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Catalytic activity of salenCo(III)OAc complex in the reaction of addition of carboxylic acids to terminal epoxides

Agnieszka Bukowska, Wiktor Bukowski*, Jarosław Noworól

Faculty of Chemistry, Rzeszów University of Technology, al. Powstańców W-wy 6, 35-959 Rzeszów, Poland

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Abstract

The catalytic activity and regioselectivity were studied of the salenCo(III)OAc complex in the reaction of addition of aliphatic carboxylic acids to a series of terminal epoxides (epichlorohydrin, 1,2-epoxybutane, propylene oxide, *tert*-butyl glycidyl ether and 2,3-epoxypropyl phenyl ether). The reduction in the activity in the order: acetic > acrylic > methacrylic acid was found. The regioselectivity of the addition was independent on carboxylic acid nature and depended on the nature of the epoxide. The best regioselectivity for the addition to epichlorohydrin was observed. The catalytic activity and regioselectivity of salenCo(III)OAc were compared with those for chromium(III) acetate catalyst.

Keywords: Epoxide; Carboxylic acid; Ring opening; Salen cobalt(III) complex

1. Introduction

For about 15 years, i.e. since asymmetric epoxidation of non-functional olefins in the presence of chiral salenMn(III) complexes was discovered [1,2] a great deal of interest was focused on the study of catalytic activity of metal salen complexes [3–11].

Besides the asymmetric epoxidation, salen catalysts are very often explored in the asymmetric ring-opening reactions involving epoxides. The Jacobsen group has shown that chiral salenCr(III) complexes are very useful in the ring-opening epoxides by trimethylsilyl azide [12,13]. They were also tested in reactions of epoxides with thiols [14] and benzoic acid [15]. Chiral salenCo(III) complexes turned out to be very effective catalysts in the addition of phenols [16] and water (*hydrolytic kinetic resolution*) [17] to terminal epoxides. Cobalt(III) complexes were also explored in other ring-opening reactions, namely in alcohol [18] and aromatic acid addition [15] to epoxides.

In particular, the mentioned findings concerning ring-opening reactions made easier the synthesis of different vicinal chiral amino alcohols, on one side, and chiral epoxides, diols and hydroxy ethers, on the other. The first can be used as precious ligands for asymmetric catalysis or chiral intermediates, and the second, as the chiral intermediates for asymmetric synthesis of pharmaceuticals.

In our present study, we tested the catalytic activity of salenCo(III)OAc complex (**1c**) in the addition of aliphatic carboxylic acid to terminal epoxides (Scheme 1). The aspects of the regiochemistry of reactions and reagent reactivity were particularly explored.

2. Experimental

2.1. Materials

Carboxylic acids (acetic, acrylic and methacrylic) and racemic terminal epoxides (epichlorohydrin, 1,2-epoxybutane, propylene oxide, *tert*-butyl glycidyl ether and 2,3-epoxypropyl phenyl ether) were reagent grade from Aldrich or Fluka.

* Corresponding author.
E-mail address: wbuk@prz.rzeszow.pl (W. Bukowski).

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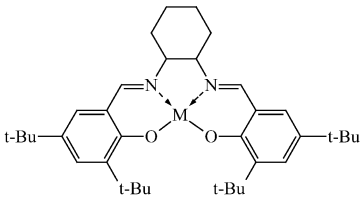

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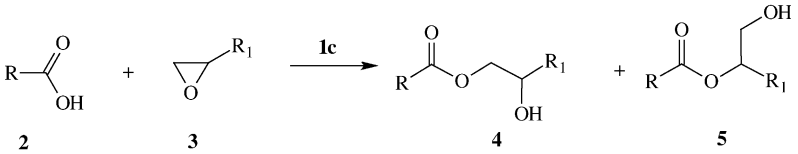
M= **1a**: H,H; **1b**: Co; **1c**: CoOAc



2 **3** **4** **5**

	R		R_1
2a	CH_3	**3a**	CH_3
2b	CH_2=CH	**3b**	CH_2Cl
2c	CH_2=C(CH_3)	**3c**	CH_2CH_3
		3d	$CH_2OC(CH_3)_3$
		3e	CH_2OPh

Scheme 1. General scheme of the addition.

Cobalt(II) acetate tetrahydrate ($C_4H_6CoO_4{\cdot}4H_2O$) and (±)-*trans*-1,2-diaminocyclohexane were reagent grade from Aldrich or Fluka.

Salen ligand (**1a**) was obtained in the classic way in the reaction of 3,5-di-*tert*-butylsalicylaldehyde and (±)-*trans*-1,2-diaminocyclohexane in 96% ethanol solution [19]. 3,5-Di-*tert*-butylsalicylaldehyde was obtained according to [20]. SalenCo(II) complexes (**1b**), the precursor of complex (**1c**), were synthesized from salen ligand (**1a**) and cobalt(II) acetate in dichloromethane/methanol solution according to the procedure described in [21]. The salenCo(III)OAc catalyst (**1c**) was prepared from the salenCo(II) complex (**1b**) by using the procedure described by Jacobsen and coworkers [21] and was used without any further purification.

Table 1
Molar fraction of regioisomers (**4** and **5**) in the reaction of acetic acid with epichlorohydrin in the presence of different catalytic systems

Catalyst	Temperature (°C)	Ratio of **4**:**5**
Chromium(III) acetate	60	92.1:7.9
SalenCr(III)Cl	60	87.8:12.2
SalenCo(III)OAc	60	87.6:12.4
SalenCo(III)OAc	40	91.5:8.5
SalenCo(III)OAc	25	93.6:6.4

2.2. General procedure

Small vials (5 ml) were charged with salenCo(III)OAc complex (**1c**) (0.2–1.0 mol%) and equimolar mixtures of carboxylic acids and epoxides (1 ml). The reaction mixtures were stirred for 10–48 h in a glycerine bath. Progress of the reaction was monitored by capillary GC analysis (HP-FFAP capillary column). The molar fractions of isomeric products **4** and **5** were calculated by measuring the surface of area of chromatographic peaks of regioisomers.

3. Results and discussion

Our previous study on the reaction of aliphatic carboxylic acids with epichlorohydrin (ECH) has shown that complexing chromium(III) ions by salen ligand exert a disadvantageous effect on their catalytic activity and regioselectivity in comparison with simple salt: chromium(III) acetate [22]. We expected salenCo(III)OAc complex to be more active and selective than the earlier tested chromium(III) compounds.

The study of the catalytic activity of **1c** was started from the reaction of acetic acid with epichlorohydrin. It turned out that the activity of the salenCo(III)OAc complex (**1c**) in this reaction was clearly higher than in the case of previous tested chromium catalyst (Fig. 1). Unfortunately, there was

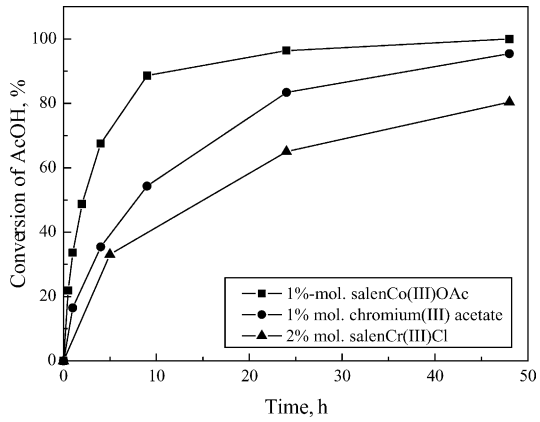


Fig. 1. Conversion of acetic acid in the reaction with epichlorohydrin in the presence of different catalytic systems (temperature: 25 °C).

Table 2
The catalytic activity of the salenCo(III)OAc complex and chromium(III) acetate in the reactions of acetic acid with a series of epoxides (temperature: 25 °C; time: 24 h)

Catalyst (1 mol%)	Conversion of **2a** (%)				
	3a	**3b**	**3c**	**3d**	**3e**
Chromium(III) acetate	73	83	82	55	70
SalenCo(III)OAc	81	96	83	85	95

no improvement in the addition regioselectivity (Table 1). The molar fraction of the abnormal addition product **5** in the presence of **1c** at 60 °C was comparable to that observed for the salenCr(III)Cl complex and higher than in the presence of chromium(III) acetate. In the presence of complex (**1c**) the improvement of regioselectivity was possible after reducing reaction temperature.

Further experiments have shown that catalyst **1c** turned out to be more catalytically active in the case of addition of acetic acid to propylene oxide, *tert*-butyl glycidyl ether or 2,3-epoxypropyl phenyl ether (Table 2). Among the epoxy compounds only 1,2-epoxybutane (**3c**) reacted with acetic acid with similar yield both in the presence of the salenCo(III)OAc complex and chromium(III) acetate.

In the presence of salenCo(III)OAc **3b** reacted with acetic acid most readily and **3a** at the lowest rate (Table 2). Among all explored oxiranes, the best regioselectivity of acetic acid addition was observed for epichlorohydrin (Table 3).

An increase of molar fraction of isomer **5** with growing acceptor character of the substituents in the epoxy ring (the order: epichlorohydrin < *tert*-butyl glycidyl ether < 2,3-epoxypropyl phenyl ether) can be explained in terms of the increasing partial charge of the more substituted carbon atom in epoxy ring. Unfortunately, the reduction of the regioselectivity in the case of propylene oxide and 1,2-epoxybutane is not consistent with this explanation.

Table 3
Molar fraction of regioisomers (**4** and **5**) in the reactions of acetic acid (**2a**) with a series of epoxides (**3**) in the presence of **1c** (temperature: 25 °C)

Epoxide	Ratio **4**:**5**
3a	85.6:14.4
3b	93.6:6.4
3c	84.1:15.9
3d	89.3:10.7
3e	85.3:14.7

Table 4
The catalytic activity of the salenCo(III)OAc complex and chromium(III) acetate in the reactions of acrylic acid with a series of epoxides (temperature: 25 °C; time: 24 h)

Catalyst (1 mol%)	Conversion of **2b** (%)				
	3a	**3b**	**3c**	**3d**	**3e**
Chromium(III) acetate	82	94	88	76	92
SalenCo(III)OAc	84	91	70	72	93

Table 5
The catalytic activity of the salenCo(III)OAc complex and chromium(III) acetate in the reactions of methacrylic acid with a series of epoxides (temperature: 25 °C; time: 24 h)

Catalyst (1 mol%)	Conversion of **2c** (%)				
	3a	**3b**	**3c**	**3d**	**3e**
Chromium(III) acetate	83	96	81	76	89
SalenCo(III)OAc	11	25	10	21	32

Further study on the addition of acrylic and methacrylic acids to the same group of oxiranes were carried out in the presence of complex **1c**. This catalyst was found less active in these reactions in comparison with acetic acid addition (Tables 4 and 5). Consequently, its catalytic activity became similar to that observed for acrylic acid addition in the presence of chromium(III) acetate (only in the case of 1,2-epoxybutane chromium(III) acetate was more active catalyst). On the other hand, its activity in the reactions with methacrylic acid was weaker than that of chromium(III) acetate.

Acrylic and methacrylic acids similarly acetic acid showed the best regioselectivity in the addition to epichlorohydrin (Table 6). However, no influence of the acid nature on the regioselectivity was observed as it had been found in the presence chromium(III) acetate [23].

Table 6
Molar fraction of regioisomers (**4**) and (**5**) in the reactions of acrylic (**2b**) and methacrylic (**2c**) acids with a series of epoxides (**3**) in the presence of **1c** (temperature: 25 °C)

Epoxide	Ratio **4**:**5**	
	2b	**2c**
3a	85.6:14.4	86.4:13.6
3b	97.0:3.0	95.4:4.6
3c	85.8:14.2	85.0:15.0
3d	94.8:5.2	91.7:8.3
3e	90.1:9.9	83.6:16.4

4. Conclusion

The study has shown that the salenCo(III)OAc complex exhibits high catalytic activity in the reaction of acetic acid addition to a series of terminal epoxides. Its activity clearly reduces in the reaction involving theoretically stronger acids, e.g. acrylic and methacrylic. Furthermore, there was no expected improvement in the regioselectivity of the addition in relation to that observed for simple chromium(III) salts, e.g. chromium(III) acetate. In the presence of the salenCo(III)OAc complex, the molar fraction of the regioisomers depends on the nature of epoxides and practically does not depend on the structure of carboxylic acids. The highest regioselectivity was observed for epichlorohydrin.

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