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CONVERSION OF EPOXIDES TO THIIRANES CATALYZED WITH $TiO(TFA)_2$ and $TiCl_3(OTf)$ IN THE PRESENCE OF AMMONIUM THIOCYANATE OR THIOUREA

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Abstract: $TiO(CF_3CO_2)_2$ and $TiCl_3(CF_3SO_3)$ are efficient catalysts for the conversion of epoxides to thiiranes in the presence of ammoniun thiocyanate or thiourea under non-aqueous conditions.

In a recent work,[1,2] we described a new catalytic technique for the conversion of epoxides to thiiranes with NH_4SCN in non aqueous solvents different from classical methods[3-8] which are generally carried out in aqueous organic homogenous or heterogeneous media. Most of these methods suffer from one or more of the disadvantages such as; low yield of the reaction, rapid increase of pH and occurrence of polymerization reaction, high temperature, long reaction time and difficult work up procedure. In our studies for finding a suitable catalyst for the reaction of styrene oxide and thiocyanate ion, different Lewis acids such as halides of Ru(III), Al(III),

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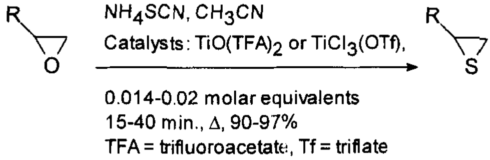
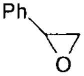
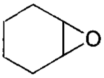
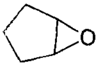
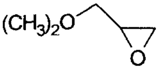
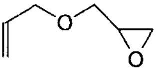
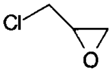
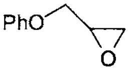
Sn(II), Mn(II), Zn(II), Fe(II), Fe(III), Co(II), Cu(II) and Ti(IV) were studied[2], but almost all of them except Ru(III) which is rather an expensive reagent failed to complete the reaction mostly due to the complex formation between SCN^- and the Lewis acid. In the course of our studies with Ti(IV), we observed that replacing of Cl with other ligands such as triflate or trifluoroacetate not only increases the efficiency of Ti(IV) as a Lewis acid, but also inhibits its complex formation with anions such as SCN^-. We, therefore, decided to prepare two known derivatives of $TiCl_4$, $TiO(CF_3CO_2)_2$[9] and $TiCl_3(CF_3SO_3)$[10], and examine their abilities for this transformation. These two solid reagents can be prepared from $TiCl_4$ and in comparison are both solid and stable. Although $TiCl_3(OTf)$ is still hygroscopic, but $TiO(TFA)_2$ is non-hygroscopic, air stable and its handling is very easy. We examined the catalytic abilities of both compounds for conversion of epoxides to thiiranes with ammonium thiocyanate in refluxing acetonitrile. Both reagents acted very efficiently and it was observed that only 0.014-0.02 molar equivalents of the catalysts are enough to convert epoxides to their corresponding thiiranes in excellent yields within 15-40 min.(scheme 1). In the case of styrene oxide, 97% and 96% of styrene episulfide were obtained after 15 min with $TiO(TFA)_2$ and $TiCl_3(OTf)$, respectively. In a similar reaction with 0.02 molar equivalents of $TiCl_4$, only 7% of styrene episulfide was obtained after 3h refluxing in acetonitrile.

Scheme 1



The results obtained from these reactions are shown in Table 1.

Table 1. Conversion of Epoxides to Thiiranes[I] with Ammonium Thiocyanate Catalyzed with $TiO(TFA)_2$ or $TiCl_3(OTf)$ in refluxing acetonitrile

Epoxide	$TiO(TFA)_2$		$TiCl_3(OTf)$.	
	Mole ratio of Sub./Cat./SCN^-	Time (min)/Yield%[II]	Mole ratio of Sub./Cat./SCN^-	Time (min)/Yield%[II]
	1/0.017/3	15/97	1/0.02/3	15/96
	1/0.017/3	20/95	1/0.02/3	40/95
	1/0.017/3	40/94	1/0.02/3	50/94
	1/0.014/2	40/93	1/0.02/3	40/93
	1/0.017/3	15/94	1/0.02/3	15/95
	1/0.017/3	15/95	1/0.015/3	20/90
	1/0.014/2	20/90	1/0.02/3	15/94
	1/0.017/3	20/93	1/0.02/3	35/98

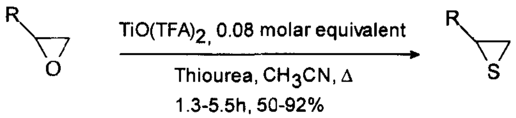
[I] The products were identified by comparison with known samples. [II] Isolated yield.

The reaction of epoxides with thiourea as another sulfured agent has also been reported to give thiiranes under wet conditions (solvent free) or in aqueous ethanol.[11] For example, the reaction of styrene oxide with wet thiourea in the absence of solvent has been reported to afford styrene episulfide in 45% yield after 10h. The reaction of epoxides with thiourea in aqueous ethanol is more or less very similar to the reaction of epoxides and KSCN,[11] with usually long reaction time and low yields in the cases of cyclic epoxides. In the absence of solvent, desulfuration to olefin has also been reported in some reactions.

It seemed interesting to complete this work by the study of the reactivity of these two catalysts for the conversion of epoxides to their corresponding thiiranes with thiourea. The reaction of styrene oxide and thiourea in refluxing acetonitrile was studied with 0.08 molar equivalents of either catalyst. Both $TiO(TFA)_2$ and $TiCl_3(OTf)$ showed similar reactivity for this transformation and styrene episulfide was obtained in 85% yield. Under similar conditions, when styrene oxide was reacted with thiourea in the absence of the catalyst, GC and TLC analysis of the reaction mixture did not show the formation of any product after 2h. The conversion of other epoxides to their corresponding thiiranes under these conditions was also studied successfully (Scheme 2).

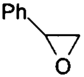
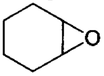
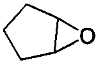
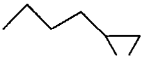
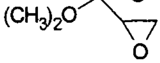
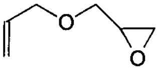
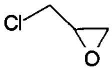
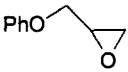
The results obtained from this study are shown in Table 2.

Scheme 2



In conclusion, $TiO(TFA)_2$ and $TiCl_3(OTf)$ can be considered as efficient catalysts for the conversion of epoxides to thiiranes with both ammonium thiocyante or thiourea under aprotic conditions. High yields of the reaction products, shorter reaction time compared to classical method of thiirane synthesis, stability and efficiency of the catalysts and easy work up, make this method an addition to the suitable procedures for this transformation.

Table 2. Conversion of Epoxides to Thiiranes with Thiourea Catalyzed With $TiO(TFA)_2$

Epoxide	Mole ratio of Sub./Cat./Thiourea	Time (h)	Yield%[1]
	1/0.08/2	1.3	85
	1/0.08/2	1.8	55
	1/0.08/2	2	50
	1/0.014/2	2.5	83
	1/0.08/2	3.3	75
	1/0.08/2	5.5	87
	1/0.08/2	5	80
	1/0.08/8	5	92

[1] Isolated yield.

Experimental: Products were characterized by comparison of their physical data IR, NMR and mass spectra with that prepared accordance with literature procedures. Infrared spectra were recorded on a Perkin Elmer IR-157 G and a Perkin Elmer 781 spectrometer. NMR spectra were recorded on a Bruker Avance DPX-250. Mass spectra were recorded on a Shimadzu GCMS-QP 1000 EX.

General Procedure for the Conversion of Epoxides to Thiiranes.

In a round-bottom flask, a solution of epoxide (1 mmol) in CH_3CN (5 ml) and NH_4SCN (3 mmol) or thiourea (2 mmol) was prepared. Then $TiO(TFA)_2$ or $TiCl_3(OTf)$ (0.014-0.02 mmol) was added to the solution and the reaction mixture was refluxed for appropriate time (Table1, 2). After completion of the reaction, the mixture was cooled to room temperature and then water (10 ml) was added to the mixture. The mixture was extracted with CH_2Cl_2 (3x20 ml) and the original layer was dried with anhydrous Na_2SO_4. The solvent was evaporated and the crude product was chromatographed on a short column of silica-gel with CCl_4 to give the pure products in 50-98% yields.

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