

# Synthesis of Azidohydrins, Nitrohydrins and Nitratohydrins from Epoxides Using Azide, Nitrite and Nitrate Exchange Resins

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## ABSTRACT

Ring opening reactions of epoxides with nucleophiles are very useful approach in organic synthesis for preparation of functionalized oxygenated compounds. Solid-phase synthesis, in particular reactions using polymer supported nucleophiles, have been widely used in organic synthesis mainly because of the ease of separation of products. Thus, as new polymeric reagents, Amberlite IRA-400 supported azide, nitrite and nitrate are introduced as polymeric reagents for efficient and regioselective conversion of epoxides to azidohydrins, nitrohydrins and nitratohydrins in good yields under mild reaction conditions. The advantages of these reagents over some of those reported in the literature, are easy work-up procedure, regeneration of the reagent, clean and neutral reaction conditions. In addition, no catalyst is required for occurrence of the reactions.

### Key Words:

polymer supported nucleophiles;  
azidohydrin;  
nitrohydrin;  
nitratohydrin;  
epoxides.

### INTRODUCTION

Epoxides are versatile intermediates in organic synthesis and their reactions with variety of reagents such as, electrophiles, nucleophiles, acids, bases, reducing agents, and some oxidizing agents are widely studied [1].

Ring opening reactions of epox-

ide with nucleophiles are considered as an interesting approach in organic synthesis of many functionalized oxygenated compounds. The reaction with nucleophiles such as oxygen compounds (water, alcohols, phenols) [2-6], nitrogen compounds

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(amine and derivatives of amines, azide, nitrate, isocyanate) [7-9], halides [10], and various carbon nucleophiles [11] have been performed in both organic and aqueous solvents.

Since the  $\beta$ -amino alcohols are very important in both organic and medical chemistry [12], the ring cleavage of epoxides with azide [13] and nitro compounds [14] presents an effective synthetic route of  $\beta$ -amino alcohols. The ring cleavage reaction of epoxides with azide compounds are often carried out under either alkaline or acidic conditions and several different methods have been devised in order to obtain the direct azidolysis of epoxides in the presence of sodium azide [7,15]. Usually these conditions require high temperatures and/or long reaction times, and as side reactions, isomerizations, epimerization, and rearrangements may be induced by alkaline conditions of the reactions with alkali azides in these systems. Furthermore, several novel methods have been introduced for this kind of transformation, for example, it has been found that sodium azide impregnated on a calcium cation exchange Y-type zeolite (CaY) induced the nucleophilic ring opening of epoxides in aprotic solvents affording azidoalcohols [16]. Other reported reagents are tributyltin azide without solvent and promoter [17], dibutyltin azide in DMF [18], triethylaluminum/hydrogen azide as a mild and efficient reagent for medium to large ring cyclic epoxides [19], diethylaluminum azide for the regio- and stereoselective ring opening of 2,3-epoxyalcohols [20], trimethylsilylazide in the presence of a Lewis acid [21] and also trimethylsilylazide in presence of Cr (salen) [22]. In addition, it has been reported that simple salts, such as lithium or magnesium perchlorate, zinc or lithium triflate, and ammonium chloride can be used as efficient catalysts for the azidolysis of epoxides in acetonitrile [23]. Use of phase transfer catalyst has also been reported for the preparation of azidoalcohols [24]. Polymer supported azide system, as a mild and efficient reagents for promoting the reaction of polycyclic aromatic hydrocarbon epoxides with azides, has also been described [25].

The simple classical method for preparing  $\beta$ -nitroalcohols consists of nucleophilic nitro addition to epoxides. But the cleavage of epoxides by nitro groups is difficult because of low nucleophilicity of nitro groups. The cleavage of epoxides by a system consisting of  $\text{MgSO}_4/\text{NaNO}_2$  in dry MeOH under reflux condition [26] and the use of micellar media for the effi-

cient ring opening of epoxides with  $\text{NO}_2^-$  catalyzed with  $\text{Ce}(\text{OTf})_4$  have been reported [27].

Nitrate containing organic compounds have useful applications in organic synthesis. They are useful reagents for the preparation of important class of nitrate compounds [28] through their reaction with carbanions.  $\beta$ -Nitroalcohols as alkyl nitrates have been prepared in low yields through the reaction of epoxides in concentrated nitric acids [29] or by nitration of haloalcohols [30] with silver nitrate. Recently, the use of Ce (IV) and  $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$  supported on  $\text{SiO}_2$  [31] as catalysts for ring opening of epoxides with nitrate anion was reported.

Polymeric reagents have proven useful for many chemical transformations in organic synthesis [32]. The advantage of polymer supported reagents chiefly lie in the fact that they require no specialized polymer synthesis and purification techniques, thus rendering them simple to use. This coupled with their insolubility, physical stability, compatibility with a wide range of solvents including, in some cases water, and their toleration of a great number of reaction conditions, make them ideal as platforms on which to perform organic synthesis [32]. In addition, many ion-exchange resins, and indeed reagents supported on them, are commercially available and are relatively inexpensive.

There has been extensive growth in the application of polymers incorporated with reactive nucleophilic anions as reagents in organic synthesis. For example, phenoxide containing resin has been successfully employed in the high yield clean conversion of alkyl halide into phenyl ethers [33], and cyanide on Amberlite IRA-400 has been used in the synthesis of nitriles [34]. The immobilization of fluoride anion on Amberlite has proved useful for clean conversion of sulphonyl chlorides to sulphonyl fluorides [35]. The thiocyanate anions have been reported for the transformation of alkyl halides into alkyl cyanates and alkyl thiocyanates [36] and the preparation of benzene sulphinate on Amberlite has been described to be employed in the convenient synthesis of sulphones [37].

As far as we know there has been no report in the literature on the use of polymer supported azide, nitrite and nitrate anions in ring opening reaction of epoxides. Now in continuation of our work on the synthesis and application of polymer supported nucleophiles in organic synthesis [38,39], we report the preparation

and use of Amberlite IRA-400 ( $N_3^-$ ), Amberlite IRA-400 ( $NO_2^-$ ) and Amberlite IRA-400 ( $NO_3^-$ ) as efficient functionalized polymers for conversion of different epoxides into their corresponding  $\beta$ -hydroxy azides,  $\alpha$ -hydroxy nitrites and  $\beta$ -hydroxy nitrates (Scheme I).

## EXPERIMENTAL

### Material and Techniques

Epoxides were purchased from Merck and Amberlite IRA-400( $Cl^-$ ) from Fluka Chemical Companies. Products were characterized by comparison of their physical data with those of known samples[13,26]. Gas chromatography was recorded on a Shimadzu GC 14-A. IR spectra were recorded on a Perkin Elmer 781 spectrometer.  $^1H$  and  $^{13}C$  NMR spectra were recorded on a Bruker DPX 250.

### Preparation of Polymer Supported Nucleophile (Azide, Nitrite and Nitrate)

Amberlite IRA-400 (chloride form) (10 g) was washed several times with distilled water to remove foreign materials. The obtained resin was then stirred in a 20% aqueous sodium salt solution of the nucleophile (100 mL) for 5 min. The mixture was then diluted with distilled water (50 mL) and stirred for additional 5 min, it was then decanted, and washed several times with water until the supernatant liquid gave a negative azide test with ferric nitrate for Amberlite IRA-400 (azide form)[40], with potassium permanganate for Amberlite IRA-400 (nitrite form) and with ferrous ammonium sulphate for Amberlite IRA-400 (nitrate form) [41]. The resin was finally dried over anhydrous  $P_2O_5$  for 5 h under vacuum at 50 C.

The exchange capacity of the resin was determined by passing 1 N sodium chloride solution (100 mL) through the resin(0.3 g) packed in a column. The amount of sodium salt of the nucleophile in the eluent was then titrated with 0.01 normal hydrochloric acid using methyl orange as indicator. The exchange capac-

**Table 1.** Reaction of epoxides with Amberlite IRA-400 supported nucleophile ( $N_3^-$ ,  $NO_2^-$ ,  $NO_3^-$ ) in different solvents.

Entry	Solvent	Time (h)	Average conversion (%)
1	THF	24	20
2	EtOH	15	100
3	$CH_2Cl_2$	24	30
4	$C_6H_6$	24	0
5	$CH_3CN$	24	40
6	$H_2O$	15	50

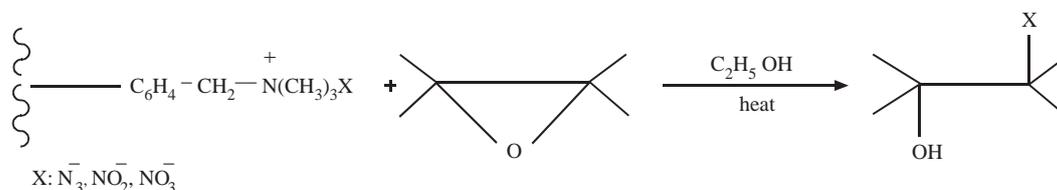
ities of polymer supported nucleophiles were calculated to be 1.0 mmol/g, 1.3 mmol/g and 1.4 mmol/g for polymer supported  $N_3^-$ ,  $NO_2^-$  and  $NO_3^-$ , respectively. The regeneration of the used resins can be easily achieved by washing them first with 1M aqueous sodium chloride and subsequently with 20% aqueous sodium salt solution of the corresponding nucleophile.

### General Procedure for Ring Opening of Epoxides with Polymer Supported Nucleophiles (Azide, Nitrite and Nitrate)

A mixture of Amberlite IRA-400 supported nucleophile resin (3 mmol/g based on the capacity), epoxide (1 mmol) and ethanol (10 mL) was stirred at 50 C for the appropriate time indicated in Table 1. Progress of reaction was followed by T.L.C using carbon tetrachloride-methanol (5:1) as eluent and/or G.C. On completion of the reaction, the resin was filtered off and washed with ethanol. The filtrate was dried with sodium sulphate and solvent evaporated. The product was identified by comparison of its spectral data with that of the known sample. The yields of reactions were 82-96%.

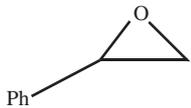
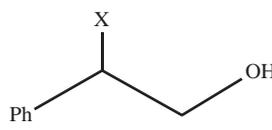
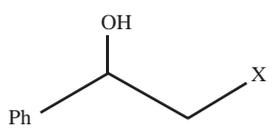
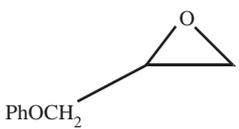
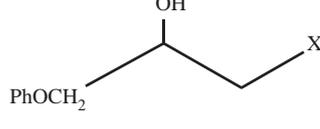
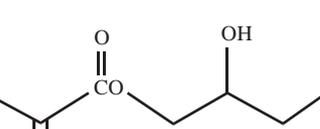
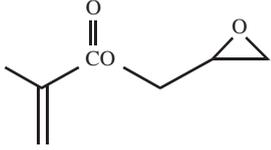
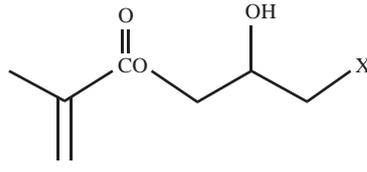
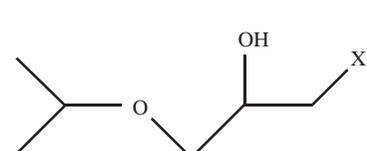
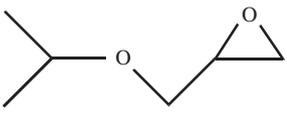
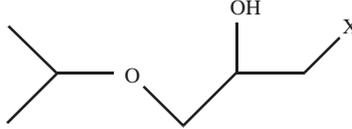
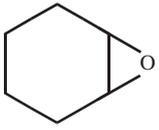
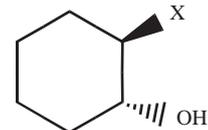
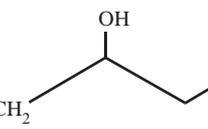
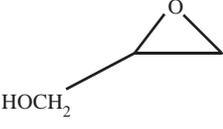
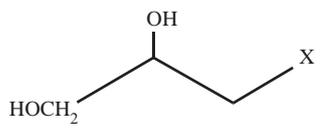
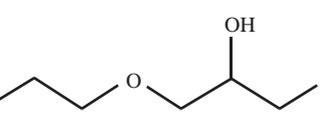
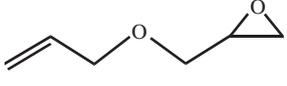
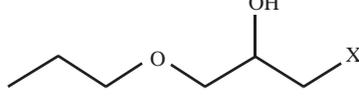
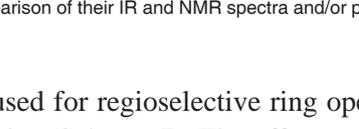
## RESULTS AND DISCUSSION

The Amberlite IRA-400 supported  $N_3^-$ ,  $NO_2^-$  and



Scheme I

**Table 2.** Reaction of epoxides with Amberlite IRA-400 supported nucleophile ( $\text{N}_3^-$ ,  $\text{NO}_2^-$ ,  $\text{NO}_3^-$ ) in ethanol<sup>a</sup>.

Entry	Epoxide	Time (h)			Product <sup>b</sup>	Yield (%) <sup>c</sup>		
		$\text{N}_3^-$	$\text{NO}_2^-$	$\text{NO}_3^-$		$\text{N}_3^-$	$\text{NO}_2^-$	$\text{NO}_3^-$
1		1	2	1.5		30	32	33
								
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
								

(<sup>a</sup>) All of the reactions were carried out at 50°C; (<sup>b</sup>) Products were identified by comparison of their IR and NMR spectra and/or physical data with the authentic samples [13,26]; (<sup>c</sup>) Yield refers to isolated product.

$\text{NO}_3^-$  were easily prepared by the reactions of Amberlite IRA-400 ( $\text{Cl}^-$  form) with aqueous sodium salt of the nucleophiles. The capacities of these polymeric reagents were determined as mmol of the nucleophile per gram of dry resin. The obtained polymers were

used for regioselective ring opening of different epoxides (Scheme I). The effects of different kinds of solvents and molar ratios of these polymeric reagents on the ring opening reactions of epoxides were investigated. The reactions were carried out in tetrahydrofuran,

benzene, acetonitrile, dichloromethane, water and ethanol. The experimental results showed that ethanol was the most suitable solvent (Table 1). Different reactivities of polymer supported nucleophiles in these solvents is presumably due to different swellability of the polymers and solubility of the substrates in the solvents. The optimum molar ratio of polymer to epoxide was found to be 3:1.

Except for the reaction of styrene oxide which produces some of the other regio-isomers as side products, the reactions of other epoxides were found to be highly regioselective and only one isomer was obtained. In the case of cyclohexene oxide as an example of cyclic epoxide, trans product was obtained. Obviously, in these reactions, the attack appears to be largely at the primary carbon atom of the epoxide ring. The direction of ring opening is that characteristically observed for reactions of monoalkyl substituted epoxides under  $S_N2$  conditions and is probably dictated by steric and electronic factors. It seems that these polymeric reagents carrying the nucleophile have an attracting effect on the epoxy substrate and the reactions proceed smoothly in the vicinity of the reagents. Probably the ring opening of the

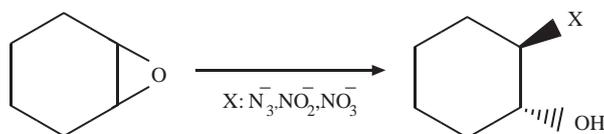
epoxide is facilitated by polar bonding between the oxygen of the epoxide molecule and quaternized nitrogen of the polymer. The results obtained for the ring opening of different substituted epoxides with the polymer supported  $N_3^-$ ,  $NO_2^-$  and  $NO_3^-$  are shown in Table 2.

Table 3 shows the comparison between different low molecular weight reagents/catalyst systems carrying  $N_3^-$ ,  $NO_2^-$  and  $NO_3^-$  nucleophiles and our polymer supported nucleophiles in the ring opening reactions of cyclohexene oxide. As seen in the case of polymer supported nucleophiles (entries 6,9 and 11) the conditions are mild, yields are good and most important of all no catalyst is used

The main advantage of using polymer supported  $N_3^-$ ,  $NO_2^-$  and  $NO_3^-$  in these ring opening reactions of epoxides is that the reactions occur under neutral condition and contrary to most reported methods in the literature no addition of any catalyst is required. The final reaction product can be simply filtered and separated without the need for a further chromatographic step in addition, the spent polymeric reagents can be regenerated and reused several times without appreciable loss in their capacities and efficiencies.

**Table 3.** Comparison of cyclohexene oxide cleavage reactions with different nucleophilic systems and polymer supported nucleophiles.

Entry	Reagent systems	Solvent	Temp (°C)	Time (h)	Yield (%)	Ref.
1	$(Bu)_3SnN_3$	THF	60	0.40	89	17
2	$Et_3Al/ HN_3$	Toluene	-70	0.25	72	19
3	$Me_3SiN_3/SmI_2(THF)_2$	$CH_2Cl_2$	25	120	58	21
4	$NaN_3/ LiClO_4$	$CH_3CN$	80	20	95	23
5	QPA/ $NaN_2$	$H_2O$	25	8	89	24
6	Amberlite /IRA-400/ $N_3^-$	EtOH	50	6	87	-
7	$MgSO_4/ NaNO_2$	MeOH	65	7	59	26
8	Micelle/ $Ce(OTf)_4/NaNO_2$	$H_2O$	25	10	78	27
9	Amberlite/IRA-400/ $NO_2^-$	EtOH	50	7	80	-
10	Micelle/ $Ce(OTf)_4/NaNO_3$	$H_2O$	25	0.2	90	42
11	Amberlite/IRA-400/ $NO_3^-$	EtOH	50	12	90	-



QPA: Poly[N-(2-aminoethyl)acrylamido]trimethyl ammonium chloride resin.

## CONCLUSION

Amberlite IRA-400 supported  $N_3^-$ ,  $NO_2^-$  and  $NO_3^-$  are important and valuable reagents for conversion of epoxides to  $\beta$ -substituted alcohols. Absence of any catalysts, easy reaction work-up, high purities of the obtained products, mild reaction conditions and regenerability of the resins make them valuable polymer supported nucleophilic reagents in organic synthesis.

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