

KİMYA
CHEMISTRY

DOI: <https://doi.org/10.36719/2707-1146/36/17-23>

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UOT 547.37:542.91

**PREPARATION AND PROPERTIES OF MONO AND DIEPOXY ETHERS BASED ON
ALICYCLIC OXIMES, DIOXIMES AND THEIR DERIVATIVES**

Abstract

The reaction of alicyclic oximes and dioximes with epichlorohydrin in the presence of a $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ catalyst to obtain chlorohydrin ethers of the corresponding dioximes was studied. A probable mechanism for the reaction is proposed. Epoxy ethers of dioximes were synthesized by dehydrochlorination of chlorohydrin ethers with alkali. The physico-chemical parameters of the synthesized compounds were determined. The composition and structure of chlorohydrin and epoxy ethers were proven by ^1H , ^{13}C NMR, IR-spectroscopy and the hydroxyl, chlorine and epoxy numbers of the synthesized compounds were determined. The synthesized epoxy compounds can be used as synthetic fibers in the textile industry.

Keywords: *condensation reaction, epichlorohydrin, alicyclic dioximes, boron trifluoride etherate, epoxidation, epoxy ethers*

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**Alisiklik oksimlər, dioksimlər və onların törəmələri əsasında mono və diepoksi efirlərinin
alınması və xassələri**

Xülasə

$\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ katalizatorunun iştirakı ilə alisiklik oksimlərin və dioksimlərin epixlorhidrinlə reaksiyası müvafiq dioksimlərin xlorhidrin efirlərini əldə etmək üçün tədqiq edilmişdir. Reaksiya üçün ehtimal olunan mexanizm təklif olunur. Dioksimlərin epoksi efirləri xlorhidrin efirlərinin qələvi ilə dehidroxlorlaşdırılması yolu ilə sintez edilmişdir. Sintez edilmiş birləşmələrin fiziki-kimyəvi parametrləri müəyyən edilmişdir. Xlorhidrin və epoksi efirlərinin tərkibi və quruluşu ^1H , ^{13}C NMR, İQ spektroskopiyası ilə sübut edilmiş və sintez edilmiş birləşmələrin hidrosil, xlor və epoksi sayları müəyyən edilmişdir. Sintezləşdirilmiş epoksi birləşmələri toxuculuq sənayesində sintetik liflər kimi istifadə edilə bilər.

Açar sözlər: *kondensasiya reaksiyası, epixlorhidrin, alisiklik dioksimlər, bor trifluorid efirəti, epoksidləşmə, epoksi efirləri*

Introduction

Epoxy compounds are one of the most important products of petrochemical synthesis, which, due to their chemical activity, find great practical use as stabilizers and plasticizers, emulsifiers, bactericides, foaming agents and foam plastics, lubricants and dyeing agents, paints and adhesives, as monomers for the production of heat-resistant epoxy polymer materials.

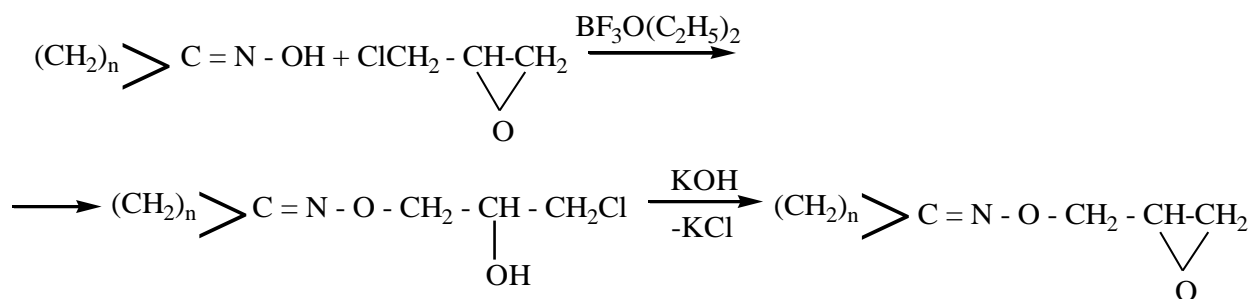
As an analysis of the literature shows, the reaction of alicyclic oximes with epichlorohydrin (ECH) is unexplored (Eselev, Bobilev, 2009: 12-14-16; Zeynalov, 1996: 222; Zeynalov, Kazımova, Sharifova, 2003: 188). Based on ECH, which contains two reactive groups in its structure an epoxy group and a chlorine atom-glycerol derivatives are obtained, which are of interest as intermediates for organic synthesis and the production of biologically active compounds. When interacting with proton-donor organic compounds containing a mobile hydrogen atom: alcohols, phenols, amines, acids, oximes, ketones, aminoacids, mercaptans, it is possible to obtain multifunctional compounds of various modifications with a complex of useful properties (Bakulina, Lazarev, Yakovlev, 1982: 26).

Previously, studies were carried out on the synthesis of alicyclic epoxy ethers by the interaction of alcohols, acids, amines, aminoacids and ECH, followed by dehydro-chlorination of chlorohydrins into epoxy ethers (Budaqova, Zeynalov, Kasımova, 2010: 245-247; Budaqova, Zeynalov, Kasımova, 2011:335; Budaqova, Zeynalov, Sharifova, 2007: 23-36; Budaqova, Zeynalov, 2012: 41).

Results and discussions.

In order to create a process for producing alicyclic epoxy ethers and expanding their range, we carried out a reaction between oximes and dioximes with ECH. The following cyclic oximes were chosen as the object of study: cyclopentanone and cyclohexanone oximes, cyclohexanedionedioxime-1,2- (nioxime-1,2), cycloheptane-dionedioxime - 1,2 (heptoxime-1,2).

Condensation reactions of ECH with oximes were carried out in the presence of a $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ catalyst according to the following scheme:



где n=4,5

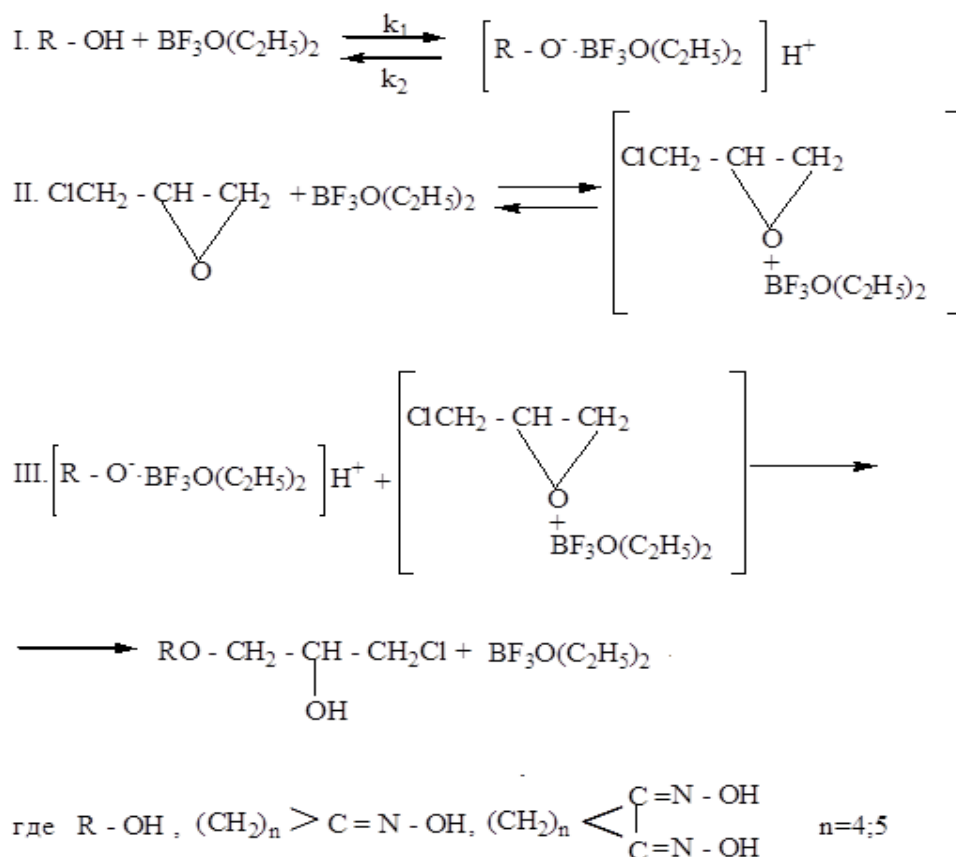
Condensation reactions of ECH with cyclic oximes were carried out in a sulfur ether medium with catalysis by $\text{BF}_3\text{O}(\text{C}_2\text{H}_5)_2$ in an amount of 0.01% relative to ECH at a temperature of 30-35 °C and a time duration of 5-6 hours.

During the research, it was found that the nature of the reactions and the properties of the resulting products depend on the properties and structure of the initial hydroxyl-containing components, the composition of the reaction medium, the type of catalyst used, and the synthesis conditions.

The opening of the epoxy ring of ECH with oximes of the alicyclic series occurs according to Krassusky's rule for compounds with the presence of an electronegative element, which exhibits a negative inductive effect.

In the structure of ECH, the chlorine atom promotes a shift in electron density, weakening the bond of the α -carbon atom, the rupture of which leads to the formation of chlorohydrin ethers of oximes. The formation of products of exactly this structure was proven in the second stage of the reaction by dehydrochlorination of the corresponding chlorohydrins to epoxy ethers.

Based on an analysis of literary and experimental materials, the following diagram of the stepwise mechanism of the reaction for the synthesis of chlorohydrins based on alicyclic oximes was proposed:



Boron trifluoride ether, as a compound with a coordination bond O---B, acts as a donor of BF₃ since the bond in the etherate is weak - 14 kcal BF₃ itself participates in the reaction. The first of them are fragile and form a [ROBF₃]H⁺ complex with oximes, where n=1 or 2, and the second complex is BF₃·(ROH)_n.

The second complex is more stable. In this complex, boron trifluoride coordinates with the oxygen of the hydroxyl group, dramatically increasing the acidity of the proton, which acts as acid catalysts since the BF₃ addition products and oximes are strong acids.

At the same time, it is known that ECH is also catalyzed by Lewis acids, in particular boron trifluoride, forming a protonated complex with the oxygen of the oxide, increasing its reactivity.

The mechanism of interaction of ECH with oximes in the presence of an acidic Lewis acid catalyst includes three stages. In the reaction mechanism proposed above, the limiting – determining stage is the interaction of the BF₃O (C₂H₅)₂ catalyst with ECH, i.e. First, an equilibrium interaction of ECH, oxime and catalyst occurs, very slowly forming an intermediate complex, which is quickly consumed in the second stage of the reaction. The decomposition of the resulting complexes with the formation of a carbocation at the α-carbon atom of ECH leads to the interaction of the cation with the oxime. The mechanism is located between S_N¹ and S_N².

At the second stage of the process of obtaining epoxy ethers, the dehydrochlorination reaction of chlorohydrin ethers of oximes was carried out. When chlorohydrins are dehydrochlorinated with alkali solutions, a side reaction occurs - the hydrolysis of chlorohydrins to diols. To avoid side processes, the dehydrochlorination reaction is carried out with dry alkali in sulfuric ether or benzene at a temperature of 30-35 °C and a time of 5-6 hours. After washing the alkali with water, separating the organic layer and drying over anhydrous CaCl₂, ether and excess alcohol were extracted by atmospheric distillation. Epoxy ethers of the corresponding oximes are obtained by vacuum distillation. In order to obtain diepoxy ethers based on cyclic dioximes and their derivatives, the

At a molar ratio of dioxime: ECH=1:1, dioxime monochlorohydrin ether is obtained, followed by dehydrochlorination of which dioxime monoepoxy ether is obtained.

2. Chlorohydrin cyclohexanone oxime.

It was obtained according to the general synthesis procedure similar to example 1. From 56.5 g (0.5 mol) of cyclohexanone oxime and 46.25 g (0.5 mol) of ECH, 90.7 g (89.3% of theoretical) chlorohydrin oxime ether was obtained, having the following physico-chemical parameters: $T_{bp}=134-136^{\circ}\text{C}$ (4 mm.hg), $n_d^{20}=1.4700$, $d_4^{20}=1.0889$.

IR spectra cm^{-1} : 3385 characteristic absorption bands for (OH), 1671 (C=N), 1456 (-CH₂-), 1240, 1110 (CO, C-OH), 740 (C-C1) bonds.

¹H NMR spectrum: 1.28 m (6H, -CH₂-), 2.43 m (4H, CH₂-C=N), 2.65 N. (2H, OH), 3.72 d. (4H, CH₂Cl), 3.94 d. (4H, -CH₂O), 4.05 sh. (2H, CH-OH).

¹³C NMR spectrum: 25.2-25.4 (2C, 25.4 (s), 26.9-27.1(2C, 27.0 (s), 27.0 (s)), 42.3 (1C, s), 55.7 (1C, s), 65.3-65.4 (2 C, 65.4 (s), 65.4 (s)), 85.6 (1 C, s), 151.6-151.8 (2 C, 151.7 (s), 151.7 (s)).

3. Dichlorohydrin cyclohexanedionedioxime.

It was obtained according to the general synthesis procedure similar to example 1. From 71 g (0.5 mol) of cyclohexanone oxime and 111 g (1.2 mol) of ECH, 165 g (91% of theoretical) of chlorohydrin oxime ether was obtained, having the following physico-chemical properties : $T_{bp}=240-242^{\circ}\text{C}$ (2 mm.hg), $n_d^{20}=1.4750$, $d_4^{20}=1.1860$.

IR spectra cm^{-1} : 3398 characteristic absorption bands for (OH), 1674 (C=N), 1456 (-CH₂-), 1243, 1110 (CO, C-O-H), 740 (C-C1) bonds.

¹H NMR spectrum: 1.27 m (6H, -CH₂-), 2.43 m (4H, CH₂-C=N), 2.65 N. (2H, OH), 3.72 d. (4H, CH₂Cl), 3.94 d. (4H, -CH₂O), 4.05 w. (2H, CH-OH).

¹³C NMR spectrum: 25.3-25.4 (2C, 25.4 (s), 26.9-27.1(2C, 27.0 (s), 27.0 (s)), 42.3 (1C, s), 55.7 (1C, s), 65.3-65.4 (2 C, 65.4 (s), 65.4 (s)), 85.6 (1 C, s), 151.6-151.8 (2 C, 151.7 (s), 151.7 (s)).

4. Cycloheptanedioxime dichlorohydrin.

It was obtained according to the general synthesis procedure similar to example 1. From 78 g (0.5 mol) of cycloheptanedione dioxime and 111 g (1.2 mol) ECH, 179.5 g (95% of theoretical) of dioxime chlorohydrin ether was obtained, having the following physico-chemical properties: $T_{bp}=263-265^{\circ}\text{C}$ (2 mm.hg), $n_d^{20}=1.4800$, $d_4^{20}=1.1211$.

IR spectra cm^{-1} : 3398 characteristic absorption bands for (OH), 1674 (C=N), 1456 (-CH₂-), 1243, 1110 (CO, C-OH), 740 (C-C1) bonds.

¹H NMR spectrum: 1.26 m (6H, -CH₂-), 2.43 m (4H, CH₂-C=N), 2.65 N. (2H, OH), 3.72 d. (4H, CH₂Cl), 3.94 d. (4H, -CH₂O), 4.05 w. (2H, CH-OH).

¹³C NMR spectrum: 25.3-25.4 (2C, 25.4 (s), 26.9-27.1(2C, 27.0 (s), 27.0 (s)), 42.3 (1C, s), 55.7 (1C, s), 65.3-65.4 (2 C, 65.4 (s), 65.4 (s)), 85.6 (1 C, s), 151.6-151.8 (2 C, 151.7 (s), 151.7 (s)).

The yields and some physico-chemical parameters of the synthesized mono- and dichlorohydrin ethers of the corresponding oximes are presented in table 1.

Table 1. Yields and some physicochemical parameters of mono – and dichlorohydrin oximes.

Titles Connections	Exit, % mass.	$T_{bp}^{\circ}\text{C}$ mm.hg	n_d^{20}	d_4^{20} g/cm ³
Chlorohydrin oxime cyclopentanone	96	118-120/3	1,4680	1,0586
Chlorohydrin oxime cyclohexanone	89	134-136/4	1,4700	1,0889
Dichlorohydrin cyclohexanedionedio-xime-1,2	91	240-242/2	1,4750	1,1860
Dichlorohydrin cyclohexanedionedio-xime-1,2	95	263-265/2	1,4800	1.1211

5. Epoxy ether of cyclopentanone oxime.

To a mixture of 28 g (0.5 mol) of powdered KOH in a medium of 150 ml of sul-furic ether, with stirring for 30 minutes, 220 g (1.2 mol) of chlorohydrin ether of cyc-lopentanone oxime was added

dropwise. The reaction was carried out for 5-6 hours at a temperature of 30-35⁰ C. After washing the alkali with water, separating the organic layer, drying over CaCl₂, sulfuric ether was distilled by atmospheric distillation, and then the epoxy ether of cyclopentanone oxime was extracted by vacuum distillation. The yield of the target product is 176.5 g (80.1% of theory) with T_{bp}= 97-99⁰ C (2 mm.hg), n_d²⁰= 0.9675, d₄²⁰= 1.4510, epoxy number - 5.42%.

IR spectra cm⁻¹: 1648 characteristic absorption bands for (C=N), 1456 (-CH₂-), 1227, 1140 (CO, C-O-C) bonds.

¹H NMR spectrum: 1.35 m (4H, -CH₂-), 2.30 d (2H, CH₂-C=N), 3.72 d., 3.94 d. (2H, -CH₂-O).

¹³C NMR spectrum: 24.1 (2C, 25.4 (s), 26.9-27.1(2C, 27.0 (s), 27.0 (s)), 42.3 (1C, s), 55.7 (1C, s), 65.3-65.4 (2C, 65.4 (s), 65.4 (s)), 85.6 (1 C, s), 151.6-151.8 (2 C, 151.7 (s), 151.7 (s)).

6. Epoxy ether of cyclohexanone oxime.

Produced similarly to example 5. From a mixture of 28 g (0.5 mol) of powdered KOH and 246.6 g (1.2 mol) of oxime chlorohydrin ether, 162.3 g (77.1% of theoretical) reaction product with T_{bp}=111-113⁰ was obtained C (4 mm.hg), n_d²⁰= 1.4525, d₄²⁰= 0.9893, epoxy number - 6.08%.

IR spectra cm⁻¹: 1655 characteristic absorption bands for (C=N), 1460 (-CH₂-), 1230, 1150 (CO, C-O-C) bonds.

¹H NMR spectrum: 1.36 m (6H, -CH₂-), 2.28 d (2H, CH₂-C=N), 3.72 d., 3.94 d. (2H, -CH₂-O).

¹³C NMR spectrum: 24.1 (2C, 25.4 (s), 26.9-27.1(2C, 27.0 (s), 27.0 (s)), 42.3 (1C, s), 55.7 (1C, s), 65.3-65.4 (2C, 65.4 (s), 65.4 (s)), 85.6 (1 C, s), 151.6-151.8 (2 C, 151.7 (s), 151.7 (s)).

7. Cyclohexanedioneoxime diepoxy ether.

Produced similarly to example 5. From a mixture of 28 g (0.5 mol) powdered KOH and 354 g (1.2 mol) dichlorohydrin cyclohexanedionedioxime, 305 g (86% of theoretical) of the reaction product with T_{bp}= 217-219⁰ C (4 mm.hg) was obtained, n_d²⁰=1.4690, d₄²⁰=1.1124, epoxy number - 12.64%. IR spectra cm⁻¹: 1657 characteristic absorption bands for (C=N), 1460 (-CH₂-), 1232, 1148 (CO, C-O-C) bonds.

¹H NMR spectrum: 1.36 m (6H, -CH₂-), 2.32 d (2H, CH₂-C=N), 3.72 d., 3.94 d. (2H, -CH₂-O).

¹³C NMR spectrum: 24.1 (2C, 25.4 (s), 26.9-27.1(2C, 27.0 (s), 27.0 (s)), 42.3 (1C, s), 55.7 (1C, s), 65.3-65.4 (2C, 65.4 (s), 65.4 (s)), 85.6 (1 C, s), 151.6-151.8 (2 C, 151.7 (s), 151.7 (s)).

8. Cycloheptanedioneoxime diepoxy ether.

Produced similarly to example 5. From a mixture of 28 g (0.5 mol) of powdered KOH and 370 g (1.2 mol) of cycloheptanedioxime dichlorohydrin, 340 g (92% of the theoretical) reaction product with T_{bp} =244-246⁰ C (2 mm.hg) was obtained, n_d²⁰=1.4745, d₄²⁰=1.1196, epoxy number - 14.05%.

IR spectra cm⁻¹: 1670 characteristic absorption bands for (C=N), 1456(-CH₂-) 1238, 1152 (CO, C-O-C) bonds.

¹H NMR spectrum: 1.36 m (6H, -CH₂-), 2.32 d (2H, CH₂-C=N), 3.72 d., 3.94 d. (2H, -CH₂ O), 4.0 d (4H, CH₂O).

¹³C NMR spectrum: 24.1 (2C, 25.4 (s), 26.9-27.1(2C, 27.0 (s), 27.0 (s)), 42.3 (1C, s), 55.7 (1C, s), 65.3-65.4 (2C, 65.4 (s), 65.4 (s)), 85.6 (1C, s), 151.6-151.8 (2C, 151.7 (s), 151.7 (s)).

The yields and some physico-chemical parameters of the obtained mono- and diepoxides of the corresponding oximes are presented in Table 2.

Table 2. Some physicochemical characteristics of mono- and diepoxy oxime ethers.

Titles connections	Exit, % mass.	T _{bp} ⁰ C mm.hg	n _d ²⁰	d ₄ ²⁰ g/cm ³	Epoxy number,%
Cyclopentanoneoxime epoxy ether	80	97-99/2	1,4510	0,9675	5,42
Cyclohexanoneoxime epoxy ether	77	111-113/4	1,4525	0,9893	6,08
Diepoxyether cyclohexanedionedioxime-1,2	86	217-219/2	1,4690	1,1124	12,64
Diepoxyether cycloheptanedionedioxime-1,2	92	244-246/2	1,4745	1.1196	14,05

IR spectra for mono- and diepoxy ethers (cm^{-1}): characteristic bands for 1648-1655 (C=N), 1456 ($-\text{CH}_2$), 1227, 1140 (CO, C-O-C) bonds.

^1H NMR spectra: 1.35 m. (4H, $-\text{CH}_2$), 2.30 d.(2H), 2.35 m.(4H, $\text{CH}_2\text{-C=N}$), 2.74 m.(1H), 3.90 d.(2H, $-\text{CH}_2\text{O}$), 2.34 in., 2.76 characteristic stripes for the epoxy ring.

Conclusion

Thus, as a result of a series of experiments, effective methods for the synthesis of new mono- and diepoxy ethers based on oximes and dioximes of the alicyclic series were developed and studied. The optimal process mode for the production of chlorohydrin and epoxy ethers has been selected. A probable mechanism for the reaction is proposed. Epoxy ethers of dioximes were synthesized by dehydrochlorination of chlorohydrin ethers with alkali. Synthesized epoxy compounds can be used in the production of plastics, as cross-linking agents, solvents, diluents, plasticizers, stabilizers, adhesives and paints, pharmaceuticals, and also as synthetic fibers in the textile industry.

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Received: 16.06.2023

Accepted: 25.08.2023