



REVIEW ARTICLE

OXIDATIVE CHLOROHYDRINATION OF CHLOROLEFINS OF ALLYL TYPE

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ABSTRACT

The reaction of low-temperature oxidative chlorohydrination of allyl chloride, 2,3-dichloropropene-1 and 1,3-dichlorobutene-2 with application of the hydrochloric acid and hydrogen peroxide has been studied. The possibility of preparation of glycerine dichlorohydrin, 1,3-dichloroacetone and 1,2-dichlorobutanone with yields 70-75% from theoretical one has been shown. Selectivity – 85-92%.

Key words:

Allyl chloride, Glycerine dichlorohydrin,
2,3-dichloropropene-1,
1,3-dichloroacetone,
1,3-dichlorobutene-2,
1,2-dichlorobutanone,
chlorohydrination, hydrogen peroxide.

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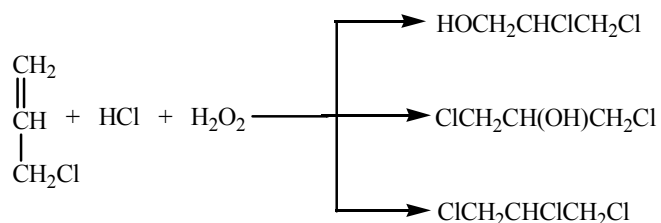
INTRODUCTION

It was known that (Muganlinskiy *et al.*, 1991) in the production of epichlorohydrin at the stage of preparation of glycerine dichlorohydrin an equimolar quantity of the hydrogen chloride is formed. In addition, per one ton of the epichlorohydrin 0,5 ton of chloroorganic products as a waste is formed (Silinskaya *et al.*, 2000). However, in spite of some recommendations (Zanaveskin *et al.*, 1996; Voronkov *et al.*, 2001; Gogotov *et al.*, 2009; Poddubniy *et al.*, 2007) these wastes are practically not utilized. In connection with above-mentioned one it has been investigated the oxidative chlorohydrination reaction of the chlorine-containing olefins of allyl type with application of hydrochloric acid and hydrogen peroxide. With the aim of study of influence of the chlorine atom on reactivity and on chlorohydrination reaction direction we have investigated the behavior of the chlorine-containing olefins, where the chlorine atoms are both in α -, and β -position of double bond. For this purpose in the comparable conditions we have considered the chlorohydrination of allyl chloride, 2,3-dichloropropene-1 and 2,4-dichlorobutene-2.

Experimental: For carrying out of reaction it was used three-necked flask with mechanical mixer and external shirt for thermostating.

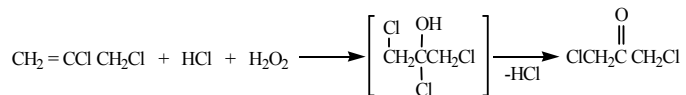
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The hydrogen peroxide solution was given to the mixture of hydrochloric acid and chlorine-containing olefin at temperature 45-50°C. Molar ratio of the reacting component HCl : H₂O₂ : chloroolefin = 2,0: 1 :1. At the end of the solution was analyzed for content of glycerine dichlorohydrin (in a case of allyl chloride). In addition, the reaction products were identified by chromatographical method. It has been established that the oxidative chlorohydrination of allyl chloride by peroxol method leads to the preparation of 1,3-dichloropropanol-2, 2,3-dichloropropanol-1 and 1,2,3-trichloropropane. It affords that the chlorohydrination of allyl chloride proceeds with chlorine generated from hydrochloric acid through stage of formation of the chloric complex, it can be easily explained the scheme of formation of isomers of glycerine dichlorohydrin and 1,2,3-trichloropropane.



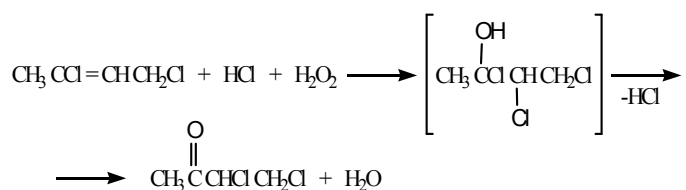
A yield of dichlorohydrin at concentration of the hydrochloric acid 5-6% and reaction temperature 45-50 °C reaches 75% from theory with selectivity 90-92%.

With the aim of elucidation of influence of the chlorine atom depending on location in molecule it was interesting to consider a behavior of α -chlorosubstituted olefins in the oxidative chlorohydration reactions, for which the reaction with 2,3-dichloropropene-2 was investigated. It has been established that at chlorohydration of 2,3-dichloropropene-1 instead of expected chlorohydrin a symmetrical 1,3-dichloroacetone is prepared.

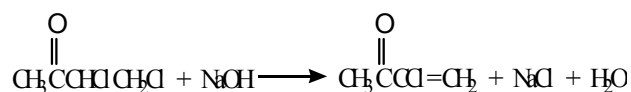


B.p. 63-65°C/15 mm merc.c., n_D^{20} -1,4850, d_4^{20} -1,4345.

Consequently, it proceeds the analogous chlorohydration reaction, where an addition of chlorine atom and hydroxyl group occurs on Markovnikov rule. However, the prepared chlorohydrin due to instability easily eliminates the hydrogen chloride with formation of symmetrical dichloroacetone. A yield of compound is 70-75% from theory. In the IR-spectrum of the prepared substance there is an intensive absorption band 1738 cm^{-1} characteristic for carbonyl group. In a case of the oxidative chlorohydration of 1,3-dichlorobutene-2 it is also formed the ketone and exactly 1,2-dichlorobutanone-3. For formation of this substance the following scheme is assumed:



B.p. 60-65°C/12 mm merc.c., n_D^{20} -1,4826, d_4^{20} -1,3292. The structure of the prepared substance has been proved by elemental analysis and spectroscopically. In the IR-spectrum of product there is an intensive band at 1725 cm^{-1} characteristic for keto-group. The dichlorohydration reaction can serve as a characteristic proof of structure of the proposed dichloroketone. At heating of the product with NaOH in the presence of hydroquinone the substance distilled off as an azeotrope was 2-chlorobuten-1-on-3 easily polymerizing during storage:



B.p. 97-98 °C, n_D^{20} -1,4826, d_4^{20} -1,1792. A yield of chlorovinyl-methyl ketone was 85% from theory.

Thus, the data on oxidative chlorohydration of the chlorine-containing olefins by peroxol method allow to assume that the reaction proceeds on trimolecular scheme between olefin generated from hydrochloric acid by chlorine and water. In this case, an electrophilic attack of molecular chlorine occurs, advantageously, from side of more hydrogenated carbon atom, i.e. an addition of the chlorine atom and hydroxyl group to multiple carbon-carbon bond in chlorolefins occurs basically on Markovnikov rule. During oxidative chlorohydration of allyl chloride, 2,3-dichloropropene-1 and 1,3-dichlorobutene-2 the reaction conditions considerably influence on yield of the purposeful products. In accordance with obtained results the most satisfactory yields of glycerine dichlorohydrin, 1,3-dichloroacetone and 1,2-dichlorobutanone-3 are observed at relatively low concentrations of hydrochloric acid (3-8%) and reaction temperature (40-50°C). At higher concentrations of the chlorine ions it takes place a considerable decrease of yields of the basic products, which has been connected with formation of the compounds of deep chlorination. So, in cases of α -chloroolefins on the chromatograms of the prepared mixture it is increased a number of peaks of unidentified impurities and in case of allyl chloride – yield of 1,2,3-trichloropropane. In the developed regime the yields of chlorohydrin and chloroketone reach 70-75%, which can be served as the efficient method for preparation of indicated compounds.

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