

# Catalytic Syntheses of Polycyclic Compounds Based on Norbornadiene in the Presence of Nickel Complexes: VI. Heterogenized Catalyst for Isomerization Reactions of Norbornene Derivatives

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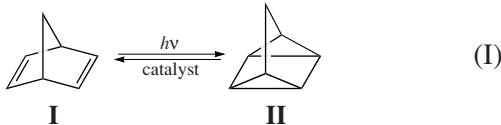
Received June 27, 2006

**Abstract**—The kinetics and mechanism of the thermal isomerization of 5-*exo*-methyl-tricyclo[3.2.1.0<sup>5,7</sup>]octene-2 into 2-methyl-tetracyclo[3.2.1.0<sup>2,7,0<sup>4,6</sup>]octane are reported. The use of catalysts based on nickel compounds is demonstrated. As compared to the other catalytic systems, the heterogenized nickel catalyst obtained by thermal treatment of nickel norbornadiene complexes shows much better performance characteristics (selectivity, specific activity, and service life).</sup>

**DOI:** 10.1134/S0023158407060092

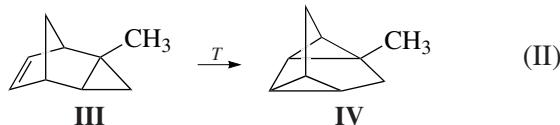
## INTRODUCTION

Bicyclo[2.2.1]hepta-2,5-diene (norbornadiene, NBD) and some other compounds of the norbornene series are capable of isomerizing into saturated derivatives. Such valence isomerization is accompanied by a transformation of the carbon backbone. The best known example of such transformation is the photoinduced conversion of NBD (**I**) into quadricyclane (**II**) [1, 2]:



The forward reaction occurs under UV irradiation and is accompanied by the accumulation of a large amount of energy (~120 kJ/mol). The reverse process can be carried out in the presence of a catalyst.

A chemical analogue of reaction (I) is the isomerization of 5-*exo*-methyl-tricyclo[3.2.1.0<sup>5,7</sup>]octene-2 (**III**) into 2-methyl-tetracyclo[3.2.1.0<sup>2,7,0<sup>4,6</sup>]octane (**IV**). This process is free of quantum chemical forbiddance and can be initiated by heating:</sup>



The opening of the cyclopropane ring of compound **III** is similar to the opening of a double bond, resulting in the formation of two new cyclopropane moieties in **IV**.

Preliminary quantum chemical calculations (DFT/PBE method, three-exponential basis set, Priroda program [3]) indicated that reaction (II) has a negative

Gibbs free energy ( $\Delta G_{298} = -68$  kJ/mol) and can, therefore, be accelerated by a catalyst.

For purposeful selection of a catalytic system, it is necessary to know the mechanism of the noncatalytic (thermal) process. For this reason, the first step of our study was the investigation of the thermal isomerization reaction **III** → **IV**.

## EXPERIMENTAL

Both domestic and foreign chemicals of 99.0–99.9% purity were used in this study. All reagents and solvents were purified before syntheses by standard procedures [4].

The thermal isomerization of 5-*exo*-methyl-tricyclo[3.2.1.0<sup>5,7</sup>]octene-2 was conducted in sealed quartz tubes (10 ml), fitted with a sampler. The temperature was controlled using an oil ultrathermostat (up to 130°C) or Wood’s alloy (up to 200°C).

The catalytic isomerization of 5-*exo*-methyl-tricyclo[3.2.1.0<sup>5,7</sup>]octene-2 was carried out in a 20-ml reactor similar to the Soxhlet apparatus. The catalyst was placed in the upper chamber. The reaction was conducted in a nitrogen atmosphere at the reactant boiling point, which was varied using a vacuum pump. The liquid phase was circulated by heating the bottom chamber.

Nickel chloride, nickel bromide, and nickel sulfate supported on  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> from aqueous solutions were used as catalysts (the nickel content was 0.2–5.0 wt %). Before use, the catalysts were heat-treated at 120°C for 5 h and then calcined at 400°C for 2 h in a nitrogen atmosphere.

**Table 1.** Temperature dependence of the yield of compound **IV**

Temperature, °C	Conversion of <b>III</b> , %	Yield, %		
		compound <b>IV</b>	other isomerization products*	resinification products
140	—	—	—	—
150	26.0	Traces	6.0	20.0
160	29.0	1.5	9.5	18.0
170	40.0	6.0	13.0	21.0
180	66.0	27.0	18.0	21.0

Note: The reaction time is 2 h; the initial weight of compound **III** is 5 g.

\* The isomerization of compound **III** yields not only **IV**, but also three other compounds with the same molecular weight of 120. Their structure is not conclusively determined, but, as judged from the fragmentation of their molecular ions, they must have a norbornane backbone (high ion intensity at  $m/z$  66, which is likely due to an ion resulting from retrodiene decomposition).

The reaction mixture was analyzed, and the course of the reaction was monitored by gas chromatography (Chrom-5 chromatograph, SPB-20 and  $\beta$ -DEX capillary columns from Supelco). The products were identified using  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy (Bruker DPX-300 spectrometer operating at 300.033 and 75.15 MHz, respectively) in  $\text{CDCl}_3$  and GC-MS (Delsi Instruments, OV-1 column, electron impact ionization, ionization energy of 70 eV). The signals were assigned using reference data [5].

## RESULTS AND DISCUSSION

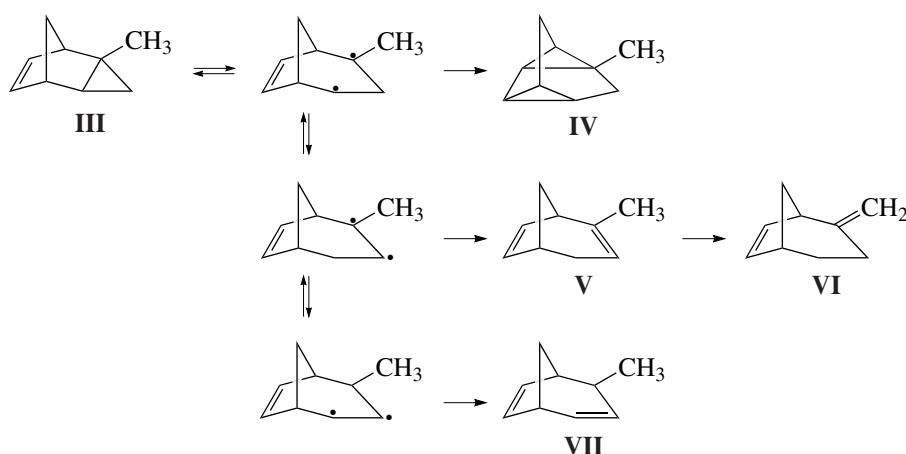
### *Thermal Isomerization of 5-exo-Methyl-Tricyclo[3.2.1.0<sup>5,7</sup>]Octene-2 into 2-Methyl-Tetracyclo[3.2.1.0<sup>2,7</sup>.0<sup>4,6</sup>]Octane*

Heating compound **III** in bulk up to 140°C does not cause any reaction. Heat treatment for 2 h at 150°C causes darkening of the solution due to the formation of

resinification products. Further raising the temperature to 180°C (compound **III** boiling point) favors the formation of isomerization products (Table 1). The yield of compound **IV** increases significantly with temperature, while the amount of resinification products remains almost invariable.

The buildup of compound **IV** in the course of the reaction was studied. The time dependence of  $\ln C$  was found to be linear, obeying a first-order kinetic equation (Fig. 1).

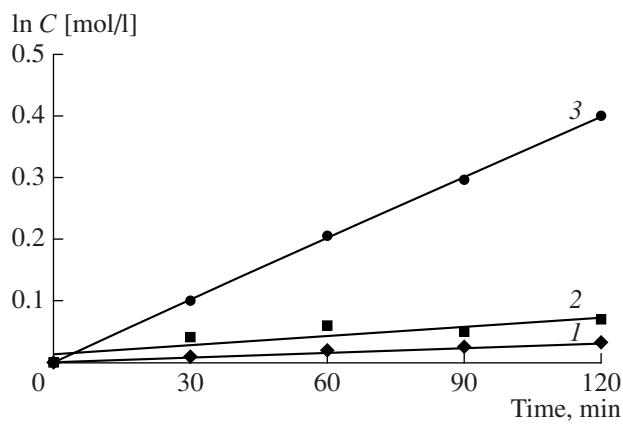
The experimental first-order reaction constants are in satisfactory agreement with the Arrhenius equation (Fig. 2). The activation energy of reaction (II) is 250 kJ/mol. This large value of activation energy, which is comparable with the C–C bond strength in the cyclopropane ring, is evidence of the biradical mechanism of ring opening (see the scheme).



Likely mechanism of the thermal isomerization **III** → **IV**.

The irreversibility of reaction (II) was confirmed experimentally. Upon heating to 200°C, compound **IV**,

which was selected to be the starting compound, neither isomerizes into **III** nor undergoes some other conversion.



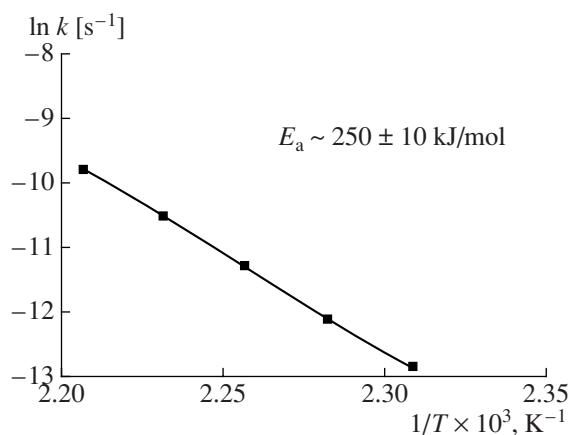
**Fig. 1.** Dependence of  $\ln C$  on the duration of the thermal isomerization of compound **III** into **IV** at  $T = (1) 160$ ,  $(2) 170$ , and  $(3) 180^\circ\text{C}$ .

#### Catalytic Isomerization of 5-exo-Methyl-Tricyclo[3.2.1.0<sup>5,7</sup>]Octene-2

Usually, hydrocarbon isomerization reactions occur under the action of heterogeneous metal and oxide catalysts [6, 7]. Since the isomerization of **III** is the  $[2\pi + 2\sigma]$  type, nickel compounds seem to be the most promising catalysts [8–10].

We tested heterogeneous catalysts consisting of nickel salts supported on  $\gamma\text{-Al}_2\text{O}_3$  from aqueous solution. Considering that the surface and the nature of the support often exert an effect on heterogeneous catalytic processes, we carried out a series of experiments in which the support ( $\text{Al}_2\text{O}_3$ ) free of the active components was pretreated before the experiment in the same way as the nickel-containing catalysts. The results of these comparative experiments are presented in Tables 2 and 3.

It follows from these data that the presence of the heterogeneous support somewhat improves the isomerization yield and selectivity. The nickel catalyst makes it possible to conduct the reaction at a temperature as low as  $100^\circ\text{C}$  without obtaining any significant amounts of resinification products. The best performance is shown by nickel halides. Probably, as the catalyst is calcined at  $400^\circ\text{C}$ , partial reduction of nickel salts occurs, which proceeds more readily for halides.



**Fig. 2.** Arrhenius plot of the compound **IV** formation rate constant.

On the assumption that reduced nickel species play a significant role in the isomerization of **III**, we performed a series of experiments for the catalytic system  $\text{NiCl}_2/\text{Al}_2\text{O}_3$  reduced at  $120^\circ\text{C}$  with hydrogen for 2 h and calcined at  $400^\circ\text{C}$  for 2 h. The results are listed in Table 4. It follows from these data that  $\text{NiCl}_2$  reduction in hydrogen proceeds readily and is complete in 0.5 h.

Furthermore, comparing the data listed in Tables 3 and 4 suggests that the thermal treatment of  $\text{NiCl}_2$  leads to the same results irrespective of whether the catalyst was pretreated with hydrogen. It is obvious that the active nickel component of the catalyst is the same species in both cases.

Next, we studied the system obtained by the reduction of nickel chloride on  $\text{Al}_2\text{O}_3$  with a heavy hydrocarbon ( $\text{C}_{16}\text{-C}_{20}$ ) at  $550^\circ\text{C}$  in a nitrogen atmosphere [11, 12]. The key step in the formation of such catalysts is high-temperature nickel salt reduction with a heavy hydrocarbon with the formation of metal–carbon bonds. It is desirable that the boiling point of the heavy hydrocarbon be above  $200\text{--}250^\circ\text{C}$ . The results are listed in Table 5.

An analysis of these data testifies that this catalytic system has significant advantages over the systems used previously. Firstly, this catalyst shows a higher specific activity (conversion of **III** at  $100^\circ\text{C}$  in 1 h is 5%

**Table 2.** Isomerization of compound **III** into **IV** in the presence of  $\text{Al}_2\text{O}_3$

$T, ^\circ\text{C}$	Reaction time, h	Conversion, %	Yield of compound <b>IV</b> , %	Selectivity, %
130	1	9.2	5.1	55.4
130	3	20.1	10.0	49.7
150	1	20.1	6.3	31.4
150	3	39.5	11.7	29.6
180	1	37.1	9.2	24.8
180	3	51.9	12.5	24.1

Note: The initial amount of compound **III** is 8.3 mmol; the support is  $\text{Al}_2\text{O}_3$ .

**Table 3.** Isomerization of compound **III** into **IV** in the presence of Ni (1 wt %)/Al<sub>2</sub>O<sub>3</sub>

Ni compound	T, °C	Conversion, %	Yield of compound <b>IV</b> , %	Selectivity, %
NiCl <sub>2</sub>	100	16.1	10.6	65.5
NiCl <sub>2</sub>	130	37.8	23.3	61.7
NiBr <sub>2</sub>	100	14.9	8.7	58.4
NiBr <sub>2</sub>	130	35.6	21.6	60.8
NiSO <sub>4</sub>	100	11.1	5.8	51.9
NiSO <sub>4</sub>	130	27.4	14.4	52.7

Note: The initial amount of compound **III** is 8.3 mmol; reaction time, 1 h; substrate/nickel = 200 : 1.

**Table 4.** Isomerization of compound **III** into **IV** in the presence of the catalytic system NiCl<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> reduced with hydrogen

Reduction time in H <sub>2</sub> , h	Temperature, °C	Conversion*, %	Yield, %		
			compound <b>IV</b>	other isomerization products	resinification products
2	100	18.4	10.3	6.5	1.6
	130	35.4	18.9	11.7	4.8
0.5	100	19.1	10.6	7.1	1.4
	130	33.8	18.3	11.4	4.1

\* Reaction time, 1 h.

**Table 5.** Parameters of the catalytic isomerization of compound **III** into **IV** in the presence of the catalytic system NiCl<sub>2</sub>/C<sub>16</sub>–C<sub>20</sub>/Al<sub>2</sub>O<sub>3</sub>

Ni content of the catalyst, %	T, °C	Conversion, %	Yield of compound <b>IV</b> , %	Selectivity, %
0.5	100	14.9	12.2	81.6
1.0	100	22.7	17.0	74.8
5.0	100	39.1	26.0	66.4
0.5	130	24.1	18.3	76.1
1.0	130	35.5	25.8	72.7
5.0	130	58.7	35.2	60.0

Note: The initial amount of compound **III** is 8.3 mmol; reaction time, 1 h.

**Table 6.** Parameters of the isomerization of compound **III** into **IV** in the presence of the catalytic system Ni(C<sub>3</sub>H<sub>5</sub>)<sub>2</sub>–NBD–Al<sub>2</sub>O<sub>3</sub>

Active component content of the catalyst, %	T, °C	Conversion, %	Yield of <b>IV</b> , %	Selectivity, %
0.3	80	7.8	7.4	95.1
0.5	80	13.4	12.8	95.6
1.0	80	20.3	18.9	93.2
0.3	100	12.6	11.7	92.5
0.5	100	18.8	17.1	90.9
1.0	100	28.7	26.3	91.6
0.3	130	22.1	20.0	90.5
0.5	130	31.6	27.2	86.1
1.0	130	48.7	41.2	84.7

Note: The initial amount of compound **III** is 8.3 mmol; reaction time, 1 h; substrate/active component = 200 : 1.

higher). Secondly, we observed a significant increase in selectivity, which is as high as 81% at 100°C. Note that raising the nickel content of the catalyst increases the total yield of compound **IV** but leads to a decrease in selectivity. This high performance of the catalyst is likely due to the generation of carbenic or carbidic nickel compounds. In an oxygen-containing atmosphere, the catalyst loses its activity.

In view of the obvious high performance of high-temperature nickel salt reduction with heavy hydrocarbons, it is pertinent to modify the approach to the formation of active nickel species so as to take into account the mechanism of NBD homodimerization via a procedure described in our earlier publication [5]. This mechanism involves the formation of organometallic compounds between reduced nickel and NBD, the formation of complexes of certain composition and structure, and subsequent thermal decomposition.

The new system (Table 6) makes it possible to conduct the isomerization reaction at a low temperature of 80°C. This enables one to reduce the by-product yield and to increase the selectivity to 95%. The other parameters of this process (conversion and the yield of compound **IV**) are also significantly higher at lower temperatures and active component contents (0.3%).

The efficiency of the new catalytic system in the isomerization of norbornane derivatives is probably due to the more uniform and homogeneous distribution of nickel atoms on the  $\text{Al}_2\text{O}_3$  surface and the absence of a wide variety of nickel clusters and other polynuclear entities. It is obvious that the formation and supporting of the active component as an individual prereduced organometallic compound can give rise to a matrix

effect, which is one of the most important approaches used in modern nanocatalyst design.

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