

CYCLOALKENES C₈ – C₁₀
AND SYNTHESIS OF A SERIES OF THEIR OXYGEN-CONTAINING
DERIVATIVES

ABSTRACT

Relevance of the research topic. To date, within the framework of a comprehensive program for the rational use of oil resources, a process has been developed and implemented in industry for the isolation and purification of one of the by-products of ethylene production - cyclopentadiene (CPD). With the current scale of ethylene production, the potential resources of CPD are very significant. Based on it, dicyclopentadiene is obtained by implementing a dimerization process, 5-vinyl-2-norbornene is obtained as a result of cyclosodimerization of CPD with butadiene-1,3, and based on the latter, as a result of a cyclodimerization reaction, 1,5-cyclooctadiene is obtained. The technology for the production of these dienes has been developed and implemented in a number of industries, both in Russia and abroad.

As a result, C₈-C₁₀ alicyclic dienes become an available raw material, and the development of effective ways of their transformation into valuable consumer products is an urgent task.

The aim of the work is to study and develop the scientific foundations of the technology for the production of vinylnorbornane and cyclooctene by the catalytic hydrogenation of 5-vinyl-2-norbornene (5-vinyl-bicyclo[2,2,1]heptene-2, VNB) and cis,cis-1,5 -cyclooctadiene (COD) with hydrogen in the liquid phase in the presence of a finely dispersed palladium catalyst (1% Pd/C), followed by their use in the synthesis of methylnorbornylketone and 1,2-epoxycyclooctane.

To achieve this goal, it is necessary to solve the following tasks:

- study the conditions and kinetics of the process of liquid-phase hydrogenation of 5-vinyl-2-norbornene and cis,cis-1,5-cyclooctadiene using a finely dispersed palladium catalyst for its optimization and modeling;

- compare the reactivity of double bonds in the structures of vinylbornene, dicyclopentadiene and cyclooctadiene during hydrogenation to justify the possibility of selective formation of the corresponding cycloalkenes on their basis;

- evaluate the ability to oxidize the vinyl group of vinylbornane by oxidizing agents of various nature, identify the resulting oxidation products using modern instrumental methods for studying their structure;

- to study in detail the kinetic and quantitative patterns of liquid-phase oxidation of cyclooctene to epoxide, as well as to determine and substantiate the conditions for its occurrence, which ensure the selective formation of the target 1,2-epoxycyclooctane.

Scientific novelty. It has been shown that under the conditions of heterogeneous catalysis using finely dispersed 1% Pd/C suspended in the liquid phase, the double bonds of VNB and DPC molecules are saturated with hydrogen successively, at an unequal rate, which makes it possible to selectively obtain vinylbornane and cyclooctene in this process.

For the first time, on the basis of experimental data and quantum chemical calculations, a comparative assessment of the reactivity of double bonds in the structures of vinylbornene (5-vinyl-bicyclo[2.2.1]heptene-2), its analogue, dicyclopentadiene (tricyclo[5.2.1.0^{2.6}]decadiene-3.8), as well as cis,cis-1,5-cyclooctadiene in the process of their catalytic hydrogenation with hydrogen in the liquid phase.

For the first time, a molybdenum-containing catalytic system was proposed and its regulating function was established in the process of liquid-phase oxidation of cyclooctene with molecular oxygen to 1,2-epoxycyclooctane, which makes it possible to increase the selectivity of the formation of the target product to 85-86 mol.% compared to the known initiated oxidation. A possible scheme of the radical-chain mechanism of epoxide formation in the catalytic process of cyclooctene oxidation is proposed, indicating the reasons for the increase in the yield of the target product.

For the first time in the oxidation of the vinyl group of 2-vinylnorbornane with peracids in the presence of a number of catalysts, a ketone, methylnorbornyl ketone (ethanon-1-bicyclo[2.2.1]hept-2yl), was obtained as the target product of the reaction, the structure of which was confirmed by physicochemical research methods, in particular, HPLC with high-resolution mass spectrometric detection, as well as H^1 NMR, C^{13} NMR and IR-spectroscopy.

Theoretical and practical significance of the work. Methods for the selective production of 2-vinylnorbornane and cyclooctene, convenient for practical use, are proposed, scientifically substantiated, and worked out in detail. Based on the analysis of mass transfer processes in a three-phase gas-liquid-solid catalyst system, taking into account the kinetic parameters of the diene hydrogenation reaction established by us, a simulation of the reaction unit was implemented, which is a batch flow reactor equipped with an effective mixing device. Methylnorbornyl ketone synthesized from 2-vinylnorbornane is of undoubted practical interest. According to the literature data, the amine obtained on its basis is an effective antiviral agent.

The obtained scientific results can be used to expand the concepts of theoretical organic chemistry in the field of reactivity of alicyclic compounds in a number of reactions and processes, as well as to develop scientifically based approaches to the selection of efficient catalytic systems both in the reaction of hydrogenation of substrates with hydrogen in the liquid phase and in the reaction liquid phase oxidation.

Provisions for defense:

– Regularities that make up the physicochemical foundations and technological principles of the catalytic hydrogenation of double bonds of 5-vinyl-2-norbornene (5-vinyl-bicyclo[2.2.1]heptene-2, VNB) and 1,5-cis,cis-cyclooctadiene (COD) with hydrogen in the liquid phase in the presence of a finely dispersed palladium catalyst suspended in the liquid phase (1% Pd/C) versus dicyclopentadiene (tricyclo[5.2.1.0^{2.6}]decadiene-3.8, DCPD).

- Kinetic parameters and kinetic model of the process of catalytic hydrogenation of cyclodienes under conditions of pseudo-homogeneity of the reacting system.
- Conditions for the production of cycloalkenes based on the reaction of hydrogenation of these cyclodienes in a three-phase system gas - liquid - solid catalyst in a flow reactor simulating an ideal mixing reactor, convenient for subsequent practical implementation.
- Results of catalytic liquid-phase oxidation of cyclooctene with molecular oxygen to 1,2-epoxycyclooctane using a catalytic system with a control function.
- information about the possibility of methylnorbornylketone formation as a result of the oxidation of 2-vinylnorbornane with oxidizing agents of various nature and methods for its identification.