SHORT PAPER

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Conversion of epoxides into 1,3-dioxolanes catalysed by high oxidation state metalloporphyrins[†]

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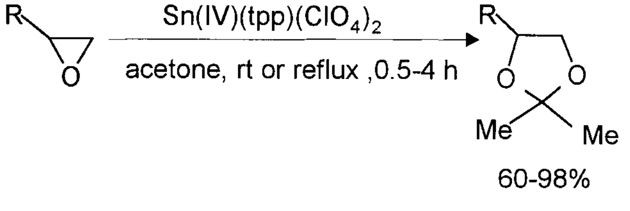
Tin(IV) tetraphenylporphyrin perchlorate, Sn(IV)(tpp)$(ClO_4)_2$, catalyses the efficient reaction of epoxides with acetone to give the corresponding 1,3-dioxolanes in good yields.

Keywords: epoxides, 1,3-dioxolanes, metalloporyphyrines

1,3-Dioxolanes are widely used as protecting groups for diols[1,2] with special application for carbohydrate and steroid chemistry. In addition, they are very suitable derivatives of diols for GLC and mass spectrometry.[3] Direct conversion of an epoxide into 1,3-dioxolane, instead of adding water to form diol with subsequent elimination in the presence of acetone, has been studied with relatively few reagents. Among these reagents, anhydrous copper sulfate[3] has been reported to produce the dioxolanes, but the yields in most cases are low with relatively long reaction times. The use of zeolite,[4a] KSF clay,[4b] HBF_4[4c] and some Lewis acids have been reported for this transformation. Most Lewis acids failed to give the desired products. Anhydrous zinc[5] and magnesium halides[5,6] have been reported to give rearranged products. The same reaction with both $FeCl_3$[7] and Me_3SiCl[8] gave the corresponding halohydrins while $SnCl_4$ and $TiCl_4$[9] produced little or no product. Among Lewis acids, BF_3.OEt_2 has been successfully applied for the conversion of different types of carbonyl compounds into their corresponding 1,3-dioxolane derivatives with ethylene and propylene oxides.[9] $RuCl_3$,[10] $TiCl_3$(OTf) and $TiO(TFA)_2$[11] can catalyse the efficient reaction of epoxides with acetone to give 1,3-dioxolane in excellent yields.

The successful applications of metalloporphyrins as mild Lewis acid catalysts,[12–16] prompted us to explore the potential of these complexes as catalysts for conversion of epoxides into 1,3-dioxolanes with acetone.

We found that tin(IV) tetraphenylporphyrin perchlorate, Sn(IV)(tpp)$(ClO_4)_2$, acts as an efficient catalyst for conversion of epoxides into 1,3-dioxolanes with acetone (Scheme 1).



Scheme 1

Reactions of different aliphatic and cyclic epoxides including those with electron-withdrawing substituents were performed in refluxing acetone (except for cyclohexene oxide) and in the presence of only 0.02 molar equivalent of Sn(IV)(tpp)$(ClO_4)_2$. The possibility of reaction with other carbonyl compounds such as cyclohexanone and cyclo-octanone was investigated, but low conversions were obtained under the same experimental conditions.

Table 1 summarises the results obtained for conversion of different epoxides to their corresponding 1,3-dioxolanes.

Although the reaction without a catalyst gave no product, the reaction proceeded catalytically upon addition of metalloporphyrin complexes. Among the catalysts tested, Sn(IV)(tpp)$(ClO_4)_2$ was found to be highly active for the reaction. The catalytic activities of the catalysts in reaction with styrene oxide appeared to be in the following order: Sn(IV)(tpp)$(ClO_4)_2$ (96%) >> Fe(tpp)ClO_4 (38%) > Fe(tF_5pp)Cl (18%) > Mn(tpp)ClO_4 (6%) > Sn(tpp)Cl_2 (5%) > Fe(tpp)Cl (4%) > Mn(tpp)Cl (2%) > Cu(tpp) (1%).

With regard to some other reported catalysts such as BF_3.OEt_2,[9] RuCl,[10] $TiO(TFA)_2$ and $TiCl_3$(OTf),[11] the following comparisons may be made: BF_3.OEt_2 has been used only for ethylene and propylene oxides and there is no reaction for epoxides with electron-releasing substituents; $RuCl_3$ and $TiO(TFA)_2$ suffer from long reaction times (up to 5 h) and the need for large amounts of catalysts (up to 0.3 molar ratio); but in the case of $TiCl_3$(OTf), the results obtained with the proposed catalyst show longer reaction times and lower yields.

In conclusion, Sn(IV)(tpp)$(ClO_4)_2$ /acetone as an efficient catalytic system expands the scope of utilisation of metalloporphyrins in useful organic synthesis.

Experimental

All chemicals used were of reagent grade. The tetraphenylporphyrin was prepared and metallated according to the literature.[17,18] Sn(IV)(tpp)$(ClO_4)_2$, Fe(tpp)ClO_4 and Mn(tpp)ClO_4 prepared as described by Arnold[19] and Suda.[13] Products were characterised by comparison of their physical data, IR and NMR with those of authentic samples and/or literature data. ^{1}H NMR spectra were obtained with a Brucker AW 80(80 MHz) spectrometer. GLC analyses were performed on a Shimadzu GC-16A instrument. Infrared spectra were recorded on a Philips PU-9716 or Shimadzu IR-4350 spectrophotometers. Refractive indices were obtained with a Carl Zeiss 51577 instrument.

General procedure for conversion of epoxides into 1,3-dioxolanes: In a round-bottomed flask (25 ml) equipped with a condenser and a magnetic stirrer, a solution of epoxide (1 mmol) in acetone (5 ml) was prepared. Sn(IV)(tpp)$(ClO_4)_2$ (0.019 g, 0.02 mmol) was added to this solution and the reaction mixture was stirred magnetically under reflux conditions. The reaction progress was monitored by GLC. After completion of the reaction, the mixture was directly passed through a short column of silica-gel (1:1 hexane–ethyl acetate) to remove the catalyst. The elute was evaporated under reduced pressure and the crude product was obtained in a quantitative yield. Distillation of product under reduced pressure resulted in the corresponding 1,3-dioxolane in 60–98% yields.

Physical and Spectral Data: Compound **2a:** n = 1.4465 (lit.[20] n = 1.448); ^{1}H-NMR($CDCl_3$) d: 4.34–4.05(2H, m), 2.58–2.07(4H, m), 1.35(6H, s), 1.24–1.00(4H, m); IR(neat): 2980, 2930, 2870, 1440, 1355, 1260, 1180, 1080, 960, 885, 835, 780 cm^{-1}.

Compound **2b:** n = 1.5270 (lit.[21] n = 1.5273); ^{1}H-NMR($CDCl_3$) d: 7.25(5H, s), 5.00(1H, dd, J = 8 Hz), 4.23(1H, dd, J = 7 Hz), 3.62(1H, dd, J = 6Hz), 1.48(3H, s), 1.40(3H, s); IR(neat): 3036, 2990, 2870, 1600, 1495, 1450, 1365, 1230, 1150, 1055, 945, 850, 755, 700 cm^{-1}.

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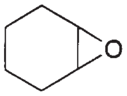
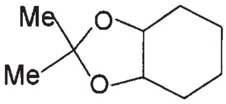
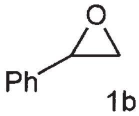
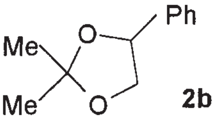
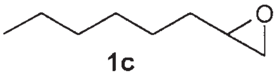
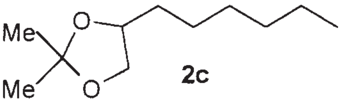
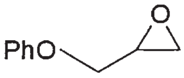
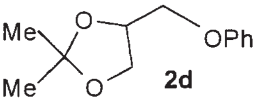
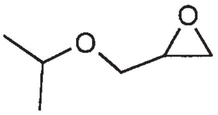
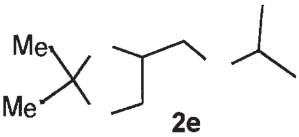
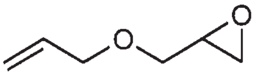
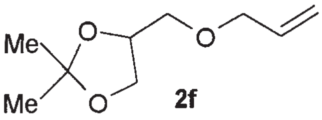
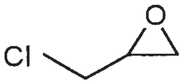
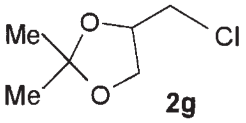
[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Table 1 Conversion of Epoxides into 1,3-Dioxolanes Catalyzed by Sn(IV)(tpp)(ClO4)2.

Run	Substrate	Product[a]	Time/h	Condition	Yield/%[a]
1	 **1a**	 **2a**	0.5	RT	98
2	 1b	 **2b**	0.5	Reflux	96
3	 1c	 **2c**	3	Reflux	86
4	 **1d**	 **2d**	3.5	Reflux	88
5	 **1e**	 **2e**	4	Reflux	83
6	 **1f**	 **2f**	4	Reflux	90
7	 1g	 **2g**	4	Reflux	60

[a] Isolated yields.

Compound **2c:** n=1.2495; ^{1}H-NMR(CDCl$_3$) d: 4.20–3.31(3H, m), 1.72–1.13(16H, m), 0.82(3H, t, $J = 7$ Hz); IR(neat): 2970, 2915, 2860, 1460, 1375, 1250, 1160, 1050, 950, 850, 730 cm^{-1}. Found: C, 70.85; H, 11.88. $C_{11}H_{22}O_2$ requires C, 70.92; H, 11.90%.

Compound **2d:** mp 63 °C (lit.[22] mp 64–65 °C); ^{1}H-NMR(CDCl$_3$) d: 7.47–6.72(5H, m), 4.65–3.64(5H, m), 1.42(3H, s), 1.30(3H, s); IR(KBr): 3070, 2990, 2920, 1600, 1585, 1490, 1445, 1344, 1240, 1210, 1170, 1035, 910, 810, 747 cm^{-1}.

Compound **2e:** n = 1.4170(lit.[23] n = 1.4168); ^{1}H-NMR(CDCl$_3$) d: 4.37–3.30 (6H, m), 1.37(3H, s), 1.27(3H, s), 1.15(6H, d, $J = 6$ Hz); IR(neat): 2970, 2930, 2870, 1460, 1380, 1365, 1260, 1125, 1070,1030,920, 850, 735 cm^{-1}.

Compound **2f:** n = 1.4318(lit.[24] n = 1.4320); ^{1}H-NMR(CDCl$_3$) d: 5.95–4.70(3H, m), 4.35–3.32(7H, m), 1.33(3H, s), 1.25(3H, s); IR(neat): 3050, 3000, 2920, 2850, 1455, 1360, 1320, 1250, 1090, 920, 840, 755 cm^{-1}.

Compound **2g:** n = 1.4359 (lit.[25] n = 1.4357); ^{1}H-NMR(CDCl$_3$) d: 4.34–3.12(5H, m), 1.32(3H, s), 1.21(3H, s); IR(neat): 2960, 2900, 2860, 1450, 1375, 1250, 1165, 1080, 1025, 935, 870, 740 cm^{-1}.

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