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Tetrahedron Letters 45 (2004) 1535–1537

Tetrahedron Letters

Synthesis of thiiranes from oxiranes in water using polymeric cosolvents

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Received 5 October 2003; revised 23 November 2003; accepted 5 December 2003

Abstract—Poly(vinylamine) (PVA) and poly(allylamine) (PAA) were prepared and used as polymeric cosolvents. Oxiranes were converted efficiently to the corresponding thiiranes under mild reaction conditions in water with ammonium thiocyanate (NH_4SCN) using these polymeric cosolvents. The polymeric cosolvents are reusable.

The toxic and volatile nature of many organic solvents, particularly chlorinated hydrocarbons that are widely used in organic synthesis have posed a serious threat to the environment. Consequently methods that successfully minimize their use are the focus of much attention. One of the recently developed methods is to use water as solvent for organic reactions.[1] Unfortunately its use is limited by the low solubility of organic compounds. One of the most important strategies to overcome this limitation of water, in order to expand the scope of water-based organic synthesis, has been the utilization of organic cosolvents.[1–3]

It is well known that low molecular weight organic solvents have been used as effective polar cosolvents for promoting nucleophilic displacement reactions.[4–6] Much research has also been done on the preparation of polymeric cosolvents with a view to their use as solid phase cosolvents and catalysts in organic reactions.[3,6,7] By virtue of their insolubility, such materials would be particularly attractive since they can be recovered by filtration and used again.

There are many methods reported in the literature for the preparation of thiiranes[8,9] and the most general one has been the conversion of oxiranes to thiiranes. For this purpose several sulfurated agents such as thiourea,[10] inorganic thiocyanates,[11] phosphine sulphides,[12] silica gel-supported KSCN,[13] dimethylthioformamide,[14] and low hydrate KSCN-liquid heterogeneous media[15] have been used. Usually with these sulfurated agents, several different Lewis acids such as Ce(IV) as ceric ammonium nitrate (CAN),[16] Ru(III) as ruthenium trichloride ($RuCl_3$),[17] $BiCl_3$,[18] $TiO(CF_3CO_2)_2$,[19] and $TiCl_3(CF_3SO_3)$[19] have been used as catalysts for the conversion of the epoxides to thiiranes. Very recently Yadav[20] used a [Bmim]PF_6–H_2O solvent system for this transformation. However, most of these methods suffer from drawbacks such as the use of organic solvents, low yields of the reactions, high temperatures, long reaction times, the need for the reactions to be carried out in the presence of acidic catalysts, difficulties in the separation of the product from the original reactant and catalysts, formation of polymeric by-products and, in most cases, use of expensive and unrecoverable catalysts. Thus it seems that convenient and general methods for this purpose especially using heterogeneous catalysts are still in demand.

Recently we reported polymer supported thiocyanate[21a] as a reagent and poly(vinylpyridine)–$Ce(OTf)_4$[21b] and polystyrene supported aluminum chloride[21c] as catalysts for the synthesis of thiiranes from oxiranes. These polymeric systems could overcome many drawbacks in the synthesis of thiiranes. As a part of our general program to investigate the use of polymer-supported reagents and catalysts in organic reactions, we now report an improved, efficient, and easy synthesis of thiiranes from oxiranes under mild reaction conditions in water with ammonium thiocyanate and utilizing poly(vinylamine) (PVA) or poly(allylamine) (PAA) as polymeric cosolvents.

Cross-linked polyacrylamide was prepared by free radical solution polymerization of a acrylamide/

Keywords: Polymeric cosolvent; Oxirane; Thiirane.

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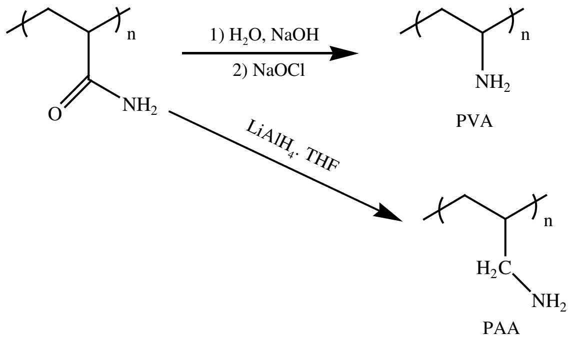
0040-4039/$ - see front matter © 2003 Elsevier Ltd. All rights reserved.
doi:10.1016/j.tetlet.2003.12.014

divinylbenzene mixture in ethanol using potassium persulfate as an initiator.[22] PVA was prepared by Hofmann rearrangement of polyacrylamide using NaOCl, and PAA was prepared by reduction of polyacrylamide using $LiAlH_4$ (Scheme 1).[3,23] The amino content of these polymers was determined by the titration method and found to be 10.9 and 10.2 meq/g of PVA and PAA, respectively.

The reaction of different epoxides with ammonium thiocyanate in the presence of NaOH was performed efficiently and in high yields in water utilizing the polymeric cosolvents (Table 1, Scheme 2). The presence of NaOH in the reaction media enhanced the formation of thiiranes.[24]

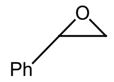
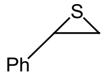
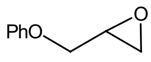
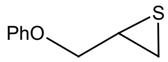
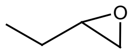
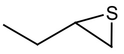
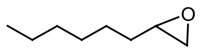
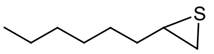
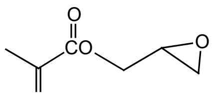
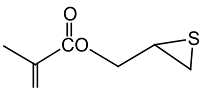
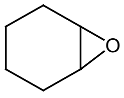
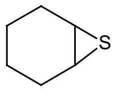
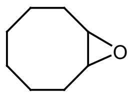
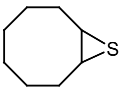


Scheme 1. Preparation of PVA and PAA.

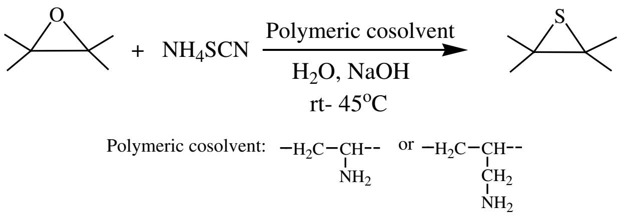
As seen in Table 1 (entry 1), in the absence of any catalyst the reaction proceeded slowly and in low yield. It is believed that these polymeric amine species can catalyze the formation of thiiranes from epoxides in the aqueous phase in two ways. Firstly by swelling in the aqueous media they can act as cosolvents for the organic substrates, namely the epoxides, and can therefore provide the necessary microenvironment for the water-soluble nucleophile, that is, SCN^-, to be in the vicinity of the epoxides for the reactions to occur. Secondly, the amino functionalities on these polymeric cosolvents can interact through H-bonding with the oxygens of the epoxides to facilitate the attack of the thiocyanate anion as the nucleophile. We have made this suggestion for other nucleophilic ring opening reactions of epoxides using cosolvents I and II,[3] and polymeric phase transfer catalysts.[22,25,26] In addition, as seen in Table 1, the efficiency of PAA as cosolvent is slightly more than PVA in the reactions of epoxides with NH_4SCN. This is probably due to the better availability of the amino groups for interactions with the oxygens of the epoxides, as the amino functionality is further from the chain of the polymer and sterically less hindered.

In conclusion, we believe that the present methodology compared to most reported in the literature offers a

Table 1. Reaction of different epoxides with NH_4SCN using PVA and PAA as polymeric cosolvents in the presence of NaOH[a]

Entry	Epoxide	Temperature (°C)	Time (min)[b]	Product[d]	Isolated yield (%)
1		25	600[c] 35 (I) 30 (II)		35 94 93
2		45	75 (I) 70 (II)		91 93
3		25	50 (I) 50 (II)		96[e] 98[e]
4		25	80 (I) 80 (II)		93[e] 94[e]
5		25	60 (I) 50 (II)		86[e] 92[e]
6		45	90 (I) 80 (II)		85 92
7		45	120 (I) 100 (II)		91 94

[a] Molar ratio of polymeric cosolvent to epoxides to NaOH was 0.2:1:1.5.
[b] I ≡ PVA; II ≡ PAA.
[c] No polymeric cosolvent.
[d] Products were identified by comparison of their NMR spectra and physical data with those reported in the literature.[14–16,18]
[e] GC yield.



Scheme 2. Preparation of thiiranes from oxiranes.

simple and efficient method for conversion of epoxides to thiiranes without the use of a Lewis acid catalyst, with high yields, mild reaction conditions, no polymeric byproducts, and an easy work-up procedure. The polymeric cosolvents can be used again without any loss in their activities. Finally, as the synthesis of thiiranes is carried out in water it can be considered as an environmentally friendly reaction.

Materials and techniques: Starting materials were purchased from Fluka and Merck companies. All products were characterized by comparison of their IR and NMR spectra and physical data with those reported in the literature.[14–16,18] The progress of the reactions was followed by TLC on silica-gel Polygram SIL/UV 254 plates or by GLC on Shimadzu GC 14-A with hydrogen flame ionization detector. FT-IR spectra were run on a Shimadzu FTIR-8300 spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker Avance DPX instrument (250 MHz).

Preparation of PVA and PAA: 2% Cross-linked polyacrylamide was prepared according to the reported procedure.[22] PVA and PAA were prepared using cross-linked polyacrylamide as reported in our previous work.[3]

Conversion of epoxides to thiiranes: To a mixture of epoxides (1.0 mmol), ammonium thiocyanate (0.23 g, 3 mmol), and NaOH (0.06 g, 1.5 mmol) in water (10 mL), the polymeric cosolvent (PVA or PAA, 0.05 g) was added. The suspension was stirred at room temperature (or at 45 °C) for the length of time shown in Table 1. The progress of each reaction was monitored by TLC, using hexane/ethyl acetate (5:1) as eluent, and/or GC. On completion of the reaction, the mixture was filtered and the filtrate was extracted with ether (2 × 10 mL). The organic portion was dried with anhydrous Na_2SO_4 and filtered. The pure product was obtained by evaporation of the solvent. The spent polymeric catalyst from different experiments was washed with water, methanol, and ether and dried overnight in vacuum oven and reused.

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