

# Catalytic Syntheses of Polycyclic Compounds Based on Norbornadiene in the Presence of Nickel Complexes: V. Codimerization of Norbornadiene and Methyl Vinyl Ketone on Heterogenized Nickel Catalysts

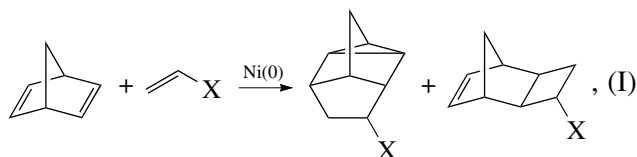
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**Abstract**—A new heterogenized nickel catalyst was developed for the codimerization of norbornadiene and methyl vinyl ketone. This catalyst considerably improved the performance characteristics of the process (selectivity, specific activity, and operating time), as compared with available analogs. A thermogravimetric study of the formation of the active component of the catalyst was performed. Factors affecting the selectivity and productivity of the process were determined.

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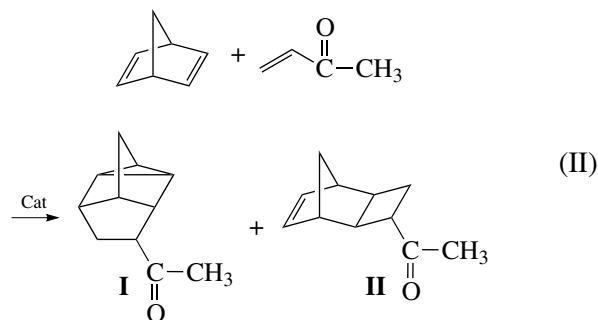
## INTRODUCTION

The codimerization of bicyclo[2.2.1]hepta-2,5-diene (norbornadiene, NBD) with functionally substituted alkenes is a promising method for the preparation of new modified carbocyclic structures, which are used in medicine, fragrance industry, microelectronics, etc. These reactions are very difficult to perform as a single-stage process. Nevertheless, the codimerization of NBD with olefins whose double bond is activated with a strong electron-acceptor substituent can be performed in the presence of homogeneous nickel catalysts:



where X = CHO, COOR, COR, or CN.

The following interaction of NBD with methyl vinyl ketone (MVK), which results in the formation of spatially isomeric 8-acetyltetracyclo[4.3.0.0<sup>2,4</sup>.0<sup>3,7</sup>]nonane (**I**) and 3-acetyltricyclo[4.2.1.0<sup>2,5</sup>]non-7-ene (**II**), is of practical interest:



The number of catalytic systems for this reaction is limited; the majority of these catalytic systems exhibit activity under conditions of homogeneous catalysis [1–3]. In this case, the reaction occurs via a [4 + 2]-cycloaddition route to form the *exo* and *endo* isomers of compound **I**. The occurrence of [2 + 2]-cycloaddition, which leads to product **II**, is characteristic of only a heterogeneous catalyst. This heterogeneous catalyst is nickel chloride supported onto aluminum hydroxide and reduced with heavy alkanes (C<sub>16</sub>–C<sub>20</sub>) in an atmosphere of nitrogen at 550°C followed by modification with triphenylphosphine [4].

The total yield of NBD and MVK codimers under optimum conditions varied from 40 to 80%; in this case, product **I** was predominant. Compound **II**, which is very promising as an intermediate for subsequent transformations with the participation of the strained norbornene double bond (linear and metathesis polymerization, allylation, etc.), was formed in minor amounts (to 20–30%).

The NiCl<sub>2</sub>/PPh<sub>3</sub>/alkane/Al(OH)<sub>3</sub> heterogeneous catalyst is characterized by sufficiently high performance characteristics and can be repeatedly used [4–6]. Note that, in this case, the efficiency of the catalytic system depends not only on the activity of the catalyst and the stability of its operation over a long time interval but also on the absence of side processes such as the homodimerization of NBD and the polymerization of MVK.

The main aim of this study was to develop a new practically feasible catalyst that improves selectivity for norbornene derivative **II** and enhances the overall performance of the process.

## RESULTS AND DISCUSSION

*Catalyst Preparation*

The reduction of a nickel salt with a heavy hydrocarbon (it is desirable that its boiling temperature be higher than 200–250°C) with the simultaneous formation of nickel–carbon bonds is a key stage in the formation of the above catalyst. Further studies on the formation of this catalyst allowed us to hypothesize the generation of carbene or carbide nickel compounds, which can form catalytically active complexes under reaction conditions [7].

In this work, we used another principle of the formation of catalytically active species with consideration for the reaction mechanism of NBD homodimerization [8–10]. It consists in the preliminary formation of organometallic compounds of reduced nickel with NBD and the formation of complexes with a particular structure and composition followed by the thermal degradation of these complexes. This approach allowed us to prepare mononuclear nickel complexes, which subsequently form the basis of catalysts with higher specific activity and selectivity because of structural homogeneity. Thus, the homoligand NBD complexes of nickel  $\text{Ni}(\text{NBD})_2$  and  $\text{Ni}(\text{NBD})_3$ , which occurred in an equilibrium, were formed from organometallic nickel compounds ( $\text{Ni}(\text{C}_3\text{H}_5)_2$ ,  $\text{Ni}(1,5\text{-COD})_2$ ,  $\text{Ni}(\text{C}_5\text{H}_5)_2$ , etc.) in the bulk of NBD.

The synthesis of the active catalyst component was performed in a vacuum (0.5–2.0 Pa) or in an atmosphere of a purified and dried inert gas (nitrogen or argon).

Bis( $\eta^3$ -allyl)nickel (1.4 g, 0.01 mol) was added to NBD (9.2 g, 0.10 mol) by vacuum recondensation. After the solution was thawed and the mononuclear homoligand NBD complexes of nickel were formed, a calculated amount of crushed aluminum hydroxide (0.1–2.0 mol), which was precalcined at 300°C for 6 h, was added from a special pocket of the reactor. In a number of cases, a required amount of toluene was added for the complete wetting and uniform impregnation of the carrier. The nickel content of the catalyst was varied from 0.5 to 10 wt %. After the carrier was impregnated, the solvent, unreacted NBD, and its allylation products were removed in a vacuum by gradually heating the reactor to 200°C. Next, after cooling, the catalyst was repeatedly washed with toluene until the complete disappearance of NBD dimers. The aluminum hydroxide carrier was uniformly red colored (the catalyst lost its color and became black after the penetration of air into the reactor). Thereafter, the reactor was placed in a muffle furnace, slowly heated in a flow

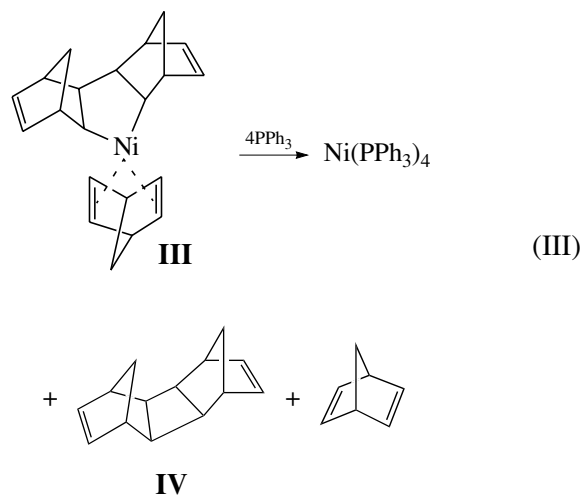
of nitrogen to 500°C, and calcined for 4 h. Under these conditions, aluminum hydroxide underwent complete dehydration, as supported by gravimetry. Thus, the support of the catalyst used in the reaction was  $\text{Al}_2\text{O}_3$ .

The resulting catalyst was tested in the codimerization reaction of NBD and MVK (catalytic system 1, CS-1). Moreover, taking into account the fact that phosphine ligands have a considerable effect on the course of reaction, CS-1 was treated in a vacuum with a solution of triphenylphosphine in NBD at 25°C. In this case, the amount of triphenylphosphine was calculated so that it was equimolar with respect to nickel (catalytic system 2, CS-2).

*Thermogravimetric Study of the Complex  $\text{Ni}(\text{NBD})_3$* 

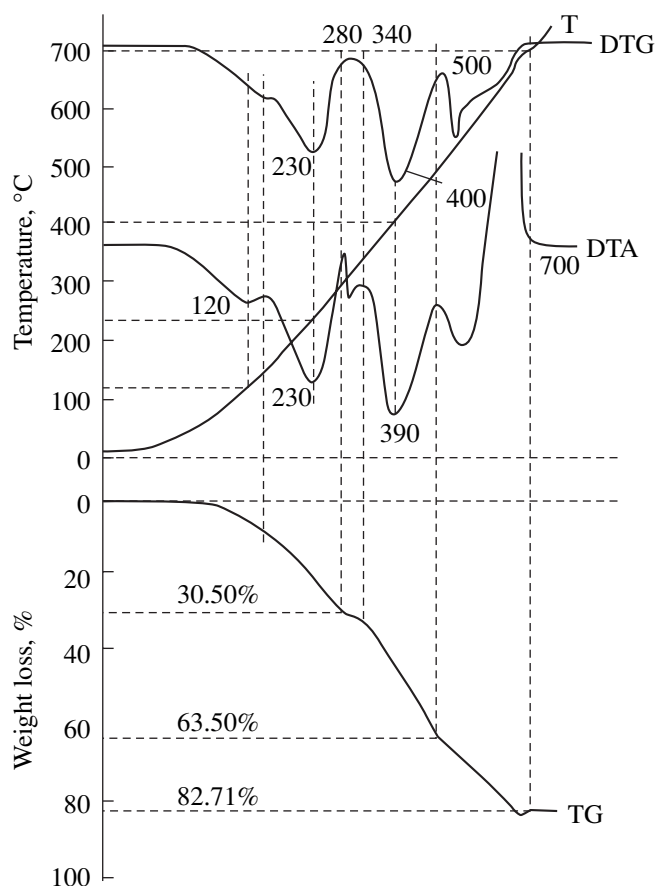
In order to obtain information on the composition of the active component of the  $\text{Ni}(\text{NBD})_n/\text{Al}_2\text{O}_3$  catalyst formed as a result of thermal treatment, we performed a thermogravimetric study of the  $\text{Ni}(\text{NBD})_n$  model system.

The procedure used for the preparation and isolation of the complex  $\text{Ni}(\text{NBD})_n$  (primarily  $\text{Ni}(\text{NBD})_3$ ) is given above and also described elsewhere [8]. The proposed structure of this complex (**III**) is based on IR- and NMR-spectroscopic data, elemental analysis, and the structures of products formed upon the decomposition of the complex in air and under the action of an excess of  $\text{PPh}_3$ :



One of the decomposition products of compound **III** was identified as the *exo-trans-endo* isomer of pentacyclo[8.2.1.1<sup>4,7</sup>.0<sup>2,9</sup>.0<sup>3,8</sup>]tetradeca-5,11-diene (**IV**) [11].

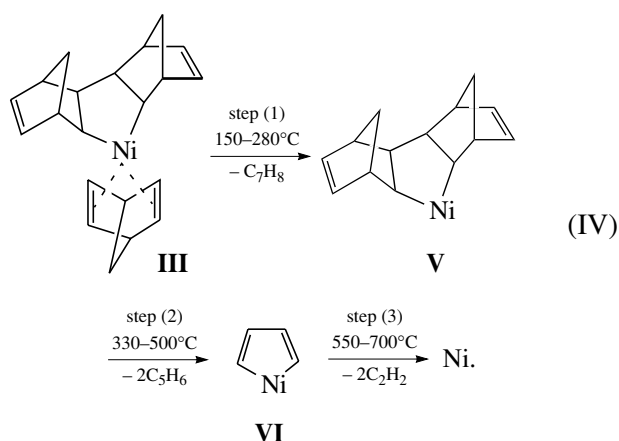
The thermal stability of complex **III** was studied by thermogravimetry over the range 30–700°C in an atmosphere of nitrogen.



Thermal analysis curves for the complex  $\text{Ni}(\text{NBD})_3$ .

The figure and Table 1 summarize the results of thermogravimetric studies.

The thermal decomposition of compound **III** occurred in three steps. The probable mechanism of this decomposition is the following:



Evidently, a weak endo effect with a maximum at 80–120°C was due to the evaporation of impurity hydrocarbons from the sample (see the figure).

A strong endothermic effect in the temperature range 150–280°C, which was accompanied by a ~30% weight loss, corresponds to the removal of a chelate-coordinated NBD molecule (step (1)). The resulting complex **V** occurs over a temperature range, although the superposition of endo and exo effects in the DTA curve suggests its metastability.

As the temperature was increased to 330–340°C, the dimer molecule formed in compound **V** underwent retrodiene decomposition accompanied by the consecutive elimination of two cyclopentadiene molecules (step (2)). It is most likely that the second decomposition product, 2,4-nickelcyclopentadiene (**VI**), was stable because of the formation of a conjugated  $d-\pi$  electron system. Compounds of this structure are well known for various metals. Nickel metal was formed upon subsequent heating (>550°C), and acetylene traces were detected in the gas phase (step (3)).

Effects that correspond to the steps of the decomposition of compounds **V** and **VI** in the DTA curves were

**Table 1.** Data on the thermal decomposition of the  $\text{Ni}(\text{NBD})_3$  complex\*

Nature of the effect	Total weight loss, %		Peak parameters in curves					
			DTG, °C			DTA, °C		
	experimental	calculated	onset	maximum	end	onset	maximum	end
Evaporation of NBD dimers	–	–	–	–	–	40	120	150
Decomposition steps:								
(1)	30.5	27.49	150	230	280	150	230	280
(2)	63.5	66.94	330	400	500	330	380	500
(3)	82.7	82.48	500	–	700	500	550–600	700

\* The purity of the complex was 95.0%.

**Table 2.** Conditions and results of the catalytic codimerization of NBD and MVK

Catalyst	Weight concentration of nickel, %	NBD : MVK molar ratio	Reagent addition procedure	MVK conversion, %	Yield of codimers, %	I/II ratio
CS-1	0.5	1.5	A	51.8	46.4	25 : 1
CS-1	1.5	1.5	A	68.1	63.0	22 : 1
CS-1	3.0	1.5	A	89.6	83.7	21 : 1
CS-1	10.0	1.5	A	100	91.4	24 : 1
CS-1	0.5	1.0	A	36.0	25.4	20 : 1
CS-1	0.5	2.0	A	56.6	54.3	22 : 1
CS-1	0.5	1.5	B	58.9	58.1	20 : 1
CS-1	1.5	1.5	B	74.6	73.1	28 : 1
CS-2	0.5	1.5	A	38.4	36.1	1 : 3
CS-2	1.5	1.5	A	48.4	45.3	1 : 4
CS-2	3.0	1.5	A	61.0	58.8	1 : 4
CS-2	0.5	2.0	A	67.1	65.1	1 : 4
CS-2	0.5	1.5	B	46.6	46.3	1 : 6
CS-2	0.5	1.0	B	36.0	35.1	1 : 6
CS-2	1.5	1.5	B	65.6	63.9	1 : 6
CS-2	10.0	1.5	B	91.1	90.0	1 : 6
CS-2*	0.5	1.5	B	5.3	5.3	1 : 18

Note: Temperature, 90°C; reaction time, 3 h; PPh<sub>3</sub>/Ni ratio, 1 : 1.

\* The ratio PPh<sub>3</sub>/Ni = 2 : 1 was used in this experiment.

partially superimposed on each other; therefore, the experimental weight loss at the first two steps (~63.5%) was somewhat smaller than the theoretically calculated value (67%).

The reaction scheme proposed for the decomposition of compound **III** is tentative. It is likely that carbene or carbide nickel compounds, from which catalytically active centers are formed, can be produced at steps 2 and 3.

#### *Catalytic Codimerization of NBD and MVK*

The codimerization reaction was performed in a Soxhlet apparatus at the boiling temperature of the reaction mixture (~90°C) for 4 h. The catalyst was placed in the upper reactor chamber because it rapidly lost its activity being placed in the flask. The reagents were introduced into the reactor in different manners:

(A) a mixture of NBD and MVK in a given ratio was loaded into the flask of the apparatus;

(B) NBD was loaded into the flask of the apparatus and MVK was added to the upper chamber with the use of a dropping funnel.

Table 2 summarizes the experimental conditions and response values: the conversion of MVK, the total yield of codimers **I** and **II**, and the ratio between the codimers.

Data given in Table 2 suggest that both of the catalytic systems exhibited higher activity than that of the

previously used catalyst [6]. Thus, under analogous conditions, CS-1 allowed us to prepare compound **I** almost quantitatively. The concentration of the active component in the proposed catalytic system was much lower. Note that procedure B for introducing the reagents was more effective; in particular, the yield of by-products considerably decreased in this case.

In our opinion, the most interesting result was obtained with the use of CS-2 modified with triphenylphosphine. The experimental results suggest that an optimum Ni/PPh<sub>3</sub> ratio is 1 : 1. In this case, the yield of ketone **II** was as high as 50–60% at selectivity higher than 80%. These high performance characteristics with respect to compound **II** are much better than those of previously known procedures (less than 20–30%) [5].

In this case, procedure B for introducing the reagents was also more effective: the conversion of MVK increased by 8–17%, whereas the formation of side NBD dimers decreased to 1%.

With the use of an excess of NBD over MVK, we managed to exclude completely the formation of MVK oligomers.

A possible explanation of the higher activity and selectivity of developed catalytic systems CS-1 and, especially, CS-2, as compared with well-known systems, consists in a more uniform and homogeneous distribution of nickel atoms over the support surface and the absence of a broad spectrum of nickel clusters or other polynuclear species. Evidently, this procedure for

generating and supporting an active component as a prereduced metal complex compound can result in a matrix effect: a promising technique for improving the selectivity of chemical reactions.

## EXPERIMENTAL

Both domestic and foreign chemicals of 99.0–99.9% purity were used in this study. All of the reagents and solvents were purified before syntheses in accordance with standard procedures [12]. The reagents NBD and MVK were distilled at a reduced pressure before use. Triphenylphosphine from Aldrich was recrystallized from ethanol.

The reaction mixture was analyzed and the course of reaction was monitored by gas chromatography (Chrom-5 chromatograph; SPB-20 and  $\beta$ -DEX capillary columns from Supelco).

The thermal properties of complex **III** were studied on a Paulik-Erdey derivatograph. Aluminum oxide was used as a reference substance. The samples were heated at a rate of 10 K/min. The sample weight was varied from 0.05 to 0.20 g. The error in weight losses was no higher than 3%.

The products were identified using IR and  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectroscopy and chromatography–mass spectrometry (GC–MS).

The IR spectra in the region 700–3100  $\text{cm}^{-1}$  were measured on a Bruker IFS-113 V spectrometer with a Karlo-Erba Strumentation 4200 chromatographic attachment using a glass capillary column 30 m in length and 0.75 mm in diameter (SPB-1 phase, film thickness of 1  $\mu\text{m}$ ). The  $^1\text{H}$  and  $^{13}\text{C}$  NMR spectra were measured on a Bruker DPX-300 instrument at operating frequencies of 300.033 and 75.15 MHz, respectively, in  $\text{CDCl}_3$ . The GC–MS studies were performed on an instrument (Delsi Instruments) with an OV-1 column; the spectra were measured in the electron impact mode with an ionization energy of 70 eV. The experimental data were consistent with published data [4].

**8-Acetyltetracyclo[4.3.0.0<sup>2,4</sup>.0<sup>3,7</sup>]nonane (I):** bp 82–84°C,  $n_{\text{D}}^{20} = 1.4955$ . IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 799, 1727, 2958. MS,  $m/z$ : 162 ( $\text{M}^+$ , 16.0% rel. int.), 147 (6.0), 120 (9.0), 119 (100.0), 118 (12.0), 117 (21.0), 115 (9.0), 104 (6.0), 103 (5.0), 92 (12.0), 91 (94.0), 79 (8.0), 78 (5.0), 77 (10.0), 66 (4.0), 65 (8.0), 51 (4.0), 41 (15.0), 39 (8.0).  $^1\text{H}$  NMR\* ( $\text{CDCl}_3$ )  $\delta$ , ppm: 3.02 (ddd,  $J = 4.5$ , 4.5, 11,  $\text{H}_8$ -endo), 2.88 (dd,  $J = 5.5$ , 8.5,  $\text{H}_8$ -exo), 2.5 (m,  $\text{H}_7$ -endo), 2.2 (m,  $\text{H}_7$ -exo), 1.5–1.95 (m, 4H-, 2H<sub>9</sub>-, H<sub>1</sub>-, H<sub>6</sub>-endo + exp), 1.55 (s, 2H<sub>5</sub>-endo), 1.51 (s, 2H<sub>5</sub>-exo), 0.75–1.06 (m, 3H-, H<sub>2</sub>-, H<sub>3</sub>-, H<sub>4</sub>-endo + exo), 2.14

(s, 3H,  $\text{CH}_3$ -endo), 2.12 (s, 3H,  $\text{CH}_3$ -exo).  $^{13}\text{C}$  NMR (exo isomer) ( $\text{CDCl}_3$ )  $\delta$ , ppm: 10.78 (CH), 13.00 (CH), 14.63 (CH), 29.00 ( $\text{CH}_3$ ), 29.89 ( $\text{CH}_2$ ), 31.00 ( $\text{CH}_2$ ), 42.52 (CH), 42.98 (CH), 45.47 (CH), 53.86 (CH), 209.08 (C).  $^{13}\text{C}$  NMR (endo isomer) ( $\text{CDCl}_3$ )  $\delta$ , ppm: 13.70 (CH), 15.08 (CH), 15.15 (CH), 28.69 ( $\text{CH}_3$ ), 29.90 ( $\text{CH}_2$ ), 31.39 ( $\text{CH}_2$ ), 39.33 (CH), 42.35 (CH), 45.78 (CH), 52.76 (CH), 208.39 (C).

**3-Acetyltricyclo[4.2.1.0<sup>2,5</sup>]non-7-ene (II):** bp 82–85°C,  $n_{\text{D}}^{20} = 1.4735$ . IR ( $\nu$ ,  $\text{cm}^{-1}$ ): 700, 1360, 1570, 1710.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$ : 2.67, 2.73 (s, 2H, CH), 5.98 (m, 2H, CH), 2.10 (s, 3H,  $\text{CH}_3$ ).  $^{13}\text{C}$  NMR ( $\text{CDCl}_3$ )  $\delta$ , ppm: 21.90 ( $\text{CH}_2$ ), 27.24 ( $\text{CH}_3$ ), 33.50 (CH), 39.93 (CH), 40.28 ( $\text{CH}_2$ ), 43.84 (CH), 43.96 (CH), 45.54 (CH), 134.31 (CH), 135.66 (CH), 207.76 (C).

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\* Multiplicity: s, d, and m refer to singlet, doublet, and multiplet, respectively.