

**PALLADIUM-CATALYZED CARBONYLATION  
OF 1,5-CYCLOOCTADIENE. EFFECTS OF TEMPERATURE  
AND PRESSURE**

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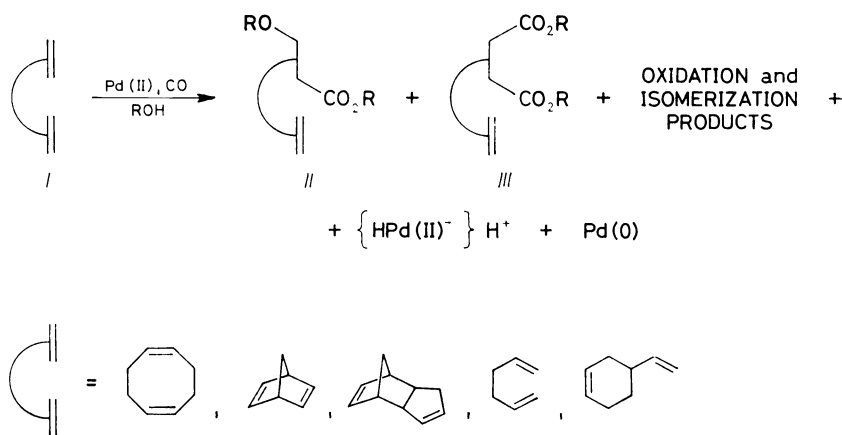
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The influence of temperature and carbon monoxide pressure on the course of oxidative carbonylation reaction of 1,5-cyclooctadiene in the presence of the palladium(II) salts as a catalyst, was investigated.

Much attention has been focused on the research of CO insertion into the metal–carbon  $\sigma$ -bond, with specific interest in the conversion of stoichiometric reactions into catalytic reactions and their possible application to the synthesis of functionalized organic compounds<sup>1–3</sup>. One of these reactions is the Pd(II)-catalyzed carbonylation of various dienes *I* with the double bonds in a spatial proximity favorable for the formation of the metal–diene and/or metal–monoene  $\pi$ -complexes<sup>4</sup> (Scheme 1).



SCHEME 1

A major difficulty in planning and interpreting experimental results of the reactions of this type, where depending on the structure of the diene *I*,  $\beta$ -alkoxy ester *II* and/or diesters *III* are principal products in alcohol as a solvent, is the competing metal-promoted isomerization<sup>5</sup> and oxidation processes<sup>6</sup>.

We were particularly interested in the study of carbonylation of 1,5-cyclooctadiene (COD) in the presence of Pd(II)-catalyst in order to promote the understanding of how different reaction conditions e.g. temperature, CO pressure, and an oxidant/catalyst molar ratio, affect the product ratio of carbonylation products versus undesired products of oxidation and isomerization. The results which are summarized in Table I and correlated with those of the stoichiometric reaction, are explained in terms of the suggested mechanisms. Consequently, experimental conditions with the optimum activity for the formation of the carbonylated compounds and a minimum of the side products are proposed.

Cu(II)-salt is required to reoxidize Pd(0) and make the whole process catalytic; since an acid is formed during the reaction, the base should be added, because acid inhibits the carbonylation reaction and therefore in the absence of base only the stoichiometric amount of  $\beta$ -elimination products is detected and Pd(II)-1,5-COD  $\pi$ -complex was isolated as well, without formation of carbonylated products.

Based solely on the GC retention times, four compounds *V*–*VIII* detected in catalytic carbonylation of COD at room temperature and 417 kPa (Table I, run 1) are identical with compounds isolated and characterized in stoichiometric

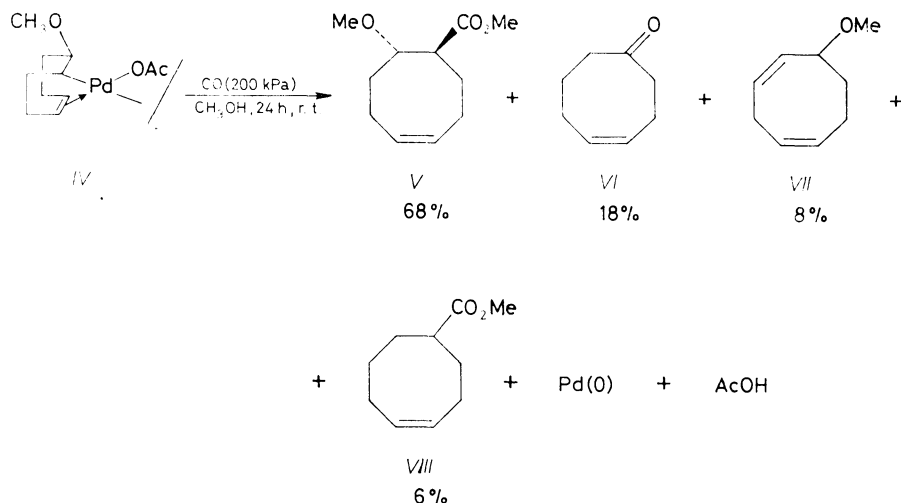
TABLE I

Pd(II)-Induced oxidative carbonylation of 1,5-COD in methanol (1,5-COD in 10% molar excess; Cu(II) : Pd(II) : base mol. ratio (in mmol) 11 : 0.56 : 22 (runs 1–3) and 40 : 0.5 : 84 (run 4))

Run	Temp. °C	Reaction time, h	CO pressure kPa	Product composition <sup>a</sup>				Unkn. %	C.T. <sup>b</sup>	Yield %
				<i>V</i>	<i>VI</i>	<i>VII</i>	<i>VIII</i>			
1	r.t.	24	417	90 <sup>c</sup>	3.5	0.5	2.5	3.5	6.4	64
2	100	24	417	91	3.5	1	3	1.5	6.3	63
3	0	24	417	23 <sup>d</sup>	46 <sup>d</sup>	12 <sup>d</sup>	4 <sup>d</sup>	1.5	3.5	35
4	r.t.	44	417	89	4	1	2	4.0	36	91

<sup>a</sup> Product composition relates to the relative ratio of the organic products; the total yield is determined by means of an internal gas chromatography standard, or based on an oxidant as a limiting reagent; <sup>b</sup> C.T. is catalytic turnover number (mmoles of organic products/mmoles of catalyst), the organic mixture contained certain amount (1.5–4%) of the unknowns, representing most likely isomerized cyclooctenones and cyclooctadienyl methyl ethers; <sup>c</sup> includes the isomers *IX* and *X*; <sup>d</sup> includes the isomers with double bond shifted.

carbonylation of di- $\mu$ -acetatobis(2-methoxy-5-cyclooctenyl)dipalladium(II) (Scheme 2)<sup>7</sup>.



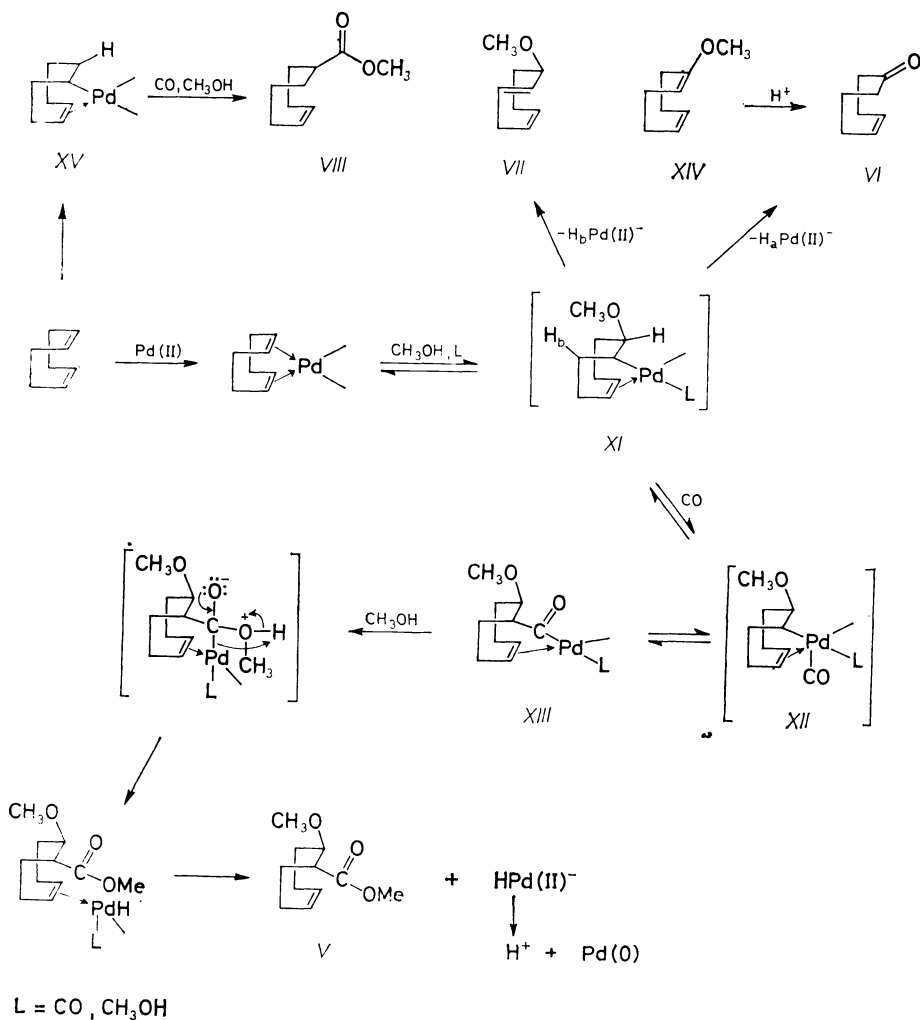
SCHEME 2

The subsequent collection of the compounds *V–VIII* by preparative GC and correlation of their IR, <sup>1</sup>H NMR and mass spectra gave further confirmation for the proposed structures (see Experimental).

The formation of the observed products *V*, *VI*, and *VII* can be explained by involving the intermediate *XI*, generated in oxymetalation reaction of 1,5-COD–Pd(II)  $\pi$ -complex with methanol (Scheme 3).

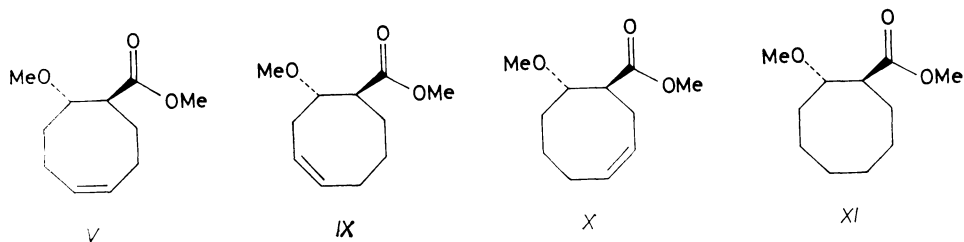
As pictured, the insertion of CO into the Pd(II)–carbon  $\sigma$ -bond (*XI*  $\rightarrow$  *XIII*) required a prior coordination of carbon monoxide<sup>8</sup>, resulting in the formation of a five-coordinate species such as *XII*. Subsequent nucleophilic attack of methanol on the acyl–Pd(II) complex *XIII*, followed by the elimination of palladium(II) hydride, leads to the formation of *V*. The  $\beta$ -elimination of Pd(II)H<sub>a</sub>— from *XI* gives rise to vinyl ether *XIV* which in the presence of an acid converts into *VI*, or into *VII*, by competitive  $\beta$ -elimination of Pd(II)H<sub>b</sub>—. The formation of methyl 4-cyclooctenecarboxylate<sup>4</sup> (*VIII*) should be attributed to *cis*-addition of palladium(II) hydride to 1,5-COD and carbonylation of *XV*. GC analysis of the reaction mixture revealed the presence of two other compounds with relatively long retention times, with IR and <sup>1</sup>H NMR spectra very similar to these of the major compound, methyl *trans*-8-methoxy-4-cyclooctenecarboxylate (*V*), indicating the structure similarity. The relative peak area of these compounds, with respect to increasing retention time, was 18 : 18 : 64, and catalytic hydrogenation of the carbonylation mixture resulted in

a residue, analysis of which showed that three peaks prior to the reduction emerged to only one peak. Therefore, the  $\beta$ -alkoxy esters *V*, *X*, and *IX* differ only in the position of the double bond, yielding upon reduction saturated methyl *trans*-2-methoxycyclooctanecarboxylate (*XI*).

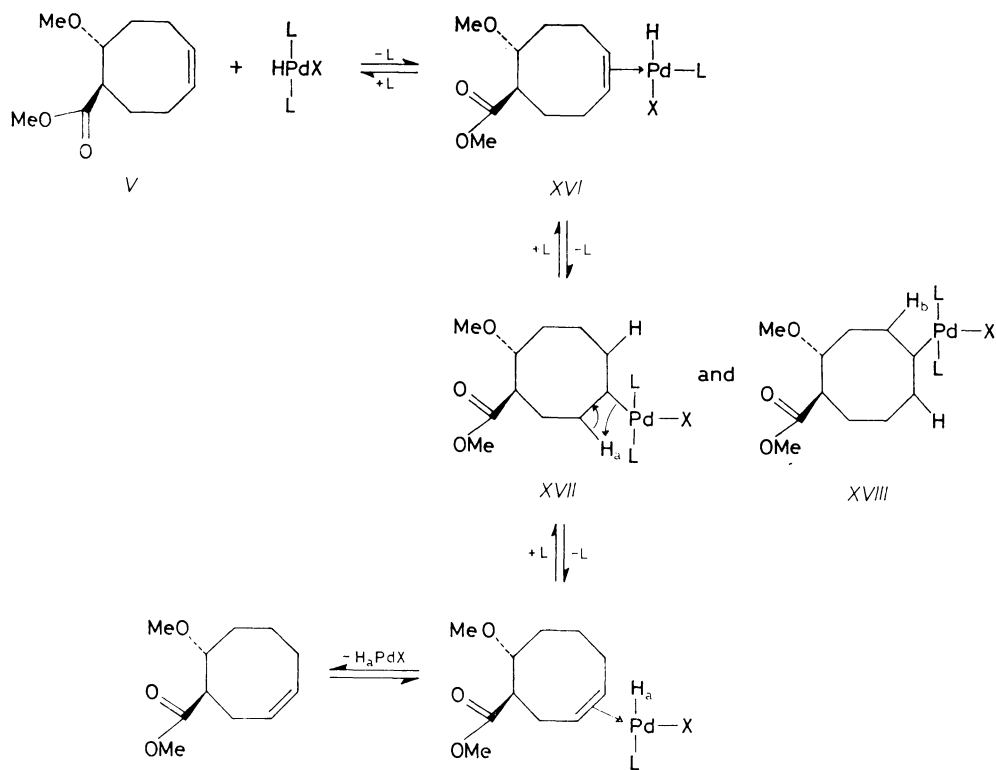


SCHEME 3

The processes leading to isomerized esters *IX* and *X* can be explained by known metal-hydride addition-elimination mechanism<sup>5</sup> depicted in Scheme 4.



An alternative  $\pi$ -allyl mechanism,<sup>5</sup> whereas  $\pi$ -allyl complex is produced by hydride abstraction, followed by readdition of a metal hydride to a different carbon atom cannot be excluded.



L = CO, CH<sub>3</sub>OH

SCHEME 4

The mechanism involves *cis*-addition of palladium(II) hydride, generated in situ, to the double bond of compound V forming via  $\pi$ -complex XVI alkylpalladium(II)

$\sigma$ -complexes *XVII* and *XVIII*. The subsequent  $\beta$ -elimination results in the migration of double bond yielding one of the isomers from *XVII*. The net result is the 1,2-hydride shift and the second isomer is formed from *XVIII*, obviously in an analogous way by the same mechanism most common also in catalysis by Rh, Ni, and Co hydrides<sup>5</sup>.

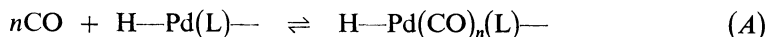
The variation of the reaction temperature has profound effect on the course of the Pd(II)-catalyzed carbonylation of COD. The reaction carried out under the same reaction conditions, but with a rising of the temperature to 100°C, led to the formation of only four products *V–VIII* as in carbonylation of Pd(II)-complex *IV* (Table I, run 2). The total yield was 63% and methyl *trans*-2-methoxy-4-cyclooctencarboxylate (*V*) is formed principally, representing 91% of the organic material. Contrary to the reaction at room temperature, there was no isomerization observed at all, most probably because of the fast decomposition of Pd(II) hydride to elementary palladium, thus preventing the occurrence of addition and  $\beta$ -elimination processes, responsible for isomerization (Scheme 4). However, the tendency to get isomerized products should be enhanced even more at the lower reaction temperature than at ambient temperature, due to the slower decomposition of Pd(II) hydride. Indeed, as the temperature was lowered to 0°C (Table I, run 3) GC analysis of the organic mixture indicated the presence of at least 15 components. The overall yield based on the oxidant was only 33%. Primary oxidation products were isomeric cyclooctenones (46% of the organic products) and cyclooctadienyl methyl ethers (12%). They comprised the main part of the organic mixture (58%), which means that  $\beta$ -elimination of HPd-species (Scheme 2) leading to primary oxidation products, and elimination-addition processes giving rise to other dienyl ethers as depicted below, compete very effectively with the CO insertion. Carbonylated products *V*, *IX*, and *X* which represent the minor part (23%) of the reaction mixture, were present in nearly same relative ratio with respect to one another. Thus, the isomerization obviously plays a very important role in the carbonylation of COD and most probably in the case of other chelating dienes at lower temperatures and to a less extent at room temperature as well.

The effect of pressure was studied under the same reaction conditions as in run 1 (Table I), but with the variable pressures of CO. The relevant experimental results which concern the relative ratio of  $\beta$ -methoxy esters *V*, *IX*, and *X*, dependent on the change of CO pressure, are collected in Table II.

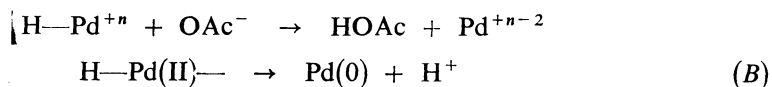
As seen from Table II (run 1), when the carbonylation was run under the pressure of 417 kPa, a considerable isomerization was observed, in regard to  $\beta$ -methoxy esters *V*, *IX*, and *X* (relative ratio 64 : 18 : 18). However, we have shown that the isomerization is remarkably sensitive to the decrease of the CO pressure, but only *V* with double bond in original position was formed at 138 kPa, whereas at the intermediate CO pressure of 276 kPa (Table II, run 2) the isomerization was drastically reduced. Even more significant, such a carbonylation at lower CO pressure proceeds in better

yield (64% of  $\beta$ -methoxy esters at 417 kPa, compared to 77% at 276 kPa and 87% at 138 kPa).

One of the possible reasons for such an effect of the CO pressure is the ability of CO to stabilize Pd(II) hydride via the coordination with palladium. It is reasonable to assume that the coordination between CO and Pd(II) hydride is most likely an equilibrium and consequently the concentration of hydridopalladium carbonyl depends on CO pressure (Eq. (A)).



The hydridopalladium carbonyl formed to a larger extent at higher CO pressure is more stable than a simple hydridopalladium and so has a longer lifetime and can isomerize more effectively. As stated out before, the lack of isomerization at higher temperatures was explained as the result of faster decomposition of the hydridopalladium species. Modes of decomposition of this hydride species may be reactions with acetate ion serving as a base or a reductive elimination (Eq. (B)).



These facts suggest that (i) the fast decomposition of hydridopalladium(II)-species at high temperature (100°C) prevents the isomerization reaction (Table I, run 1), but (ii) subambient temperatures (<20°C) favor the slower decomposition of the same hydridopalladium(II) compound and consequently the isomerization processes play the main role during the Pd(II)-catalyzed carbonylation of 1,5-COD (Table I, run 3). On the other hand (iii) low CO pressures, causing the faster decomposition of palladium hydride (below 276 kPa) suppress the same isomerization process (Table II, run 2 and 3). In view of an inverse temperature and CO pressure effect on the stability of Pd(II)-species, it is significant that the catalytic car-

TABLE II

The effect of the pressure on the isomerization reaction

Run	$p(\text{CO})$ kPa	The relative preparation, %			Overall yield %
		<i>IX</i>	<i>X</i>	<i>V</i>	
1	417	18	18	64	64
2	276	2.5	2.5	95	77
3	138	0	0	100	87

bonylation of 1,5-COD can proceed satisfactorily, yielding carbonylated products *V* and *VIII* (Table II, run 3) without isomerization products *IX* and *X*, even at room temperature, but at a very low CO pressure (138 kPa).

Finally, in order to obtain more information on the preparative aspects of this reaction, we have tested the possibility of a rising the catalytic number by increasing the molar ratio of an oxidant versus the catalyst. Typically, the molar ratio Cu(II)/Pd(II) was 11/0.56 (Table I, runs 1, 2 and 3) and the corresponding catalytic numbers were around 6 (maximum possible 6.4). Thus, it is noteworthy that under mild experimental conditions (Table I, run 4) and upon rising the oxidant/catalyst ratio (Cu(II)/Pd(II) = 40), the yield and the catalytic number were much higher, i.e. 90% and 36, respectively.

## EXPERIMENTAL

*General.*  $^1\text{H}$  NMR spectra were recorded on a Varian F-60 and Varian XL-100 spectrometers and are reported in parts per million ( $\delta$ ) downfield from internal  $\text{Me}_4\text{Si}$ . Infrared spectra were obtained on a Perkin-Elmer Model 283 spectrometer. Mass spectra were obtained on a AEI MS-902 spectrometer. Gas chromatography (GC) was carried out on a Loenco model 15 C-E and Hewlett-Packard model 775, both equipped with a thermal conductivity detector. GC columns used for analytical and preparative analysis were packed with 10% and 20% Carbowax 4000 on Chromosorb W 60/80 mesh, non-acid washed. For higher temperatures Carbowax 20 M on Chromosorb W 60/80 mesh, non-acid washed was used.

*Palladium(II) complexes.* Dichloro(1,5-cyclooctadiene) palladium(II) was prepared by the published method of Chatt et al.<sup>9</sup> Di- $\mu$ -acetatobis(2-methoxy-5-cyclooctenyl)dipalladium(II) (*IV*) was prepared by the method of Anderson and Burreson<sup>10</sup>.

### General Procedure for the Oxidative Carbonylation of 1,5-COD Catalyzed by Palladium(II) Compounds

The reactions requiring CO pressure above 100 kPa were performed in 250 cm<sup>3</sup> heavy-walled Pyrex bottle used for hydrogenation with the Parr apparatus. The bottle is equipped with a stainless steel adapter, that has a pressure gauge, pressure release safety valve and a needle valve connected to the Parr hydrogenation tank which contained CO. A suspension of copper(II) salt, sodium acetate, Pd(II)-catalyst and 1,5-COD in methanol was placed into the flask with magnetic stirring bar. The flask was evacuated on a vacuum line and carbon monoxide introduced to desired pressure (up to 417 kPa). Generally, the temperature of the reaction mixture is adjusted (0–100°C) by placing the bottle in an ice or oil bath. Catalytic carbonylation of 1,5-COD at atmospheric pressure was carried out in a 250 cm<sup>3</sup> round bottom flask equipped with a capillary inlet and outlet connected to a ballast CO tank to keep the carbonylation mixture under one atmosphere of CO pressure. At the end of the reaction when palladium black precipitates, indicating the total consumption of copper(II) salt for the oxidation of Pd(0), the solution is separated by filtration from the precipitated metal and some of the undissolved inorganic salts. The large part of the solvent was distilled off, the residue was treated with ether, or alternatively extracted with pentane or petroleum ether (30–50°C). Combined organic extracts were dried and concentrated until the solvent was removed by distillation at atmospheric pressure and finally under reduced pressure at room temperature. The residue was further purified by



passing it through a neutral alumina column to eliminate the traces of the remaining inorganic salts. The analysis and separation of the organic mixture was done by the analytical and preparative gas chromatography. The identification of the compounds was performed by IR,  $^1\text{H}$  NMR, mass spectra and by the comparison of the GC retention times and spectral data with these of the authentic samples synthesized in the independent ways.

#### Catalytic Carbonylation of 1,5-COD at Room Temperature

The suspension of  $3\text{ cm}^3$  (24 mmol) of 1,5-COD, 1.5 g (11 mmol) of copper(II) chloride, 1.8 g (22 mmol) of sodium acetate and 0.1 g (0.56 mmol) of palladium chloride in  $50\text{ cm}^3$  of methanol was treated with CO over the period of 24 h (CO pressure 417 kPa), according to the procedure just described. After the work-up the organic mixture was analyzed by GC on a 3 m, 0.25 inch column of 10% Carbowax 4000 on non-acid washed 60/80 mesh Chromosorb W operated at  $120^\circ\text{C}$  and 70 kPa. Based on the comparison of the retention times with those of authentic samples, three minor compounds were identified as: 2,5-cyclooctadienyl methyl ether<sup>6</sup> (*VII*) (0.5%; retention time 11.5 min), 4-cyclooctenone<sup>6</sup> (*VI*) (3.5%; retention time 22 min) and methyl 4-cyclooctenecarboxylate<sup>4</sup> (*VIII*) (2.5%; retention times 38 min) (there were some other minor peaks around the peaks of the compounds *V*, *VII*, and *VIII* indicating partial isomerization of the double bond). Three other compounds (retention times 105, 100, and 87 min) were separated by preparative gas chromatography. Relative peak area of these three components with respect to increasing retention time was 18 : 18 : 64. The structure of the compound with the longest retention time was determined as methyl *trans*-8-methoxy-4-cyclooctenecarboxylate (*V*):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ )  $\delta$  5.57 (2 H, m,  $\text{HC}=\text{CH}$ ); 3.57 (3 H, s,  $\text{CO}_2\text{CH}_3$ ); 3.5 (1 H, m,  $\text{CHOCH}_3$ ); 3.29 (3 H, s,  $\text{OCH}_3$ ); 2.8 (1 H, m,  $\text{HCCO}_2\text{CH}_3$ ); 2.2 (4 H, b, allylic); 1.7 (4 H, bm, methylene protons). IR spectrum (neat):  $\tilde{\nu}_{\text{max}}$  1 735, 3 020  $\text{cm}^{-1}$ . Mass spectrum:  $m/z$  198  $\text{M}^+$ . Two other compounds with long retention times (87 and 100 min) have  $^1\text{H}$  NMR spectra very similar to those of the known methyl *trans*-8-methoxy-4-cyclooctenecarboxylate (*V*). Reduction of the carbonylation mixture by hydrogen over 10% palladium on charcoal afforded in addition to cyclooctanone, cyclooctyl methyl ether and methyl *trans*-2-methoxycyclooctanecarboxylate (*XI*) (retention time 80 min):  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta$  3.64 (3 H, s,  $\text{CO}_2\text{CH}_3$ ); 3.59 (1 H, m,  $\text{CHOCH}_3$ ); 3.25 (3 H, s,  $\text{OCH}_3$ ); 2.58 (1 H, m,  $\text{HCCO}_2\text{CH}_3$ ); 1.2–1.8 (8 H, m). IR spectrum (neat):  $\tilde{\nu}_{\text{max}}$  2 970, 1 740, 1 085  $\text{cm}^{-1}$ . All spectral and physical data of *XI* were identical to those of the independently synthesized authentic sample<sup>7</sup>. Accordingly, the two compounds in the original carbonylation mixture prior to the reduction were established as the unsaturated *trans*-methoxy esters *IX* and *X*, that differ in the position of the double bond. The overall yield of the organic material based on the limiting reagent copper(II) salt was 64%, and from that amount 90% corresponds to carbonylated bifunctional esters *V*, *IX*, and *X*.

Catalytic carbonylation of 1,5-COD under the same reaction conditions, but changing the temperature to  $100^\circ\text{C}$ , resulted in the formation of only four compounds, that were separated by preparative GC. Their structures were determined by comparison of the IR and NMR spectra with those of the authentic samples<sup>4,6</sup>. As listed in Table I, run 2, they are: methyl *trans*-8-methoxy-4-cyclooctenecarboxylate (*V*) (91%), 2,5-cyclooctadienyl methyl ether (*VII*) (1%), 4-cyclooctenone (*VI*) (3.5%) and methyl 4-cyclooctenecarboxylate (*VIII*) (3%) (1.5% unknowns). The total yield based on copper(II) salt was 63%. Carbonylation of 1,5-COD under the same experimental conditions, but without oxidant afforded only stoichiometric amount of the same compounds.

Catalytic carbonylation of 1,5-COD in the presence of large amount of oxidant was performed under exactly the same conditions as described above for carbonylation at room temperature and 417 kPa CO pressure, but with disodium tetrachloropalladate instead of palladium chloride as a catalyst, and a much larger amount of the oxidant with respect to catalyst (molar ratio

Cu(II)/Pd(II) = 80; Table I, run 4). The reaction time was 44 hours and after usual work-up four compounds were isolated and identified: methyl *trans*-8-methoxy-4-cyclooctenecarboxylate (IV) (89%), 2,5-cyclooctadienyl methyl ether (VII) (1%), 4-cyclooctenone (VI) (2%) and methyl 4-cyclooctenecarboxylate (VIII) (2%) and 4% of the unknown organic compounds. The total yield of organic compounds was 91% (catalytic turnover number = 36).

Catalytic carbonylation of 1,5-COD at 276 kPa CO pressure (Table II, run 2) afforded after 24 h, the same four compounds V–VIII. The major compound methyl *trans*-8-methoxy-4-cyclooctenecarboxylate (V) (85%) was 5% isomerized giving rise to compounds IX and X (ratio 95 : 2.5 : 2.5).

At 138 kPa CO pressure (Table II, run 3) isomerization of methoxy ester V was not observed. Overall yield for carbonylation at 276 kPa was 77% and at 138 kPa 87% (see also Table II concerning the effect of CO pressure).

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