Journal of Molecular Catalysis, 83 (1993) 301-310
Elsevier Science Publishers B.V., Amsterdam

M178

Oxidation of cycloalkenes and methylenecycloalkanes by palladium(II) complexes. Part 2. NMR study on the mechanism of the ring expansion of methylenecyclobutane

I.E. Beck*, E.V. Gusevskaya, A.V. Golovin and V.A. Likholobov

Boreskov Institute of Catalysis, Pr. Akad. Lavrentieva 5, Novosibirsk 630090 (Russian Federation); tel. (+7-383)2351453, fax. (+7-383)2355766; e-mail LIKHV1@CATALYSIS.NSK.SU

(Received September 10, 1992; accepted March 20, 1993)

Abstract

The reaction of methylenecyclobutane (**1**) with bis(acetonitrile)chloronitropalladium(II) in methylene chloride yields cyclopentanone. Two intermediates - π-olefin complex of palladium and product of β-nitritopalladation of **1** in a Markovnikov fashion - are observed by ^{1}H and ^{13}C NMR. Palladium-catalyzed ring expansion of **1** is suggested to involve heterolysis of the palladium-carbon bond and rearrangement of the resulting cyclobutyl to cyclopentyl cations. The selective formation of ring-expanded and ring-contracted carbonyl products from methylenecyclobutane and 1-methylcyclobutene, respectively, is discussed in terms of proposed mechanism.

Key words: cycloalkene oxidation; methylenecyclobutane; oxidation; palladium

Introduction

Olefins are known to be stoichiometrically and, in the presence of oxygen, catalytically oxidized by nitro complexes of palladium(II) [1–5]. Depending on the olefin structure, solvent nature, and composition of the palladium complex, these interactions may give carbonyl compounds, epoxides, alcohols, vinyl derivatives, or glycol esters. Experiments with palladium nitrite complexes, labelled with heavy isotopes of oxygen, revealed the O atom transfer from the nitro group to the olefin as a distinctive feature of such reactions [1–3]. The key intermediates are σ-organopalladium compounds, which are formed as a result of the insertion of coordinated olefin into Pd–O or Pd–N bonds and were observed by IR or/and NMR for ethylene [6,7], propylene [1], 1-methylcyclobutene [8], and norbornene [9]. Eventually, the decomposition step of these intermediates does determine the nature of the oxidation products.

The oxidation of small ring olefinic compounds by transition metal complexes is usually accompanied by skeletal rearrangements resulting in the formation of ring-expanded, ring-contracted, ring-intact, or ring-opened products

*Corresponding author.

0304-5102/93/$06.00 © 1993 - Elsevier Science Publishers B.V. All rights reserved.

[10-12]. The detailed mechanism of such transformations has not yet been clarified. It has been found that the structure of the products depends, in particular, upon the position of the double bond in the parent olefin. The oxidative palladium-induced ring contraction of 1-methylcyclobutene was the subject of our previous report [8]. The aim of the present study was to investigate *in situ* by ^{1}H and ^{13}C NMR spectroscopy the mechanism of the interactions of an isomeric olefin, methylenecyclobutane, with $PdCl_2L_2$ and $PdCl(NO_2)L_2$ ($L=CD_3CN$) in methylene chloride.

Experimental

The synthesis of $PdCl_2(CD_3CN)_2$ and $PdCl(NO_2)(CD_3CN)_2$ (residual protium 0.3%) as well as the results of their elemental analysis were described

TABLE 1

The characteristics of lines in ^{1}H and ^{13}C NMR spectra of the compounds **1-5** observed in reaction solutions[a]

Compound	Hydrogens[b]				
	on C^1 and C^1	on C^2 and C^2	on C^3 and C^3	on C^4 and C^4	on C^5 and C^5
1	-	2.62 (tt, 4H) $J_{2-5}=2.4$ $J_{2-3}=8.1$	1.86 (p, 2H) $J_{3-2}=8.1$ $J_{3-4}=8.1$	2.62 (tt, 4H) $J_{4-5}=2.4$ $J_{4-3}=8.1$	4.61 (p, 2H) $J_{5-2}=2.4$ $J_{5-4}=2.4$
	150.5 (s, 1C)	31.9 (t, 2C)	16.7 (t, 1C)	31.9 (t, 2C)	104.7 (t, 1C)
2	-	2.81 (br, 4H)	2.06 (br, 2H)	2.81 (br, 4H)	4.84 (br, 2H)
	140.9 (s, 1C)	40.4 (t, 2C) $J_{C-H}=135$	18.3 (t, 1C) $J_{C-H}=145$	40.4 (t, 2C) $J_{C-H}=135$	89.3 (t, 1C)
3	-	2.86 (br, 4H)	2.07 (br, 2H)	2.86 (br, 4H)	4.91 (br, 2H)
	-	40.0 (br, 2C)	18.2 (br, 1C)	40.0 (br, 2C)	-
4	-	δ_b^c 2.48 (q, 2H) $J_{b-c}=12$ $J_{b-d}=10$ $J_{b-i}=8$ $J_{b-c'}=2$	δ_d^c 1.90 (m, 1H) $J_{d-i}=14$ $J_{d-b}=10$ $J_{d-c}=4$	δ_b^c 2.48 (q, 2H) $J_{b-c}=12$ $J_{b-d}=10$ $J_{b-i}=8$	δ_a (3.40 (s, 2H)
		δ_c^c 2.37 (m, 2H) $J_{c-b}=12$ $J_{c-i}=8$ $J_{c-d}=4$ $J_{c-b'}=2$	δ_i^c 1.74 (m, 1H) $J_{i-d}=14$ $J_{i-c}=8$ $J_{i-b}=8$	δ_c^c 2.37 (m, 2H) $J_{c-b}=12$ $J_{c-i}=8$ $J_{c-d}=4$	
	71.7 (1C)	41.2 (t, 2C)	32.8 (t, 1C)	41.2 (t, 2C)	100.0 (1C)
5	-	1.86 (m, 4H)	2.04 (m, 4H)	2.04 (m, 4H)	1.86 (m, 4H)
	217.4 (s, 1C)	36.6 (t, 2C)	21.9 (t, 2C)	21.9 (t, 2C)	36.6 (t, 2C)

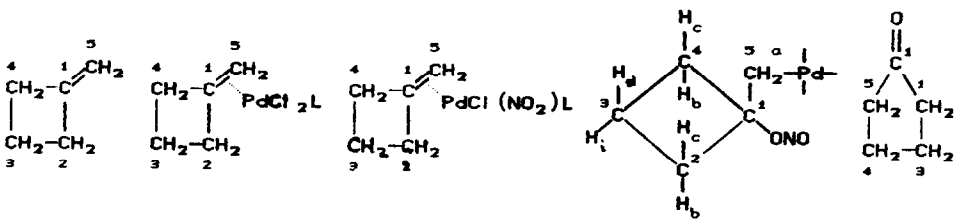
[a]Spectra recorded in CD_2Cl_2 solution at 303 K at 300 MHz; chemical shifts are in ppm *vs.* HMDSO (^{1}H) and TMS (^{13}C). s=singlet, d=doublet, t=triplet, q=quartet, p=pentuplet, m=multiplet, br=broad signal; coupling constants J_{H-H} and J_{C-H} are in Hz.

[b]Figures refer to the center of gravity of the multiplet lines.

[c]The corrected chemical shifts of the second-order spectrum have been deduced by the procedure described in ref. 14.

previously [5]. NMR spectra were recorded using Bruker CXP-300 spectrometer with a magnetic field induction of 7 T. The temperature of the samples was continuously monitored with a precision of 1°C by a VT-1000 thermocouple. The reactions were carried out in methylene-d_2 chloride (residual protium 0.5%) at 303 K. The concentrations of palladium and **1** in solution were 4×10^{-2} M. ^{1}H and ^{13}C NMR chemical shifts, δ, were determined using hexamethyldisiloxane and tetramethylsilane as internal standards, respectively.

Methylenecyclobutane and cyclopentanone were kindly donated by Dr. O.E. Batalin (Sankt-Peterburg). The compounds were purified by fractional distillation up to 99.0 and 99.5% of the main component, respectively, and characterized by GLC, ^{1}H and ^{13}C NMR (10^{-1} M, CD_2Cl_2, 298 K). The spectra obtained (Table 1) of the complexes depicted below were compared to standard spectra [13].



1 2 3 4 5

Results and discussion

Methylenecyclobutane was found to undergo oxidation by $PdCl(NO_2)L_2$ in methylene chloride to yield almost exclusively cyclopentanone. The NMR experiments *in situ* permitted us to detect a number of intermediates formed in the course of this reaction and suggest the routes of their decomposition.

After the addition of **1**, the solution of $PdCl_2L_2$ goes rapidly from a dark yellow colour to pale yellow. The ^{1}H NMR spectrum of the solution of **1** and $PdCl_2L_2$ consists of three lines: at δ 2.81 (4H), 2.06 (2H), and 4.84 (2H), which are much more broadened compared to the starting olefin (Table 1). The ^{13}C NMR spectrum shows a singlet at δ 140.9 and triplets at δ 40.4, 18.3 and 89.3 ppm. The intensities of these lines, which we attributed to product **2**, do not change over prolonged periods (at least 7 days). Like the molecule of the starting olefin, product **2** seems to contain four methylene groups, two of which are magnetically equivalent, and a carbon not bound to hydrogens. Analysis of the spectral data, listed in Table 1, prompted us to suggest that during the interaction of **1** with $PdCl_2L_2$ no substantial changes in olefin structure occur. So, the equilibrated formation of π-olefin complex of palladium is likely to take place in the solution. The group of broadened lines, **2**, seem to be an

averaged spectrum that arises as a result of the rapid (on the NMR time scale) exchange between olefin molecules bound and not bound to palladium.

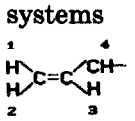
The addition of $PdCl(NO_2)L_2$ to a solution of **1** leads to the appearance of a number of lines in the NMR spectra. The group of lines whose intensities varied in the same manner with reaction time were attributed to the same compounds. For this purpose the coupling constants for the resolved multiplets were also used. As a result, we isolated four groups of lines (**1**, **3**, **4**, **5**). The dependence of their intensities on time is shown in Fig. 1, and the spectral characteristics in Table 1.

On the basis of the chemical shifts, the group of lines **5** belongs to cyclopentanone, the end product of the reaction. Cyclopentanone accumulates in the solution with an appreciable induction period (Fig. 1), during which the maximum concentrations of **3** and **4** are observed. Hence, compounds **3** and **4** could be the kinetic precursors of cyclopentanone. The intensities of the groups of lines **3** and **4**, which appear in the spectra after the addition of palladium complex, tend to decrease with time, and disappear by the end of the reaction. Therefore, these lines can be attributed to the reaction intermediates.

The ^1H NMR spectrum of **3** is similar to that of **2** (the differences in chemical shifts are about 0.05 ppm) as well as the ^{13}C NMR spectrum (the carbon signals of **3** are more broadened than those of **2**). We suggest that intermediate **3** is the π olefin complex formed as a result of the displacement of the neutral ligand from $PdCl(NO_2)L_2$. So, **3** is different from **2** only in the nature of the ligands on the palladium ion.

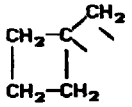
The ^{13}C NMR spectrum of compound **4** consists five lines at δ 71.7, 41.2, 32.8, and 100.0 ppm. The ^1H NMR spectrum of **4** shows a broadened quartet at δ 2.48, multiplets at δ 2.37 and 1.96, a broadened multiplet at δ 1.90, and a singlet at δ 3.40 ppm. As can be seen, intermediate **4** contains five non-equivalent groups of hydrogens, designated as H_a–H_i (Table 1). The differences in the chemical shifts of H_b and H_c, as well as H_d and H_i, are comparable to the coupling between them, therefore the second-order spectra are observed. The coupling constants were determined on the basis of homonuclear decoupling. Analysis of spectra led to the corrected chemical shifts of multiplet lines given in Table 1 being deduced by the procedure described in ref. 14.

Presuming that intermediate **4** involves five carbons, like the starting olefin and the end product, it can be supposed that **4** contains one carbon not bound to hydrogens and four $-CH_2-$ groups, two of which are equivalent. Unlike the starting olefin, in **4** no coupling of the hydrogens on C^5 with the other hydrogens of the molecule is observed (Table 1). Hence, the $-C^5H_2-$ group seems to be isolated from the other proton-containing groups and bound to C^1 by a C–C single bond rather than by a double bond as in **1**. Note that in allylic systems



the coupling might be observed between the allylic hydrogens and the vinylic hydrogens across four bonds ($J_{H^1-H^4}$ or $J_{H^2-H^4}$ is generally 0–3 Hz) [15].

So, the intermediate **4** contains the following fragment

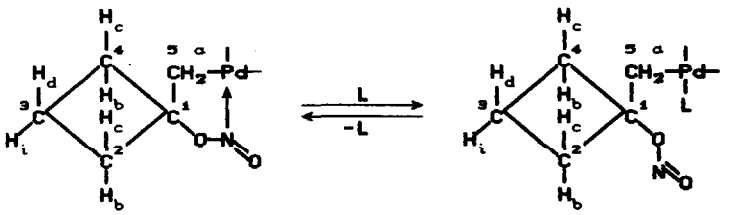


and appears to be a product of the β-nitritopalladation of **1**.

The ^{1}H-NMR spectra show that the protons on the carbon bearing the nitrite group resonate between 4.0 and 5.1 ppm similar to that of free alkyl nitrites [16], with the α-protons *cis* to the nitroso group being shifted up-field with respect to those that are *trans* (*e.g.*, for ethyl nitrite: δ_{cis}=4.0 ppm, δ_{trans}=5.1 ppm). The protons on the carbon, bound to palladium resonate between 1.5 and 4.5 ppm [6,17,18] depending on the number of alkyl substituents present on both the carbon atoms, which initially was bound by a double bond. The carbon atom bonded to the nitrite group in intermediate **5** seems to have a ^{13}C chemical shift of about 68 ppm (comparable to 68.2 ppm for the corresponding carbon in *n*-butyl nitrite [13], to 66.8 ppm is isoamyl nitrite [13], to 69.5 ppm in β-nitritonorbornyl palladacycle [17] and to 67.5 ppm in the analogous 1-methylcyclobutene derivative [8]) and the carbon atom bound to palladium should be expected to resonate at about 94.9 ppm as in [8] or in [17].

Therefore, it should be supposed taking into account the spectrum characteristics of intermediate **4** (Table 1) that the Markovnikov addition to the C=C bond in **1** takes place to result in the palladium attaching to the primary carbon atom (a ^{13}C signal at 100.0 ppm and ^{1}H multiplet at 3.40 ppm) and nitrite bound to the tertiary carbon atom (a ^{13}C signal at 71.7 ppm). The interaction with the palladium atom could be the reason for some broadening of the H_b and H_i signals. These hydrogens seem to be on the same side of the ring with the $-CH_2Pd$ group.

Thus, the spectrum observed can be assigned to a heteropalladacyclopentane (chelated alkyl nitrite) complex **4a**, such as the one characterized by a single-crystal X-ray structure determination [17], or to its open ring isomer **4b**:



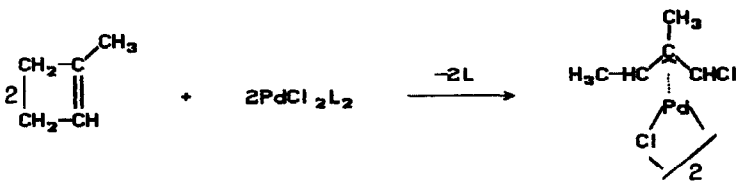
4a **4b** (1)

In spite of the lack of direct evidence for the proposed equilibrium (eqn. (1)), the significant downfield shift of the protons of the CH_2Pd group of compound

4 compared to that for palladaorganic compounds without nitrogen able to bind with the Pd atom [6,7,18], may be due to the ring closure. The metallacyclic ring opening must be occurring because of the kinetic lability of Pd(II), the poor donor character of alkyl nitrites towards Pd(II) [17] and the broadening and changing the chemical shifts of the β-nitritoalkyl palladium intermediates which are formed from other olefins during the reaction [6,17].

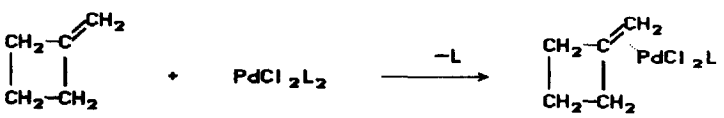
Mechanism of the methylenecyclobutane oxidation

The reactions between olefins and palladium complexes $PdCl_2L_2$ ($L=CH_3CN$, PhCN) in chloroform or methylene chloride lead to the products of differing structure depending on the nature of the olefin. Acyclic α-olefins, *e.g.*, ethylene and propylene, give π complexes, whose oxidation proceeds only in the presence of oxygen-containing agents such as acetic acid or water. Three-membered rings usually undergo ring cleavage, *e.g.*, vinylcyclopropanes form ring-opened 1–3-η^3-π-allyl palladium complexes [19–21]. Five- or more-membered ring cycloalkenes and methylenecycloalkanes react with palladium(II) chlorides giving exocyclic and/or endocyclic ring-intact palladium π-allyls [22,23]. In our previous publication [8], stable ring-opened 1–3-η^3-π-allyl complex formed in virtually quantitative yield as a result of a non-reversible reaction of 1-methylcyclobutene with $PdCl_2(CD_3CN)_2$ in methylene chloride, has been characterized for the first time (reaction 2).



(2)

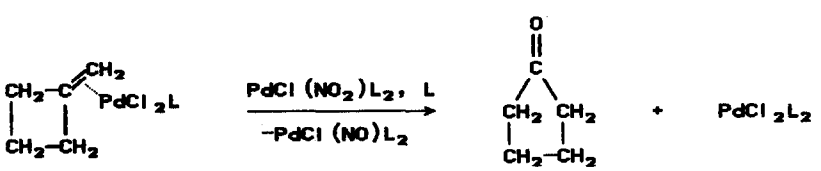
We have found that, unlike 1-methylcyclobutene, another isomeric olefin, methylenecyclobutane, reacts with $PdCl_2L_2$ to give only a π-olefin complex:



(3)

1 2

The addition of agents which serve as oxygen sources further transforms **2** into an oxygen-containing product (like with acyclic α-olefins):



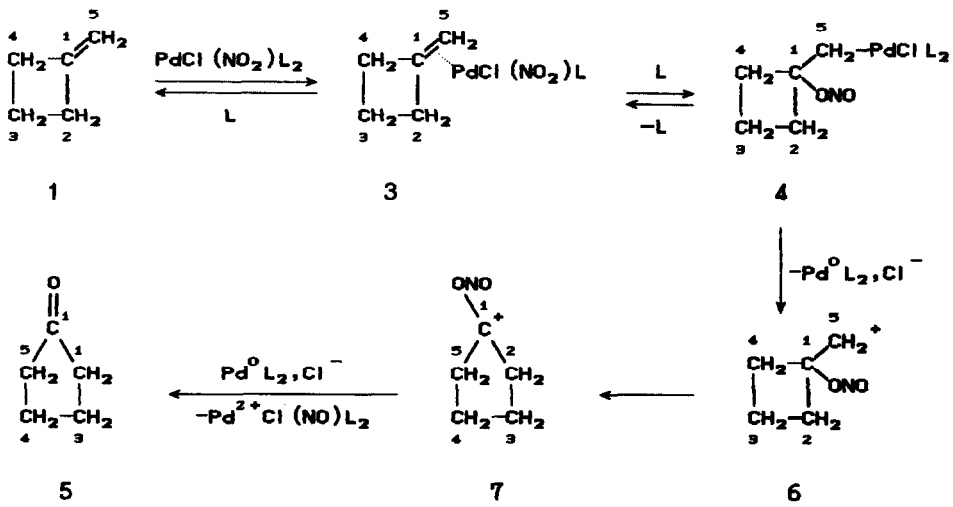
(4)

2 5

The oxidation of methylenecyclobutane to cyclopentanone was first of all described by Boontanonda and Grigg [11] for the "$PdCl_2$–$CuCl_2$–O_2–H_2O–C_6H_6" system. The substituted methylenecyclobutanes undergo analogous ring expansions. In other solvents, such as ethyl acetate or isopropyl alcohol, ring-opened and ring-intact products (acetopropyl chloride and 1-methylcyclobutanol) are formed from **1** [11]. The mechanism of these reactions has not yet been studied. 1-Methylcyclobutene can be oxidized by palladium(II) complexes into a ring-contracted product, cyclopropyl methyl ketone [8,10]. The oxidation of a number of cycloalkenes and methylenecycloalkanes by thallium(III) has been studied by Abley *et al.* [12]. The carbonyl products of the oxidation of cycloalkenes are typically ring-contracted aldehydes; of the 1-methylcycloalkenes, ring-contracted ketones; and of the methylenecycloalkanes, ring expanded cyclo ketones. These reactions have been interpreted in terms of carbonium-ion mechanisms. Most probably, **1** reacts with palladium(II) complexes by a similar mechanism. There are several alternative rearrangements possible for the intermediate carbonium ions produced in the most of these reactions. Therefore, it is remarkable that in each case only one carbonyl product is formed. The reasons for this selectivity remain unclear.

In this work we attempted to explain these observations on the basis of knowledge about the structure of the intermediates formed during the reactions of **1** and 1-methylcyclobutene with $PdCl(NO_2)L_2$.

The proposed mechanism of ring expansion of **1** is presented by Scheme 1. In the first step of the reaction, the displacement of a neutral ligand from palladium complex takes place and π-olefin complex **3** is formed. The insertion of coordinated olefin into the Pd–O bond gives an equilibrium concentration of the Markovnikov addition product **4**. It is somewhat surprising that the



Scheme 1.

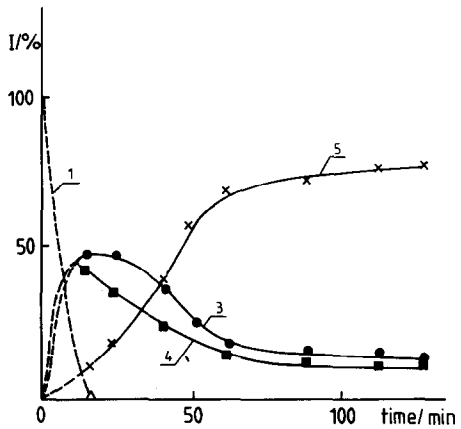


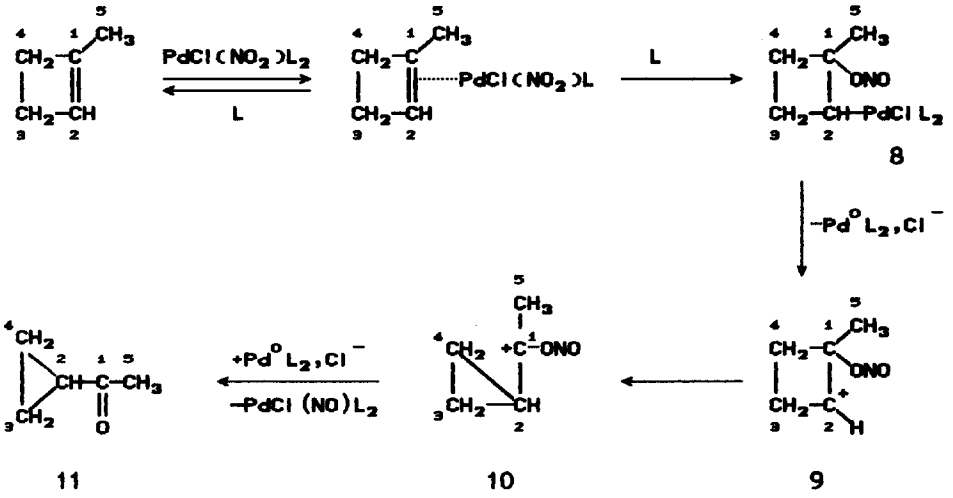
Fig. 1. The dependence of line intensities in the ^1H NMR spectrum on time during methylenecyclobutane oxidation by the $PdCl(NO_2)(CD_3CN)_2$ complex in CD_2Cl_2 at 303 K.

formation of a β-oxypalladation product is readily reversible, as can be seen from the reaction kinetics (Fig. 1), since the cycloreversion reaction involves the breaking of a carbon–oxygen bond. However another example of such a cycloreversion reaction has been reported by Andrews *et al.* [17].

Further rearrangement of **4** with the formation of ring-expanded cyclo ketone **5** most probably proceeds through carbonium ion intermediates. The heterolysis of the palladium–carbon bond in **4**, which is an atypical decomposition for organopalladium compounds, presumably is favoured by the absence of hydrogen atoms on β-carbon(1) that prevents the alternative decomposition of intermediate **4** by the β-hydride shift. Then the rearrangement of the incipient primary carbonium ion into a more stable ring-expanded secondary oxo-carbonium ion **7** occurs. This reaction is additionally favoured by the relief of the strain on going from a four- to a five-membered ring. The intermediate **4** decomposes finally to cyclopentanone and nitrosyl palladium complex.

The mechanism of the palladium(II)-catalyzed ring contraction of 1-methylcyclobutene discussed in our previous publication [8] is presented in Scheme 2.

The organopalladium intermediate, **8**, as well as **4** were detected and identified by detailed analysis of the ^1H and ^{13}C NMR spectra. The palladation of the C=C bonds in both olefins in Markovnikov fashion gives compounds **4** and **8**, in which the nitrite group is attached to the tertiary carbon atom. This reinforces the possibility of the decomposition of **4** and **8** through an atypical mechanism, namely through heterolysis of the palladium–carbon bonds and the formation of cyclobutyl cations **6** and **9**. The rearrangement step of the latter on going to the most stable (in the reactions described) secondary carbonium ions **7** and **10**, additionally stabilized by the nitrite substituent, ultimately determines the structure of the oxidation products. Although the cleavage of the C^1–C^4 bonds takes place in both carbonium ions (**6** and **9**), in **6** the



Scheme 2.

transfer of the positive charge to C^1 causes the release of one of the bonds on C^5, whereas in **9**, it is one bond on C^2. Therefore, the C^4–C^5 and C^4–C^2 bonds arise with the formation of cyclopentyl cation and cyclopropyl carbonium ion (**7** and **10**), respectively.

As was mentioned above, in intermediates **4** (eqn. (1)) and **8** [8] the intramolecular coordination of the nitrite group on the palladium ion through the nitrogen atom should be expected. So, the schematic presentation of the rearrangement of **4** into **5**, depicted in Scheme 1, or **8** into **11** (Scheme 2), does not exclude the opportunity for the skeletal rearrangements to proceed within the coordination sphere of palladium due to the coordination of palladium atom (independent of its oxidation step) with nitrogen atom of the nitrite through all the steps of the reaction. Especially in low polarity aprotic media, ionic pairs are more likely to participate in these reactions rather than isolated ions.

The carbonyl compounds, cyclopentanone and cyclopropyl methyl ketone, and nitrosyl palladium(II) complexes are finally formed in these reactions, *i.e.*, the nitro group virtually acts as an oxidant. Thus, the factor that determines the structure of the final carbonyl products is the position of the nucleophilic group in the organopalladium intermediates (in the ring or in the substituent), which in turn depends upon the position of the double bond in the parent olefin.

References

1 M.A. Andrews and K.P. Kelly, *J. Am. Chem. Soc.*, *103* (1981) 2894.

2 N.I. Kuznetsova, V.A. Likholobov, M.A. Fedotov and Yu.I. Yermakov, *J. Chem. Soc., Chem. Commun.*, (1982) 973.
3 F. Mares, S.E. Diamond, F.J. Regina and J.P. Solar, *J. Am. Chem. Soc., 107* (1985) 3545.
4 A. Heumann, F. Chauvet and B. Waegell, *Tetrahedron Lett., 23* (1982) 2767.
5 I.E. Beck, E.V. Gusevskaya, V.A. Likholobov and Yu.I. Yermakov, *React. Kinet. Catal. Lett., 33* (1987) 209.
6 E.V. Gusevskaya, I.E. Beck, A.G. Stepanov, V.A. Likholobov, V.M. Nekipelov, Yu.I. Yermakov and K.I. Zamaraev, *J. Mol. Catal., 37* (1986) 177.
7 E.V. Gusevskaya, I.E. Beck, A.G. Stepanov, V.A. Likholobov and K.I. Zamaraev, *Stud. Surf. Sci. Catal., 55* (1990) 213.
8 I.E. Beck, E.V. Gusevskaya, A.V. Golovin and V.A. Likholobov, *J. Mol. Catal., 83* (1993) 301.
F9 Chauvet, A. Heumann and B. Waegell, *Tetrahedron Lett., 25* (1984) 4393.
10 J.E. Byrd, L. Cassar, P.E. Eaton and J. Halpern, *Chem. Commun.*, (1971) 40.
11 P. Boontanonda and R. Grigg, *J. Chem. Soc., Chem. Commun.*, (1977) 583.
12 P. Abley, J.E. Byrd and J. Halpern, *J. Am. Chem. Soc., 95* (1973) 2591.
13 *The Sadtler Standard Spectra: Nuclear Magnetic Resonance Spectra,* Vols. 1-86, Nos. 1M-48000M, Sadtler Research Laboratory, Philadelphia, PA, 1966-1988.
14 J. Emsly, J. Finey and L. Satklif, *High Resonance NMR Spectroscopy,* Vol. 1, Mir, Moscow, 1968.
15 A.J. Gordon and R.A. Ford, *The Chemist's Companion,* Wiley, New York, 1972.
16 H.W. Brown and D.P. Hollis, *J. Mol. Spectrosc., 13* (1964) 305.
17 M.A. Andrews, T.C.-T. Chang, C.-W.F. Cheng, T.J. Emge, K.P. Kelly and T.F. Koetzle, *J. Am. Chem. Soc., 106* (1984) 5913.
18 I.E. Beck, E.V. Gusevskaya, A.G. Stepanov, V.A. Likholobov, V.M. Nekipelov, Yu.I. Yermakov and K.I. Zamaraev, *J. Mol. Catal., 50* (1989) 167.
19 A.D. Ketley and J.A. Braatz, *J. Organomet. Chem., 9* (1967) P5.
20 T. Shono, T. Yoshimura, Y. Matsumura and R. Oda, *J. Org. Chem., 33* (1968) 876.
21 M. Parra-Hake, M.F. Rettig, J.L. Williams and R.M. Wing, *Organometallics, 5* (1986) 1032.
22 B.M. Trost and P.E. Strege, *Tetrahedron Lett., 30* (1974) 2603.
23 B.M. Trost, P.E. Strege, L. Weber, T.J. Fullerton and T.J. Dietsche, *J. Am. Chem. Soc., 100* (1978) 3407.