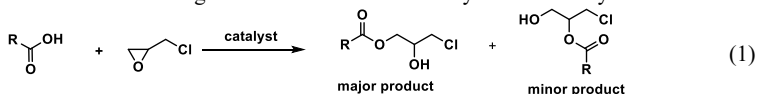


**SALOPHEN METAL COMPLEXES AS CATALYSTS FOR NUCLEOPHILIC
OXIRANE RING OPENING: SYNTHESIS, STRUCTURAL AND ELECTRONIC
FACTORS OF REGIOSELECTIVITY**

*Yutilova K. S.*¹, Sokolovskyi D. A.², Shved O. M.³, Gorden A. E. V.⁴

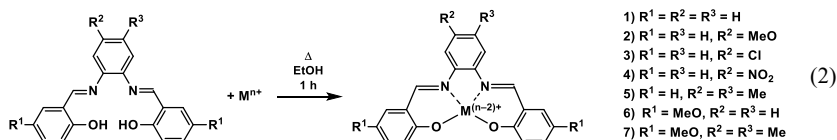
- ¹Institute of Organic Chemistry, National Academy of Sciences of Ukraine, Kyiv, Ukraine
²Vinnitsia Scientific Research Expert and Forensic Center of the Ministry of Internal Affairs of Ukraine, Vinnitsia, Ukraine
³L. M. Litvinenko Institute of Physical Organic and Coal Chemistry, National Academy of Sciences of Ukraine, Kyiv, Ukraine
⁴Texas Tech University, Lubbock, Texas, USA
 k.yutilova@ioch.kiev.ua

Epichlorohydrin (2-(chloromethyl)oxirane, ECH) is an industrially important and structurally distinctive epoxide widely employed in organic synthesis owing to the presence of three electrophilic carbon atoms and a nucleophilic oxygen center. The pronounced reactivity of its strained three-membered ring, together with its availability and multifunctional character, makes ECH a valuable precursor for the synthesis of bi- and trifunctional molecules. Such transformations frequently exhibit significant chemo-, regio-, and stereoselectivity (1), especially in reactions involving chiral substrates or under asymmetric catalysis.



The objective of this study was to synthesize and characterize salophen and substituted salophen complexes of transition metals, and to assess their catalytic activity and regioselectivity in the ring-opening acetolysis of epichlorohydrin.

Salophen ligands and their complexes with transition metals Cu(II), Fe(II), Fe(III), and Co(II) were synthesized (2) and characterized by UV–Vis, IR, and ¹H NMR spectroscopy. The catalytic performance of these complexes in epoxide transformations was investigated using the acetolysis of epichlorohydrin as a model reaction (1). Kinetic analysis showed that the reaction orders with respect to both the acid and the catalyst are consistent with those observed for conventional catalytic systems (tetraalkylammonium salts and trialkylamines). It was demonstrated that the catalytic activity of salophen complexes is controlled by the electronic properties of the ligands, with electron-donating substituents leading to an acceleration of the reaction (1).



- 1) R¹ = R² = R³ = H
- 2) R¹ = R³ = H, R² = MeO
- 3) R¹ = R³ = H, R² = Cl
- 4) R¹ = R³ = H, R² = NO₂
- 5) R¹ = H, R² = R³ = Me
- 6) R¹ = MeO, R² = R³ = H
- 7) R¹ = MeO, R² = R³ = Me

The products obtained in the presence of Co(II) salophen complexes were identified, and their structures and ratios were determined by ¹H NMR spectroscopy. Substituted Co(II) salophen complexes provided higher regioselectivity than traditional catalysts, preferentially yielding β-hydroxypropyl esters, which are important precursors of epoxy compounds. Steric characteristics of the synthesized complexes were assessed using SambVca software through calculation of the percent buried volume and construction of steric maps. Quantitative structure–selectivity relationships revealed that regioselectivity is controlled by both steric and electronic properties of the ligand substituents. A mechanistic pathway for catalysis by salophen metal complexes has also been proposed.