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Poly(N- bromosuccinimide) (PNBS) as a mild, efficient, non-acidic, polymeric and heterogeneous catalyst applied for easy conversion of epoxides into thiiranes by treatment with KSCN or $(NH_2)_2CS$ at room temperature

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Abstract

Poly (*N*-bromosuccinimide) (PNBS) as a mild, efficient, non-acidic, polymeric and heterogeneous catalyst was applied for simple conversion of epoxides into thiiranes by treatment with KSCN or $(NH_2)_2CS$ at room temperature. Aliphatic and aromatic epoxides converted into their corresponding thiiranes under mild conditions. All reactions proceeded in short reaction times and afforded the corresponding products in good to excellent yields. The catalyst could be recycled and reused for several times without any deterioration in its activity. Advantages such as easy preparation of the catalyst, simple work up, excellent yields of the products and recyclability of the catalyst makes this method more useful compared to the known methodologies.

Keywords: polymer, catalyst, thiirane, epoxide, heterogeneous catalyst

1.Introduction

Thiiranes have found applications in pharmaceutical, pesticide and polymer industries. Various methods have been developed for the preparation of these compounds. [1] The most general one is based on the conversion of oxiranes to thiiranes by an oxygen–sulfur exchange reaction [2]. For this purpose, several sulfur-introducing agents, including inorganic thiocyanates [3], 3-methylbenzothiozole-2-thione [4], dimethylthioformamide [5], thiourea [6], and phosphine sulfide [7] have been utilized. Besides a sulfurated reagent, a protic acid such as TFA [4,5,7], or a Lewis acid such as $RuCl_3$ [8], $BiCl_3$ [9], $TiO(CF_3COO)_2$ [8], $TiCl_3(CF_3SO_3)$ [10], and $InBr_3$ [11] is employed. Conversion of epoxides to thiiranes with NH_4SCN and thiourea in the presence of a suitable catalyst is important in organic chemistry [12].

However, some of these methods suffer from drawbacks such as low yield, rapid increase of pH during the reaction (which leads to ready polymerization of thiirans and lowering of the yield), high acidity of the catalyst or reagent, the non-catalytic nature of the reagents, long reaction times, inconvenient handling and limitation of the substrates

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(epoxides).

Considering the above-mentioned limitations, it seems that the introduction of more convenient and general method for this purpose especially using heterogeneous catalysts is still of demand.

Herein, we describe a simple and highly efficient method for the preparation of thiirane in the presence of catalytic amounts of poly(*N*-bromosuccinimide) (PNBS) as heterogeneous catalyst containing a good source of positive bromine under mild conditions with thiourea or KSCN.

2.Materials and Methods

All chemicals were supplied by either Merck or Fluka. The progress of the reactions was followed by TLC. The identities of the products were determined by comparison of their physical and spectral data with those reported in the literature. FT-IR spectra were recorded on a Shimadzu DR-8001 spectrophotometer. NMR spectra were recorded on a Brucker Avance DPX instrument (operating at 250 MHz for ^{1}H and 62.9 MHz for ^{13}C).

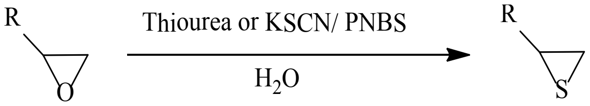
3.Experimental

General procedure for the preparation of thiirane from epoxide:

To a stirred suspension of PNBS (0.1g, 0.6 mmol) and oxirane (1 mmol) in H_2O (5 mL) was added KSCN or $(NH_2)_2CS$ (2 mmol) in H_2O (3 mL) slowly at room temperature. The reaction mixture was stirred for appropriate time. After completion of the reaction (as monitored by TLC), the resulting mixture was filtered and the filtrate washed with H_2O (3 ×5 mL) and the organic layer was dried over anhydrous Na_2SO_4. After evaporation of the solvent on a rotary evaporator, the pure product was obtained in high to excellent yield (Table 2). The characterization of the products was performed by comparison of their IR, ^{1}H-NMR, ^{13}C-NMR, and physical data (melting point or boiling point) with those of authentic samples.

4.Results and Discussion

In continuation to our work on the development of useful synthetic methodologies [13], we have recently observed that oxiranes can conveniently be converted into thiiranes by treatment with KSCN or $(NH_2)_2CS$ in the present of catalytic amounts of PNBS [14] at room temperature (Scheme 1).



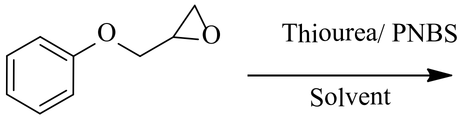
Scheme 1

A series of preliminary experiments were performed on phenyl gelycidyl ether in order to determine the best reaction conditions (Table 1). In the absence of PNBS, the reaction occurred after prolonged reaction time. Reaction in solvents such as THF, CH_2Cl_2, $CHCl_3$, acetone, and DMF resulted in lower yields of the desired product. The choice of solvent in organic reactions using polymer-supported catalysts are extremely important. A solvent should be chosen in which the insoluble polymeric catalyst swell well and the particular substrate dissolves completely. Water was found to be a suitable solvent for this purpose. In the present conversion, the role of H_2O is possible to activate the oxiranes through hydrogen bonding.

The best reaction condition was found when we used 0.6 equivalents of PNBS in water as solvent at room temperature. The reaction was carried out with simple procedure by mixing directly the KSCN or thiourea (2 mmol), the epoxides (1 mmol), and PNBS (0.6 mmol, 0.1 g) at room temperature, in water (5 mL) (Table 1, entry 5 and 6).

In the present study, both KSCN and $(NH_2)_2CS$ showed a similar activity as the reaction times were the same (30 min) and the yields were very analogous. The structures

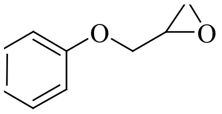
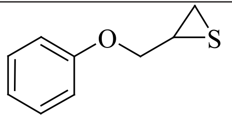
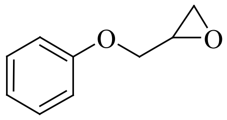
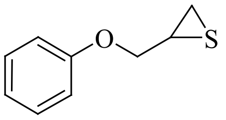
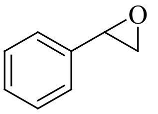
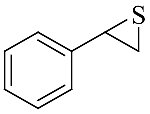
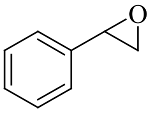
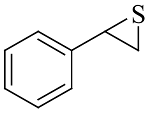
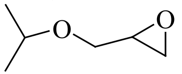
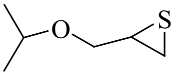
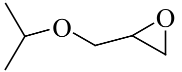
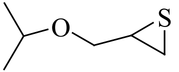
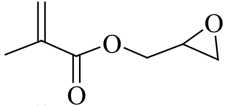
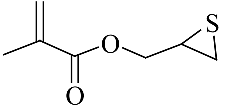
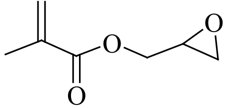
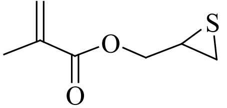
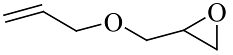
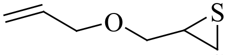
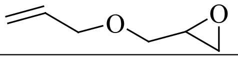
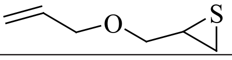
Table 1. Effect of different molar ratios of PNBS on the reaction of phenyl glycidyl ether with $(NH_2)_2CS$ in water as a solvent



Entry	PNBS(mmol)	Time	Conversion (%)
1	-	24h	80[a]
2	5	30 min	100
3	2	1h	100
4	1	1h	100
5	**0.6**	**30min**	**100**
6	**0.6**	**30min**	**100[b]**
7	0.3	2.5	100
8	0.2	3h	80

a) Under reflux condition (100℃) b)KSCN used instead $(NH_2)_2CS$

Table 2: Conversion of epoxides to thiiranes using PNBS as a catalyst in water

Entry	Substrate	Product	reagent	Time (h)	Yield(%)[a]
1			KSCN	0.5	96
2			$(NH_2)_2CS$	1	95
3			KSCN	0.75	96
4			$(NH_2)_2CS$	70	87
5			KSCN	1.5	92
6			$(NH_2)_2CS$	2	89
7			KSCN	2	95
8			$(NH_2)_2CS$	2.2	89
9			KSCN	1	87
10			$(NH_2)_2CS$	1	83

a) Isolated yield.
b) All products were characterized by comparison of their IR, ^1H NMR and ^{13}C NMR with those of an authentic sample.

of the products were established from their spectra (^{1}H NMR, ^{13}C NMR and IR) data.

To show the generality and scope of PNBS promoted thiirane synthesis, the reaction was examined with various structurally divers epoxides. The results are shown in Table 2. The data clearly show that all reactions proceeds smoothly under these conditions and afforded the desired thiirane in excellent yields.

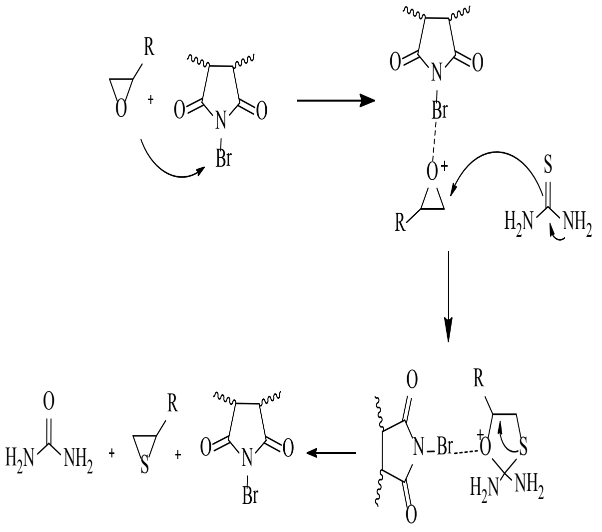
The products were obtained in excellent yields and no side products were detected. Work up procedure was very simple, and in the most cases the crude products were pure and did not need any further purifications (Table 2)

In this method, due to the neutrality of the catalyst no polymeric by-product was observed.

One of the most important advantages of the polymeric catalysts over their monomeric analogous is that, in most cases the used polymeric catalyst can be recycled. For the synthesis of 2-(phenoxymethyl)thiirane using phenyl gelycidyl ether as starting material and PNBS as a catalyst, it could be used several times without an appreciable loss of catalytic activity and there is no need for regeneration. The spent polymeric catalyst from different experiments was combined, washed with chloroform and dried overnight in vacuum oven and reused. (Table 3)

As it can be observed in Table 3, the PNBS was recovered from the reaction mixture and recycled without loss of activity.

We propose the following mechanism to account for the formation of thiiranes from epoxides with $(NH_2)_2CS$ in the presence of PNBS as a catalyst (Scheme 2):



Scheme 2

5.Conclusion

In conclusion, we have developed a simple and efficient protocol for the synthesis of thiiranes from oxiranes by treatment it with KSCN or $(NH_2)_2CS$ in H_2O at room temperature. The mildness, non-acidic and eco-friendly nature of the method, short reaction time and excellent yields are notable advantages of this protocol. PNBS is heterogeneous catalyst, eco-friendly and a biologically acceptable inexpensive polymer.

References

[1] A. Hassner. The Chemistry of Heterocyclic Compounds, John Wiley and Sons, New York 2009.

[2] (a) A. R. Katritzky, Handbook of heterocycle chemistry, Pergamon press, 2013; (b) M. Sander, Thiiranes, Chem. Rev. 66 (1966), 297-339; (b) E. Vedejs, G. A. Krafft, Cyclic sulfides in organic synthesis, Tetrahedron, 38 (1982), 2857–2881.

Table 3. Recyclability of PNBS for the synthesis of thiiranes

Run	Time (min)	Conversion (%)
Initial Run (Fresh Catalyst)	60	100
1st Recycle	60	100
2nd Recycle	80	90
3rd Recycle	100	90

[3] (a) H. M. Chen, P. Y. Chen, C. F. Wang, J. C. Tsai, E. C. Wang, An improved method for the conversion of oxiranes to thiiranes and the discrimination of their base peaks in EI-MS ARKIVOC (2012) 157-168; (b) J. S. Yadav, B. V. S. Reddy, G. Baishya, Indium Tribromide: A Novel and Highly Efficient Reagent for the Conversion of Oxiranes to Thiiranes, Synlett (2003), 396-398.

[4] V. Calo, L. Lopez, L. Marchese, G. J. Pesce, A simple method for converting oxirans into thiirans stereospecifically, Chem. Soc., Chem. Commun. (1975), 621-622.

[5] T. Takido, Y. Kobayashi, K. Itabashi, A Convenient Synthesis of Thiirans by the Use of Dimethylthioformamide, Synthesis (1986) 779–780

[6] (a) H. Bouda, M. E. Borredon, E. Delmas, A. Gaset, Synthesis of Thiiranes from Epoxides in the Presence of Thiourea in a Weakly Hydrated Organic Medium, Synth. Commun. 19 (1989) 491-500; (b) S. Brown, M. M. Bernardo, Z.H, Zi, P. K. Lakshmi, Y. Tanaka, F. Fridman, S. Mobashery, Potent and Selective Mechanism-Based Inhibition of Gelatinases J. Am. Chem. Soc. 122 (2000), 6799-6800.

[7] S. E. Denmark, S. Rossi, M. P. Webster, H. Wang Catalytic, Enantioselective Sulfenylation of Ketone-Derived Enoxysilanes J. Am. Chem. Soc., 136 (2014), 13016-13028

[8] N.Iranpoor, F. Kazemi, Stereospecific formation of S (−) styrene sulfide: Efficient conversion of epoxides to thiiranes catalysed with Ru (III) Tetrahedron, 53 (1997) 11377-11382.

[9] I. Mohammadpoor-Baltork, H. Alian, Bismuth(III) Chloride: A Mild and Efficient Catalyst for Synthesis of Thiiranes from Oxiranes, Synth. Commun. 28 (1998), 3943–3947.

[10] N. Iranpoor, B. Zeynizadeh, Conversion of Epoxides to Thiiranes Catalyzed with $TiO(TFA)_2$ and $TiCl_3(OTf)$ in the Presence of Ammonium Thiocyanate or Thiourea Synth. Commun. 28 (1998), 3913-3918.

[11] J. S. Yadav, B. V. S. Reddy, G. Baishya, Synlett (2003) 396–398.

[12] (a) B. Tamami, A. R. Kiasat, Synthesis of Thiiranes From Oxiranes Under Mild and Nonaqueous Conditions Using Polymer Supported Thiocyanate, Synth. Commun. 26 (1996) 3953-3956; (b) N. Iranpoor, F. Kazemi, Cerium (IV) Catalysis: Efficient Conversion of Epoxides to Thiiranes, Synthesis (1996), 821-823.

[13] (a) B. Tamami, H. Firouzabadi, F. Ebrahimzadeh, A. Fadavi, Poly(*N*-bromoacrylamide): an Efficient and Useful Catalyst for the Protection of Carbonyl Compounds as Dithiolanes, Dithianes and Oxathiolanes under Solvent-Free and Microwave Conditions J. Iran. Chem. Soc. (2009) 722-728; (b) F. Ebrahimzadeh, R. Rooydell, Poly (*N*-bromoacrylamide) as highly efficient, regioselective and recyclable catalyst for preparation of β-azidoalcohols, β-cyanoalcohols, β-nitroalcohol and β-nitratoalcohols from epoxides under aqueous conditions Der Chemica Sinica, 3 (2012), 1146-1152; (c) F. Ebrahimzadeh, New applications of poly(*N*-bromoacrylamide) in organic synthesis: highly efficient and regioselective transformation of alkenes into bromohydrins, bromoethers and bromoacetates, Der Chemica Sinica, 3 (2012), 1140-1145; (d) F. Ebrahimzadeh, poly (*N*-bromoacrylamide) as highly efficient, regioselective and recyclable catalyst for preparation of β-azidoalcohols, β-nitroalcoholsand β-nitratoalcohol from epoxides under aqueous condition Chemica Sinica, 3 (2012), 1185-1190.

[14] B. Tamami, A. Nasrolahi Shirazi, F. Ebrahimzadeh. Synthesis and Applications of Cross-linked Poly(*N*-bromomaleimide) in Oxidation of Various Organic Compounds, Iranian Polymer Journal 18 (2009), 957-967.