

CATALYTIC REACTION  
MECHANISMS

## Unconventional Allylation of Norbornadiene Catalyzed by Palladium Complexes

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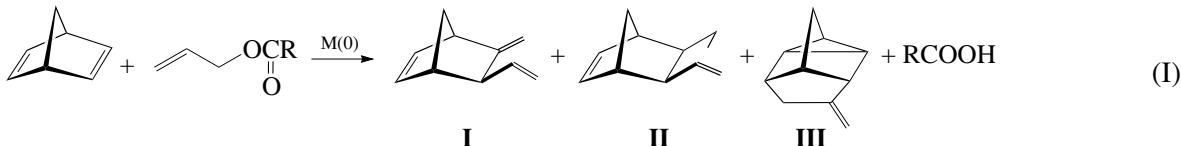
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**Abstract**—A new catalytic system based on palladium complex compounds for the unconventional allylation of norbornadiene with allylic esters of carboxylic acids is developed. The structure of reaction products is determined and the factors affecting their ratio are found. Comparative analysis of the palladium and nickel catalytic systems is performed.

### INTRODUCTION

The interaction of bicyclo[2.2.1]hepta-2,5-diene (norbornadiene, NBD) with allylic esters of carboxylic acids and allylic derivatives of transition metals fills a special place among cycloaddition reactions involving this diene. An uncommon character of this reaction is associated with the structure of the adducts. The [2+2]

or [2+4] cycloaddition of an allylic group to NBSD can result in the allyl C–C bond rupture either to form methylenevinyl derivative **I** or to become a fragment of the methylenecyclobutane (**II**) or methylenecyclohexane (**III**) ring (reaction (I)). In all cases, the allyl group loses a hydrogen atom, which is eliminated as part of the carboxylic acid formed.



The  $\text{Ni}[\text{P}(i\text{-C}_3\text{H}_7\text{O})_3]_4$  complex is used as a catalyst in this reaction, which was first described by Catellani and Chiusoli [1]. Other catalytic systems based on nickel complexes were used later for such processes involving the NBN and NBD derivatives [2–4].

On the basis of a mechanistic study of unconventional NBD allylation, a model for a unit catalytic cycle (see Scheme) was proposed [5].

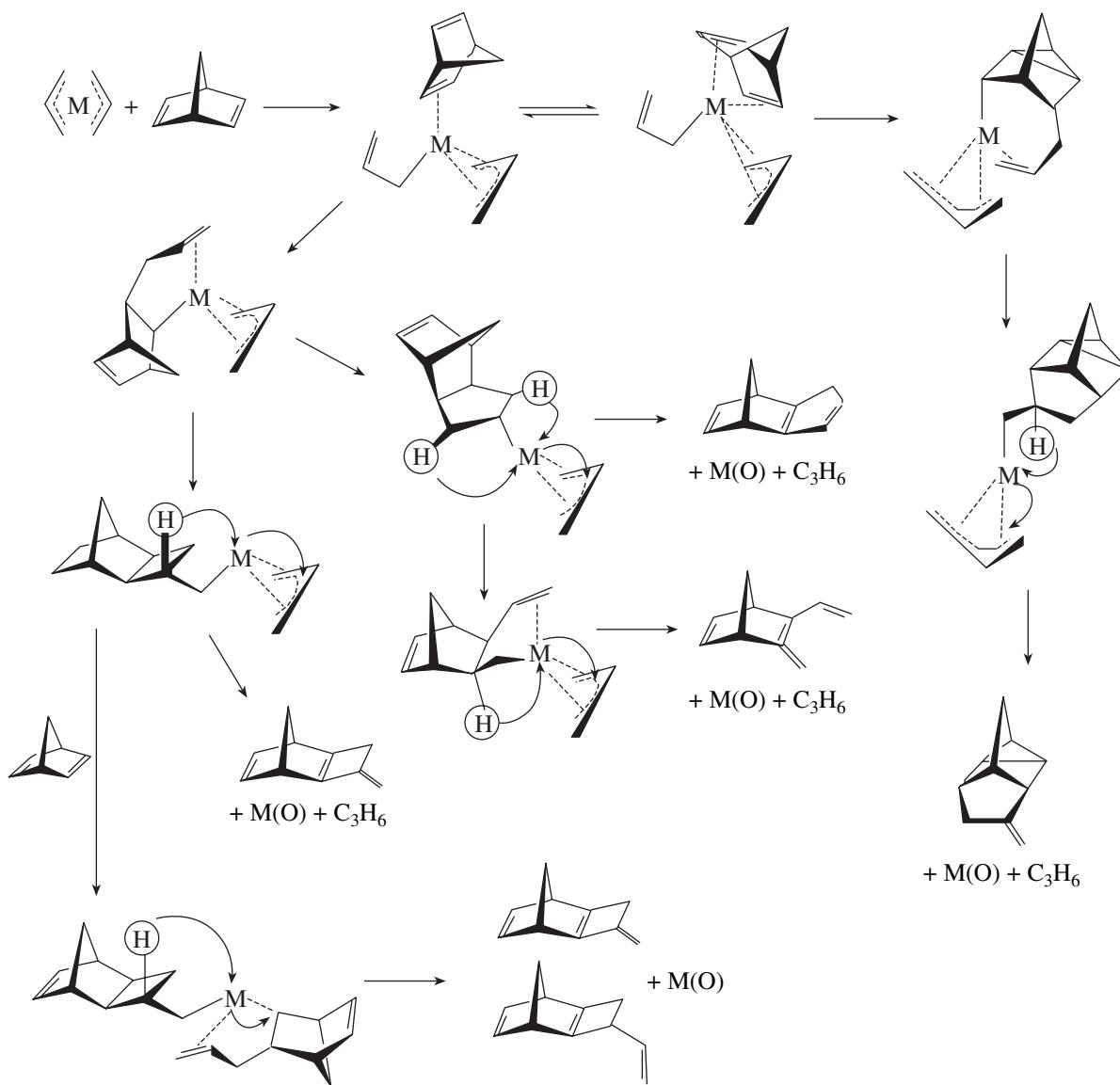
This model proved to be very useful for studying the main routes of the cycloaddition of the allyl fragment to NBD and looking into the reaction mechanism in detail. The redox disproportionation of the allyl ligands is central to the reaction, whose key stage is  $\beta$ -hydride transfer. This reaction is common to compounds with an unsubstituted intracyclic norbornene double bond and allyl fragments with various structures. It was shown that allylic complexes of other metals, such as iron, cobalt, rhodium, palladium, and platinum, can be used along with nickel compounds in this stoichiometric reaction. Based on the available data, it was suggested [5] that new catalytic systems involving a variety of transition metals can be developed. Recently a palladium catalyst for NBN allylation has been reported [6]. However, palladium catalytic systems were not used for the NBD allylation. To develop new catalysts for

unconventional NBD allylation, we studied the catalytic performance of palladium phosphine systems:  $\text{Pd}(\text{dba})_2 + 2\text{PPh}_3$ ,  $\text{Pd}(\text{OAc})_2 + 2\text{PPh}_3$ ,  $\text{PdCl}_2(\text{PPh}_3)_2$ ,  $[(\text{C}_3\text{H}_5)\text{Pd}]\text{NO}_3 + 2\text{PPh}_3$  as precursors of catalytically active species in reaction (I). Allyl acetate (AA) was used as an allylation agent.

### EXPERIMENTAL

Acetonitrile (high purity grade) was distilled over phosphorus pentoxide, methanol was purified by distillation, and ethanol was boiled and distilled over calcium oxide. Triphenylphosphine (Aldrich) was used without additional purification. Palladium acetate [7] and  $\text{Pd}(\text{dba})_2$  [8] (palladium *trans,trans*-dibenzylideneacetone) were prepared from palladium chloride according to the known procedures. A solution of the  $(\eta^3\text{-C}_3\text{H}_5)\text{PdNO}_3$  cationic complex was prepared by adding the equivalent amount of silver nitrate to a solution of allylpalladium chloride and separating the silver chloride precipitate by centrifugation.

The reaction was carried out in a nitrogen atmosphere in a temperature-controlled reactor equipped with a magnetic stirrer, a reflux condenser, and a sampler. The reactor, loaded with a weighed portion of a



**Scheme.** Mechanism of stoichiometric allylation of NBD by homoligand allyl complexes of transition metals (M = Fe, Co, Ni, Rh, Pd, and Pt).

catalyst, was evacuated and filled with nitrogen, and the deoxygenated solvent and reactants were introduced by a syringe through the sampler. Then a solution of the complex ( $\eta^3\text{-C}_3\text{H}_5\text{PdNO}_3$ ) was charged into the reactor.

The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectra were recorded on a Bruker DPX 300 spectrometer with an operating frequency of 121.458 MHz (80%  $\text{H}_3\text{PO}_4$  as an external standard). The formation of products was monitored by GLC (Chrom-5 chromatograph, Supelco capillary columns), and the identification of the products was performed by chromatography/mass spectrometry and  $^1\text{H}$  NMR (Bruker AC 300 P, operating frequency for protons is 300.13 MHz). The products were separated by distillation at 20 Torr.

5-Methylene-6-*exo*-vinylbicyclo[2.2.1]heptane-2 (**I**). B.p. (20 Torr) = 54°C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta$ : 6.19 (m,

1 H), 6.13 (m, 1 H), 5.75 (ddd, 1 H), 5.14 (m, 1 H), 5.03 (m, 2 H), 4.97 (m, 1 H), 3.22 (s, 1 H), 2.79 (s, 1 H), 2.62 (d, 1 H), 1.67 (m, 2 H). MS, m/e: M<sup>+</sup> 132 (1.7), 131 (4.0), 117 (33.0), 105 (2.5), 104 (6.7), 91 (33.3), 79 (6.7), 78 (16.7), 77 (9.2), 66 (100), 65 (25.0), 51 (17.0), and 39 (50.0).

3-Methylene-*exo*-tricyclo[4.2.1.0<sup>2,5</sup>]nonene-7 (**II**). B. p. (200 Torr) = 63°C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta$ : 6.01 (m, 2 H), 4.78 (s, 2 H), 2.76 (s, 2 H), 2.64 (m, 2 H), 2.05 (s, 1 H), 2.01 (s, 1 H), 1.76 (d, 1 H), 1.28 (d, 1 H). MS, m/e: M<sup>+</sup> 132 (8.3), 131 (18.3), 117 (100.0), 105 (4.2), 104 (15.0), 91 (50.0), 79 (4.6), 78 (15.0), 77 (8.3), 66 (58.3), 65 (13.3), 51 (5.0), and 39 (8.0).

8-Methylenetetracyclo[4.3.0.0<sup>2,4</sup>0<sup>3,7</sup>]nonane (**III**). B.p. (200 Torr) = 67.5°C.  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ),  $\delta$ : 4.67 (m, 1 H), 4.52 (m, 1 H), 2.36 (s, 1 H), 2.32 (m, 2 H),

Results for unconventional NBD allylation with allyl acetate (AA) catalyzed by palladium complexes

Run	Catalyst	Solvent	T, °C	Yield, %	Products ratio, %		
					<b>I</b>	<b>II</b>	<b>III</b>
1	Pd(OAc) <sub>2</sub> + 2PPh <sub>3</sub>	CH <sub>3</sub> CN	70	86	46	20	34
2	Pd(dba) <sub>2</sub> + 2PPh <sub>3</sub>	CH <sub>3</sub> CN	70	82	49	22	29
3	Pd(OAc) <sub>2</sub> + 2PPh <sub>3</sub>	CH <sub>3</sub> CN	80	98	36	22	42
4	Pd(OAc) <sub>2</sub> + 2PPh <sub>3</sub>	CH <sub>3</sub> CN	40	76	52	31	17
5	Pd(OAc) <sub>2</sub> + 2PPh <sub>3</sub>	CH <sub>3</sub> CN	25	62	58	36	6
6	Pd(OAc) <sub>2</sub> + 2PPh <sub>3</sub>	CH <sub>3</sub> ON	70	94	46	32	22
7	Pd(OAc) <sub>2</sub> + 2PPh <sub>3</sub>	C <sub>2</sub> H <sub>5</sub> OH	70	96	38	38	24
8*	Pd(OAc) <sub>2</sub> + 2PPh <sub>3</sub>	CH <sub>3</sub> CN	70	99	44	25	31
9**	Pd(OAc) <sub>2</sub> + 2PPh <sub>3</sub>	CH <sub>3</sub> CN	70	88	—	70	30
10	PdCl <sub>2</sub> (PPh <sub>3</sub> ) <sub>2</sub>	CH <sub>3</sub> CN	70	10	50	20	30
11	[(C <sub>3</sub> H <sub>5</sub> )Pd]NO <sub>3</sub> + 2PPh <sub>3</sub>	CH <sub>3</sub> CN	70	90	44	26	28

\* Allyl formate was used instead of allyl acetate.

\*\* Methyl acetate was used instead of allyl acetate.

2.00 (s, 1 H), 1.72 (s, 1 H), 1.62 (m, 1 H), 1.48 (d, 1 H), 1.35 (m, 1 H), 1.12 (m, 1 H), and 0.92 (d, 1 H). MS, m/e: M<sup>+</sup> 132 (44.4), 131 (22.2), 117 (100.0), 105 (4.4), 104 (15.5), 91 (66.7), 79 (6.7), 78 (13.3), 77 (8.9), 66 (6.7), 65 (8.9), and 51 (5.6).

## RESULTS AND DISCUSSION

The structure of the products of NBD allylation in the presence of palladium complexes is similar to those of the nickel-catalyzed reaction (I) studied by us earlier [3–5]. Nearly the same activity and close ratios of the reaction products were found for different palladium catalysts (Table), indicating the *in situ* generation of possibly the same catalytically active complexes.

This hypothesis is confirmed by the fact that the <sup>31</sup>P NMR signals of the reaction solutions, which are due to different palladium phosphine species, are characterized by the same chemical shifts (15.1, 18.3, 27.3, 37.6, and 37.7 ppm) irrespectively of the structure of the starting complex.

Palladium catalysts exhibit activity both in air and in an inert atmosphere, whereas nickel-based catalytic systems are only active in the absence of oxygen. Although the presence of oxygen does not lead to the destruction of the palladium catalytic system, the reaction rate is low under these conditions. Therefore, it is

preferable to carry out this reaction in an inert atmosphere.

The <sup>31</sup>P NMR findings allowed us to conclude that a side reaction, triphenylphosphine oxidation, is the reason for the catalyst deactivation. The signal from free PPh<sub>3</sub> ( $\delta$  = –4.5 ppm) rapidly disappears simultaneously with a fast increase in the intensity of the signal from Ph<sub>3</sub>P=O ( $\delta$  = 29.8 ppm).

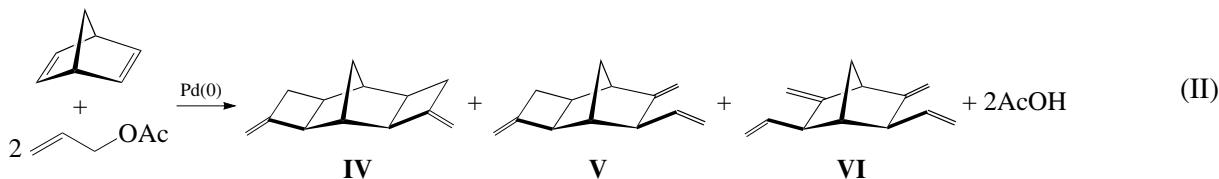
The ratio of the NBD allylation products depends on the temperature. Compounds **I** and **II**, in which the norbornadiene double bond is retained, are formed predominantly at 25–60°C. An increase in the relative amount of compound **III**, which is a [2+4]-cycloadduct, is observed at a higher temperature (80°C).

Alcohol media (see table, runs 6 and 7) favor a slight increase in the relative amount of compound **I**. When methyl acetate is used instead of AA, a compound similar to **II** is absent from the reaction products. This fact is in agreement with the suggested reaction scheme and confirms the key stage of the  $\beta$ -hydride transfer, giving evidence of the qualitative similarity of the mechanisms for the nickel and palladium complexes.

The catalyst containing chlorine ions is less active (see table, run 10), and this is in agreement with the data in [6]. The removal of chlorine ions from the coordination sphere of the allylic complexes (see run 11) leads to a substantial increase in the total yield of the reaction products.

When the molar ratio AA/NBD is higher than unity, the unsubstituted double bond of norbornene in com-

pounds **I** and **II** undergo a secondary allylation to form a great number of regio- and stereoisomers (**IV**–**VI**):



A comparison of the catalytic performance of the palladium phosphine and nickel phosphite complexes in reaction (I) leads us to the following conclusions. The nickel catalysts are more active, and their selectivity to each product can be improved up to 80–95% by optimizing the parameters of the catalytic process (temperature, phosphite/nickel ratio, and acid removal). The palladium catalysts exhibit lower specific activity, but they are more stable in the presence of oxygen and can be easily regenerated.

## CONCLUSION

Thus, the catalysts based on palladium complexes are capable of unconventional NBD allylation with allylic esters of carboxylic acids in high yields. The structures of reaction products are similar to those in the reaction catalyzed by nickel complexes but their ratio varies within narrower limits. A further study of the reaction mechanism on the basis of kinetic and spectral data as well as the development of catalysts immobilized in an ionic liquid is believed to essentially improve the parameters of the process and its synthetic potential.

## ACKNOWLEDGMENTS

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