Catalytic hydroallylation of norbornadiene with allyl formate

I. P. Stolyarov,[a]★ A. E. Gekhman,[a] I. I. Moiseev,[a] A. Yu. Kolesnikov,[b] E. M. Evstigneeva,[b] and V. R. Flid[b]

[a]*N. S. Kurnakov Institute of General and Inorganic Chemistry, Russian Academy of Sciences, 31 Leninsky prosp., 119991 Moscow, Russian Federation. Fax: +7 (495) 954 1279. E-mail: stolarov-igic.ras@rambler.ru*

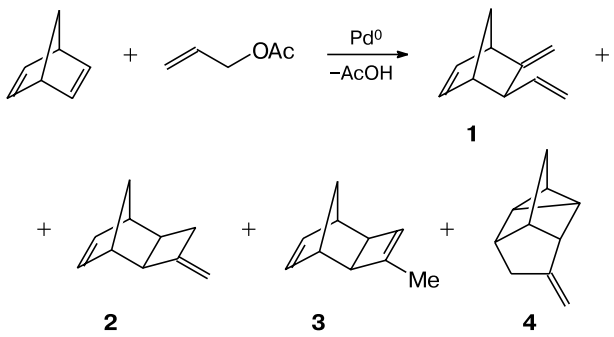
[b]*M. V. Lomonosov Moscow State Academy of Fine Chemical Technology, 86 prosp. Vernadskogo, 117571 Moscow, Russian Federation. Fax: +7 (495) 952 1274. E-mail: vflid@rol.ru*

Norbornadiene (NBD) reacts with allyl esters All—OC(O)R (R = Me, Bu^t, Ph, CCl_3, CF_3) in acetonitrile solutions of palladium(0) complexes to give a mixture of four isomeric nontraditional allylation products and the corresponding carboxylic acids. Under similar conditions, the reaction of NBD with allyl formate in solutions of Pd^0 and Pd^{II} complexes occurs selectively, resulting in the product of addition of the allyl fragment and the H atom to an NBD double bond, 5-allylbicyclo[2.2.1]hept-2-ene, and CO_2. The hydroallylation of NBD is accompanied by catalytic addition of formic and acetic acids to one double bond of the diene to give bicyclo[2.2.1]hept-2-en-5-ol and nortricyclan-3-ol acetates and formates. Unlike most known palladium-based catalyst systems, these complexes exhibit catalytic activity also in the absence of phosphines.

Key words: norbornadiene, allylation, catalytic hydroallylation, palladium(0) complexes, palladium(II) complexes, allyl esters.

The catalytic reaction of norbornene[1] and norbornadiene[2] (NBD) with allyl acetate readily proceeds in the presence of palladium complexes and triphenylphosphine (L) to give new C—C bonds in various isomeric products of nontraditional allylation and acetic acid (Scheme 1).

Scheme 1



1 **2** **3** **4**

In the presence of triphenylphosphine, 5-methylidene-6-vinylbicyclo[2.2.1]hept-2-ene (**1**), 3-methylidenetricyclo[4.2.1.0^{2,5}]non-7-ene (**2**), and 8-methylidenetetracyclo[4.3.0.0^{2,4}.0^{3,7}]nonane (**4**) are usually formed in commensurable amounts, while only traces of 3-methyltricyclo[4.2.1.0^{2,5}]nona-3,7-diene (**3**) are formed, and the possibilities of controlling the selectivity by varying the reaction conditions are limited. Irrespective of the type of the precursor of the homogeneous catalyst ($Pd_3(OAc)_6$, $Pd(dba)_2$ (dba is *trans*,*trans*-dibenzylideneacetone) or $[AllPd]NO_3$) and the solvent, the selectivity with respect to each of isomers **1**—**4** does not exceed 20—40%.[2] Recently, it was found[3] that the reaction of NBD with allyl acetate in an ionic liquid in the presence of nanoclusters Pd55/147 and L is highly selective giving rise to only one allylation product, methylidenevinyl derivative of norbornene **1**, although this reaction is markedly slower than those in solutions of Pd^0 and Pd^{II} compounds in polar organic solvents.

In the search for new approaches to the control of the selectivity of the process shown in Scheme 1, we studied the reactions of NBD with various allyl esters All—OC(O)R (R = H, Me, Bu^t, CCl_3, CF_3, Ph) in acetonitrile in the presence of palladium complexes containing no phosphine ligands. Both the homonuclear palladium complexes ($Pd(dba)_2$, $Pd(Bu^tdba)_2$ (Bu^tdba is $(4\text{-}Bu^tC_6H_4CH{=}CH)_2CO$), $phenPd(OAc)_2$ (phen is 1,10-phenanthroline), $Pd_3(OAc)_6$, $[AllPdCl]_2$, $[AllPdOAc]_2$) and recently synthesized[4—6] heteronuclear carboxylate complexes $[PdM(\mu\text{-}RCOO)_mL_n]_x$ (M = Zn, Co, Ni, Mn, lanthanides; R = Me, Bu^t; $m = 4, 5$; $x = 1, 2$) and $Pd_2Cu(\mu\text{-}OAc)_6$ were used as catalyst precursors. Preliminary experiments have shown that these complexes are rather stable in acetonitrile solutions at 20—60 °C.

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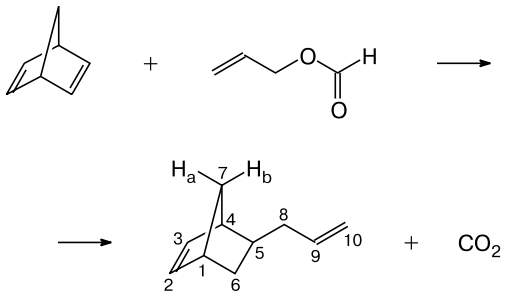
Results and Discussion

In solutions of Pd^{II} complexes without triphenylphosphine, the reaction of NBD with esters All—OC(O)R (R = Me, Bu^t, Ph, CCl_3, CF_3) at 20—60 °C is very slow and nonselective. In solutions of Pd^0 complexes without phosphine, the allylation occurs faster, but gives all of the four isomeric products (Table 1).

The most essential feature distinguishing these catalysts from the catalyst systems based on palladium complexes with triphenylphosphine is the presence of noticeable amounts of isomer **3** among the products.

Under similar conditions, NBD reacts with allyl formate through an unusual route. The major reaction is the addition of the allyl fragment and the H atom to a double bond of NBD to give 5-allylbicyclo[2.2.1]hept-2-ene (**5**) (Scheme 2).

Scheme 2



5

Previously,[7] allylnorbornene was obtained in the stoichiometric reaction of NBD with bis(allyl)nickel. Under our experimental conditions with palladium complexes, the reaction (see Scheme 2) is catalytic and proceeds much faster than the reaction shown in Scheme 1 involving other allyl esters. In addition, the use of homo- and heteronuclear Pd^{II} complexes as catalyst precursors also results in compound **5** as the major product, though after a long induction period. Presumably, during this period, Pd^{II} is reduced to Pd^0 under the action of components of the reaction mixture. After additional introduction of the stoichiometric (with respect to palladium) amount of formic acid to the reaction mixture, the induction period disappears due to acceleration of Pd^{II} reduction to give catalytically active Pd^0 compounds (Scheme 3).

Scheme 3

$$Pd^{II} + HCOOH = Pd^0 + 2\,H^+ + CO_2$$

The results of chromatographic analysis of reaction mixtures after the experiments are summarized in Table 2.

After Pd^{II} reduction, stabilization of Pd^0 in the reaction mixture is apparently provided due to coordination to NBD.

The highest selectivity to product **5** equal to 93—95% is achieved by using zerovalent palladium complexes $Pd(dba)_2$ and $Pd(Bu^tdba)_2$ as the catalyst precursor. The allylation by-products **1**—**4** are formed in all cases, their

Table 1. Composition of the products of allylation of NBD with allyl esters All—OC(O)R in a solution of $Pd(dba)_2$*

R in AllOC(O)R	Distribution of allylation products (%)			
	1	**2**	**3**	**4**
Me	30	23	32	14
Bu^t	26	35	21	18
Ph	20	28	33	19
CCl_3	8	79	5	8
CF_3	28	19	45	8

* The reaction time was 24 h at 20 °C.

Table 2. Composition of NBD allylation products in the reaction with allyl formate[a]

Catalyst or its precursor	Selectivity with respect to allylation products **1**—**5** (%)				
	1	**2**	**3**	**4**	**5**
$Pd(dba)_2$[b]	1	4	2	—	93
$Pd(Bu^tdba)_2$[b]	1	3	1	—	95
$Pd(MeCN)_2(OAc)_2$	5	10	4	3	78
$(AllPdCl)_2$[c]	1	16	—	4	79
$Pd(acac)_2$	—	22	15	—	63
$Pd_3(OAc)_6$	1	12.5	6.5	—	80
$Pd_3(OCOEt)_6$	1	11	5	1	82
$Pd_3(Bu^tCOO)_6$	—	15	4	5	76
$Pd_2Zn_2(OAc)_8$	1	17	14	—	68
$Pd_2Cu(OAc)_6$	7	11	5	5	72
$Pd_2Co_2(OAc)_8$	3	15	5	1	76
$Pd_2Ni_2(OAc)_8$	1	13	7	—	79
$Pd_2Mn_2(OAc)_8$	12	9	—	—	79
$Pd_2Ce_2(OAc)_{12}$	—	16.5	9.5	—	74
$Pd_2Eu_2(OAc)_{10}$	—	12	9	—	79
$Pd_2Er_2(OAc)_{10}$	—	18	11	—	71
$Pd_2Gd_2(OAc)_{10}$	—	19	12	—	69
$Pd_2Nd_2(OAc)_{10}$	7	16	5	5	67
$Pd_2Cu(Bu^tCOO)_6$	15	12	5	—	68
$PdNi(Bu^tCOO)_4$	12	25	8	5	50
$PdMn(Bu^tCOO)_4$	5	15	8	3	69

[a] Reaction conditions: 0.1 mg-at. of complex Pd (relative to palladium metal), 1 mmol of NBD, 1 mmol of allyl formate, 0.1 mmol of HCO_2H, 1 mL of MeCN, 20 °C, duration 24—72 h.
[b] Without the addition of HCO_2H.
[c] In the presence of a stoichiometric amount of HCO_2K with respect to palladium.

Table 3. Dependence of selectivity of NBD hydroallylation with respect to product **5** (*S*) on the reaction duration (*t*)*

t/min	*S* (%)	*t*/min	*S* (%)
15	65	90	83
30	75	120	83
45	83	150	83
75	83		

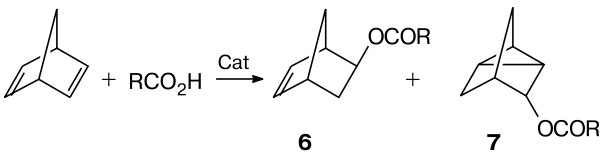
* $[Pd_3(OAc)_6]$ = 0.033 mol L^{-1}, [NBD] = [AllOC(O)H] = 1 mol L^{-1}, $[HCO_2H]$ = 0.1 mol L^{-1}, MeCN, 40 °C.

amount being much higher when Pd^{II} compounds are used as catalyst precursors. In addition, changes in the composition of the allylation products in solutions of various heteronuclear complexes are insignificant and do not suggest a substantial effect of carboxylates of other metals on the allylation.

When Pd^{II} complexes are used as catalyst precursors and a stoichiometric amount of reducing HCOOH is added to the reaction mixture, the selectivity to the hydroallylation product **5** increases (Table 3) and, hence, the selectivity to nontraditional allylation products **1**—**4** decreases following the reduction of palladium.

The hydroallylation and allylation of NBD is accompanied by parallel catalytic hydrocarboxylation to give bicyclo[2.2.1]hept-2-en-5-ol and nortricyclan-3-ol acetates and formates (Scheme 4). When heteronuclear complexes are used as catalyst precursors, this process competes significantly with hydroallylation.

Scheme 4



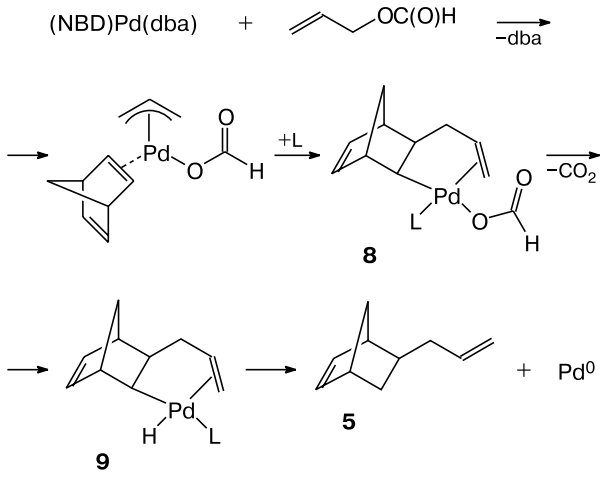
R = H, Me; Cat is catalyst

The total amount of esters **6** and **7** approximately corresponds to the number of moles of acetic acid formed from the OAc^- ligands upon the reduction of heteronuclear Pd^{II} complexes to Pd^0. In a typical experiment, the yield of compounds **6** and **7** does not exceed 4—5 moles per g-atom of palladium.

A possible mechanism of catalytic hydroallylation of NBD is presented in Scheme 5. The first step, *viz.*, reversible replacement of one dba ligand in the Pd^0 coordination sphere by NBD, is omitted for clarity.

The proposed mechanism includes the oxidative addition of allyl formate to Pd^0 to give Pd^{II} allyl complex, followed by the insertion of the NBD double bond into the palladium—allyl bond to give π,σ-complex **8**. The

Scheme 5



L is dba, MeCN, NBD

latter reaction was reported;[8,9] some of complexes of this type are stable; their structures were studied by NMR and X-ray diffraction. Unlike other carboxylates, the formate ligand coordinated to palladium in complex **8** readily eliminates CO_2 to be converted into hydride. The attack of the hydride ligand on the Pd—C σ-bond in molecule **9** results in diene **5** in the Pd^0 coordination sphere. The possibility of a synchronous reaction mechanism involving a cyclic transition state[10] in which the hydride formed simultaneously with the formate decarboxylation attacks the allyl ligand is completely ruled out, although in the absence of NBD, allyl formate slowly decomposes to propylene and CO_2. At the following reaction steps, the initial form of the catalytically active complex is regenerated under the action of dba and NBD and product **5** passes to the solution.

The reaction mixture was also found to contain traces of NBD hydrogenation products, namely, norbornene and norbornane. The absence of propylene among the products is consistent with the proposed reaction mechanism.

Previously,[11] we demonstrated that hydrogenation of organic compounds of various classes proceeds smoothly under the action of formic acid in the presence of giant palladium clusters but does not occur in the presence of palladium metal. Apparently, these hydrogenation processes also involve the coordinated formate. When formate is replaced by any other carboxylate incapable of elimination of CO_2, these reactions do not proceed. It is noteworthy that the route of reaction of NBD with allyl formate markedly changes in the presence of other carboxylate ions: for example, upon addition of sodium acetate to the reaction medium, nontraditional allylation according to Scheme 1 occurs in parallel with hydroallylation of the diene at a comparable rate. This change in the reaction route is due to the replacement of the

formate ligand in the intermediate complex by the acetate ligand. Similar reasons can be used to interpret the parallel allylation and hydroallylation of NBD in solutions of various Pd^{II} complexes (see Table 2).

This hydroallylation reaction is a rather rare case of catalysis by Pd^0 complexes, which does not require the presence of phosphine ligands.

Experimental

Acetonitrile (for liquid chromatography, Merck) was used as received. Formic acid (99%, OJSC ChromResurs) was dehydrated by freezing. Palladium acetate (pure grade, TU 6-09-05-684-86) was purified from nitrogen-containing impurities by long-term refluxing in glacial acetic acid followed by recrystallization from benzene. Palladium propionate and pivalate were obtained from the acetate by exchange with the corresponding acids in benzene by a known procedure.[12] Palladium acetylacetonate[13] and binuclear allylpalladium chloride[14] were prepared by reported procedures. The complex $Pd(MeCN)_2(OAc)_2$ was synthesized similarly to $Pd(MeCN)_2X_2$ by a published procedure.[15] Heteronuclear complexes were synthesized by known procedures,[4–6] the pivalate derivatives were prepared from acetates by exchange with pivalic acid, as described previously,[12] followed by recrystallization from pentane. Palladium(0) π-complexes were obtained from palladium chloride by a known procedure.[16] Stabilized 2,5-norbornadiene of 96% purity (Acros Organics) was distilled under argon prior to use. Allyl acetate of 99% purity produced by the same company and allyl trifluoroacetate of 98% purity (Fluorochem) were used as received. Other esters were prepared by esterification of allyl alcohol with appropriate carboxylic acids in the presence of anhydrous $CaCl_2$ followed by fractional distillation under argon; according to chromatographic analysis, the product purity was 97—98%.

Reaction of NBD with allyl esters. The reactions were carried out in a thermostated glass reactor equipped with a stirrer, a reflux condenser, and a sampling device. The reactor was charged with acetonitrile (1 mL), NBD and allyl esters (1 mmol each), and palladium compounds (0.1 mg-at. relative to the metal). The reaction mixture was stirred under argon or in air at 20—60 °C, samples for chromatographic analysis being taken at intervals by a microsyringe. The order of elution of the NBD allylation products from the chromatographic column was as follows: **1**, **5**, **3**, **4**, and **2**.

5-Allylbicyclo[2.2.1]hept-2-ene (5). $Pd(dba)_2$ (0.574 g, 1 mmol), NBD (2.16 mL, 20 mmol), allyl formate (1.82 mL, 20 mmol), and acetonitrile (10 mL) were placed into a 50-mL conical flask equipped with a hydraulic seal with silicone oil. All reactants were freshly distilled, the content of the base substance was ≥96%. The reaction mixture was stirred for 24 h at 20 °C. Carbon dioxide was evolved and bubbled away through the hydraulic seal. After 24 h, the reactant conversion exceeded 70% at a selectivity of up to 95% with respect to product **5**. To separate the volatile products from the catalyst and esters **6** and **7**, the reaction mixture was poured into a 50—100-mL round-bottom flask, and the content was recondensed *in vacuo,* the product being collected in a liquid-nitrogen-cooled trap. The round-bottom flask containing the catalyst and the solution of products was carefully (to avoid overrunning of the solution into the trap) heated for 30 min on a water bath at 30—40 °C with evacuation. The trap containing frozen acetonitrile and reaction products was left for some time at 20 °C for evaporation of liquid nitrogen and for condensate unfreezing. Distilled water (30 mL) was added to the unfrozen content of the trap and the separated organic phase was extracted with pentane (5×5 mL). The extract was dried with anhydrous sodium sulfate and pentane, norbornene, and allyl formate were evaporated *in vacuo* on a rotary evaporator at 20 °C. The resulting colorless liquid with a pungent odor (~1 mL) contained 93—95% of 5-allylbicyclo[2.2.1]hept-2-ene (**5**) and traces of usual allylation products **1**—**4** and esters **6** and **7**. The product was kept in the dark under argon.

Chromatographic analysis was carried out on a GC-17A chromatograph (Shimadzu, Japan) with a flame ionization detector and a 25 m × 0.2 mm capillary column with grafted XE-60 phase. The organic reaction products were identified by GC/MS analysis (Agilent instrument, design 5973) and ^1H and ^{13}C NMR spectroscopy (Bruker Advanced 600 spectrometer). Mass spectrum of compound **5**, m/z (I_{rel} (%)): 134 $[M]^+$ (5), 119 (3), 105 (2), 93 (4), 92 (5), 91 (12), 79 (6), 77 (10), 67 (10), 66 (100), 65 (8). The NMR signals of compound **5** were assigned using homo- and heteronuclear ($^1H—^1H$ and $^1H—^{13}C$, respectively) correlation spectroscopy and DEPT 90 and DEPT 135 experiments. ^1H NMR (600.13 MHz, $CDCl_3$), δ: 6.08 (dd, 1 H, H(2), J = 3.1 Hz, J = 5.7 Hz); 6.03 (dd, 1 H, H(3), J = 3.1 Hz, J = 5.7 Hz); 5.83 (ddt, 1 H, H(9), J = 17.1 Hz, J = 10.5 Hz, J = 6.6 Hz); 5.01 (dm, 1 H, H_a(10), J = 17.1 Hz); 4.96 (dm, 1 H, H_b(10), J = 10.5 Hz); 2.79 (s, 1 H, H(1)); 2.57 (s, 1 H, H(4)); 2.13 (pseudotriplet, 2 H, H(8), J = 7.2 Hz); 1.43 (m, 1 H, H(5)); 1.33 (m, 2 H, H(7)); 1.27 (dd, 1 H, H_a(6), J = 11.4 Hz, J = 2.2 Hz); 1.13 (dt, 1 H, H_b(6), J = 11.4 Hz, J = 3.8 Hz). ^{13}C NMR (150.92 MHz, $CDCl_3$), δ: 138.31 (C(9)); 136.75 (C(3)); 136.44 (C(2)); 114.78 (C(10)); 45.87 (C(4)); 45.05 (C(7)); 41.99 (C(1)); 40.70 (C(8)); 38.14 (C(5)); 32.69 (C(6)). The *exo*-position of the allyl substituent in the norbornene fragment is indicated by low chemical shifts of the bridging carbon atom (δ 45.05). For *endo*-substituted norbornenes, this value is normally higher (δ 48.8).

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