Journal of Organometallic Chemistry, 255 (1983) 263–268
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands

PALLADIUM-CATALYZED REACTION OF BUTADIENE AND CARBON DIOXIDE

ARNO BEHR and KLAUS-D. JUSZAK

Institut für Technische Chemie und Petrolchemie der Rheinisch-Westfälischen Technischen Hochschule Aachen, Worringer Weg 1, D-5100 Aachen (F.R.G.)

(Received May 12th, 1983)

Summary

The selective syntheses of the δ-lactone 2-ethylidene-6-hepten-5-olide and of the γ-lactone 2-ethyl-2,4-heptadien-4-olide by the palladium-catalyzed reaction of carbon dioxide and butadiene are described. Mechanistic studies showed that the formation of the γ-lactone proceeds by a consecutive reaction via the δ-lactone. The products are accounted for in terms of a reaction path involving an allylic palladium carboxylate complex as a key intermediate.

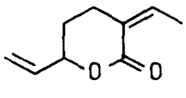
Introduction

In recent years transition metal catalyzed reactions of carbon dioxide aimed at the utilization of CO_2 as building block in organic syntheses have attracted considerable attention. For instance, the telomerization of butadiene with carbon dioxide yielding lactones, acids and esters has been the subject of several investigations [1–5]. Recently we found that CO_2 and butadiene can be converted selectively into the δ-lactone 2-ethylidene-6-hepten-5-olide **1** [6], and this enabled us to study the mechanism of this synthesis and the succeeding reactions of the δ-lactone.

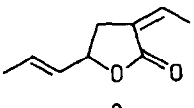
Results and discussion

Synthesis of 2-ethylidene-6-hepten-5-olide (1)

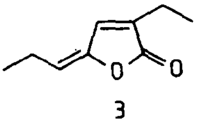
The palladium-catalyzed reaction of carbon dioxide and butadiene yields, among other products, a mixture of the lactones **1–3** and the esters of the 2-ethylidene-4,6-heptadienoic acid **4** and **5** [1–5].



1

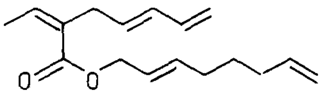


2

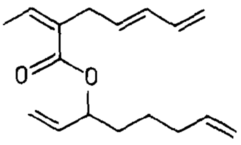


3

0022-328X/83/$03.00



4



5

The δ-lactone **1** was obtained very selectively (> 95%) by reacting butadiene and carbon dioxide in the presence of a palladium catalyst modified by a phosphine ligand of high basicity and with a large cone angle [6]. As palladium catalysts palladiumbis(acetylacetonate), palladiumbis(hexafluoroacetylacetonate), palladiumbis(dibenzylideneacetone) and the dimeric palladiumallylacetate proved to be active. The use of nitriles such as propionitrile, benzonitrile or acetonitrile as solvents proved necessary, and acetonitrile was by far the best. Use of other polar and unpolar solvents such as acetone, hexamethylphosphoric acid triamide, tetrahydrofurane, chloroform, ether or benzene led to drastically decreased activity and selectivity. It seems that the CH-acidity of the solvent plays an important role in the formation of the catalytically active palladium species. However, it is disadvantageous to use solvents of too high CH-acidity, such as nitromethane, which reacts with butadiene to give telomers containing nitro-groups [7,8].

Some typical examples of the reaction of butadiene and carbon dioxide are given in Table 1. The results illustrate the controlling effect of the phosphorus ligand: Phosphines with linear alkyl substituents such as triethylphosphine gave a mixture containing large amounts of the esters **4** and **5**, whereas phosphines with alkyl groups branched at the α-carbon atom, such as tricyclohexylphosphine or triisopropylphosphine, yielded selectively the δ-lactone **1**. Use of comparable chelating ligands, such as 1,2-bis(dicyclohexylphosphino)ethane (dcpe), led to decreased selectivity towards formation **1**.

When a mononuclear palladium species such as $Pd(acac)_2$ is used as the catalyst precursor the optimum ratio of palladium to added phosphine amounts about 1/3, whereas dinuclear species such as $[Pd(C_3H_5)(OAc)]_2$ require a ratio of 1/1.5 (Table 2).

The isolation of the δ-lactone was achieved either by a distillation at 4 μbar or by steam distillation at normal pressure. In this way lactone **1** was obtained about 99% pure.

TABLE 1

VARIATION OF THE PHOSPHORUS LIGAND[a]

Ligand	Conversion of butadiene (%)	Yield (Sel.)[b] (%)			
		1	**2**	**4**	**5**
PEt_3	31	4 (24.2)	0.3 (1.8)	6.9 (41.8)	5.3 (32.1)
PBu^n_3	27	3 (16.9)	0.1 (0.6)	8.6 (49.1)	5.9 (33.4)
PCy_3	44	39 (96.2)	0.1 (0.2)	0.9 (2.2)	0.5 (1.2)
PPr^i_3	44	40 (96.2)	0.3 (0.7)	0.8 (1.9)	0.5 (1.2)
dcpe	19	11 (69.6)	0.1 (0.6)	2.8 (17.7)	1.9 (12.0)

[a] 0.16 mmol $Pd(acac)_2$; 0.48 mmol phosphorus ligand; solvent: CH_3CN; T 90°C, t 15 h. [b] Sel. = selectivity.

TABLE 2

VARIATION OF THE PALLADIUM/PHOSPHORUS RATIO[a]

Pd/P	Yield of δ-lactone 1 (%)	
	$Pd(acac)_2$	$[Pd(C_3H_5)(OAc)]_2$
1/1	10	16
1/1.5	18	40
1/2	36	36
1/2.5	39	28
1/3	40	23
1/4	39	–
1/6	24	–

[a] 0.16 mmol Pd complex; x mmol PPr^i_3; other conditions as listed in Table 1.

Syntheses of 2-ethyl-2,4-heptadien-4-olide 3

The δ-lactone **1** can be isomerized selectively to the γ-lactone **3** by using the same catalysts as for the synthesis of the δ-lactone **1**. Whereas the synthesis of **1** is performed at low palladium concentrations, e.g. at ratios of butadiene to palladium as 1000/1 until 5000/1, the isomerization of **1** to **3** proceeds very fast at much higher catalyst concentrations. The lactone **3** can also directly be synthesized from butadiene and CO_2 using butadiene/palladium ratios of 20/1. A typical example is given in Fig. 1: The δ-lactone **1** was reacted in the presence of the catalyst system $Pd(acac)_2/PPr^i_3$ at a ratio of lactone to palladium of 20/1. After about 2 h the δ-lactone **1** was isomerized almost quantitatively to the thermodynamically more stable γ-lactone **2**. After a further 8 h the non-conjugated γ-lactone **2** had isomerized to the most stable conjugated γ-lactone **3**, which was present in two stereoisomeric forms; these could be separated by GLC analysis and proved to have the same mass spectra.

After distillation at about 4 μbar the lactone **3** was obtained 97% pure. Prior to the distillation of the pure γ-lactone **3** it is advantageous to remove the palladium

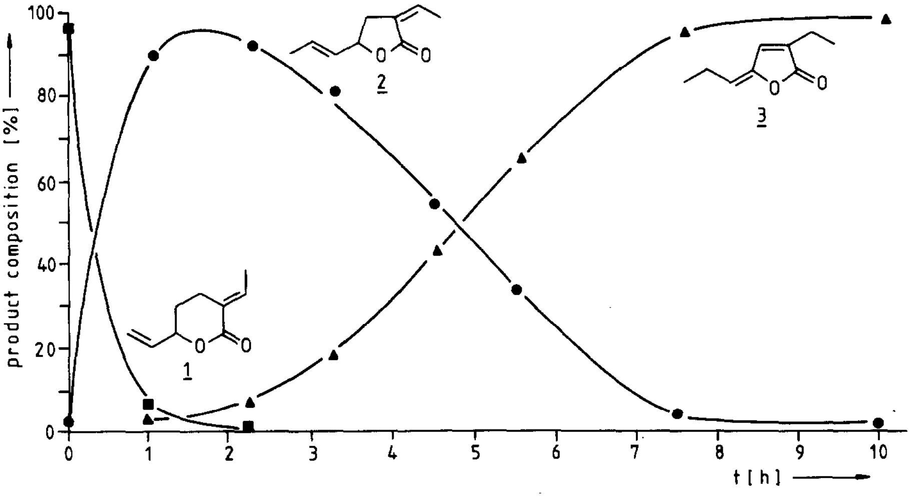


Fig. 1. Isomerization of the δ-lactone 1.

catalyst; this can be done by column chromatography using silicagel and a mixture of cyclohexane and ethylacetate.

Isolation of the intermediate lactone **2** in comparable purities by distillation was not possible. A product mixture obtained after a 90 min isomerization of **1** (compare Fig. 1) contained both **1** and the conjugated lactone **3**.

Conversions of the lactones with butadiene

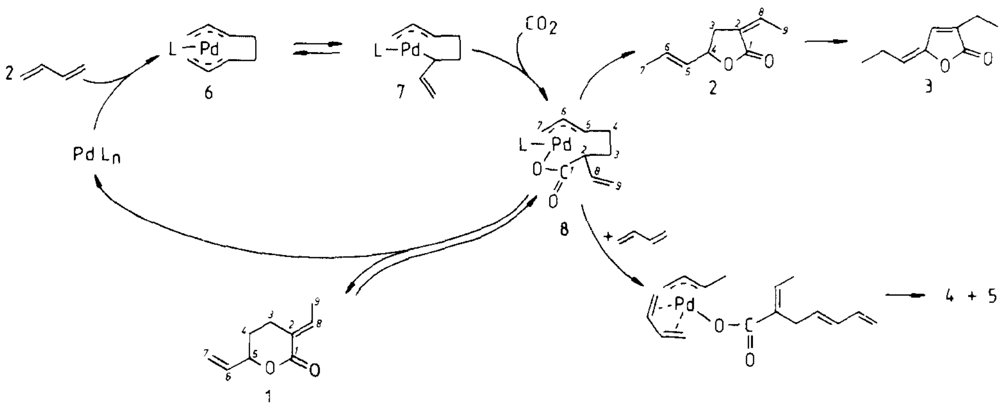
The reaction of the δ-lactone **1** in presence of the catalyst system Pd(acac)$_2$/PPr$^i_3$ and butadiene yielded a mixture of the γ-lactone **2** and the esters **4** and **5**. A quantitative study by a GLC analysis using an internal standard however proved that two thirds of the reagent **1** decomposed into acids or octatrienes. The reaction of the γ-lactone **3** and butadiene yielded only decomposition products and no esters were obtained. These findings support the view that the formation of the esters proceeds via the intermediate δ-lactone **1**.

Reaction mechanism

To account for the formation of **1**, its isomerization to **2** and **3**, and its reaction with butadiene to give the esters **4** and **5**, we propose the following mechanism:

Phosphine-palladium complexes PdL$_n$ react with butadiene to give the bis-η^3-allyl complex **6**, which is in equilibrium with the corresponding η^1-η^3-intermediate **7**. In this equilibrium basic phosphines favour the formation of **7**. Here the influence of basic phosphines, shown in Table 1, can be understood. Intermediates similar to **7** were discussed by Wilke and Jolly in their elegant work on butadiene oligomerization and telomerization by nickel [9] and palladium [10] complexes.

SCHEME 1



After insertion of CO$_2$ into the palladium–carbon σ-bond of the intermediate **7** complex **8** is formed (Scheme 1). Complex **8** has several possibilities for further reactions:

(a) Cyclization and hydrogen-transfer, with formation of the ethylidene group, to give the δ-lactone **1**.

(b) Cyclization to a five-membered ring by attack of the oxygen bonded to the palladium on carbon atom number 4 to give lactone **2**, which can isomerize by palladium-catalyzed hydrogen transfer to give lactone **3**.

(c) Reaction with two further molecules of butadiene to give the octadienyl esters **4** and **5**.

It is noteworthy that the δ-lactone **1** can also become coordinated to palladium through an oxidative addition to form the intermediate **8**. Through this ring opening the δ-lactone gives the same products as are formed from butadiene and carbon dioxide.

Experimental

The reactions were carried out in 75 ml steel autoclaves or in glass autoclaves fitted with a manometer, a valve and a magnetic stirrer. All experiments were performed under argon which was dried with a 4 Å mol sieve. The solvents were dried and distilled under argon. The analysis of the product mixtures was by GLC using a 100 m OV 101 glass capillary and a temperature program from 100 to 230°C. The identification of the products was by IR, ^1H and ^{13}C NMR spectroscopy and GLC/MS.

Synthesis of lactone 1

A mixture of 14 g (0.26 mol) butadiene, 15 g (0.34 mol) carbon dioxide, 0.05 g (0.16 mmol) $Pd(acac)_2$, 0.08 g (0.48 mmol) PPr^i_3 and 30 ml acetonitrile was heated in a steel autoclave for 15 h at 90°C. After removal of unreacted CO_2 and butadiene, GLC analysis revealed a 40% yield of lactone **1**. Distillation of the crude oil gave 7.54 g (50 mmol) of lactone **1** of 99% purity.

Syntheses of lactone 3

(a) A mixture of 10 g (66 mmol) lactone **1**, 1 g (3.2 mmol) $Pd(acac)_2$, 1.6 g (9.8 mmol) PPr^i_3 and 200 ml acetonitrile was stirred in a glass autoclave for 15 h at 90°C. After cooling the solvent was removed in vacuo. GLC analysis of the crude oil revealed a 90% yield of lactone **3**. Distillation gave lactone **3** of 97% purity.

(b) A mixture of 14.8 g (0.27 mol) butadiene, 13.8 g (0.30 mol) carbon dioxide, 0.95 g (3.2 mmol) $Pd(acac)_2$ and 1.5 g (9.4 mmol) PPr^i_3 and 30 ml acetonitrile was heated in a steel autoclave for 15 h at 90°C. After cooling the solution was concentrated and analyzed by GLC. Lactone **3** was formed in 17% yield with a selectivity of 97%.

Reaction of lactones with butadiene

A solution of 1 g (6.6 mmol) lactone (**1** or **3**), 0.2 g (0.66 mmol) $Pd(acac)_2$ and 0.33 g (2.06 mmol) PPr^i_3 in 20 ml acetonitrile was treated with 5.4 g (100 mmol) butadiene, and the mixture was heated for 15 h at 90°C. Analysis was by GLC.

Acknowledgements

Financial support from the Deutsche Forschungsgemeinschaft is gratefully acknowledged. The authors wish to express their gratitude to Professor W. Keim for helpful discussions and suggestions.

References

1 Y. Sasaki, Y. Inoue and H. Hashimoto, J. Chem. Soc., Chem. Commun., (1976) 605.
2 Y. Inoue, Y. Sasaki and H. Hashimoto, Bull. Chem. Soc. Jpn., 51 (1978) 2375.
3 A. Musco, C. Perego and V. Tartiari, Inorg. Chim. Acta, 28 (1978) 147.

4 A. Musco, J. Chem. Soc., Perkin Trans. I, (1980) 693.
5 J.A. Daniels, Eur. Pat. Appl. EP 50.445 (28.4.1982).
6 A. Behr, K.-D. Juszak and W. Keim, Synthesis, 7 (1983) 574.
7 T. Mitsuyasu, M. Hara and J. Tsuji, Chem. Commun. (1971) 345.
8 T. Mitsuyasu and J. Tsuji, Tetrahedron, 30 (1974) 831.
9 G. Wilke, B. Bogdanović, P. Hardt, P. Heimbach, W. Keim, M. Kröner, W. Oberkirch, K. Tanaka, E. Steinrücke, D. Walter and H. Zimmermann, Angew. Chem., 78 (1966) 157.
10 A. Döhring and P.W. Jolly, Z. Naturforsch. B, 36 (1981) 1198.