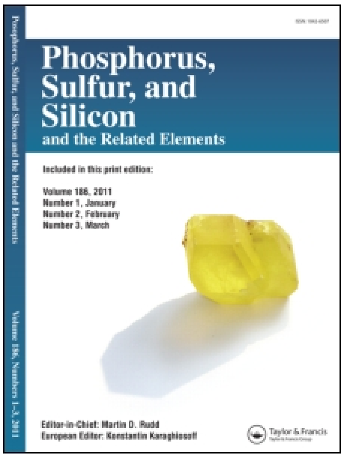

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Highly Regioselective Ring Opening of Epoxides with Thiols Catalyzed by $SbCl_3$ Under Solvent-Free Conditions

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The ring-opening reaction of epoxides with thiols by $SbCl_3$ supported on Kieselguhr under solvent-free conditions, afforded high yields of β-hydroxy sulfides. Nucleophilic attack of the thiols occurs regioselectively at the less hindered side of the epoxides.

Keywords β-hydroxysulfides; epoxides; ring opening; $SbCl_3$; solvent-free reaction; thiols

INTRODUCTION

Ring opening of epoxides with thiols is an important part of organic synthesis and has found much use in pharmaceutical[1] and natural product chemistry,[2] particularly for the synthesis of leukotrienes.[3] The classical approach for the synthesis of β-hydroxy sulfides involves nucleophilic ring opening of epoxides with thiols catalyzed by species such as $InCl_3$,[4,5] $ZnCl_2$,[6,7] $B(C_6F_5)_3$,[8] hexafluoroisopropyl alcohol,[9] lithium bistrifluoromethanesulfonamide,[10,11] aluminal,[12] gallium complexes,[13] $NiCl_2$, $6H_2O$, [14]CsF on celite,[15] HBF_4-SiO_2 under solvent-free conditions,[16] etc.

In many of the these cases, the ring opening of epoxides is carried out in a halogenated solvent normally requiring long time treatment under refluxing temperatures or environmentally unfriendly conditions.

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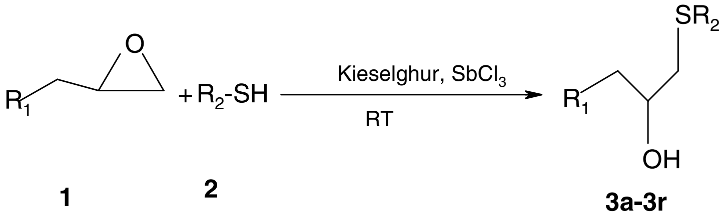


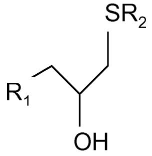
SCHEME 1

Stringent environmental protection laws in recent years prompted an increasing emphasis on the use and design of eco-friendly reagents, solid state procedures, and solvent–free reactions.[17] Dry procedures have recently attracted much attention because they can be carried on in open vessels, and the use of expensive and hazardous organic solvents can be avoided.[18] We extended our previous experience on solid supported reagents.[19–24] Here, we wish to report the results of using a simple procedure for efficient thiolysis of epoxides using $SbC1_3$ supported on Kieselguhr, as a non toxic and convenient heterogeneous catalyst surface under solvent- free conditions at room temperature. The $SbC1_3$ was used as a convenient catalyst for ring opening of epoxides with aniline and its derivatives at room temperature to afford the corresponding β-amino alcohols.[25]

RESULTS AND DISCUSSION

Our approach to a clean and simple procedure for efficient thiolysis of epoxides, makes use of $SbCl_3$ supported on Kieselguhr. This heterogeneous catalyst was used in ring opening of various epoxide in thiolysis reaction under solvent-free conditions. Initially, 2-(chloromethyl)oxirane was treated with an equimolar amount of p-methoxythiophenol in the presence of $SbCl_3$ impregnated on Kieselguhr under solvent-free conditions. The experiments were complete within 8 h, as monitored by TLC showing the disappearance of the starting epoxide. The IR and ^{1}H NMR spectrum of the crude reaction mixture revealed the formation of the β-hydroxysulfide **3a** indicating that the nucleophilic attack of the p-methoxythiophenol occurred at the less hindered side of the epoxide (Scheme 1). Moreover, in the crude mixture the other regioisomer was detected in a very small amount (about 3%) proving the high regioselectivity of the reaction. Purification of product by column chromatography (silica gel 60, petroleum ether/ EtOAc; 6 : 1) gave 96% of the desired product **3a** (Table I, entry 1).Control experiments confirmed the combined promoting effect of

TABLE I Synthesis of β–Hydroxysulfides 3

Entry	Epoxides 1 R_1	Thiols 2 R_2	Time (h)	 3^a	Yield [%]^b
1	Cl	$4\text{-}OCH_3C_6H_4$	8	**3a**	96
2	Cl	Ph	8	**3b**	94
3	Cl	$4\text{-}CH_3C_6H_4$	8	**3c**	92
4	OPh	$4\text{-}OCH_3C_6H_4$	8	**3d**	96
5	OPh	Ph	8	**3e**	95
6	OPh	$4\text{-}CH_3C_6H_4$	8	**3f**	94
7	O-allyl	$4\text{-}OCH_3C_6H_4$	9	**3g**	90
8	O-allyl	Ph	9	**3h**	91
9	O-allyl	$4\text{-}CH_3C_6H_4$	10	**3i**	88
10	Ph	$4\text{-}OCH_3C_6H_4$	9	**3j**	94
11	Ph	Ph	9	**3k**	92
12	Ph	$4\text{-}CH_3C_6H_4$	8	**3l**	92
13	O-n-butyl	$4\text{-}OCH_3C_6H_4$	10	**3m**	88
14	O-n-butyl	Ph	10	**3n**	88
15	O-n-butyl	$4\text{-}CH_3C_6H_4$	12	**3o**	80
16	$4\text{-}CH_3C_6H_4$	$4\text{-}OCH_3C_6H_4$	8	**3p**	89
17	$4\text{-}CH_3C_6H_4$	Ph	8	**3q**	90
18	$4\text{-}CH_3C_6H_4$	$4\text{-}CH_3C_6H_4$	10	**3r**	85

[a] All compounds were characterized by IR and^{1}H NMR and compared with authentic samples.; and [b] isolated yields.

catalyst and solid support. When a mixture of 2-(chloromethyl)oxirane and *p*-methoxythiophenol was reacted in a similar conditions without the $SbCl_3$ for more than 20 h, only about 15% of the product was detected. An alternative reaction without Kieselguhr led to formation only 45% of **3a** after 14 hours, at room temperature. To asses the generality of the method, a variety of epoxides (**1**) and thiols (**2**) reacted in a similar manner, producing **3b–3r** (Table I, entries 2–18).

CONCLUSION

In summary, we have achieved an efficient protocol for the highly regioselectivity ring opening reaction of epoxides with thiols, by use of $SbCl_3$ supported on Kieselguhr under solvent-free conditions. Compared to previous methods, this simple procedure uses more friendly reaction conditions at room temperature and generally gives high yields.

EXPERIMENTAL

General

All chemicals were purchased from Merck, Aldrich, and Riedel Haen AG, and were used without further purification. IR and NMR spectra were recorded on a FT–IR Unicam Mattson 1000 using KBr disks or as neat samples and Bruker AC (80-MHz) with $CDCl_3$ as solvent and TMS as internal reference, respectively.

Ring Opening of Epoxides with Thiols—General Procedure

A mixture of epoxide (**1**; 10 mmol), thiol (**2**; 10 mmol), was added to $SbCl_3$ (0.112 g, 1 mmol) that was impregnated on Kieselguhr (0.1 g, 12%, w/w). The mixture was magnetically stirred initially under solvent-free conditions at 15°C, which was gradually raised to room temperature (30°C) at specified time (*cf.* Table I). The course of the reaction was monitored by TLC until complete disappearance of the starting material was observed. Chloroform (15 ml) was added then filtered through a celite column and catalyst filtered off. The solvent was removed at reduced pressure and the respective product (**3**) was purified by column chromatography over a short silica gel pad (peterelium ether/EtOAc; 6: 1) or by bulb to bulb distillation. The ^1H NMR and IR spectra of pure products were obtained and compared with the literature value as well as with authentic samples.[26,27]

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