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A study on the addition of some carboxylic acids to epichlorohydrin in the presence of salen chromium(III) complexes

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Abstract

The effect of salen ligands on the catalytic activity and regioselectivity of chromium(III) ions in the addition reaction of aliphatic carboxylic acids to epichlorohydrin was studied. It was found that coordination of chromium(III) ions by tetradentate Shiff's bases decreased their catalytic activity in comparison to chromium(III) acetate. Slightly worse regioselectivity was also detected. Moreover, an increase of the regioselectivity of the addition with decreasing temperature was observed.

Keywords: Oxiranes; Carboxylic acid; Ring opening; Salen chromium(III) complexes

1. Introduction

The ring opening reactions affected by nucleophilic compounds is one of the basic transformations of epoxy compounds. It makes it possible to form new bonds such as C–O (addition of alcohols, phenols, carboxylic acids), C–S (thiols, thiophenols, or thioacids), C–N (reactions with amines and their derivatives or azides), C–X (reactions with halogenhydrins or their salts) and C–C (addition of hydrogen cyanide, metalorganic compounds), etc.

The products of the addition contain hydroxy groups capable of reacting in the subsequent-parallel reactions with oxiranes. In some cases, e.g. in the synthesis of polyglycols or polyetherols used in manufacturing of non-ionic detergents or polyurethane semi-products, the subsequent-parallel reactions are expected to proceed. In most cases, however, these reactions are suppressed by selecting suitable conditions of addition, e.g. by using selective catalysts or an excess of nucleophiles.

Regardless of the type of catalysis, the asymmetric derivatives of epoxy compounds react yielding two isomeric products: the normal addition products and the abnormal one. The yield of isomers depends on many factors, e.g. the structure of reagents, catalysts, solvents, etc. [1–7]. Generally, in the neutral or basic medium formation of the normal product is enhanced, while in acidic medium probability of forming the abnormal isomer increases.

Sometimes, the abnormal products of addition are dominant. It happens for compounds having double bounds or an aromatic ring in the direct neighborhood of epoxy group. In these derivatives, mesomeric stabilization of carbocation formed after breaking C–O bond in epoxy group may occur.

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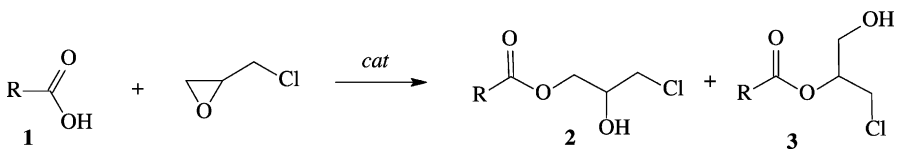
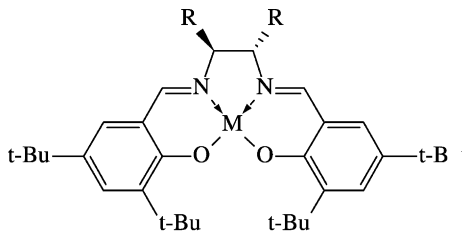


Fig. 1. General scheme of the addition; cat.: $(AcO)_3Cr$; $(AcO)_3Cr + \mathbf{4}$ or **5**; **1**–**3a**: R = CH_3, **b**: R = CH_3CH_2, **c**: R = $CH_3(CH_2)_3$, **d**: R = $CH_3(CH_2)_4$, **e**: R = $CH_3(CH_2)_6$, **f**: R = CH_2=CH, **g**: R = CH_2=C(CH_3).

In our previous studies concerning the reaction of aliphatic carboxylic acids with some monosubstituted oxiranes, we have shown that formation of the abnormal addition product is limited by Cr^{3+} ion (from chromium(III) acetate) [7–9] as compared with basic catalysts [10]. The high catalytic activity of chromium(III) acetate and high regioselectivity of the addition result from coordination of reagents by chromium(III) ions leading to activation of an epoxy ring. The ring opening in oxiranes becomes possible by an internal attack of coordinated carboxylate ions. Introduction into the coordination sphere of the metal bulky ligands ought to limit at theoretically, the chance least of formation of abnormal isomers.

In this work, some salen chromium(III) complexes were tested in order to check this assumption. We tried to follow Jacobsen et al. who used salenCr(III) and salenCo(III) complexes in ring opening of epoxides by various nucleophiles [11–19]. Our study concentrated on the regioselectivity of addition of some aliphatic carboxylic acids to epichlorohydrin (Fig. 1) and catalytic activity of chromium(III) ions in the presence of selected salen ligands (Fig. 2).



4: M = H, H
5: M = Cr(III)Cl
a: R = H
b: R = $(CH_2)_4$

Fig. 2. General structure of salen ligands and their chromium(III) complexes.

2. Experimental

2.1. Materials

Carboxylic acids and *rac*-epichlorohydrin were reagent grade from POCh, Aldrich or Fluka. Chromium(III) acetate (grade p.a.) was purchased from Sverdlovskij Khimicheskij Zavod.

Most of salicylaldehydes, ethylenediamine, (±)-*trans*-1,2-diaminocyclohexane, and anhydrous $CrCl_2$ were reagent grade from Aldrich, Avocado or Fluka.

Salen ligands (4) were obtained in stoichiometric reaction of salicylic aldehyde and diamine in 96% ethanol solution of [20]. SalenCr(III)Cl complexes (5) were synthesized according to procedure described in [17]. 3,5-di-*tert*-Butylsalicylaldehyde was obtained according to [21].

2.1.1. Experimental data of salen ligands

4a: yellow solid, m.p. 190–191 °C; IR (KBr): 2963, 2909, 2870, 2704 (br), 1629 (C=N), 1595, 1482, 1466, 1440, 1394, 1360, 1294, 1271, 1253, 1235, 1213, 1203, 1174, 1042, 974, 880, 839, 830, 774, 730, 711, 645 cm^{-1}.

^{1}H NMR ($CDCl_3$, 200 MHz), δ: 13.6 (s, 2H), 8.38 (s, 2H), 7.36 (d, J = 2.4 Hz, 2H), 7.06 (d, J = 2.4 Hz, 2H), 3.91 (s, 4H), 1.43 (s, 18H), 1.28 (2, 18H); ^{13}C NMR ($CDCl_3$, 50 MHz): 167.56, 158.01, 140.03, 136.57, 127.00, 126.03, 117.79, 59.59, 34.99, 34.0, 31.45, 29.40; Anal. calc. for $C_{32}H_{48}N_2O_2$ (492.74): C, 78.00; H, 9.82; N, 5.69. Found: C, 77.78; H, 9.83; N, 5.61.

4b: yellow solid, m.p. 183–184 °C; IR (KBr): 2962, 2936, 2863, 2700 (br), 1630, 1594, 1469, 1439, 1390, 1362, 1270, 1253, 1241, 1203, 1174, 1135, 1086, 1038, 879, 862, 828, 773, 711, 644: ^{1}H NMR ($CDCl_3$, 200 MHz), δ: 13.72 (s, 2H), 8.35 (s, 2H), 7.34 (d, J = 2.4 Hz, 2H), 7.05 (d, J = 2.4 Hz, 2H), 3.62–3.52 (m, 2H), 2.05–1.50 (m, 8H), 1.40 (s, 18H), 1.27 (2, 18H),

^{13}C NMR ($CDCl_3$, 50 MHz): 165.81, 158.17, 139.86, 136.33, 126.72, 126.02, 117.92, 72.40, 35.00, 34.02, 33.26, 29.42, 24.34.

Anal. calc. for $C_{36}H_{54}N_2O_2$ (546.83): C, 79.07; H, 9.95; N, 5.12. Found: C, 79.11; H, 9.95; N, 5.11.

2.1.2. Experimental data of salenCr(III)Cl

5a: brown solid; IR (KBr): 3195 (br), 2957, 2906, 2869, 1625 (C=N), 1532, 1461, 1437, 1412, 1387, 1362, 1331, 1316, 1272, 1256, 1234, 1200, 1169, 832, 785, 748, 541; Anal. calc. for $[C_{34}H_{53}N_2O_4CrCl^{\bullet}(3/2)H_2O^{\bullet}\ (1/2)THF]$ (641.25): C, 63.68; H, 8.33; N, 4.37; Cr, 8.11; Cl, 5.53. Found: C, 63.71; H, 8.42; N, 4.49; Cr, 8.06; Cl, 5.70.

5b: brown solid; IR (KBr): 3376 (br), 2953, 2906, 2867, 1620 (C=N), 1532, 1462, 1435, 1381, 1361, 1320, 1255, 1200, 1170, 1029, 837, 785, 748, 564, 544; Anal. calc. for $[C_{38}H_{59}N_2O_4CrCl^{\bullet}(3/2)H_2O^{\bullet}(1/2)THF]$ (689.29): C, 65.64; H, 8.55; N, 4.03; Cr, 7.48; Cl, 5.10. Found: C, 65.60; H, 8.53; N, 4.03; Cr, 7.56; Cl, 5.00.

2.2. General procedure

Small vials (5 ml) were charged with the catalytic system $(AcO)_3Cr$, **4** + $(AcO)_3Cr$ or **5** (0.5, 1, or 2 mol%, suitable for 60, 40 and 25 °C) and equimolar mixtures of carboxylic acid and epichlorohydrin (1 ml). The reaction mixtures were stirred for 10–48 h in glycerin bath. Progress of the addition reaction was monitored by capillary GC analysis (HP 5890 chromatograph with an FFAP capillary column, 10 m/0.53 mm/1 μm). Cyclohexanone was used as external standard. The molar fractions of isomeric products **2** and **3** were calculated by measuring the surface area of the chromatographic peaks due to regioisomers. Experiments were carried out at least twice.

3. Results and discussion

In the initial stage of our study, the reaction of acetic acid addition to epichlorohydrin in the presence chromium(III) acetate was explored. Two series experiments were carried out. In the first series of 0.5 mol% chromium(III) acetate and the same quantity of salen ligands **4** were used as catalytic systems. In the second series of reactions, 0.5 mol% salenCr(III)Cl complexes **5** were the catalysts. For reference, a blank experiment with 0.5 mol% chromium(III) acetate without salen additives was carried out. In all experiments, stoichiometric quantities of the reagents were used. The reactions were carried out at 60 °C. Progress of the addition was monitored by capillary GC analysis.

Table 1
The effect of salen ligand 4 on the catalytic activity of chromium(III) ions in acetic acid addition to epichlorohydrin; concentration of catalytic system—0.5 mol%, temperature—60 °C.

Time (h)	Conversion of **1a** (%)				
	$(AcO)_3Cr$	$(AcO)_3Cr$ + **4a**	$(AcO)_3Cr$ + **4b**	**5a**	**5b**
1.5	49	44	48	26	23
3	74	66	72	44	43
4.5	87	84	85	58	55
8	96	93	95	84	80
24				97	99

It turned out that addition of free salen ligands to the mixture of acetic acid, epichlorohydrin and chromium(III) acetate practically did not change the rate of substrate conversion in comparison to the blank experiment (Table 1). In spite of that some worsening of the addition regioselectivity was detected (Fig. 3).

The absence of the an effect of salen ligands on the catalytic activity of chromium(III) ions in the first series of experiment indicates a lack of complexing of metal by the tetradendate ligands.[1] Probably, the detected slightly negative effect of the salen ligand additives on the regioselectivity of addition is caused by the fact that the ligands are Shiff's bases. It is well known that the addition carboxylic acid to epoxy compound is catalyzed, beside some transition metal complexes also by many substances of acidic and basic character. Generally, basic compounds favor formation of the normal addition product, but are less selective than chromium(III) acetate.

Two additional experiments with tertiary amines (triethylamine and tributylamine used in concentration

[1] It seems to be caused by the inertness of chromium(III) ions in complexing reactions. Stoichiometric mixtures of acetic acid and epichlorohydrin have a dark green colour, and addition of the yellow coloured salen ligand into this solution caused only a little lightening of the initial colour of the mixture. Solution of salenCr(III)Cl has a dark brown colour.

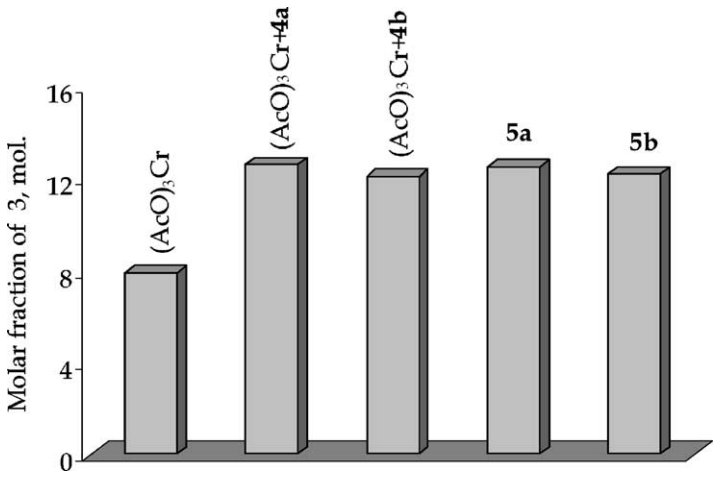


Fig. 3. Molar fraction of abnormal product (**3**) of addition of acetic acid to epichlorohydrin in the presence of different catalytic systems; temperature 60 °C.

of 12 mol% clearly showed disadvantageous effect of the basic type catalyst on the regioselectivity of addition. The yield of abnormal product in the presence of amines was as high as 16–17 mol%. Therefore, the regioselectivity of addition was close to that observed for the alkali metal acetate catalyzed reactions [10].

The slightly negative effect of salen ligands on the regioselectivity of acetic acid addition to epichlorohydrin carried out in the presence of complexes **5** was observed, as well (Table 1). It turned out that only the steric hindrances caused by introducing tetradentate salen ligand into coordination sphere of chromium(III) ions was insufficient to limit the amount of abnormal product as compared to chromium(III) acetate (Fig. 3), even in the presence of bulky substituents such as *tert*-butyl group. Also in this case, the basic properties of ligands in salenCr(III)Cl complexes are probably responsible for worsening addition regioselectivity.

Table 2
The conversion of some carboxylic acids in the reaction with epichlorohydrin in the presence of **5b**; concentration of **5b**—2 mol%; temperature—25 °C.

Time (h)	Conversion of **1** (%)						
	1a	**1b**	**1c**	**1d**	**1e**	**1f**	**1g**
12	60	65	36	41	48	29	20
24	96	98	43	47	52	54	34
48			60	59	60	87	42

Limited access to chromium ions is undoubtedly the reason for reduction of the addition rate of acetic acid to epichlorhydrin in the presence of salen complexes **5** in comparison to chromium(III) acetate (Table 1). Moreover, considerable changes in addition rates when passing from acetic to more bulky acids were also observed (Table 2). The highest rate was recorded for acetic and propionic acid addition and the smallest for methacrylic acid. The others homologues of acetic acid reacted with epichlorohydrin in a similar way.

Generally, in the presence of salen complex **5** the situation observed was different than in the case of chromium(III) acetate. Methacrylic acid reacted

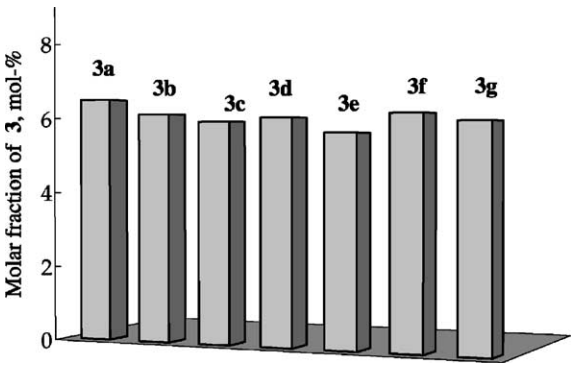


Fig. 4. Molar fraction of regioisomers **3** in the addition of a series of carboxylic acids to epichlorohydrin in the presence of 2 mol% of **5b**; temperature 25 °C.

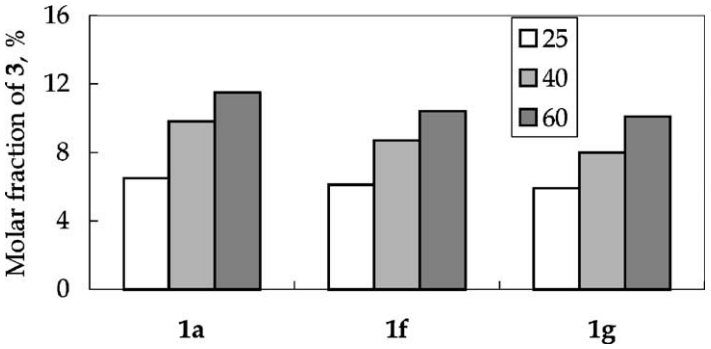


Fig. 5. The effect of temperature on the addition carboxylic acids to epichlorohydrin carried out in the presence of **5b**.

approximately three times faster than acetic acid and its reactivity was very close to that of acrylic acid [9].

From comparison of molar fractions of regioisomers **2** and **3** it follows that addition of series carboxylic acids **1** to epichlorohydrin in the presence salen complex **5** runs with comparable regioselectivity (Fig. 4).

Finally, we studied the effect of temperature on carboxylic acids addition to epichlorohydrin in the presence of **5b**. In turned out that temperature was an essential factor with respect to the yield of abnormal product. A clear decrease of the molar fraction of **3** with decreasing reaction temperature was observed (Fig. 5). However, a reduction in reaction temperature requires more catalyst and the time of addition does increase.

4. Conclusion

The study has shown that salenCr(III)Cl complexes are catalytically less active in the addition of aliphatic carboxylic acids to epichlorohydrin than simple chromium(III) salt, e.g. chromium(III) acetate. Also the sterical limitations by salen ligands do not improve the regioselectivity of addition, but, in opposite, slightly worsen the regioselectivity. In our view it may be caused by the basic properties of salen ligands.

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