

A possible way to control the course of hydride transfer in allylation of norbornadiene in the presence of palladium phosphine catalysts

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Features of allylation of norbornadiene (NBD) with allyl formate were investigated in the presence of Pd catalysts. In addition to the products of single or double allylation and hydroallylation of NBD, the products of secondary transformations, hydration and hydroformylation, have been found. An effect of triphenylphosphine on the reaction direction was studied.

Key words: norbornadiene, allyl formate, palladium acetate, allylation, hydroallylation, homogeneous metal complex catalysis.

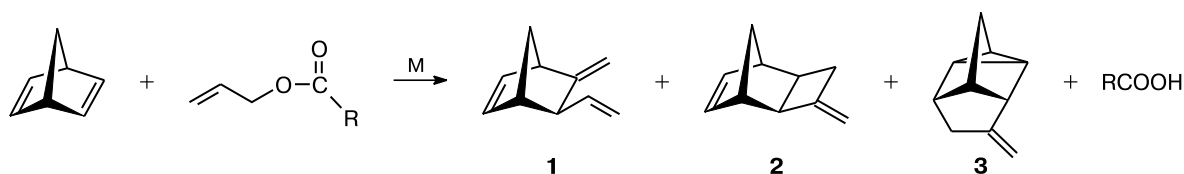
Reactions of allyl esters of carbonic acids (Scheme 1) take a special place in the catalytic chemistry of bicyclo[2.2.1]hepta-2,5-diene (norbornadiene, NBD).^{1–3}

Unique structures of the adducts account for the features of the reaction mechanism:^{4,5} addition of allyl fragment to NBD yields methylene vinyl derivative (**1**) or products in which this fragment inserts into methylenecyclobutane (**2**) or methylenecyclohexane (**3**) ring.

In all cases, allyl group loses hydrogen atom which is removed with carboxylic acid. In the case of excess of the allylating agent in the reaction mixture, compounds **1** and **2**, which retain a double bond inside the cycle, undergo secondary allylation resulting in the isomers **4–6** (Scheme 2).

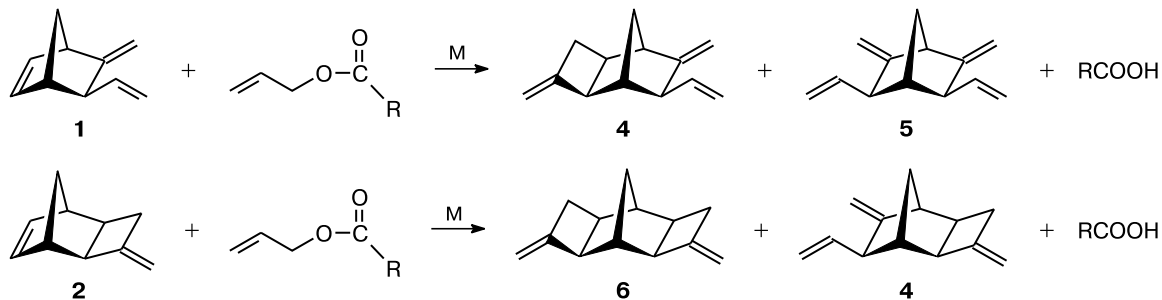
Using allyl formate (AF) in the reaction in the presence of Pd complexes gives rise to 5-allylbicyclo[2.2.1]-

Scheme 1



M = Ni, Pd
R = Me, Et, Bu^t, Ph, CCl₃, CF₃

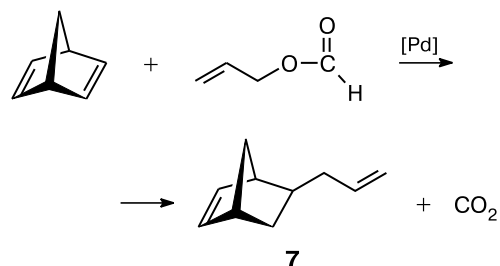
Scheme 2



M = Ni, Pd
R = Me, Et, Bu^t, Ph, CCl₃, CF₃

hept-2-ene (7) (Scheme 3). Moreover, in the absence of phosphine ligands, this product predominates.⁶

Scheme 3



A principal difference between the reactions shown in Schemes 1 and 3 is a course of hydride transfer. In the first case, allyl ligand is attached to NBD as C₃H₄ fragment, so it loses a hydrogen atom (oxidative allylation). In the second case, hydroallylation takes place, *i.e.* reductive allylation, in which NBD molecule formally attaches C₃H₆ fragment. Pd complexes catalyze both reactions. Thereby, a study of particularities in behavior of palladium phosphine catalytic systems is significant for clarifying the mechanism of hydride transfer and process selectivity. Relationships between quantitative characteristics of allylation of NBD with methyl formate and composition of the catalytic system have never been investigated earlier.

Results and Discussion

Palladium(II) acetate (Pd₃(OAc)₆) was applied as a precursor of the catalyst and triphenylphosphine (TPP) was added to it in various ratio. The reaction between equimolar amounts of NBD and AF give compounds, composition of which shows a wider variety of products than product distribution observed in similar reactions of other allyl esters (Scheme 4).

The main reaction products are compounds **1**, **2**, **3** and **7** with molecular weights of 132 and 134. The yields of these compounds depend on the reactant ratio, catalyst composition and reaction conditions (Table 1).

The products of the double allylation of NBD (compounds **4–6**) with molecular weights of 172 are also observed. Other compounds are formed when only AF is used and have molecular weights of 174 and 176 and result from hydroallylation of compounds **1**, **2**, **7**. Those are mainly regio- and stereoisomers **9–11**. Compounds **12–14** with a molecular weight of 134 are produced *via* hydrogenation of compounds **2** and **3**. In this case, the most active double bond inside the cycle participates in the reaction. The products of hydrogen attachment to methylene groups have been not found under the given conditions. In addition to the substances indicated above the products of hydroformylation of NBD, compounds **15** and **16**, were detected. The total yield of the products of the secondary reactions does not exceed 30%.

Scheme 4

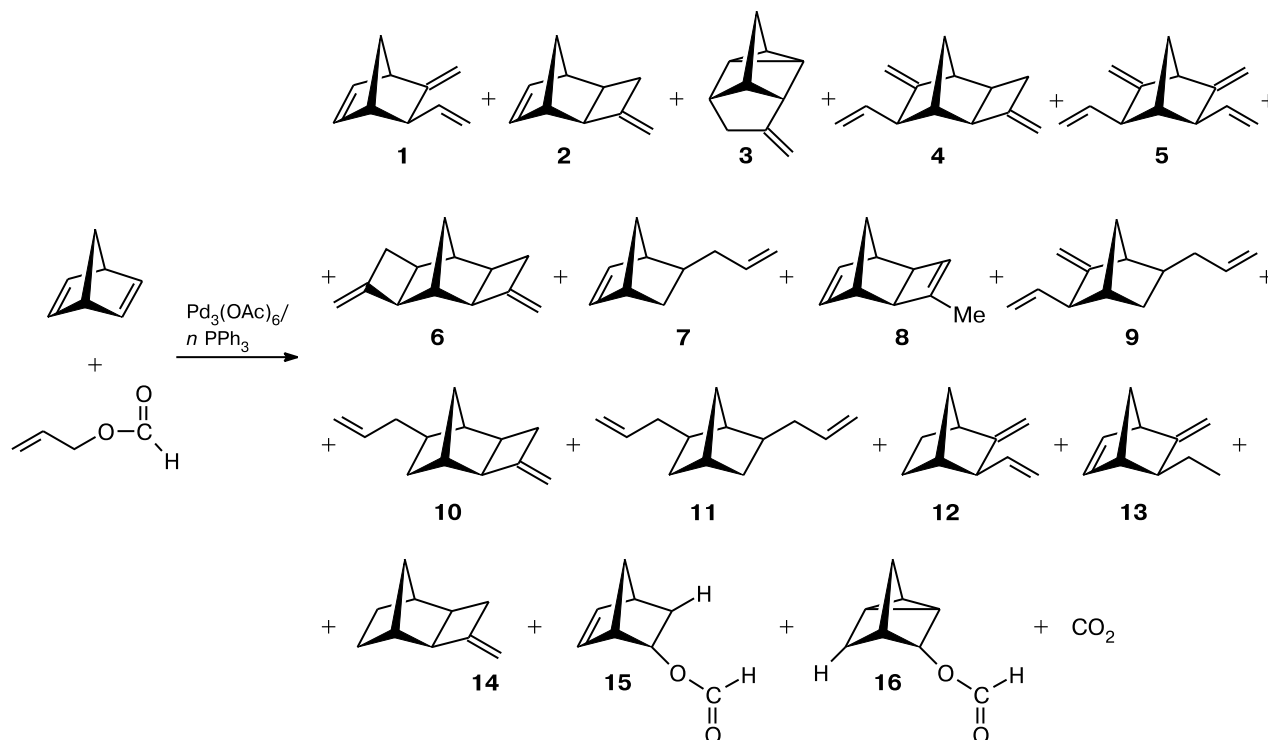


Table 1. The results of the reaction between NBD and AF at various mole ratio of TPP : Pd in argon atmosphere*

TPP : Pd	Conversion (%)		Selectivity (%)					Products of secondary reaction	Contribution of the products of single allylation (%)	
	NBD	AF	1	2	3	7	8		C ₁₀ H ₁₂	C ₁₀ H ₁₄
No phosphine	95	97	—	—	8	91	1	—	9	91
1 : 3	77	98	14	16	17	30	1	22	61	39
1.5 : 3	78	99	19	15	18	27	2	19	67	33
2 : 3	80	99	23	14	20	23	3	17	72	28
3 : 3	79	99	24	14	20	19	2	21	75	25
4 : 3	78	98	25	14	20	16	2	23	79	21
5 : 3	78	99	26	14	22	11	3	24	86	14
6 : 3	77	99	22	12	22	9	5	30	87	13

* $C_{\text{NBD}}^0 = C_{\text{AF}}^0 = 0.5 \text{ mol L}^{-1}$, Pd : NBD = 1 : 100, $T = 25 \text{ }^\circ\text{C}$, $\tau = 48 \text{ h}$, acetonitrile is applied as a solvent.

Thus, we selected the basic conditions at which reaction between NBD and AF can follow two mechanisms. First one results in the products of oxidative allylation (C₁₀H₁₂), whereas the second one leads to the products of reductive allylation (C₁₀H₁₄). The mechanism depends on the molar ratio of TPP : Pd. At an equimolar ratio of NBD to AF and high conversions of the reactants, secondary reactions involving the products of single allylation of NBD occur. Thereby, it is interesting to study the effect of TPP introduced into catalytic system on the course of the process when it is kinetically controlled. The highest selectivity to the products of single allylation of NBD is achieved at the reactant conversion of 30% ($\tau = 2.5 \text{ h}$) (Table 2). Further growth in conversion significantly increases the amount of products of double allylation of NBD from the compounds which retained the intracycle double bond.

In the absence of TPP in the catalytic system, a high selectivity (91%) to compound **7** is achieved. Elevating the TPP : Pd ratio considerably enhances the contribution

of the products of oxidative allylation of NBD (compounds **1**–**3**). The total yield of compound **7** is remarkably improved. Nevertheless, increase in conversion of NBD and AF (see Table 1) increases the yield of the products of secondary processes involving compounds **1**, **2** and **7** (double allylation, hydrogenation and hydroformylation). Since compound **3** has no intracycle double bond, it is not active in following reactions.

Maximum selectivity to the products of oxidative allylation is attained with a double excess of the TPP in TPP : Pd ratio. Further rise of the amount of phosphine decreases the conversion of the reactants up to 10–15%. This experimental fact may be accounted for by the formation of Pd(PPh₃)₄ complex which is inactive under the given conditions.

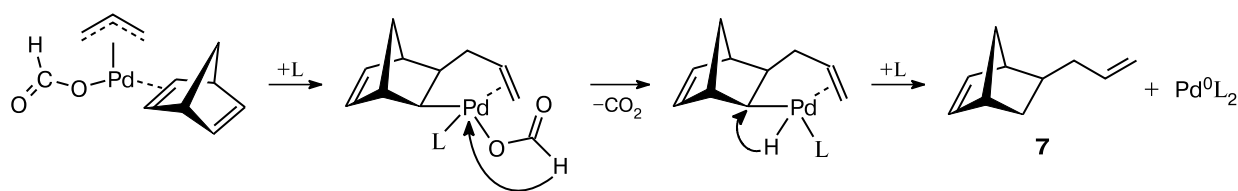
It has been shown earlier that the mechanism of interaction between NBD and allyl esters of carbonic acids is complicated. The first step of the process is oxidative addition of the ester to palladium to form π -allyl Pd^{II} complex. Then allyl fragment undergoes π – σ -isomerization,

Table 2. The results of the reaction between NBD and AF at various mole ratio of TPP : Pd in argon atmosphere*

TPP : Pd	Conversion (%)		Selectivity (%)					Products of secondary reaction	Contribution of the products of single allylation (%)	
	NBD	AF	1	2	3	7	8		C ₁₀ H ₁₂	C ₁₀ H ₁₄
No phosphine	28	28	—	—	8	91	1	—	9	91
1 : 3	29	30	18	21	23	36	1	1	64	36
1.5 : 3	28	29	20	25	24	29	1	1	71	29
2 : 3	29	30	24	27	23	24	1	1	76	24
3 : 3	29	30	27	25	23	22	2	1	78	22
4 : 3	28	30	30	25	24	18	1	2	82	18
5 : 3	28	30	32	24	23	17	2	2	83	17
6 : 3	29	31	33	26	23	13	3	2	87	13

* $C_{\text{NBD}}^0 = C_{\text{AF}}^0 = 0.5 \text{ mol L}^{-1}$, Pd : NBD = 1 : 100, $T = 25 \text{ }^\circ\text{C}$, $\tau = 2.5 \text{ h}$, acetonitrile is applied as a solvent.

Scheme 5



L = NBD, MeCN

and coordination of NBD molecule with metal atom takes place. Afterwards, the way of the process may differ depending on structure of allyl ester and presence of phosphine ligands.^{5–9}

As it was described above, the reaction of AF with NBD over palladium catalyst without TPP admixture gives the product of hydroallylation on NBD (compound **7**) with high selectivity. The mechanism of this process might be related to the hydrogen transfer from the formyl fragment and generation of the hydride complex of palladium, ensuing conversion of which brings about the formation of compound **7** and dioxide carbon as well as regeneration of the catalyst (Scheme 5).

These reactions are observed when other allyl esters are used. Therefore, catalytic hydroallylation of NBD with allyl formate is unique and application of phosphine ligands may radically change the course of hydride transfer in the process of interest.

Moreover, molar ratio of TPP : Pd seems to exert a relevant effect on the ratio of compounds **1–3** in the reaction products. The resulting product composition in oxid-

ative allylation of NBD is likely to be directly associated with an effect of various palladium complexes which are different in the number of phosphine ligands in the coordinating sphere of palladium (Scheme 6).

The results on regularities in generation of the product of oxidative allylation of NBD (compounds **1–3**) are similar to the experimental results on the process performance in the presence of nickel phosphine catalysts.¹⁰ The present experiments reveal quantitative effect of the ligands inside the coordination sphere of the metal on the course of β -hydride transfer.

Experimental

NBD and allyl formate were used with a purity grade of $\geq 99.5\%$. $\text{Pd}_3(\text{OAc})_6$ produced by the known procedures^{11,12} was applied as a catalyst precursor. Triphenylphosphine (Aldrich) was recrystallized from a methanol–chloroform mixture (4 : 1, vol.; 15 mL g⁻¹) in nitrogen atmosphere. Acetonitrile, used as a solvent, was distilled over P_2O_5 before the experiment.

The reactions were performed in a thermostated evacuating reactor equipped with a magnetic stirrer and a sampling device. After all the components were mixed, oxygen was removed from the reactor and the reaction was carried out in argon atmosphere at 25 °C.

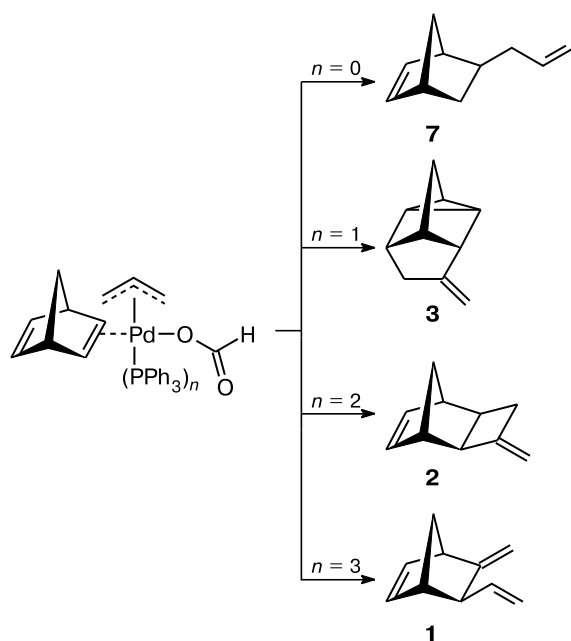
Product composition was controlled by gas chromatography using a Kristall PM-2000 instrument equipped with an Agilent J&W HP-50+ capillary column (Agilent Technologies) and a flame-ionization detector. GC/MS analysis and ¹H and ¹³C NMR spectroscopy served to identify the resulting compounds. GC/MS analysis was performed on a 689 ON gas chromatograph (Agilent Technologies) equipped with a mass-selective detector and a CPS CP-Syl 5 capillary column. NMR spectra were recorded on a Bruker DPX 300 instrument (¹H, 300.13 MHz; ¹³C, 75.033 MHz). The data of the earlier published works^{1–6,13} were applied at spectra interpretation.

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Scheme 6



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