction work-up, and the regeneration and reuse of the polymeric reagent.

3. EXPERIMENTAL

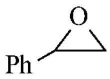
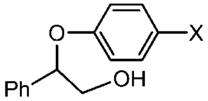
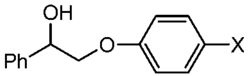
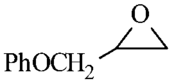
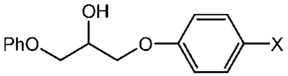
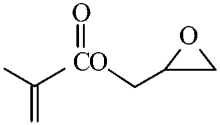
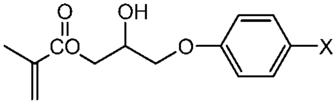
3.1. Material and Techniques

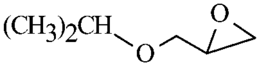
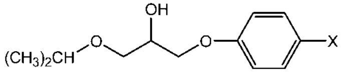
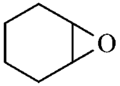
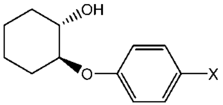
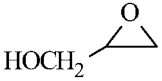
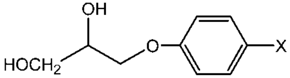
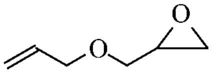
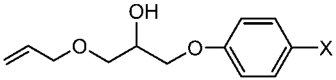
Products were characterized by the comparison of their physical data with those of known samples. Gas chromatography was recorded on a Shimadzu GC 14-A. IR spectra were recorded on Perkin Elmer 781 spectrometers. ^{1}H and ^{13}C NMR spectra were recorded on Bruker DPX 250.

3.2. Preparation of Polymer Supported Aryloxides

Commercially available Amberlite IRA-400 (Cl^- form) placed in a column was washed by an aqueous sodium salt of phenol or β-naphthol (0.25 N) until complete removal of Cl^- ions ($AgNO_3$ test). Then, the resin was successively washed with water, ethanol, and ether until the excess of aryloxide anion was removed (alcoholic $FeCl_3$ test). The resin was finally dried over anhydrous phosphorous pentoxide for 10 hr under vacuum at 50°C. The exchange capacity was determined by passing 1 M aqueous

Table 1. Reaction of epoxides with Amberlite IRA-400 supported X–$C_6H_5O^-$ in ethanol.[a]

		Time (hr)				Yield (%)[c]		
Entry	Epoxide	X = H	X = Cl	X = CH_3	Product[b]	X = H	X = Cl	X = CH_3
1		1	2	1.5		38	30	37
						57	55	60
2		1.5	2	1.5		90	80	93
3		1.5	2	1.5		93	82	95

4		1.5	2	1.5		95	85	96
5		1	2	1.5		87	80	90
6		1	2	1.5		90	85	92
7		1	2	1.5		95	85	96

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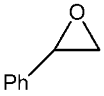
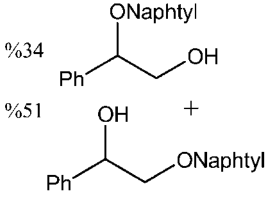
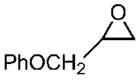
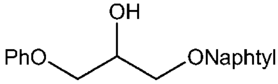
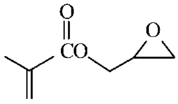
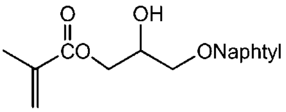
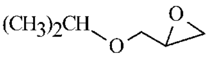
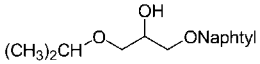
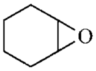
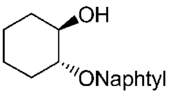
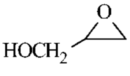
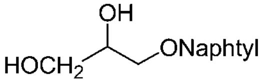
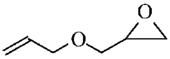
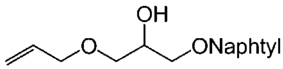
[a] Reactions were carried out at 50°C.

[b] Products were identified by comparison of their IR and NMR spectra and/or physical data with the authentic samples.[7d]

[c] Yield refers to an isolated product.

Table 2. Reaction of epoxides with Amberlite IRA-400 supported β-naphthoxide in ethanol.[a]

Entry	Epoxide	Time (hr)	Product[b]	Yield (%)[c]
1		2		85
2		2		80
3		2		82
4		2		85
5		2		85
6		2		80
7		2		85

[a] Reactions were carried out at 50°C.

[b] Products were identified by comparison of their IR and NMR spectra and/or physical data with the authentic samples.[7d]

[c] Yield refers to an isolated product.

sodium chloride (100 mL) through the resin (0.3 g) placed in a column. The amount of aryloxide anion in the eluent was determined by titrating against 0.01 N hydrochloric acid using methyl orange as indicator. The exchange capacity of polymer supported aryloxide anion reagent was found to be in the range of 1.3–1.4 mmol/g of dry resin.

3.3. General Reaction

Amberlite IRA-400 phenoxide (naphthoxide) anion resin (3 mmol), epoxide (1 mmol), and ethanol (10 mL) were stirred at 50°C for 1 hr. Progress of the reaction was followed by TLC and/or GC. After completion of the reaction, the resin was filtered-off and washed with ethanol. The filtrate was dried with sodium sulfate and the solvent evaporated to give high to excellent yield of the product. The regeneration of the used resin can be easily achieved by washing it first with 1 M aqueous sodium chloride and subsequently with sodium aryloxide solution.

ACKNOWLEDGMENT

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