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Ru(III) Catalyses the Conversion of Epoxides to 1,3-Dioxolanes

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Ru(III) CATALYSES THE CONVERSION OF EPOXIDES TO 1,3-DIOXOLANES.

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Abstract: *Anhydrous $RuCl_3$ catalyses the efficient reaction of epoxides with acetone to give the corresponding* 1,3-dioxolanes *in high yields.*

1,3-dioxolanes are widely used protecting groups for diols[1,2] with special interest in carbohydrates and steroid chemistry. In addition, they are very suitable derivatives of diols for GC, GLC and mass spectrometry.[3] Direct conversion of an epoxides to 1,3-dioxolane instead of adding water to form diol with subsequent elimination in the presence of acetone has been studied with only a few reagents. Among these reagents, anhydrous copper sulfate[3] has been reported to produce the dioxolanes, but the reported yields on the bases of glc analysis in most cases are low

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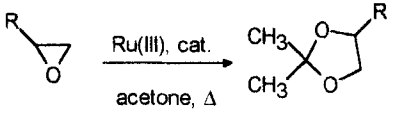
with relatively long reaction times. The use of KSF clay[4a], HBF_4[4b] and some Lewis acids has been studied for this transformation. Most of these Lewis acids failed to give the desired product.[5,6]. Among Lewis acids, $BF_3.OEt_2$ has been successfully used for conversion of different types of carbonyl compounds to their corresponding 1,3-dioxalone derivatives with only ethylene and propylene oxides.[7] In the course of our studies on catalytic reactions of Ru(III), epoxides and SCN ion[8], we observed that Ru(III) as anhydrous $RuCl_3$ can catalyse the efficient reaction of epoxides with acetone to give their corresponding 1,3-dioxalone in high yields. Epoxides with both electron releasing and withdrawing groups were reacted with 0.2 molar equivalents of anhydrous $RuCl_3$ in refluxing acetone for 1.5-4h. The products were isolated in 86-91% yields (Scheme).

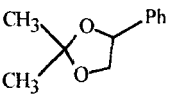
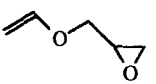
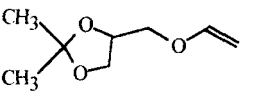
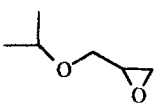
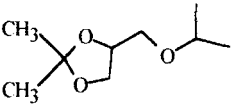
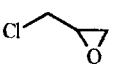
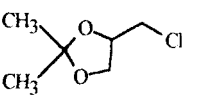
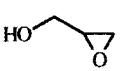
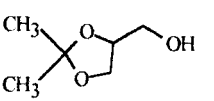
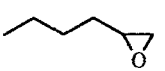
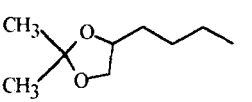
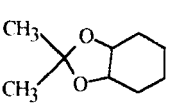
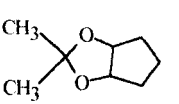


86-91%

scheme

The results obtained from these observations are shown in the Table. In conclusion this catalytic method can be applied for conversion of different classes of epoxides to their corresponding 1,3-dioxalanes. High yields of the reactions, simple work up and mild reaction conditions make this procedure a useful method for this transformation.

Table 1. Formation of acetonides from epoxides in refluxing acetone in the presence of 0.2 molar equivalents of anhydrous $RuCl_3$

Entry	Epoxide	Reaction Time (h)	Yield [I] %	Product [II]
1		5	90	
2		2	87	
3		2	86	
4		2	91	
5		2	89	
6		1.5	87	
7		1.5	88	
8		2	87	

[I] GC analysis shows 100% conversion but yield refers to isolated product.

[II] The products were identified by comparison with authentic samples.

Experimental: Products were characterised by comparison of their physical data IR, NMR and mass spectra with those prepared accordance with literature procedures. Infrared spectra were recorded on 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. The purity determination of the substrates and reactions monitoring were accomplished by TLC on silica gel polygram SILG/UV 254 plates or GLC on a Shimadzu GC-10A instrument.

Reaction of styrene oxide with acetone in the presence of Ru(III) as typical procedure: Styrene oxide (0.36 g, 3 mmol) and anhydrous $RuCl_3$(0.125 g, 0.6 mmol) were refluxed in acetone (5 mL) for 5h. The solvent was evaporated and the residue was chromtographed on a column of silica gel using CCl_4 or petroleum ether as eluent. The pure product was obtained as colourless liquid (0.481 g, 90%).

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