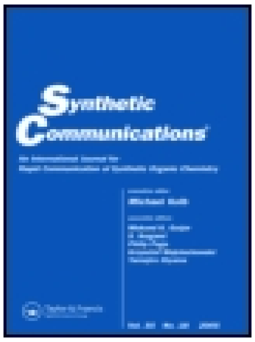

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REGIOSELECTIVE RING OPENING OF OXIRANES CATALYSED BY MONTMORILLONITE CLAY : A SIMPLE SYNTHESIS OF β-HYDROXY SULFONES

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ABSTRACT: *Oxiranes and sodium p-toluene sulfinate salt react smoothly in a regioselective manner in the presence of montmorillonite clay to furnish the corresponding β-hydroxy sulfones in good to excellent yield.*

β-Hydroxy sulfones[1] are synthetically very useful intermediate in organic transformations such as elimination reaction of β-acetoxy or β-alkoxy sulfones leading to the acetylenic or polyenic bond formation[2,3], olefins by reductive elimination[4-6] etc. Very recently, synthesis of β-hydroxy sulfones has been reported[7] from β-epoxy sulfones using Grignard reagents. We now want to report here the successful application of montmorillonite clay in the regioselective ring cleavage of different oxiranes under very mild condition to produce the β-hydroxy sulfones in fairly good yield. Our findings, however, reveal the fact that montmorillonite clay facilitates actively the nucleophilic attack of sulfinate anion leading to the oxirane ring cleavage within few hours of stirring at room

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*To whom correspondence should be made.

temperature. It seems probable to us that the Lewis acidic nature of the montmorillonite clay encourage to coordinate with the oxirane oxygen to welcome the participation of the better nucleophile sulfinate anion in the cleavage. All the reactions were done under the liquid-liquid phase transfer condition using the solvent system water, benzene, acetone (10:5:5) to get a cleaner phase difference at the end of the reaction (monitored by TLC). It has been seen that the reactions generally proceed with high regio-selectivity and definitely with anti stereoselectively. However the anti stereoselectivity could be well demonstrated by the reaction with cyclohexene oxide (entry 1, Table 1) which produced the trans-2-[p-toluene sulfonyl] cyclohexanol (1a) exclusively. The epichlorohydrin (entry 7, Table 1) gave a somewhat interesting product as recorded in table. It is expected that the epoxysulfone was generated first which undergoes β-elimination to give (E)-3-[p-toluene sulfonyl]-2-propen-1-ol (7a) exclusively. Some other observations are summarised in the Table 1.

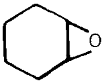
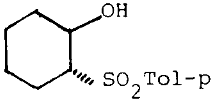
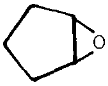
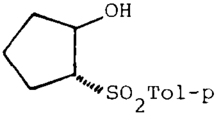
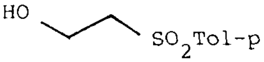
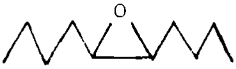
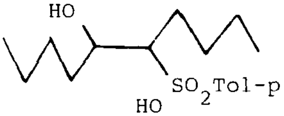
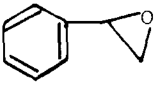
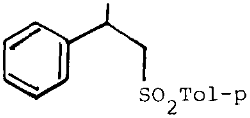
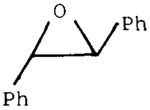
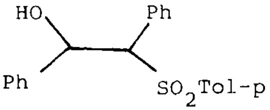
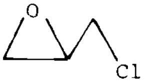
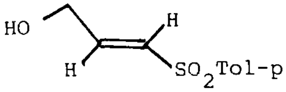
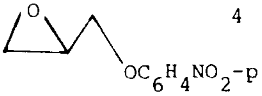
Experimental

Melting points are uncorrected and were determined on a Toshniwal melting point apparatus. IR spectra were recorded on a Shimadzu IR-408 model. ^1H NMR spectra were recorded on a ZEOL 100 MHz instrument using $CDCl_3$ as the solvent and TMS as the internal standard. Column chromatography was performed on silica gel [60-120 mesh; Merck] etc.

General Procedure

To a suspension of montmorillonite clay (3 gm) and sodium p-toluene sulfinate salt (9 gm, 0.09 mol) in the solvent system water, benzene, acetone (10:5:5), oxirane (0.06 mol) was added in drops and stirred vigorously at room temperature for the

Table 1 : Montmorillonite catalysed regioselective ring opening of oxiranes with sodium salt of p-toluene sulfinic acid

Entry	Oxiranes	Reaction Time(hrs)	Yield^a(%)	Products^b (1a-8a)	
1.		15	75		**1a**
2.		20	52		**2a**
3.		6	78		**3a**
4.		12	52		**4a**
5.		4	80		**5a**
6.		7	58		**6a**
7.		10	70		**7a**
8.		4	75		**8a**

^{a}Yield refer to pure isolated product

^{b}All β-hydroxy sulfones are properly characterised by m.p., IR & ^{1}HNMR [compared in case of the compounds **1a** (ref. 9); **6a** (ref. 2) **7a** (ref. 9) etc.

stipulated period (as mentioned in the table). The course of the reaction was monitored by TLC. After the indicated period, the whole contents was filtered and the clay-free material was extracted with ether, dried and finally chromatographed over the silica gel producing the β-hydroxy sulfone in pure form.

Physical and spectral datas of compounds **3a, 5a, and 8a**

Compound **3a** : m.p[8] 53-54°C; IR(KBr) 3500, 1600, 1290, 1140 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.40 (s, 3H); δ 2.90 (m, 1H) δ 3.30 (t, 2H); δ 4.00 (t, 2H); δ 7.40 (d, 2H Ar), δ 7.85 (d, 2H Ar).

Compound **5a** : m.p. 130-131°C; IR (KBr) 3500, 1600, 1300, 1150 cm^{-1}; ^1H NMR ($CDCl_3$) δ 2.40 (s, 3H); δ 2.96 (brs, 1H) δ 4.00-4.72 (m, 3H); δ 7.08-7.48 (m,9H) etc.

Compound **8a** : m.p. 105-106°C; IR (KBr) 3500, 1600, 1300, 1145 cm^{-1}; ^1H NMR ($CDCl_3$) 2.40 (s, 3H); δ 3.42 (d, 2H); δ 4.15 (d, 2H); δ 4.50-4.70 (m, 1H); δ 7.40, δ 7.90 (d, 2H Ar) and δ 7.00, δ 8.20 (d, 2H Ar) etc.

In conclusion, the utilization of montmorillonite clay in the regioselective ring cleavage of different oxiranes is manupulatively very simple and convenient. This offers a very good method for the synthesis of β-hydroxy sulfones under mild condition in good to excellent yield.

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