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Cyclododecene Cometathesis with Hexene-1 on the $MoCl_5/SiO_2$–Me_4Sn Catalytic System

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Abstract—The stereochemistry of the cometathesis of cyclododecene (CDD) with hexene-1 in the presence of the $MoCl_5/SiO_2$– Me_4Sn heterogeneous catalytic system has been studied. It has been established that CDD is the mixture of *cis*- (*Z*) and *trans*- (*E*) stereoisomers with the ratio of 30/70, respectively. It has been shown that the reactivity of the *E*-stereoisomer of CDD in the reaction of cometathesis is higher when compared to the *Z*-stereoisomer. Thus, when the conversion of CDD is 92%, the ratio $E/Z = 6 : 94$, i.e., the amount of the *E*-stereoisomer decreases from 70 to 7%, while the amount of the *Z*-stereoisomer increases from 30 to 93%, respectively.

Keywords: stereochemistry, cometathesis, cyclododecene, heterogeneous catalysis

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INTRODUCTION

Cyclododecene (CDD) is one of the most available petrochemical cyclic olefins. CDD is produced industrially via the partial hydrogenation of cyclododecatriene, which is formed with high selectivity during the cyclotrimerization of butadiene in the presence of Ni-containing catalysts [1].

Earlier, the chemoselectivity and stereoselectivity of the cometathesis of C_5 and C_7–C_{10} cyclic olefins with α-olefins in the presence of the $MoCl_5/SiO_2$–Me_4Sn heterogeneous catalytic system was studied by us [2–4] and a new few-stage strategy for the synthesis of a wide range of pheromones and other natural compounds was developed on this basis [5–7].

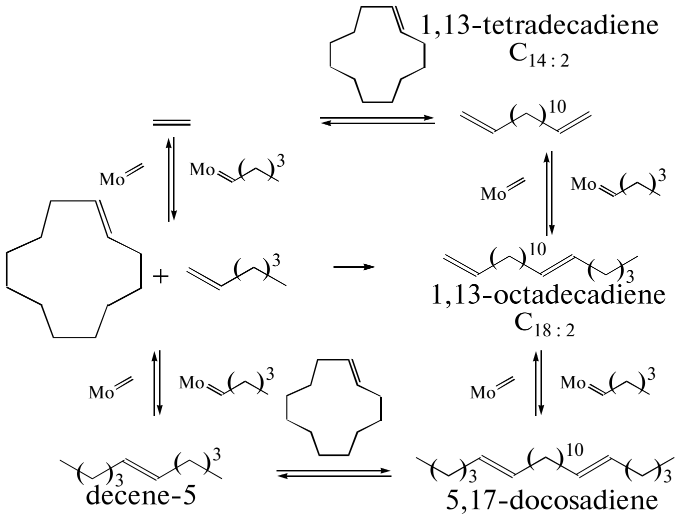
The cometathesis of CDD with 1-hexene is interesting from both practical and theoretical points of view because 1,13-octadecadiene, from which it is easy to obtain 1,13-octadecenol, as well as the corresponding aldehyde and acetate, which are the components of the pheromones of the pest insects of the Lepidoptera order, is one of the target products.

EXPERIMENTAL

The cometathesis of CDD with 1-hexene was carried out in a thermostated glass reactor with a magnetic stirrer equipped with a dropping funnel, reflux condenser, and gas burette for the measurement of the volume of ethylene evolving during the reaction. A weighed amount of the catalyst and 1-hexene was loaded into the reactor, while a certain amount of CDD 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 220°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 Finnigan 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 cometathesis of CDD with hexene-1 proceeds according to the scheme that is general for cyclic olefins



Scheme.

The chain growth reaction proceeds with the participation of CDD, while the chain termination, with the participation of hexene-1. The reaction of homometathesis of hexene-1 resulting in decene-5 and ethylene competes with these processes. According to the data of the ^{1}H NMR (Fig. 1), initial CDD is a mixture of *trans*- and *cis*-stereoisomers. The ratio of the isomers of CDD $E/Z = 70/30$ was estimated by the integral intensities of the resolved multiplets of the *trans* (*E*)-protons (the chemical shift of 5.36–5.4 ppm) and *cis* (*Z*)-protons (the chemical shift of 5.3–5.35 ppm). This stereo-composition is in agreement with the data of the capillary GLC.

The composition of the main products of the cometathesis is shown in the table. It is seen that, with the increase in the conversion of CDD, the content of 1,13-octadecadiene drops from 71 to 55%, while the content of 1,13-tetradecadiene changes slightly. The reaction proceeds quite quickly and the conversion reaches 75% within 30 min (Fig. 2).

It is interesting that reactivity of the *E*-stereoisomer of CDD in the reaction of cometathesis is higher when compared to the *Z*-stereoisomer. Thus, the initial ratio of the stereoisomers of CDD is $E/Z = 70:30$, while it is $E/Z = 6:94$ when the conversion of CDD is 92%. The content of the *E*-stereoisomer decreases from 70 to 7%, while, on the contrary, the content of the *Z*-stereoisomer increases from 30 to 93%.

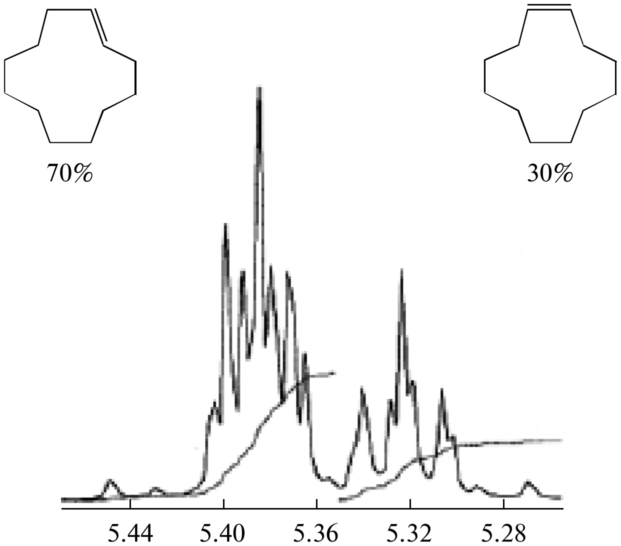


Fig. 1. A fragment of the ^{1}H NMR spectrum of initial cyclododecene.

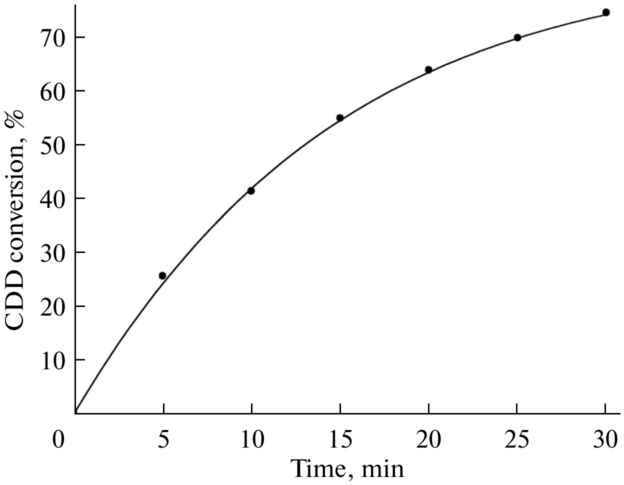


Fig. 2. Cyclododecene conversion as a function of the reaction time.

Content of the cometathesis product at various conversions of cyclododecene

Conversion of CDD, %	Amounts of cometathesis products, %		
	$C_{18:2}$	$C_{14:2}$	$C_{22:2}$ and others
40	71	14	15
58	66	14	20
81	58	14	28
92	55	13	32

As for the stereo-composition of 1,13-octadecadiene, the thermodynamically equilibrium stereo-composition $Z/E = 16 : 84$ is already observed within 5 min.

Therefore, it was established that CDD, as well as *Z*-cyclodecene, does not exhibit any *cis* (*Z*)-regulating action typical for cyclopentene, cycloheptene, cyclooctene, and cyclononene.

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