SHORT PAPER

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Montmorillonite K-10: a mild, inexpensive and convenient catalyst for synthesis of thiiranes from oxiranes under non-aqueous conditions†

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Montmorillonite K-10 catalyses the conversion of oxiranes to the corresponding thiiranes in the presence of thiourea efficiently and the yields obtained are excellent.

Many methods have already been reported for the preparation of thiiranes.[1,2] The reaction of oxiranes with inorganic thiocyanate or thiourea in water, aqueous solvents or in the presence of sulfuric acid has been considered as the most convenient method for the preparation of thiiranes.[1–4] But the yield of thiiranes, such as cyclohexene and styrene sulfides, as well as higher thiiranes by these methods is not satisfactory.[5,6] In addition, the increase in pH of the reaction medium, difficulty in separation of the product from the reaction mixture and the formation of polymeric by-products are other drawbacks of these methods. Other sulfur-introducing reagents such as phosphine sulfide,[7,8] 3-methylbenzothiazole-2-thione,[9] dimethylthioformamide,[10] polymer supported thiocyanate,[11] low hydrated KSCN-liquid heterogeneous medium,[12] silica-gel supported KSCN,[13] ceric ammonium nitrate[14] and ruthenium trichloride[15]-NH_4SCN, $TiO(CF_3CO_2)_2$ and $TiCl_3(CF_3SO_3)$ in the presence of NH_4SCN and NH_2CSNH_2[16] and tin(IV) porphyrin[17]-NH_2CSNH_2 have also been reported for this purpose. However, some of these methods show limitations such as long reaction times, low yields of the products, expensive reagents, tedious work-up, requirement for aqueous reaction conditions and presence of trifluoroacetic acid. Therefore, there is a need to develop and introduce efficient and inexpensive methods and reagents for the conversion of oxiranes to thiiranes.

In recent years, montmorillonite clays, a class of acidic clay minerals, have been found to be useful catalysts in a variety of organic reactions due to their acidity, noncorrosive, inexpensive and non-pollution.[18,19] The reactions catalysed by montmorillonite clays are usually carried out at mild conditions with high yield and selectivity. The work-up of the reaction is very simple, usually only removal of the catalyst by filtration and evaporation of the solvent are involved.

Recently, we have reported a convenient method for the conversion of oxiranes to thiiranes in the presence of NH_4SCN under catalysis of bismuth(III) chloride.[20] Little attention has been paid to the conversion of oxiranes to thiiranes in the presence of thiourea under non-aqueous conditions and only a few reports are available for this purpose.[16,17] In continuation of our research in this area, we were interested in finding a more efficient and inexpensive method for the synthesis of thiiranes from oxiranes. In this respect, we report an efficient conversion of oxiranes to thiiranes in the presence of thiourea under catalysis of montmorillonite K-10.

As shown in Table 1 different aliphatic, cyclic, activated and deactivated oxiranes react rapidly with thiourea in the presence of montmorillonite K-10 in refluxing acetonitrile affording thiiranes in excemlent yields.

In comparison with acetonitrile, the reaction times were longer and the yields of thiiranes were lower when acetone, dichloromethane and chloroform were employed as solvents. It is worth mentioning that in aqueous medium the control of pH is important for obtaining high yields and to avoid polymerization of thiiranes.[1] In this method, since the reactions occur under non-aqueous conditons, thiiranes are obtained in excellent yields wjthout any polymerization.

In conclusion, we have shown that montmorillonite K-10 is an efficient, mild, and inexpensive catalyst for the conversion of oxiranes to thiiranes in the presence of thiourea. In addition, availability of the reagents, high yields and short reaction times, and ease of work-up make this method a useful and important addition to the modern organic synthetic methodologies.

Experimental

General procedure for the conversion of oxiranes to thiiranes To a solution of oxirane (2 mmol) in MeCN (10 ml), were added thiourea (0.304 g, 4 mmol) and montmorillonite K-10 (0.4 g) and the mixture was stirred under reflux conditions for the appropriate time according to Table 1. The progress of the reaction was monitored by GLC. The reaction mixture was filtered and the solid material was washed with MeCN (10 ml). Evaporation of the solvent afforded the essentially pure product. Further purification was achieved by chromatography on a short column of silica-gel (eluent: *n*-hexane-EtOAc, 4:1) wherever necessary. The results are shown in Table 1.

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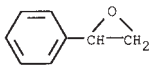
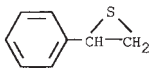
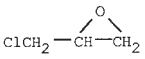
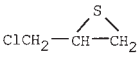
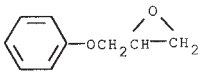
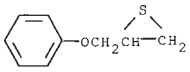
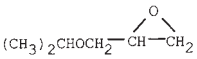
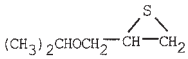
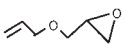
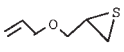
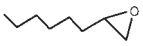
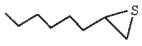
† This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Table 1 Conversion of oxiranes to thiiranes with NH_2CSNH_2/K-10 clay in refluxing MeCN

Entry	Substrate	Product[a]	*t*/min	Yield (%)[b]
1			40	98
2			45	98
3			60	92
4			45	95
5			60	97
6			60	98
7			120	92

[a]All products were identified by comparison of their physical and spectral data with those of authentic samples.
[b]Isolated yields.

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