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Catalytic Syntheses of Polycyclic Compounds Based on Norbornadiene in the Presence of Nickel Catalysts

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Abstract—The cycloadditions of olefins containing an electron-withdrawing substituent to norbornadiene are reported. The influence of the substituent and solvent nature on the [2+2+2]-cycloadduct yield and stereoselectivity is elucidated. The competitive cycloaddition of pairs of olefins to norbornadiene is discussed. Hypotheses about the structure of key intermediates of the process are considered. The consistent generalized mechanism for the cycloaddition of unsaturated compounds of various classes to norbornadiene is suggested.

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Cycloaddition reactions involving bicyclo[2.2.1]heptadiene-2,5 (norbornadiene, **I**) and an activated olefin make it possible to obtain various carbocyclic compounds. The double bond in the olefin participating in these reactions is usually activated due to the electron-withdrawing group or is an element of a strained cycle [1, 2]. Owing to the specific features of the structure of norbornadiene and activated olefins, these reactions proceed via multiple routes [3]. The problems of isomerism are of supreme significance.

We demonstrated earlier that, in the presence of bis(η^3-allyl)nickel, norbornadiene reacts with acrylic acid esters to form the corresponding [2+2+2]-cycloadducts with *endo* and *exo* structures and norbornadiene homodimers [4].

In the present work, the range of substrates was considerably widened to reveal specific features of the mechanism of this reaction. We studied the reactions of norbornadiene with unsaturated compounds of various classes: acrylic esters (methyl, ethyl, *n*-butyl, *tert*-butyl, and 2-methyladamantyl acrylates), acrolein, methacrolein, methyl vinyl ketone, acrylonitrile, 2-methylacrylonitrile, furanone, vinyl acetate, and maleic anhydride.

EXPERIMENTAL

Toluene, diethyl ether, 1,2-dichloroethane, acetone, and methanol (all high-purity grade) were purified using standard methods and stored according to the requirements imposed on these solvents.

The reagents were distilled under reduced pressure prior to use. Bis(η^3-allyl)nickel was synthesized by a standard procedure [5].

The general procedure of the cycloaddition reaction involving norbornadiene was as follows. Appropriate amounts of the starting compounds and the solvent were placed in an evacuated 10-ml batch reactor. Dissolved oxygen was removed by three cycles of freezing to the liquid nitrogen temperature and thawing. Then a weighed sample of bis(η^3-allyl)nickel was introduced into the reactor in vacuo. The reactor was filled with high-purity argon containing $<10^{-4}$ vol % oxygen and was brought to a preset temperature. The reaction was carried out at 60°C for 8 h. After the reaction was complete, the reaction solution was purged with air until the catalytic system decomposed entirely. The decomposed catalyst was filtered from soluble products using a silica gel bed on a porous filter. The filtrate was concentrated on a rotary evaporator and analyzed.

The reaction products were analyzed by gas chromatography (Kristall 2000 M chromatograph, flame-ionization detector, Zebron ZB-5 and HP-50+ capillary columns) and gas chromatography coupled with mass spectrometry (Agilent Technologies 6890 GC/5973N MSD instrument, HP-1 capillary column). The spectral characteristics of the compounds were compared with earlier data [4].

RESULTS AND DISCUSSION

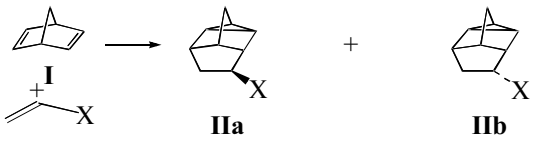
The analysis of the reaction solutions shows that the reactions of norbornadiene with a wide range of activated olefins are characterized by common regularities and afford *endo* and *exo* isomers (**IIa** and **IIb**,

Table 1. Reactions of norbornadiene with activated olefins

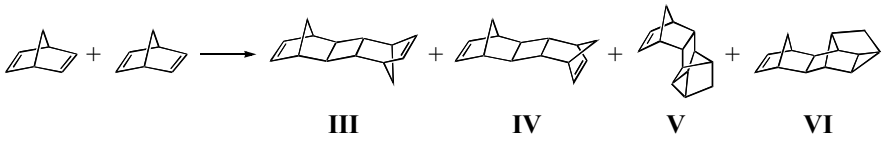
Olefin	Norbornadiene conversion, %	Yield, %		Ratio	
		norbornadiene jomodimers	[2+2+2]-cycloadducts of norbornadiene and olefin	**III** : **IV** : **V** : **VI**	**IIa/IIb**
Methyl acrylate	79.4	29	71	traces : 77 : 20 : 3	48 : 52
Ethyl acrylate	49.7	36	64	traces : 76 : 21 : 3	49 : 51
n-Butyl acrylate	95.2	40	60	traces : 78 : 20 : 2	51 : 49
tert-Butyl acrylate	57.2	52	48	traces : 77 : 20 : 3	56 : 44
2-Methyladamantyl acrylate	47.2	75	25	3 : 77 : 15 : 5	71 : 29
Acrylonitrile	31.6	12	88	2 : 73 : 22 : 3	58 : 42
2-Methylacrylonitrile	18.4	98	2	traces : 92 : 7 : 1	91 : 9
Acrolein	8.9	6	93	6 : 88 : 5 : traces	95 : 5
Methyl vinyl ketone	4.4	3	97	traces : 75 : 22 : 3	97 : 3
Furanone	22.2	5	95	traces : 76 : 22 : 2	95 : 5

Note: Reaction conditions: toluene solvent, $[norbornadiene]_0/[Ni(C_3H_5)_2]_0 = 20 : 1$, $[norbornadiene]_0 = 2.3$ mol/l, $[olefin]_0 = 1.2$ mol/l.

respectively) of the [2+2+2]-cycloadducts between an olefins and norbornadiene (reaction (1)) and various [2+2]- and [2+2+2]-homodimers of norbornadiene (**III**–**VI**) (reaction (2)).



(1)



(2)

(X – electron-withdrawing substituent)

Under these conditions, some olefins (vinyl acetate, methacrolein, maleic anhydride) undergo no cycloaddition to norbornadiene. In these cases, high-molecular-weight compounds are formed as a rule.

It follows from the data in Table 1 that the reactions involving all of the substrates proceed via various routes, including those leading to the formation of diverse regio- and stereoisomers.

In all cases, no formation of olefin homodimers was observed, although the possibility of this process in the presence of norbornadiene was established by carrying out the reaction involving methyl vinyl ketone on a heterogeneous nickel catalyst [6].

It is well known that norbornadiene is an efficient stabilizer of the zero-valence nickel catalysts even in the absence of ligands traditional in metal complex catalysis (phosphines, phosphites, amines, and others). To reveal the specific features of the behavior of the nickel systems, we attempted the homodimerization of olefins under similar conditions in the absence of norbornadiene. However, no products were observed. Moreover, in several cases, bis(η^3-allyl)nickel was unstable and decomposed into nickel metal and 1,5-hexadiene.

The homodimerization of norbornadiene under the same conditions, but without an olefin, affords *exo-trans-exo* (**III**), *exo-trans-endo* (**IV**) pentacyclic and *endo-endo* (**V**) and *exo-endo* (**VI**) hexacyclic

Table 2. Codimerization of norbornadiene with acrylic acid esters

Composition of the olefin mixture		Norbornadiene conversion, %	Yield, %			Ratio		
			norbornadiene dimers	[2+2+2]-cycloadducts of norbornadiene and acrylates		**III** : **IV** : **V** : **VI**	**IIa** : **IIb**	
$olefin_1$	$olefin_2$			$olefin_1$	$olefin_2$		$olefin_1$	$olefin_2$
Ethyl acrylate	*n*-Butyl acrylate	95	38.5	31.5	30.0	1 : 76 : 20 : 3	49 : 51	51 : 49
Methyl acrylate	*tert*-Butyl acrylate	96	38.5	36.0	25.5	traces : 77 : 20 : 3	48 : 52	56 : 44

Note: Reaction conditions: toluene solvent, $[norbornadiene]_0/[Ni(C_3H_5)_2]_0 = 20 : 1$, $[norbornadiene]_0 = 2.3$ mol/l, $[olefin_1]_0 = [olefin_2]_0 = 0.6$ mol/l.

dimers as the reaction products. In addition, the products of norbornadiene allylation form in stoichiometric amounts. In this case, the major reaction product is the *exo-trans-exo* dimer of norbornadiene (**III**) (up to 90%), and the hexacyclic isomers (**V** and **VI**) are formed in small amounts (<2% in aggregate) [7–9].

In the presence of activated olefins, the composition of the norbornadiene dimers becomes different: the *exo-trans-exo* homodimer of norbornadiene (**III**) is almost absent and the major product is the *exo-trans-endo* isomer (**IV**). In addition, the hexacyclic *endo-endo* (**V**) and *endo-exo* (**VI**) isomers are formed.

It is important that the ratio between the norbornadiene homodimers remains almost unchanged in the reactions involving all substrates except 2-methylacrylonitrile and acrolein. With these two substrates, the ratios of the norbornadiene dimers also differ insignificantly (Table 1).

The total yield of the [2+2+2]-cycloadducts increases and the yield of the norbornadiene homodimers decreases with the enhancement of the electron-acceptor strength of the substituent in the olefin (in the 2-methyladamantyl acrylate < *tert*-butyl acrylate < *n*-butyl acrylate < ethyl acrylate < methyl acrylate < acrylonitrile <acrolein < furanone < methyl vinyl ketone order). It is likely that 2-methylacrylonitrile falls out of this series.

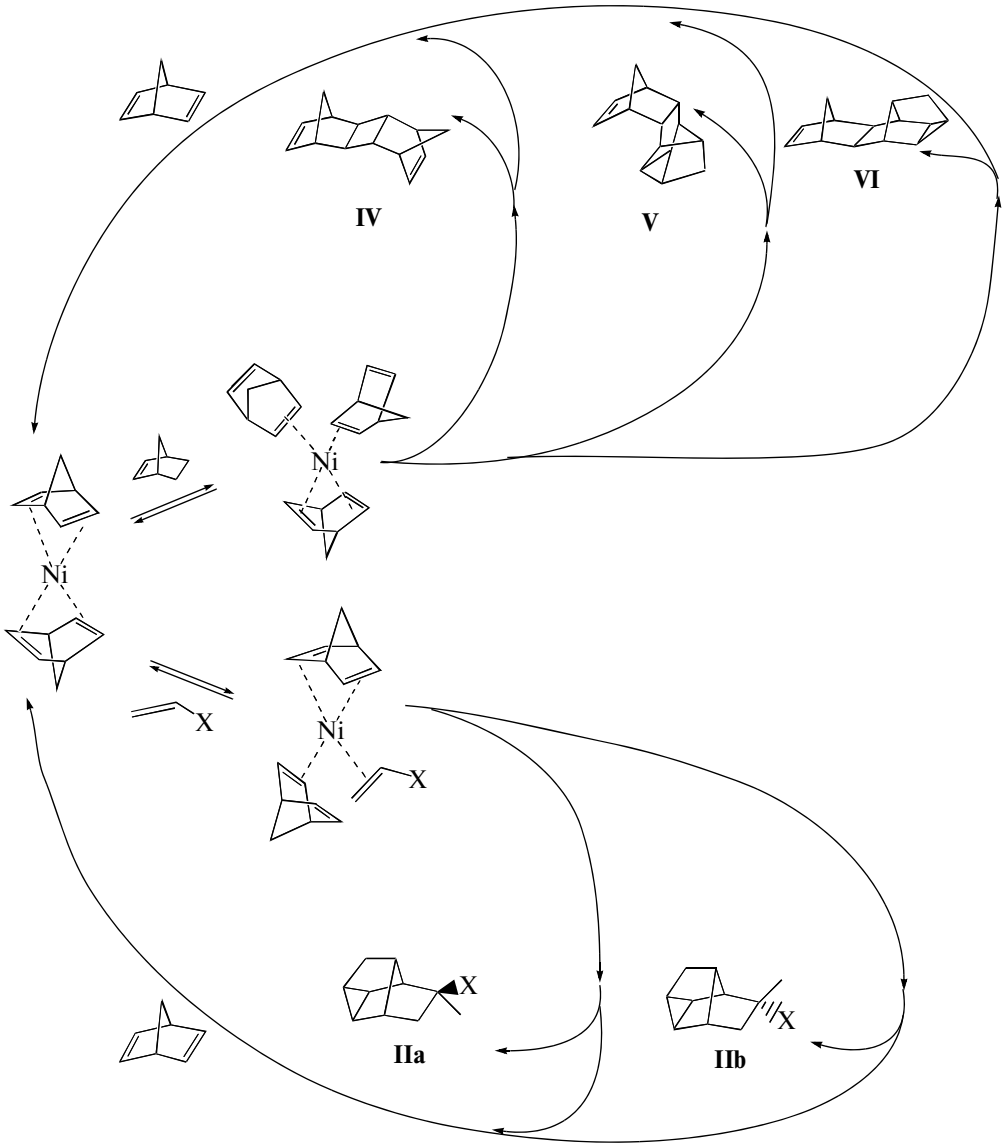
The reactions of norbornadiene with acrylic acid esters and acrylonitrile differ insignificantly in stereoselectivity. The reactions involving methyl and ethyl acrylates afford *exo* and *endo* cycloadducts with norbornadiene in equal amounts, and the *exo* isomers are formed in the other cases. The reaction of norbornadiene with the olefin having the most bulky substituent, namely, 2-methyladamantyl acrylate, affords 71% *exo* isomer. The other olefins containing a strong electron-withdrawing group give more *exo* isomers (up to 95–97%).

To elucidate the character of the coordination of the molecules in the key intermediates of the catalytic process, we carried out experiments in which norbornadiene competitively interacted simultaneously with two olefins (with ethyl and *n*-butyl acrylates or with methyl and *tert*-butyl acrylates) (Table 2). An analysis of the reaction products shows that the reaction affords norbornadiene homodimers and the [2+2+2]-cycloaddition products of each olefin. No products of olefin cross-coupling were found. The stereoselectivity of [2+2+2]-cycloadduct formation and the ratio of the norbornadiene homodimers remain the same as in individual reactions (Table 1). These results indicate that the key intermediate should contain only one olefin molecule, because the mutual influence of olefins is absent for the hypothetical intermediate and all processes proceed via independent parallel routes.

The constant ratio of the norbornadiene homodimers also indicates their formation from intermediates containing only norbornadiene molecules—another route (scheme).

The data obtained confirm the earlier suggested mechanism of [2+2+2]-cycloaddition of acrylates to norbornadiene [4]. The homodimers of norbornadiene and cycloadducts are formed via parallel routes from the common intermediate $Ni(norbornadiene)_2$ [7–9]. The intermediates $Ni(norbornadiene)_3$ and $Ni(norbornadiene)_2(olefin)$ are formed in the initial complex after the change in the coordination mode of one of the norbornadiene molecules. The subsequent successive formation of the metallocycles and reductive elimination yield the reaction products.

The ratio between the rates of the parallel reactions determines the selectivity of the process. Olefins with a stronger electron-withdrawing substituent are more easily coordinated, increasing the fraction of heteroligand complexes, and, accordingly, the yield of the [2+2+2]-cycloadducts increases. Evidently, the stereo-



(X, electron-withdrawing substituent)

Scheme. Mechanism of the interaction between norbornadiene and olefins in the presence of nickel (0) complexes.

selectivity of the process depends on the spatial structure of the intermediates.

The role of the stabilization of the key intermediates by the solvent molecules should be taken into account at each stage of the reaction. The influence of the medium was studied for the reaction of norbornadiene with *tert*-butyl acrylate (TBA). The reaction was carried out in toluene, diethyl ether, 1,2-dichloroethane, acetone, and methanol. A linear dependence of the logarithm of the ratio of the *exo* to *endo* cycloadducts of norbornadiene and TBA on the molar polarizability of the solvent was observed (figure).

The solvent effect on the cycloaddition reaction can be explained by the stabilization of the key intermediates. The polarity of the medium affects considerably the ratio of the heteroligand nickel complexes, which results in a change in the stereoselectivity of formation of the cycloadducts of norbornadiene and olefin [10]. The ratios between various norbornadiene homodimers remain almost unchanged. This influence of the solvent confirms that the *exo* and *endo* products form from the intermediates with different spatial orientations of the molecules and indirectly indicates that these intermediates contain a single olefin molecule.

A tendency to lower reactant conversions is observed as the polarity of the medium is increased (Table 3). This can be due to the stabilization of the

Table 3. Reaction of norbornadiene and TBA in various media

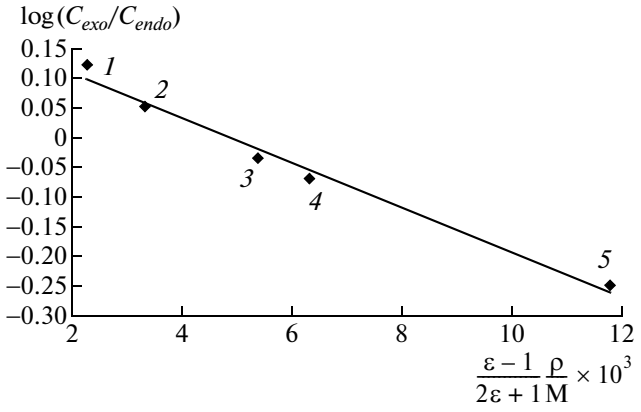
Solvent	Dielectric constant*	Norbornadiene conversion, %	Yield, %		Ratio	
			norbornadiene homodimers	[2+2+2]-cycloadducts of norbornadiene and TBA	**III** : **IV** : **V** : **VI**	**IIa** : **IIb**
Toluene	2.38	52.2	52	48	traces : 77 : 20 : 3	57/43
Diethyl ether	4.34	40.5	39	61	1 : 76 : 20 : 3	53/47
1,2-Dichloroethane	10.4	21.2	52	48	2 : 75 : 21 : 2	48/52
Acetone	20.7	19.5	61	39	traces : 80 : 15 : 5	46/54
Methanol	32.6	26.3	38	62	traces : 82 : 15 : 3	36/64

Note: Reaction conditions: toluene solvent, $[\text{norbornadiene}]_0/[Ni(C_3H_5)_2]_0 = 20 : 1$, $[\text{norbornadiene}]_0 = [\text{TBA}]_0 = 0.8$ mol/l.
* According to [11].

intermediates by solvent molecules. According to the mechanism proposed, the starting intermediate in both reaction routes is low-polarity Ni(norbornadiene)$_2$, which is more stable in nonpolar media.

It should be mentioned that the solvent effect is weaker than the influence of the nature of the olefin involved in the reaction.

Thus, the cycloadditions of the olefins to norbornadiene are of the same character. This study revealed specific features of the mechanism of the process and established the factors affecting the regio- and stereoselectivity.



Influence of the molar polarizability of the solvent on the ratio of stereoisomers (*exo*/*endo*) in the cycloaddition of TBA to norbornadiene: (*1*) toluene, (*2*) diethyl ether; (*3*) 1,2-dichloroethane, (*4*) acetone, and (*5*) methanol.

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