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Stereochemical Features of 1,7-Octadiene Metathesis on the $MoCl_5/SiO_2{-}Me_4Sn$ Catalytic System

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Abstract—It has been established that the metathesis reaction of 1,7-octadiene (OD) proceeds smoothly by two pathways in the direction of the formation of the product of the chain growth, 1,7,13-tetradecatriene, and intramolecular cyclization into cyclohexene. It has been shown that, at the low (9%) conversion of OD, the content of cyclohexene is 72%, while that of 1,7,13-tetradecatriene is 28%. As the reaction proceeds, the content of cyclohexene increases and becomes 97% at the conversion of 99%, i.e., almost all 1,7,13-tetradecatriene formed cyclizes into cyclohexene. At relatively low conversions of OD (9–55%), the stereo-composition of 1,7,13-tetradecatriene does not differ from the stereo-composition of the products of the homometathesis and cometathesis of the linear structures (Z/E=(25–18)/(75–82)). The content of 1,Z-7,13-tetradecatriene decreases sharply from 8.0 to 0.9% with the increase in the conversion. This is explained by a higher proneness of the Z-stereoisomer to the cyclization.

Keywords: olefin metathesis, heterogeneous catalysis, stereochemistry, 1,7-octadiene

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INTRODUCTION

The catalytic metathesis of olefins is one of the most interesting and promising reactions for modern petroleum chemistry and fine organic synthesis. This reaction possesses a high synthetic and technological potential and several industrial processes have been implemented on its basis [1]. In 1964, the employees of Phillips Petroleum Company Banks & Bailey obtained ethylene and butene-2 with high selectivity while passing propylene over $Mo(CO)_6/Al_2O_3$ under mild conditions (150°C) [2]. Later, the industrial Triolefin Process was implemented on the basis of this reaction [1]. The Nobel Prize in Chemistry 2005 was awarded for the development of the metathesis approach in organic synthesis.

Particular interest is associated with the use of the metathesis for the synthesis of biologically active natural compounds. At the Topchiev Institute of Petrochemical Synthesis, Russian Academy of Sciences, a new flexible few-stage strategy for the synthesis of a wide range of pheromones (environmentally friendly insecticides) and other natural compounds on the basis of the cometathesis of the petrochemical feedstock (α-olefins, cyclic olefins, cyclooctadiene, ethylene) [3–5] and heterogeneous catalytic systems on the basis of molybdenum halides developed by us was proposed [6–8].

The sex pheromones of the insects of the Lepidoptera order are long-chain unsaturated compounds in the form of the mixtures of *cis*- and *trans*-stereoisomers of a certain composition, which is why the study of the stereochemical regularities of the metathesis of olefins is of both practical and theoretical interest.

It was shown by us earlier that, during the cometathesis of cyclopentene (CP) with α-olefins, the content of the Z-isomers of 1,Δ-dienes was lower when compared to cyclooctene (CO), cycloheptene (CH), and cyclononene (CN) across the range of conversions of CP. This is explained by the fact that, in the case of CP, the reverse reaction of cyclization of the products of the cometathesis into initial CP proceeds to a significant extent and the equilibrium conversion does not exceed 77%. The reverse reaction proceeds to a much smaller extent in the case of CH. In this case, the equilibrium conversion is 94%, while there is almost no reverse reaction of metathesis cyclization in the case of CO and CN and the equilibrium conversions reach the values of 99% and above. In order to confirm the fact that the reverse reaction of metathesis cyclization of linear olefins into cycloolefin affects the stereo-composition, the stereochemical features of the metathesis of 1,7-octadiene (OD) were studied in this work.

EXPERIMENTAL

The metathesis of OD was carried out in a thermostated glass reactor with a magnetic stirrer equipped with a dropping funnel, reflux condenser, and gas

Dependence of metathesis chemoselectivity and stereoselectivity on the conversion of octadiene

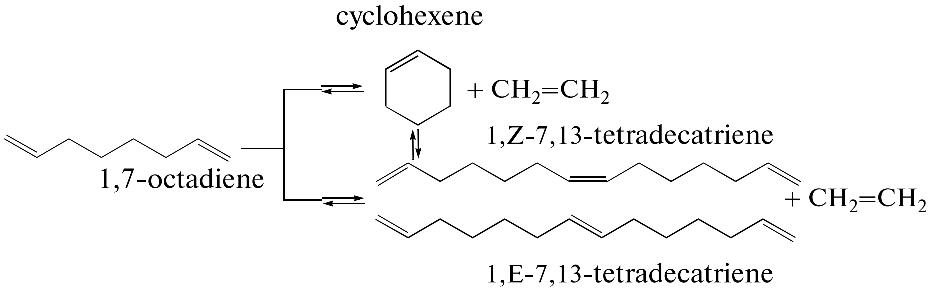
Conversion of 1,7-octadiene $C_{8:2}$, wt %	Cyclohexene content $C_{(6:1)}$, wt	1,7,13-Tetradecatriene content $C_{14:3}$, wt %	1,Z-7,13-Tetradecatriene content Z-7 $C_{14:3}$, wt %
9	72	28	25
21	73	27	22
55	79	21	18
90	91	9	8
99	97	3	0.9

burette for the measurement of the volume of ethylene evolving during the reaction. A weighed amount of the catalyst was loaded into the reactor and a certain amount of OD and cocatalyst (tetramethyltin) was loaded into the dropping funnel. The reaction was carried out with the continuous removal of forming ethylene.

The monitoring of the purity of the initial reagents as well as of the reaction progress was performed by means of gas–liquid chromatography (GLC) using an LKhM-8MD chromatograph equipped with a flame ionization detector (FID) (50 m × 0.2 mm quartz capillary column), the stationary phases were SKTFP or SE-30 and the carrier gas was H_2. The analyses were performed under the conditions of linear temperature programming (12°C/min) from 35 to 210°C. The ^1H and ^{13}C NMR spectra were recorded on a Bruker MSL-300 spectrometer in $CDCl_3$ relative to Me_4Si. The mass spectra (EI) were registered on a Finigan MAT 95 XL 70 instrument (70 eV). All the reactions, as well as the preparation of the initial compounds and solvents, were performed in the atmosphere of extra-pure-grade argon using $LiAlH_4$ as the drying agent.

RESULTS AND DISCUSSION

The features of the stereochemistry of the metathesis of OD in the presence of the $MoCl_5/SiO_2–Me_4Sn$ heterogeneous catalytic system have been studied. It has been shown that the reaction proceeds according to the Scheme by two pathways in the direction of the formation of the products of the chain growth, *Z*- and *E*-stereoisomers of 1,7,13-tetradecatriene, and in the direction of the formation of cyclohexene due to the intramolecular cyclization of initial OD and products of metathesis:



Cyclohexene is a very thermodynamically stable structure; therefore, from the two directions, the process of closure into cyclohexene occurs predominantly.

It is seen from the table that the content of cyclohexene is 72% and that of tetradecatriene is 28% at the conversion of OD of 9%. As the reaction proceeds, the content of cyclohexene increases and becomes 97% at the conversion of 99%, i.e., almost all tetradecatriene formed cyclizes into cyclohexene. At low conversions of OD (9–55%), the stereo-composition of 1,7,13-tetradecatriene, which has two possible stereoisomers, does not differ from the stereo-composition of the products of homometathesis and cometathesis of the linear structures. With the increase in the conversion, the content of 1,*Z*-7,13-tetradecatriene drops sharply. This is explained by the higher proneness of the *Z*-stereoisomer to the cyclization.

The thermodynamically equilibrium concentrations of the stereoisomers of the linear structures possessing one internal double bond are $E : Z \approx 84 : 16$. In case of the stereoisomers of 1,7,13-tetradecatriene, this value differs substantially. Thus, when the conversion of OD is 90%, the content of *Z*-tetradecatriene is 8%, while when the conversion of OD is 99%, less than 1%. Apparently, such a difference is explained by the specific features of the process (see the reaction scheme), in which there is a reaction of selective cyclization of the *Z*-isomer into cyclohexene along with the equilibrium between the isomers.

Thus, the results obtained for the metathesis of OD confirm the assumption about the possibility of the predominant closure of the *Z*-stereoisomers into cyclic olefins including CP.

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