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CATALYTIC REACTION MECHANISMS

Catalytic Syntheses of Polycyclic Compounds Based on Norbornadiene in the Presence of Nickel Complexes: IV. Problems of Regioselectivity in Norbornadiene Codimerization with Activated Olefins

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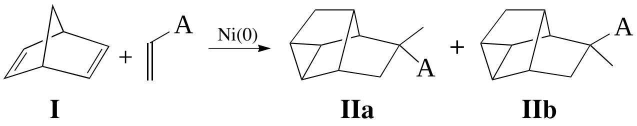
Abstract—Cyclocodimerization of norbornadiene with acrylates in the presence of bis(η^3-allyl)nickel is studied. The regio- and stereoselectivities of cycloaddition depend on the catalyst composition, temperature, reactant ratio, and the nature of acrylate. Conditions excluding the side direction (norbornadiene homodimerization) are selected. A mechanism that explains the main regularities of codimerization is proposed.

INTRODUCTION

The codimerization of bicyclo[2.2.1]heptadiene-2,5 (norbornadiene) with modified olefins is a promising method for the synthesis of new functionalized carbocyclic structures [1]. The development of catalytic systems favoring the formation of individual regio- and stereomers is especially urgent today.

Nickel(0) complexes are known to catalyze the cycloaddition of norbornadiene and some activated olefins. These reactions mainly produce [2+2+2]-cycloadducts with the *endo* (**IIa**) and *exo* (**IIb**) structures



A = CHO, COOR, COR, and CN

Compounds that can be involved in this reaction are mostly olefins containing an electron-withdrawing group, such as acrylonitrile, acrolein, methyl vinyl ketone, acrylates, vinylsulfones, and vinyl sulfoxides [2, 3].

The reaction is complicated by the formation of a considerable amount of by-products: norbornadiene dimers and oligomers. Among the substrates used, acrylates are characterized by the lowest reactivity and the yield of their codimers with norbornadiene does not exceed 15% [2].

We studied the codimerization of norbornadiene with methyl acrylate, *tert*-butyl acrylate, and 2-methyladamantyl acrylate.

The purpose of this work is to enhance the yield of codimerization products, to establish side directions of the reaction and prevent them, and to reveal factors affecting the regio- and stereoselectivities of the reaction.

Bis(η^3-allyl)nickel was used as a catalyst precursor. As shown previously [4], norbornadiene (NBD) easily substitutes allyl ligands in nickel complexes to form the $Ni(NBD)_2$ complex, which is an efficient catalyst of norbornadiene homodimerization.

The following parameters were varied in the study of the reactions of acrylates with norbornadiene: the initial reactant and catalyst concentrations, temperature, and the composition of the catalytic system (by the introduction of phosphine additives).

EXPERIMENTAL

The reaction mixture was analyzed and the course of the process was monitored by gas chromatography (Chrom-5 chromatograph, SPB-20 capillary columns, β-DEX (Supelco)). The products were identified by ^1H and ^{13}C NMR spectroscopy and chromatography coupled with mass spectrometry.

^1H and ^{13}C NMR spectra were recorded on a Bruker DPX-300 instrument at working frequencies of 300.033 and 75.15 MHz, respectively, in $CDCl_3$ and C_6D_6.

Studies by chromatography coupled with mass spectrometry were carried out on a Delsi Instruments instrument using an OV-1 column, and the spectra were recorded in the electron impact mode with an ionization energy of 70 eV.

Diethyl ether and toluene were distilled and stored above a sodium wire. Norbornadiene was distilled before experiments. Methyl acrylate, *tert*-butyl acrylate, and 2-methyladamantyl acrylate were distilled under reduced pressure and stored with a 2% hydroquinone additive. Bis(η^3-allyl)nickel was synthesized, stored, and charged into a reactor according to the procedures described in [4]. Bis(1,2-diphenylphosphino)ethane (Fluka) was used without additional purification. Triphenylphosphine was recrystallized from ethanol before use.

Experiments were carried out in closed evacuated 10-ml reactors operating at a constant temperature and equipped with a sampling device.

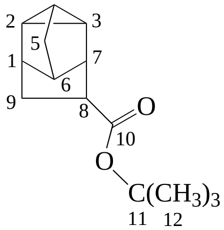
The general procedure of experiments was as follows. The reactor was charged with the weighed samples of initial substances and phosphine. Oxygen removal from the mixture was repeated three times (freezing–evacuation–thawing cycles in liquid nitrogen). Then a weighed sample of bis(η^3-allyl)nickel was transferred to the reactor in a vacuum. The reactor was filled with argon, and the temperature was brought to a constant level. A color change due to the formation of a catalytic system was observed. For different reactant ratios and catalyst compositions, the color changed from light yellow to dark red but the solution remained homogeneous. After the end of the reaction, air was passed through the reaction mixture for 30 min to decompose the catalyst. The resulting mixture was centrifuged to remove solid residues of the catalyst and filtered through a silica gel layer using dichloromethane for washing. The solvent residue was distilled off under reduced pressure. The codimerization products were separated from the norbornadiene dimers by column chromatography a column with a length of 1 m and a diameter of 20 mm packed with silica gel 230/400 mesh, 6 nm (Aldrich); hexane–diethyl ether (20 : 1) system of solvents). The material balance was calculated from the weights of the obtained products and GLC data.

Reaction of Norbornadiene with tert-Butyl Acrylate

Norbornadiene (0.34 ml, 3.36 mmol) and *tert*-butyl acrylate (0.84 ml, 5.76 mmol) were added to toluene (1 ml). Oxygen removal from the mixture was repeated three times. Then a weighed sample of bis(η^3-allyl)nickel (0.0235 g, 0.17 mmol) was charged into the reactor, and the reactor was filled with argon from which oxygen and moisture traces were preliminarily removed. The color change from yellow to orange–red due to catalyst formation was observed during defreezing. The reaction was carried out at 50°C for 6 h. After catalyst residues, unreacted initial substances, and the solvent were removed, a yellow oil was obtained. Separation by column chromatography gave norbornadiene dimers (82.32 mg, 0.447 mmol) and *tert*-butyl heterocyclo[4.3.0.0$^{2.4}$.0$^{3.7}$]nonane-8-carboxylate (247.66 mg, 1.17 mmol, 34.8% yield, *endo*/*exo* = 56 : 44).

Reaction of Norbornadiene with tert-Butyl Acrylate in the Presence of Triphenylphosphine

Norbornadiene (0.28 ml, 2.75 mmol) and *tert*-butyl acrylate (0.37 ml, 2.53 mmol) were added to toluene (1 ml), and then triphenylphosphine (0.048 g, 0.18 mmol) was added to the mixture. After three cycles of oxygen removal, bis(η^3-allyl)nickel (0.02 g, 0.18 mmol) was added to the reactor. After defreezing, the solution became yellow. The reaction was carried out at 50°C for 8 h. Chromatography gave 260 mg (1.24 mmol) *tert*-butyl tetracyclo[4.3.0.0$^{2.4}$.0$^{3.7}$]nonane-8-carboxylate (49% yield, *endo*/*exo* = 76 : 24)



^{13}C NMR (CDCl$_3$, 75 MHz, δ, ppm): 175.86(C10), 79.57(C11), 46.82(C8), 45.71(C7), 42.44, 39.85(C1,6), 31.62 (C5), 31.60(C9), 28.11(C21), 15.11, 14.94(C2,3), 13.65(C4); finer peaks (second isomer, δ, ppm): 175.13(C10), 80.50(C11), 46.29(C8), 46.12(C7), 42.83, 42.73(C1,6), 31.30(C5), 28.90(C9), 28.06(C12), 14.75, 13.09(C2,3), 11.14(C4).

^{1}H NMR (CDCl$_3$, 300 MHz, δ, ppm): 1.8–2.2 (m, H2, H3, H4), 1.45 (s, 3CH$_3$), 1.5 (s, 2H5), 1.5–2.1 (m, H1, H6, 2H9), 2.1–2.3 (m, H7), 2.78 (ddd, J = 4.5, 4.5, 11.0 Hz; H8); second isomer (δ, ppm): 0.8–1.2 (m, H2, H3, H4), 1.5 (s, 3 CH$_3$), 1.6 (s, 2 H5), 1.7–2.2 (m, H1, H6, 2H9), 2.14 (br.s, H7), 3.63 (dd, J = 5.5, 8.5 Hz, H8).

Mass spectrum, m/z (I % of the main peak): 220(2.5)-M$^+$, 164(20.8), 147(5.0), 105(1.7), 119(25.0), 118(4.2), 117(5.0), 105(2.5), 91(16.7), 79(2.5), 66(5.8), 65(4.2), 57(100.0), 41(31.7), 39(10.0), 29(5.8).

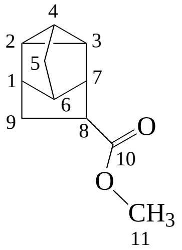
Reaction of Norbornadiene with Methyl Acrylate

Norbornadiene (0.25 ml, 2.47 mmol) and methyl acrylate (0.45 ml, 5 mmol) were added to toluene (1.1 ml). Oxygen removal was repeated three times from the mixture. Then a weighed sample 0.017 g (0.012 mmol) of bis(η^3-allyl)nickel was placed in the reactor, and the reactor was filled with argon from which oxygen and moisture traces were removed. Defreezing resulted in a change in the color from yellow to orange–red due to catalyst formation. The reaction was carried out at

50°C for 8 h. After catalyst residues, unreacted initial substances, and the solvent were removed, a yellow oil was obtained. Separation by column chromatography gave norbornadiene dimers (25.6 mg, 0.014 mmol) and methyl tetracyclo[4.3.0.0$^{2.4}$.0$^{3.7}$]nonane-8-carboxylate (114.36 mg, 0.64 mmol, 25.9% yield, *exo*/*endo* = 43 : 57).

Reaction of Norbornadiene with Methyl Acrylate in the Presence of Triphenylphosphine

Norbornadiene (0.25 ml, 2.47 mmol) and methyl acrylate (0.23 ml, 2.54 mmol) were added to toluene (1.3 ml), and triphenylphosphine (0.0316 g, 0.012 mmol) was introduced. After oxygen was triply removed from the mixture, bis(η^3-allyl)nickel (0.017 g, 0.012 mmol) was introduced into the reactor. The solution became yellow within the course of defreezing. The reaction was carried out at 50°C for 8 h. Chromatography gave methyl tetracyclo[4.3.0.0$^{2.4}$.0$^{3.7}$]nonane-8-carboxylate (210 mg, 1.17 mmol, 47% yield, *exo*/*endo* = 42 : 58)



^{13}C NMR (CDCl$_3$, 100 MHz, δ, ppm): 175.90(C10), 51.39(C11), 45.99(C8), 44.99(C7), 42.76, 42.60(C6,1), 31.31(C5), 29.31(C9), 14.77, 13.13(C2,3), 11.29(C4); second isomer (δ, ppm): 176.87(C10), 51.52(C11), 46.75(C8), 44.44(C7), 42.41, 39.94(C6,1), 31.59(C5), 31.53(C9), 15.08, 14.90(C2,3), 13.70(C4).

^{1}H NMR (CDCl$_3$, 300 MHz, δ, ppm): 0.8–1.0 (m, H2, H3), 1.0–1.2 (m, H4), 1.51 (s, 2H5), 1.6–2.1 (m, 2H9), 1.79 (s, H6), 1.99 (s, H1), 2.2–2.3 (m, H7), 2.7–3.0 (m, H8), 3.65 (s, OCH$_3$); second isomer (δ, ppm): 0.8–1.0 (m, H2, H3), 1.0–1.2 (m, H4), 1.54 (s, 2H5), 1.7–2.1 (m, 2H9), 1.95 (s, H6), 2.00 (s, H1), 2.15 (s, H7), 2.5–2.8 (m, H8), 3.60 (s, OCH$_3$).

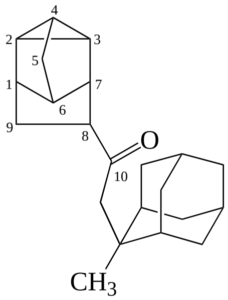
Mass spectrum, *m*/*z* (*I*% of the main peak): 178(55.4)–M$^+$, 179(8.3), 163(4.1), 147(16.5), 146(13.2), 137(4.1), 132(3.3), 124(2.5), 120(11.6), 119(95.0), 118(66.1), 117(52.9), 116(16.5), 105(23.1), 104(14.9), 92(26.4), 91(100.0), 90(9.9), 87(24.0), 79(33.1), 78(16.5), 77(23.1), 66(31.4), 65(28.9), 58(15.7), 55(15.7), 53(14.9), 51(20.7), 41(81.0), 39(54.5), 27(19.8).

Reaction of NBD with MMA

Toluene (0.3 ml) was added to 0.15 ml NBD (1.48 mmol) and 0.60 ml (2.86 mmol) MMA. The mixture was triply deoxygenated by cycled freezing-evacuation-unfreezing in liquid nitrogen. Then, a sample of bis(η^3-allyl)nickel (0.017 g, 0.012 mmol) was charged into the reactor. The reactor was filled with argon purified from traces of oxygen and moisture. During unfreezing the color changed from yellow to orange due to catalyst formation. The reaction was carried out at 50°C for 8 h. Upon the removal of the catalyst residue, unreacted reactants, and the solvent, yellow oil remained. As a result we obtained 51 mg (0.028 mmol) of NBD dimers and 99 g (0.32 mmol) 2-methyladamantyltetracyclo[4.3.0^{2,4}.0^{3,7}]nonane-8-carboxylate with a yield of 21.6% and an exo/endo ratio of 74/26.

Reaction of NBD with MMA in the Presence of Triphenylphosphine

Toluene (0.7 ml) was added to 0.17 ml NBD (1.68 mmol) and 0.35 ml MMA (1.67 mmol). Then, 0.035 g (0.013 mmol) of triphenylphosphine was added. Upon triple deoxygenation of the mixture, the reactor was charged with 0.0172 g (0.012 mmol) of bis(η^3-allyl)nickel. During unfreezing, the solution turned yellow. The reaction was carried out at 50°C for 8 h. As a result we obtained 190 mg (0.61 mmol) 2-methyladamantyltetracyclo[4.3.0^{2,4}.0^{3,7}]nonane-8-carboxylate with a yield of 36% and an exo/endo ratio of 83/17:



Mass spectrum, *m*/*z* (*I*% of the main peak):

312 (1.4)-M$^+$, 266 (0.16), 207 (0.13), 166 (0.16), 165 (1.9), 164 (16.2), 150 (11.6), 149 (100), 148 (64.0), 133 (8.7), 120 (3.9), 119 (18), 118 (2.5), 117 (4.6), 107 (9.2), 106 (13.9), 105 (14), 94 (3.9), 93 (16), 92 (20.3), 91 (33.5), 81 (6.5), 80 (6.7), 79 (18.7), 78 (4.7), 77 (10), 67 (5.1), 66 (2.5), 65 (4.2), 55 (2.8), 53 (2.7), 41 (6), 39 (3.8)

In the ^{1}H NMR spectra of the mixture of exo/endo isomers, the following signals were observed: 2.9 (ddd, 0.17 H, J = 4.5, 4.5, 11.0 Hz; H8), 2.70 (dd, 0.83 H, J = 5.5, 8.5 Hz, H8). However, we failed to assign other signals in the range 0.7–2.5 ppm.

RESULTS AND DISCUSSION

In the first series of experiments, bis(η^3-allyl)nickel without phosphine additives was used as a catalyst.

The cycloaddition of methyl acrylate and *tert*-butyl acrylate to norbornadiene leads to the formation of the *endo* and *exo* isomers **IIa** and **IIb**, respectively, with a tetracyclic structure and a considerable amount of norbornadiene dimers **III**–**IV**, whose structures were confirmed by spectroscopic methods

Table 1. Characteristics of the catalytic dimerization of norbornadiene (NBD) with *tert*-butyl acrylate (TBA)

No.	$[NBD]_0$, mol/l	$[NBD]_0/[TBA]_0$	T, °C	Ratio of reaction products, %				Conversion of NBD, %	Conversion of TBA, %
				NBD dimers	**III–IV–V–VI**	codimers	*exo*/*endo*		
1	2	1/0.5	30	59	0.5 : 81 : 16 : 2.5	41	56 : 44	46	23
2			50	57	1 : 81 : 16 : 2	43	56 : 44	72	35
3			70	47	0 : 81 : 16 : 2	53	60 : 40	87	61
4	2	1/1	30	55	1 : 83 : 14 : 2	45	54 : 46	57	16
5			50	56	0 : 83 : 15 : 2	44	56 : 44	90	24
6			70	42	0 : 82 : 16 : 2	58	56 : 44	87	32
7	1	1/2	30	40	1 : 81 : 16 : 2	60	55 : 45	46	10
8			50	25	0 : 83 : 15 : 2	75	57 : 43	60	20
9			70	28	1 : 82 : 14 : 3	72	56 : 44	70	20
10	1.5	1/2.7	50	25	0 : 81 : 16 : 3	75	56 : 44	54	11

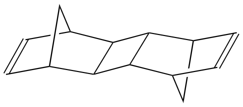
Note: $[Ni(all)_2]_0 = 0.05$, $[NBD]_0$, solvent toluene, reaction time 8 h.

Table 2. Characteristics of the catalytic codimerization of norbornadiene with methyl acrylate (MA) and methyl metacrylate (MMA)

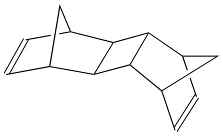
No.	$[NBD]_0/[MA]_0$	Ratio of reaction products, %				Conversion of NBD, %	Conversion of acrylate, %
		NBD dimers	**III–IV–V–VI**	codimers	*endo*/*exo*		
11	1/0.5	49	0.3 : 80 : 18 : 1.7	51	43 : 57	27	19
12	1/1	19	0.6 : 81.4 : 16 : 1	81	42 : 58	33	22
13	1/2	18	0 : 80 : 18 : 2	82	43 : 57	37	12
14	1/0.5	68	0 : 82.3 : 15.7 : 3	32	73 : 27	53	18
15	1/1	62	0 : 82.2 : 15 : 2.8	38	73 : 27	80	12
16	1/2	34	0 : 82 : 15 : 3	66	74 : 26	58	11

Note: $[NBD]_0 = 1.4$ mol/l, $[Ni(all)_2]_0 = 0.05\ [NBD]_0$, $T = 50$°C, solvent toluene, reaction time 8 h.
Acrylates: MA (runs 11–13), MMA (runs 14–16).

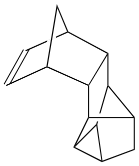
and independent experiments on norbornadiene dimerization. Trace amounts of dimer **III** are formed, probably in the initial steps of formation of the catalytic system.



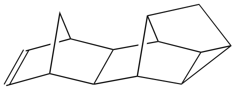
III



IV



V



VI

It is of interest that the compositions of isomers in different groups of products (norbornadiene dimers and copolymerization products) slightly depend on the temperature, the ratio of the initial concentrations of the reactants, and substituent in acrylate. The **IV**/**V**/**VI** norbornadiene dimer ratio is 82 : 16 : 2 and remains unchanged during experiment. The *exo*/*endo* ratio of codimers **IIa** and **IIb** for different acrylates is also constant in time.

The initial concentrations of reactants affect the ratio of the total amount of norbornadiene homodimers to the amount of the norbornadiene codimers with acrylates. The fraction of the codimers increases with an increase in the initial concentration of acrylate (Table 1, entries 2, 5, 8, and 10; Table 2, entries 11–16). For the twofold methyl acrylate excess, the yield of the codimers is higher than 80% (Table 2, entries 12 and 13), for *tert*-butyl acrylate it is 75% (Table 1, entries 8 and 10), and for MMA it is 66% (run 16). The kinetic studies show that the norbornadiene dimers/codimers ratio changes during experiment.

Table 3. Characteristics of catalytic norbornadiene codimerization with acrylates in the presence of tertiary phosphines

No.	Olefin	Phosphine	$[PR_3]_0/[Ni(all)_2]_0$	The ratio of reaction products, %			Yield, %
				NBD dimers	codimers	*exo*/*endo*	
17	TBA	TPP	1/1	1.6	98.4	62 : 37	48
18	″	″	1.4/1	1	99	76 : 23	45
19	″	″	2/1	0	100	84 : 16	21
20	MA	″	1/1	0	100	42 : 58	47
21	″	″	2/1	0	100	54 : 46	19
22	MMA	″	1/1	0	100	83 : 17	42
23	TBA	DPPE	0.5	26	74	44 : 56	19
24	″	″	1/1	0	100	39 : 61	20
25	MA	″	0.5	11	89	32 : 68	15
26	″	″	1/1	0.5	99.5	15 : 85	10

Note: $[NBD]_0$ = 1.4 mol/l, $[olefin]_0$ = 1.4 mol/l, $[Ni(all)_2]_0 = 0.05[NBD]_0$, T = 50°C, solvent toluene, reaction time 8 h.

The ratio of stereomers in all series of experiments for each olefin remains unchanged. In the reaction involving *tert*-butyl acrylate, the *exo/endo* isomer ratio is 56 : 44, in the case of MMA is 73 : 27 (run 16), and the *endo* isomer dominates in the case of methyl acrylate (43 : 57).

Temperature influences the rates of both the direct and side reactions. The conversion of reactants increases significantly with temperature (Table 1), and the fraction of norbornadiene dimers decreases. In our experiments, the highest yield of the codimers is observed at 70°C.

Thus, to prevent norbornadiene dimerization, the reaction should be carried out in excess acrylates and at an elevated temperature. However, a considerable excess of acrylate is needed for the complete prevention of dimerization, due to which the isolation of the target reaction products becomes more difficult. These drawbacks were eliminated and side norbornadiene dimerization was prevented by the modification of the catalytic system with tertiary phosphines.

Triphenylphosphine (TPP) and bis(1,2-diphenylphosphino)ethane (DPPE) were used and the phosphine/Ni ratio was varied in the next series of experiments (Table 3).

When triphenylphosphine was used, norbornadiene dimerization completely ceases if norbornadiene is in 20% excess over nickel in the codimerization of norbornadiene with *tert*-butyl acrylate (Table 3, entries 17–19) and if the equimolar ratio P/Ni is 1 : 1 in codimerization with methyl acrylate (MA) (Table 3, entries 20 and 21).

Bidentate BPPE eliminates side reactions only at a P/Ni ratio equal to 1 : 1 (Table 3, entries 24 and 26). However, the reaction completely ceases at an insignificant DPPE excess (DPPE/Ni = 1.2 : 1).

The reaction rate as a whole and the yield of the codimerization products decrease substantially with an increases in the P/Ni ratio.

The use of phosphines affects the stereoselectivity of the reaction and changes the ratio of stereomers **IIa** and **IIb**. The use of triphenylphosphine increases the content of the *exo* isomer (Table 3, entries 19, 21, and 22), whereas the use of DPPE increases the content of the *endo* isomer (Table 3, entries 24 and 26). This regularity is valid for all acrylates.

Reaction Mechanism

The experimental data can conveniently be analyzed in the framework of a mechanism proposed previously for the catalytic homodimerization of norbornadiene [4, 5].

According to this mechanism, the structure of the reaction products is formed in key intermediates. Norbornadiene molecules in such intermediates should occupy at least three coordination sites. These regularities can be assumed to be valid for norbornadiene codimerization with olefins as well. The necessary condition for the formation of codimers should be the formation of mixed heteroligand π-complexes containing norbornadiene and olefin molecules. Olefin should be characterized by the capability of coordination on the Ni atom, being intermediate between monodentate and bidentate norbornadiene [6].

The experimental results show that the reaction occurs via two routes. The key intermediates **IX** (codimerization route) and **VIII** (norbornadiene homodimerization) are formed from the common complex **VII** containing two chelate norbornadiene molecules (Fig. 1). Their formation requires a change in the character of coordination of one of the norbornadiene molecules. The third norbornadiene molecule (complex **VIII**) or the olefin molecule (complex **IX**) is coordinated to the freed vacancy. The equilibrium constants of these steps determine the ratio of the reaction products. Further transformations include the formation of metallacyclic intermediates **X**–**XII** (homodimerization) and

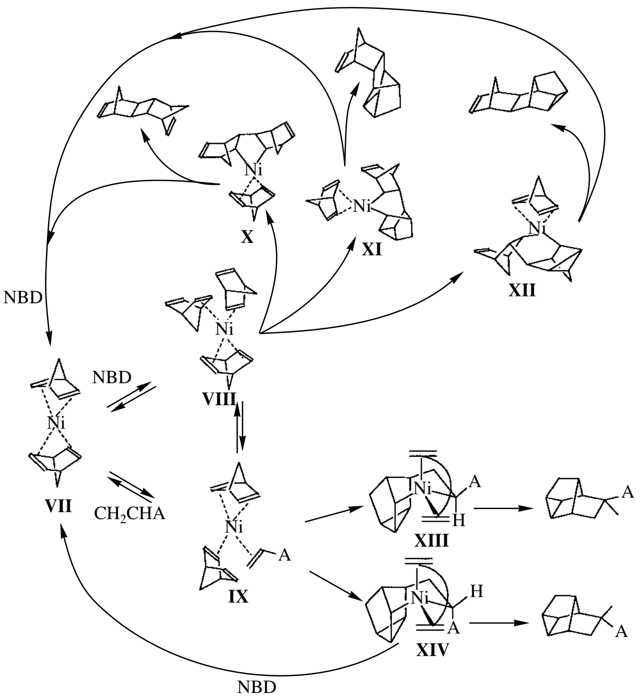


Fig. 1. Mechanism of norbornadiene (NBD) codimerization with acrylates.

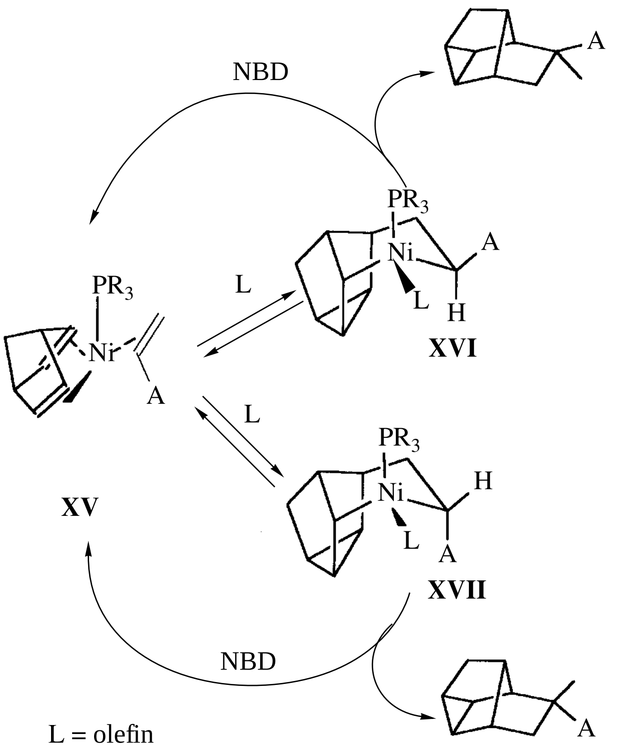


Fig. 2. Fragment of the mechanism of norbornadiene codimerization with acrylates in the presence of phosphines.

XIII, **XIV** (codimerization) and their decomposition due to reductive elimination. After these processes, nickel complex **IX** is stabilized by the remaining norbornadiene molecule, which is transformed from the monodentate into the chelate molecule.

The proposed mechanism explains the regioselectivity of cycloaddition. The constant ratio of isomers in each group of the products (norbornadiene dimers and codimers) indicates that they are formed from different intermediates via parallel routes.

This assumption is also confirmed by the following facts. First, dimer **III**, which predominates under the conditions of Ni-catalyzed norbornadiene dimerization, is virtually absent from all experiments. Evidently, the coordinating acrylate does not produce intermediates resulting in the formation of dimer **III** [4]. Second, the ratio between the norbornadiene dimers is independent of the nature of the acrylate.

Products **IIa** and **IIb** are formed from complexes containing the chelate-coordinated norbornadiene molecule. This explains the formation of only [2+2+2]-cycloadducts.

Thus, to prevent the formation of norbornadiene dimers, one of the coordination sites on the nickel atom should be blocked under the codimerization conditions.

With this purpose, we used tertiary mono- and diphosphines, whose bonds with nickel are stronger that those with π-olefins. The nickel–phosphine matrix formed is characterized by the template effect and affects stereoselectivity to a great extent.

The fragment of the codimerization mechanism involving phosphines is presented in Fig. 2.

π-Complex **XV** containing the chelate norbornadiene molecule, phosphine, and olefin $CH_2{=}CHA$ is transformed into the σ-metallocyclic intermediates **XVI** and **XVII**, whose spatial structures are determined by the stereoselectivity of codimerization.

In the case of monodentate triphenylphosphine, the formation of complex **XVI** is preferable for steric reasons resulting in an increase in the *endo* isomer content. The *exo* isomer is predominantly formed from complex **XVII** when bidentate DPPE is used. This is also caused by steric factors. In both cases, a change in the *endo*/*exo* isomer ratio is only determined by the phosphine structure and is independent of the acrylate nature.

CONCLUSIONS

Thus, a catalytic system for the synthesis of the products of norbornadiene codimerization with activated olefins was selected. Experiments using triphenylphosphine and bis(1,2-diphenylphosphino)ethane showed that the introduction of an equimolar amount of phosphine completely stopped the formation of dimers. Only cycloadducts with olefin are products of the reaction. The structures of the cycloadducts are determined by steric features of the key intermediate of the reaction. The kinetic regularities of codimerization involving a wide range of activated olefins will be discussed in our forthcoming publications.

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