

Oxidative esterification of alkenes via π - and σ -organopalladium complexes: new pathways for the reaction

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Dedicated to Professor Oleg M. Nefedov in recognition of his outstanding contribution to organometallic chemistry

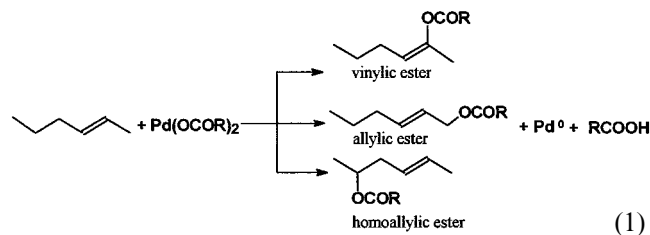
Abstract

New mechanistic data on the oxidative esterification of alkenes were obtained in the study of the reaction of Pd(II) acetate with hex-1-ene, methylcyclohex-1-ene and racemic α -pinene in a chloroform solution. High yields of unsaturated esters with terminal alcohol group were found in the oxidation of hex-1-ene, while the exocyclic methyl groups in methylcyclohex-1-ene and α -pinene remain untouched. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Palladium; Hex-1-ene; Methylcyclohex-1-ene; α -Pinene; π -Complex; σ -Complex; Oxidative esterification; Regioselectivity; Carbocation; Reaction mechanism

1. Introduction

Redox reaction of Pd(II) carboxylates with alkenes produces α -, β - or γ -alkenyl esters and Pd⁰ (Eq. (1))



via successive formation of the intermediate palladium π -(η^2 -Pd(OCOR)₂) and σ -bound (RCOOPd)-(η^1 -OCOR) complexes [1–4]. The reaction Eq. (1) is assumed to proceed through synchronous insertion of the π -coordinated alkene into the Pd–OCOR bond [1–3] or outer-sphere attack of the RCOO[−] anion on the π -coordinated alkene molecule [5] with simultaneous formation of the σ -Pd–C and C–OCOR bonds. Recently new data were obtained [6] that suggest the Pd–C σ -bond formation

and RCOO[−] anion addition to occur asynchronously. First, the (RCOO)₂ Pd(II) group adds to one of C atoms of the alkene double bond, producing a positive charge on the neighboring C atom. Then, the palladium σ -carbenium complex RCOOPd- \langle C⁺ that formed undergoes successive deprotonation and reductive elimination of the Pd⁰(OCOR)[−] group producing an allylic ester. Due to the asynchronism of the Pd–X across C=C bond addition, a carbenium moiety of the hydrocarbon ligand has a chance to isomerize, for instance via 1,2-hydride shift, before the deprotonation and elimination stages, thus resulting in a homoallylic ester.

In our previous study [6] we found that the regio- and stereoselectivity effects overlap. The aim of this work is restricted to the regioselectivity of reaction (1). To diminish the stereoselectivity problems, we chose the following series of optically inactive substrates: (1) hex-1-ene (unbranched acyclic alkene without stereo- and conformational limitations); (2) methylcyclohex-1-ene (achiral cyclohexene derivative with low ring-conformational barrier); and (3) racemic α -pinene (chiral cyclohexene derivative with rigidly fixed ring conformation). In this work we studied the regioselectivity of the reaction of Pd(II) acetate with the above alkenes in a chloroform solution.

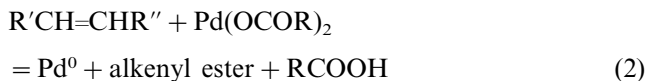
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2. Results and discussion

2.1. Reactive palladium species

Alkene oxidative esterification shown in Eq. (1) is a redox reaction that converts a soluble Pd(II) complex into colloidal Pd clusters or aggregates of small Pd metal species, so-called palladium black. The latter species are efficient catalysts for alkene dehydrogenation, isomerization and redox disproportionation. These undesired side reactions are usually precluded by the addition of *p*-benzoquinone (BQ), which re-oxidizes the Pd⁰ formed by reaction Eq. (2)



and recover Pd(II) as shown by Eq. (3) [1].

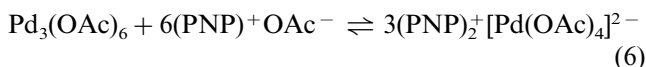
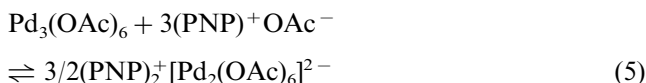


In an aprotic solvent and in the absence of free carboxylic acid RCOOH, re-oxidation of Pd⁰ by Eq. (2) does not occur. Instead of this, *p*-benzoquinone (BQ) and the alkene molecule (Un) bind the Pd⁰ species *in statu nascendi* to the π -complex BQ·Pd·Un (see Eq. (4))



which is stable in aprotic media [8,9], thus preventing the formation of the dispersed palladium phase and alkene side reactions.

Palladium(II) was introduced into reaction solutions as the complex Pd₃(OAc)₆. The reaction of the latter with alkenes is very slow at room temperature but is noticeably accelerated when 0.1–0.5 mol of additional AcO[−] anions per Pd(II) atom is added. The excess AcO[−] anions were introduced in the form of the bis(triphenylphosphoranilidene)ammonium acetate, (PNP)⁺OAc[−]. The corresponding anionic Pd(II) complexes formed according to Eqs. (5) and (6)



are well soluble in chloroform, so that the reaction between Pd(II) and alkene proceeds in a homogeneous system smoothly.

Under the experimental conditions (0.05 mol l^{−1} of the total Pd(II) and 0.01–0.02 mol l^{−1} of the (PNP)⁺OAc[−] added, preliminary equilibrated during 12–20 h at 20°C), practically all the additional AcO[−] anions were involved into the composition of the anionic Pd(II) complexes. Estimation by ¹H-NMR spectra showed that a fraction of ‘free’ (unbound with Pd(II)) AcO[−] anions in the equilibrated CDCl₃ solution was

much less than 1% of its initial concentration. Therefore, the participation of ‘free’ AcO[−] anions in the reactions under study can be neglected. The equilibrated reaction solutions contained the Pd₃(OAc)₆ and [Pd₂(OAc)₆]^{2−} as the Pd(II) species.

2.2. Reaction products

The products of the oxidative esterification of hex-1-ene, 1-methylcyclohexene and α -pinene are presented in Table 1. Even traces of vinylic esters were not found in all experiments. As can be seen in Table 1, allylic esters are the main reaction products in the oxidation of all alkenes under study.¹

2.2.1. Hex-1-ene oxidation

The most plentiful allylic esters, *cis*- and *trans*-hex-2-en-1-ol acetates (Table 1), are expected to form via the ‘carbenium’ mechanism [6], in which (1) Pd(II) atom adds to the terminal C atom of the hex-1-ene molecule and (2) σ -carbenium complex that formed successively splits off H⁺ and eliminates the Pd⁰(OAc)[−] group (see Scheme 1).

The formation of the homoallylic ester, hex-3-en-1-ol acetate, also follows reasonably from this mechanistic scheme. Meanwhile, the origin of hex-4-en-3-ol acetate is not so obvious and needs additional comments.

The appearance of the OAc group at the third position of the hexenyl moiety can be due to the reversible isomerization of σ -allyl complex **1** to complex **3** via π -allyl intermediate **2** as depicted in Scheme 2.

Hex-1-en-3-ol acetate, the expected product of Pd(OAc)[−] reductive elimination from complex **3**, was not found. We suggest that hex-4-en-3-ol acetate is formed via a series of the ‘protonation–H-shift–deprotonation’ transformations of complex **3**.

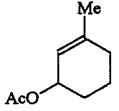
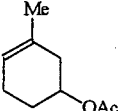
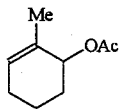
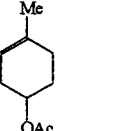
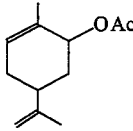
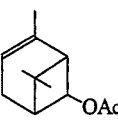
The allylic esters found could have also been considered as the products of *anti*-Markovnikov addition of the Pd–OAc group to the 1-alkene molecule followed by Pd–C bond heterolytic cleavage or H–Pd elimination. There is no reason, however, to expect the *anti*-Markovnikov addition.

2.2.2. Methylcyclohex-1-ene oxidation

As seen in Table 1, allylic esters are also the main products of methylcyclohex-1-ene oxidative esterification. In the frameworks of the known ‘allylic’ mechanism [4], the allylic esters **4** and **5** are expected to form according to Scheme 3. However, neither **4** nor **5** ester was found among the reaction products. It is noteworthy that the methyl group of the initial cycloalkene remains untouched in all of the esters formed in the reaction.

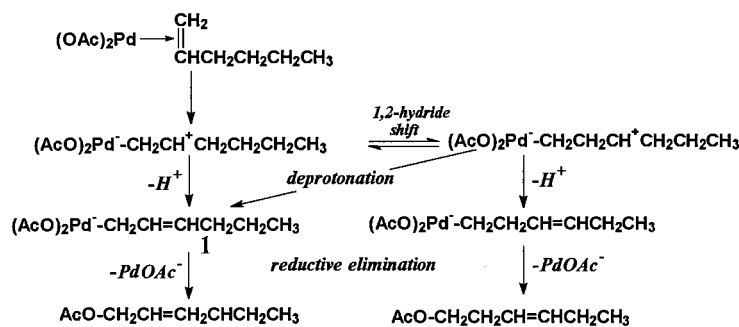
¹ Nearly the same results were obtained in experiments with the use of tetraethylammonium acetate, (NEt₄)⁺OAc[−], instead of (PNP)⁺OAc[−].

Table 1
Oxidative acetoxylation of alkenes by Pd(II) acetato complexes in chloroform at 20°C

Alkene	Allylic acetates (%) ^a	Homoallylic acetates (%) ^a
Hex-1-ene ^b	<i>cis+trans</i> -Hex-2-en-1-ol (59) <i>cis+trans</i> -Hex-4-en-3-ol (33)	<i>cis+trans</i> -Hex-3-en-1-ol (8)
Methylcyclohex-1-ene	 Methylcyclohex-1-en-3-ol (40)	 Methylcyclohex-1-en-5-ol (3)
	 Methylcyclohex-1-en-6-ol (49)	 Methylcyclohex-1-en-4-ol (8)
α -Pinene	 Carvyl acetate (10)	 α -Pinene-7-ol acetate (90)

^a Yield based on the total content of the esters formed.

^b In several experiments with the use of Pd^{II} 2-methylbutyrate- instead of Pd^{II} acetato complexes the yield of *cis+trans*-hex-2-en-1-ol 2-methylbutyrate was 90%, and the minor reaction products were the hex-3-en-1-ol and hex-4-en-3-ol 2-methylbutyrate.

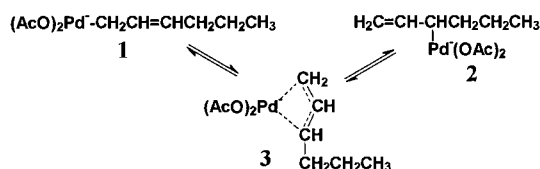


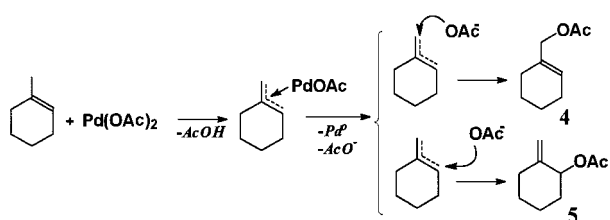
Unlike the 'allylic' mechanism [4], the 'carbenium' mechanism [6] reasonably explains the formation of the most abundant reaction product, methylcyclohex-1-en-6-ol acetate, as shown in Scheme 4.

The ways of formation of the other esters are not so obvious. The main problem is why the location of the OAc group in their molecules relatively to the Me group is different from that expected for the three known mechanisms, viz., synchronous 'classical' [1–3], 'allylic' [4] and asynchronous 'carbenium' [6] mechanisms. The resolution of the issue was found by the results for α -pinene oxidative esterification.

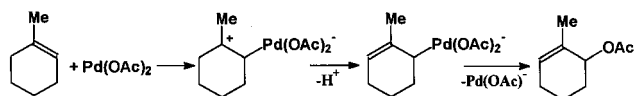
2.2.3. α -Pinene oxidation

Our experiments showed that the 2-methyl group of the α -pinene molecule undergoes no transformations by the action of Pd(II) acetates, similarly to that found for



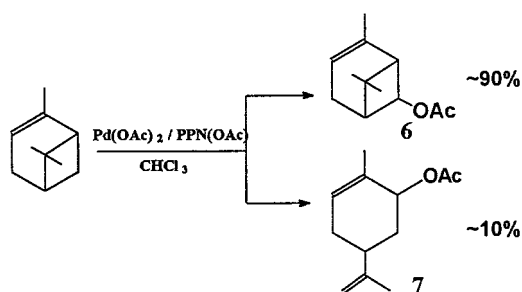


Scheme 3.



Scheme 4.

methylcyclohex-1-ene (see above). Only two esters, α -pinene-7-ol acetate (**6**) and carvyl acetate (**7**) were formed by the oxidative esterification of α -pinene (see Eq. (7) and Table 1).



(7)

The origin of these reaction products can be rationalized taking into account a carbenium nature of the hydrocarbon group of the σ -complex (**8**). The carbocation moiety of complex **8** has some similarities with the 'non-classical' homoallylic systems [9,10]. The positive

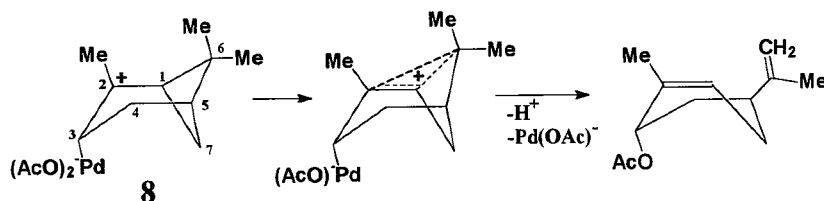
charge is partly distributed over the C atoms of the hydrocarbon cyclic system. The highest positive charge is expected to be in position six, thus inducing the cleavage of the strained C–C bond of the four-membered cycle and producing carvyl acetate as shown in Scheme 5.

The vicinity of the Pd atom to the H–C(7) bond opens up a new avenue for transformation of complex **8** including its rearrangement via migration of the Pd atom from positions three to seven, affording finally α -pinene-7-ol acetate, as shown in Scheme 6. The tendency of the Pd atom to capture an H atom seems to facilitate the insertion of the Pd atom, while it is splitted from the C(3) atom, into the C(7)–H bond.

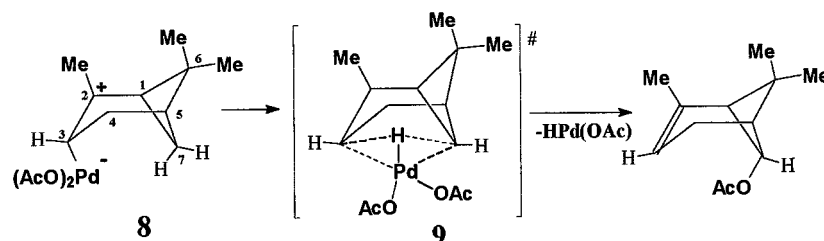
The driving force for this rearrangement seems to be a rather strong Pd–H interaction in transition state **9**, resulting in the elimination of HPdOAc, similarly to that proposed by Heck [11] for phenylacetylene carbonylation with Pd complexes. A similar rearrangement occurring in the reaction of cyclohex-1-ene (in a boat conformation) with Pd(II) acetate can result in the found products of oxidative esterification, methylcyclohex-1-en-3-ol, methylcyclohex-6-en-3-ol and methylcyclohex-1-en-4-ol (Table 1).

3. Experimental

Solvents (chloroform, acetic acid and benzene, all Reakhim (Russia), reagent grade) were purified by standard procedures [12]. Hex-1-ene (Aldrich, 99 + % purity), methylcyclohex-1-ene (Aldrich, 97 + % purity) and α -pinene (Aldrich, 98% purity, racemate, $[\alpha]^{22}_D 0^\circ$ (neat)) were distilled and stored under argon with molecular sieve 4 Å. *p*-Benzoquinone (Reakhim (Rus-



Scheme 5.



Scheme 6.

sia), reagent grade) was sublimated in vacuum before experiments. Palladium(II) chloride and sodium borohydride (both Reakhim (Russia), reagent grade) were used as received. Bis(triphenylphosphoranilidene)-ammonium chloride, tetraethylammonium hydroxide (40% aqueous soln. and (\pm)-2-methylbutyric acid (all Fluka, reagent grade) were used as received.

3.1. Analysis methods

Elemental C,H,N-microanalysis of the Pd(II), PNP and NEt_4^+ carboxylates were performed on an automatic C,H,N-analysator 'Carlo Erba Strumentazione', Italy. $^1\text{H-NMR}$ spectra were recorded on a 'Bruker WP-200' spectrometer. GC/MS analyses of the reaction products were performed on an 'Automass 150' chromatomass-spectrometer ('Delsi Nermag', France, capillary columns with OV-1). GLC analyses were conducted on chromatographs 'Varian 3600' (USA) and '3700' (Russia) with different capillary columns, stationary phases OV-1, HP-1, SE-30 and XE-60.

3.2. Palladium(II) acetate

Palladium(II) acetate was obtained by the oxidation of fresh-prepared Pd black (prepared from PdCl_2 and NaBH_4) with concentrated HNO_3 in glacial AcOH by the method [13]. The raw acetate was purified from traces of nitrate and nitrite complexes by refluxing in glacial AcOH with fresh-prepared Pd black and recrystallized from hot AcOH .

3.3. Palladium(II) (\pm)-2-methylbutyrate

(\pm)-2-Methylbutyric acid (1 g 10 mmol) in 5 ml of benzene was added to a solution of 0.5 g of palladium(II) acetate (2.23 mmol) in 30 ml of benzene and refluxed under mixing during 2 h. The dark precipitate formed after cooling was filtered off, the mother liquid was evaporated on a rotary evaporator until a viscous orange oil was formed. The oil was dissolved in pentane, the excess acid was washed off with water (three to four times by 200 ml), and the oil was dried over CaCl_2 and then over a molecular sieve. Yield 0.52 g (75% based on Pd). According to GC/MS data, the substance obtained as a viscous orange oil contains $\sim 1\%$ of excess (\pm)-2-methylbutyric acid. The sample was used in experiments on hex-1-ene oxidation in the form of solutions in chloroform without additional purification. IR spectrum (vaseline oil), $\nu\text{CO}/\text{cm}^{-1}$: 1637, 1425. $^1\text{H-NMR}$ spectrum (CDCl_3 , δ/ppm , J/Hz): 0.62 (t, 3H, $^3J = 7.36$); 0.83 (d, 3H, $^3J = 7.01$); 1.41 (m, 2H); 2.2 (m, 1H). The molecular structure of $\text{Pd}_3(\mu^2\text{-S}(+) \text{-MeC}^*\text{H}(\text{Et})\text{COO})_6$ has been established by X-ray diffraction study of the single crystal [14].

3.4. bis(Triphenylphosphoranilidene)ammonium acetate

bis(Triphenylphosphoranilidene)ammonium acetate was prepared by the modified method [15]. To a solution of $(\text{Ph}_3\text{P})_2\text{NCl}$ (1 g, 1.75 mmol) in 40 ml of CHCl_3 a solution of AgOAc (0.44 g, 2.62 mmol, 20% excess) in 30 ml of CHCl_3 was added. The reaction mixture was stirred during 1 h and the AgCl precipitated was filtered off. The solution was evaporated on a rotary evaporator to a volume of 10 ml, and diethyl ether was added to the beginning of crystallization. The main amount of PNP acetate was first precipitated as a colorless oil, which crystallizes on storing in a fridge for 10–12 h. The substance was purified by recrystallization from CHCl_3 –diethyl ether. Yield 0.94 g (90% based on $(\text{Ph}_3\text{P})_2\text{NCl}$). Anal. Found: C, 76.43; H, 5.61; N, 2.37. Calc. for $\text{C}_{39}\text{H}_{33}\text{NO}_2\text{P}_2$: C, 76.37; H, 5.57; N, 2.34%. $^1\text{H-NMR}$ spectrum (CDCl_3 , δ/ppm): 1.95 (s, 3H, OAc^-); 7.3–7.7 (m, 30H, Ph).

3.5. Tetraethylammonium (\pm)-2-methylbutyrate

Tetraethylammonium (\pm)-2-methylbutyrate was prepared by the method for the synthesis of tetraethylammonium acetate [16].

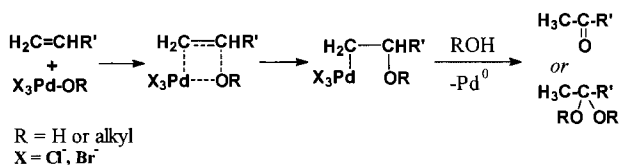
3.6. General procedure for the oxidation of hex-1-ene, methylcyclohex-1-ene and α -pinene

Palladium carboxylate (0.111 mmol), PNP or tetraethylammonium carboxylate (0.042 mmol) and *p*-benzoquinone (0.223 mmol) were placed into a two-neck flask. The flask was evacuated and filled with argon. 1.5–2.0 ml of chloroform and 0.223 mmol of alkene were added in an argon flow. The reaction mixture was stirred at a room temperature for 10–24 h, and the reaction products were analyzed by GLC and GC/MS and identified by mass spectra. Our attempts to separate the reaction products by microrectification (in accessible for us scale, 2–3 g) gave samples inadequate to ^1H - and ^{13}C -NMR analyses. Therefore, we used the GC/MS techniques. Our GS/MS findings were preliminarily compared with the Wiley 275 Database and then the MS and GLC (repeated analyses with a variety of stationary phases) data were checked by both the mass spectra and retention indices with the NIST/EPA/NIH Standard Reference Database (version 1.7).

The results are presented in Table 1.

3.7. Mass spectra of the reaction products (Automass 150, EI, 70 eV)

Our attempts to separate the reaction products by microrectification (in accessible for us scale, 2–3 g) gave samples inadequate to ^1H - and ^{13}C -NMR analyses. Therefore, we used the GC/MS techniques. Our



Scheme 7.

GS/MS findings were preliminarily compared with the Wiley 275 Database and then the MS and GLC (repeated analyses with a variety of stationary phases) data were checked by both the mass spectra and retention indices with the NIST/EPA/NIH Standard Reference Database (version 1.7).

Hex-2-en-1-ol acetate ($M_w = 142$); 100 (5.5); 82 (9.1); 67 (16.5); 55 (9.7); 43 (100).

Hex-4-en-3-ol acetate ($M_w = 142$); 142 (0.1); 100 (11.1); 85 (3.1); 71 (50.5); 58 (6.8); 43 (100).

Hex-3-en-1-ol acetate ($M_w = 142$); 82 (6.7); 67 (17.7); 54 (40.4); 43 (100).

Methylcyclohex-1-en-3-ol acetate ($M_w = 154$); 154 (7.4); 112 (16.6); 97 (29.6); 95 (25.9); 94 (33.3); 79 (100); 67 (14.8); 55 (25.9); 43 (40.7).

Methylcyclohex-1-en-6-ol acetate ($M_w = 154$); 154 (1.8); 112 (9.3); 94 (55.5); 79 (100); 67 (11.1); 55 (16.7); 43 (44.4).

Methylcyclohex-1-en-5-ol acetate ($M_w = 154$); 112 (7.4); 97 (100); 84 (37.0); 69 (37.0); 55 (35.2); 41 (29.6).

Methylcyclohex-1-en-4-ol acetate ($M_w = 154$); 110 (36.5); 95 (1.9); 82 (100); 67 (15.4); 54 (55.8); 39 (28.8).

α -Pinene-7-ol acetate ($M_w = 194$); 152 (1.8); 134 (11.1); 119 (29.6); 108 (11.1); 92 (31.5); 91 (100); 79 (12.9); 76 (11.1); 65 (5.5); 55 (3.7); 53 (7.4); 43 (48.1); 40 (14.8); 38 (7.4).

Carvyl acetate ($M_w = 194$); 152 (1.8); 150 (9.2); 134 (51.8); 132 (74.1); 121 (11.1); 119 (18.5); 107 (29.6); 106 (14.8); 91 (18.5); 79 (7.4); 77 (11.1); 67 (3.7); 57 (7.4); 43 (100); 41 (11.1).

4. Conclusions

The oxidation of alkenes higher than ethylene by Pd(II) halides in aqueous and alcohol solutions normally produces ketones or ketals [1–3]. These are the expected products when the lyate ion (OH⁻ in water and RO⁻ in alcohol) and electrophilic species PdX₃⁻ add to the C=C double bond according to the Markovnikov rule (see Scheme 7). Both electronic and steric factors are believed to facilitate this pathway.

The first evidence for the violation of the Markovnikov rule was found when propylene was oxidized with Pd(II) complexes in acetic acid [1,3]. In this case, the ‘anomalous’ reaction products, allyl acetate and *cis*- and *trans*-*n*-propenyl acetates, were found along with the ‘normal’ oxidation product, *iso*-propenyl acetate.

The ‘abnormal’ product of propylene oxidation with Pd(II) acetate, allyl acetate, was recently uncovered to be a sole reaction product in aprotic solvents (e.g. chloroform, dichloromethane, liquid CO₂ and THF) [6,7]. An additional example of the *anti*-Markovnikov oxidation was found in this work: hexen-1-ol esters prevail among the products of hex-1-ene oxidation by Pd(II) carboxylato complexes in a chloroform solution. As seen in Table 1, the total yield of hexen-1-ol acetates is 67% and that of hexen-1-ol 2-methylbutyrates reaches 90%.

Such a pronounced change in the reaction regioselectivity is barely attributable to a change in the direction of the Pd(II) electrophilic attack on the alkene C=C bond. The formation of homoallylic esters is much less rationalized in the frameworks of the conventional mechanism of alkene into Pd–OAc bond insertion [1–4]. At the same time, all facts available can be rationalized by assuming a scheme involving the Pd(II) atom attack on the least-branched position of the alkene molecule (C₁ in 1-alkenes and C₃ in α -pinene) according to the Markovnikov rule. The following reductive elimination of the Pd(OCOR)⁻ group, after deprotonation of the palladium σ -carbenium complex, should give rise to the reaction products found. In this scheme, the AcO group appears at the C atom of the starting alkene at which the Pd(II) initial attack was directed.

Acknowledgements

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References

- [1] I.I. Moiseev, π -Complexes in Liquid-Phase Olefin Oxidation, Nauka, Moscow, 1970 (in Russian).
- [2] R. Jira, in: E. Becker, M. Tsutsui (Eds.), Organometallic Reactions, vol. 3, Wiley, New York, 1972, p. 44.
- [3] P.M. Henry, Palladium Catalyzed Oxidation of Hydrocarbons, Reidel, Doordrecht, 1980.
- [4] H. Grennberg, J.-E. Bäckvall, in: M. Beller, C. Bolm (Eds.), Transition Metals for Organic Synthesis, Wiley–VCH, Weinheim, 1998, p. 200.

- [5] J.E. Bäckvall, B. Åkemark, S.O. Ljunggren, *J. Am. Chem. Soc.* 101 (1979) 2411.
- [6] N. Yu. Kozitsyna, M.N. Vargaftik, I.I. Moiseev, *J. Organometal. Chem.* 593–594 (2000) 274.
- [7] N.Yu. Kozitsyna, M.N. Vargaftik, A.E. Gekhman, I.I. Moiseev, *Dokl. Akad. Nauk* [Engl. Ed.: *Dokl. Chem.* 346 (1996) 29] 346 (1996) 48629 (in Russian).
- [8] M. Hiramatsu, K. Shiozaki, T. Fujinami, S. Sakai, *J. Organometal. Chem.* 246 (1983) 203.
- [9] (a) H. Grennberg, A. Gogoll, J.-E. Bäckvall, *Organometallics* 12 (1993) 1790;
(b) S. Winstein, *Quart. Rev. (Lond.)* 23 (1969) 1411.
- [10] P. Storey, B. Clark, *Carbonium Ions*, v.3, Wiley, New York, 1972.
- [11] R.F. Heck, *J. Am. Chem. Soc.* 94 (1972) 2721.
- [12] D.D. Perrin, W.L.F. Armarego, *Purification of Laboratory Chemicals*, 3rd edn., Pergamon, Oxford, 1988.
- [13] T.A. Stephenson, S.M. Morehouse, A.R. Powell, J.P. Heffer, G. Wilkinson, *J. Chem. Soc.* (1965) 3632.
- [14] N.Yu. Kozitsyna, M.V. Martens, I.P. Stolarov, S.E. Nefedov, M.N. Vargaftik, I.L. Eremenko, I.I. Moiseev, *Zh. Neorg. Khim.* 44 (1999) 1915 [Engl. Transl.: *Russ. Inorg. Chem.* (1999), no. 11].
- [15] N. Walker, D. Stuart, *Acta Crystallogr.* 39 (1983) 158.
- [16] J. Steigman, L.P. Hammett, *J. Am. Chem. Soc.* 59 (1937) 2540.