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Ring Opening of Propylene Oxide by Transition Metal (Ti, Zr, V) Complexes

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Propylene oxide inserts into metal–chlorine bonds to give 2-chloro-iso-propoxy and 2-chloro-n-propoxy compounds. The presence of the cyclopentadienyl ligand in the environment of the central atom leads mainly to the formation of 2-chloro-isopropoxy compounds, in relation to the π donor character of this ligand. Insertion in the metal–oxygen bond is obtained with an electronegative substituent as the fluoroethoxy ligand (OCH_2CF_3).

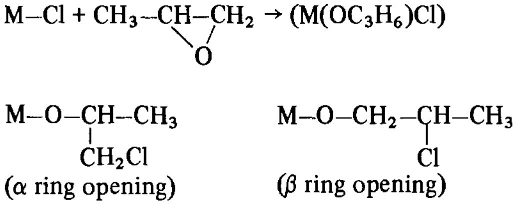
Introduction

Transition metal chloride compounds [1] ($MoCl_5$, $TaCl_5$, WCl_6) were recently used as catalysts for reacting 1,2-epoxyalkane and ethanol to give a mixture of $RCH(OH)CH_2OC_2H_5$ and $RCH(OC_2H_5)CH_2OH$ according to the α or β ring opening direction of the oxirane. It was also previously reported that ethylene oxide was inserted into the metal–chlorine bond of $TiCl_4$ and $ZrCl_4$ to give chloroethoxide compounds [2].

The aim of this work is to follow the ring opening direction of the 1,2-propylene oxide when inserting in different metal–chlorine compounds in relation to the influence of the central atom environment.

Results and Discussion

Various chloro derivatives of titanium, zirconium, vanadium and tungsten moieties (reported in Table I) react with 1,2-propylene oxide according to the scheme:



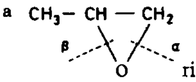
$$M{-}Cl + CH_3{-}\underset{\diagdown\,O\,\diagup}{CH{-}CH_2} \rightarrow (M(OC_3H_6)Cl)$$

$$M{-}O{-}\underset{CH_2Cl}{CH}{-}CH_3 \qquad M{-}O{-}CH_2{-}\underset{Cl}{CH}{-}CH_3$$

(α ring opening) (β ring opening)

TABLE I. Ring Opening of the 1,2-Propylene Oxide[a] with M–Cl Bond.[b]

Compound	% α $HO\underset{CH_2Cl}{C}HCH_3$	% β $HOCH_2\underset{Cl}{C}HCH_3$
$TiCl_4$	30	70
$ZrCl_4$	30	70
$VOCl_3$	58	42
WCl_6	42	58
$TiCl_2(OEt)_2$	56	44
$CpTiCl_3$	73	27
Cp_2ZrCl_2	90	10
Cp_2VCl_2	100	

[a] 

ring opening direction. [b] The reaction of 1,2-propylene oxide with HCl gives 83%and 17%of α and β ring opening form, respectively.

The direction of the ring opening is determined by GLC analysis after hydrolysis of the product.

As a general feature, 2-chloroisopropanol and 2-chloro-n-propanol are produced, whatever the nature of the central atom, with a predominance of the β ring opening direction for $TiCl_4$ and $ZrCl_4$. In the mixed derivative $TiCl_2(OEt)_2$, an inversion of the ratio is observed. This trend increases with the presence of a cyclopentadienyl group to reach formation of the 2-chloro-isopropanol as a main product in the case of Cp_2VCl_2. This situation may be explained by the modification of the Lewis acidity of the central atom due to the presence of a cyclopentadienyl group as a π electron donor, as we previously reported [3]. On the other hand, electronegative substituents on the metal would perform oxirane insertion. This is especially true with $Ti(Oi\text{-}Pr)_2(OCH_2CF_3)_2$ which gives $Ti(Oi\text{-}Pr)_2(OC_3H_6OCH_2CF_3)_2$ by insertion into a metal–oxygen bond.

It appears that the more ionic the metal halogen or oxygen bond, the more α ring opening direction occurs and selectivity is increased.

We find that treatment of 1,2-propylene oxide with $(Cp_2TiCl)_2$ in tetrahydrofurane solution at room temperature deoxygenates the epoxide and leads to the well-known orange solid $(Cp_2TiCl)_2O$ and gaseous propylene [4].

Experimental

All manipulations were carried out under argon in conventional Schlenk type apparatus using CH_2Cl_2 as solvent. Microanalyses were carried out by the Service Central de Microanalyse du CNRS. Starting materials were purchased from Alfa or prepared according to literature methods [5, 6]. Determination of the ring opening direction of the 1,2-propylene oxide was performed by GLC analysis after hydrolysis of the product.

General Procedure

A large excess of 1,2-propylene oxide in 20 ml CH_2Cl_2 (4.0 g, 68.9 mmol) is added slowly dropwise to $VOCl_3$ (2.0 g, 11.5 mmol) in 20 ml CH_2Cl_2 to avoid an exothermic reaction. The yellow solution is stirred overnight, volatiles removed *in vacuo* and the viscous liquid left is distilled as $VO(OC_3H_6Cl)_3$ (b.p. 110 °C/0.01 mmHg). *Anal.* for $VC_9H_{18}O_4Cl_3$: % exp (calcd.); C: 31.0 (31.0); H: 4.9 (5.2); V: 15.0 (14.7).

$Ti(OEt)_2(OC_3H_6Cl)_2$ (b.p. 125 °C/0.01 mm Hg): *Anal.* for $TiC_{10}H_{22}O_4Cl_2$: % exp. (calcd.): C: 36.2 (36.9); H: 6.7 (6.8); Ti: 14.5 (14.8); $Ti(Oi\text{-}Pr)_2(OC_3H_6OCH_2CF_3)_2$ (b.p. 200 °C/0.01 mm Hg): *Anal.* for $TiC_{16}H_{30}O_6F_6$: % exp (calcd.): C: 40.5 (40.0); H: 6.5 (6.2); Ti: 9.7 (10.0).

The following chloroalkoxides are undistillable oils: $CpTi(OC_3H_6Cl)_3$: *Anal.* For $TiC_{14}H_{28}O_3Cl_3$: % exp. (calcd.) C: 42.5 (42.7); H: 5.8 (5.8); Ti: 12.9 (12.2); $Ti(OC_3H_6Cl)_4$: *Anal.* for $TiC_{12}H_{24}O_4Cl_4$: % exp. (calcd.): C: 35.0(34.1); H: 6.0 (5.7); Ti: 11.0 (11.4). Other products contain polymeric propylene oxide as by-product formed during the preparation stage.

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