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Preliminary Communication

Carbonylation of organic allyl moieties

IV *. Unexpected formation of cyclic esters from the carbonylation of alkoxyoctadienes in the presence of rhodium catalysts **

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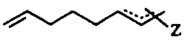
Abstract

Mixtures of 1-methoxy- and 3-methoxy-octadienes are readily converted into epimeric 2-vinylcyclopentylacetates, under moderate pressures of CO in the presence of rhodium chloride and hydrochloric acid.

We recently reported that the selective carbonylation of alkoxyoctadienes, **1a**, to alkyl nona-3,8-dienoates, **2**, can be performed in the presence of a bifunctional Pd–HCl catalyst [1]. Examination of the product selectivity and further studies [2] show that the reaction occurs through the intermediacy of an allylpalladium complex. Structure **3** is suggested for this intermediate which is stabilized by coordination of the terminal double bond. It is noteworthy that no interaction occurs between this double bond and the allyl ligand, thus preventing any C–C coupling between the ligands, despite the numerous reports of Oppolzer *et al.* [3] on the Pd^0-catalyzed cyclization of dimethylallyl(4-acetoxy-2-butenyl)malonate into 2-vinyl-methylenecyclopentane derivatives.



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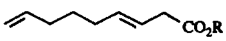
1a-1, Z = 1-OMe
1a-2, Z = 3-OMe
1b-1, Z = OAc
1c-1, Z = OCO$_2$Me



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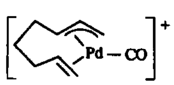
2a, R = Me



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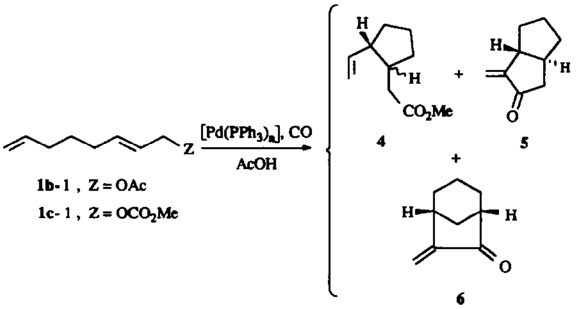
Moreover, Yamamoto *et al.* observed the cyclization–carbonylation of the acetate, **1b**-1, and carbonate, **1c**-1, in acetic acid solution (reaction 1) [4]. The cyclization process may also be favoured with other transition metal centres. For instance, a process patented by National Distillers [5] claims the use of nickel, cobalt and iron in the carbonylation of alkoxyoctadienes and reports the formation of the cyclic compounds **7**, and **8**, albeit in low yields.



The cyclization–carbonylation of a mixture of the ethers **1a**-1, **1a**-2 (isomer ratio 92:8) occurs with rhodium only, as [Rh$_2$(CO)$_4$Cl$_2$] in toluene under CO (30 bar), but with a low conversion (Table 1). Addition of 5 eq. HCl (generated *in situ* from the reaction of acetyl chloride with methanol) increased dramatically the conversion of **1a**-1, **1a**-2. In the low-boiling cut (b.p. 20 < 60°C) the linear ester **2a** and only two additional compounds were detected (capillary GC) in addition to the starting ethers. These compounds could be separated (20% AgNO$_3$ impregnated silica gel) and were stable under the reaction conditions used. They were identified as **7** and **8** by ^{1}H and ^{13}C NMR spectroscopy.

In order to improve the yields of **7**, **8**, other reaction conditions and other rhodium compounds have been investigated. RhCl$_3 \cdot$3H$_2$O provides better results, which can be explained by the formation of HCl in the course of the conversion of the RhII precursor into the RhI active species. The reaction also occurs without added HCl. The blank experiment shows a high con-

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* For Part III, see ref. 1.

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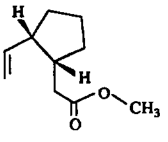

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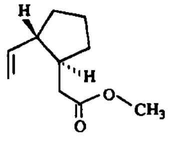

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version of **1a**-1, **1a**-2 to high boiling new ethers, a process under investigation that should be similar to the one reported by Poirier during his study of the reaction of butadiene and alcohols leading to higher telomers [6]. The absence of 1-methylene-2-vinylcyclopentane that could be produced in the cyclization process of **1a**-1, **1a**-2 and which is observed when reaction (1) is carried out without CO is noteworthy [4].

The reaction is slow for a carbonylation process using rhodium, and requires a rhodium-to-substrate ratio of 50 to be effective. Inspection of Table 1 shows that a large excess of HCl does not decrease activity. However, the reaction does not proceed in the presence of an excess of chloride ion alone, presumably because of the formation of kinetically inert anion $[Rh(CO)_2Cl_2]^-$. No positive effect of non-coordinating anions such as BF_4^- is observed.

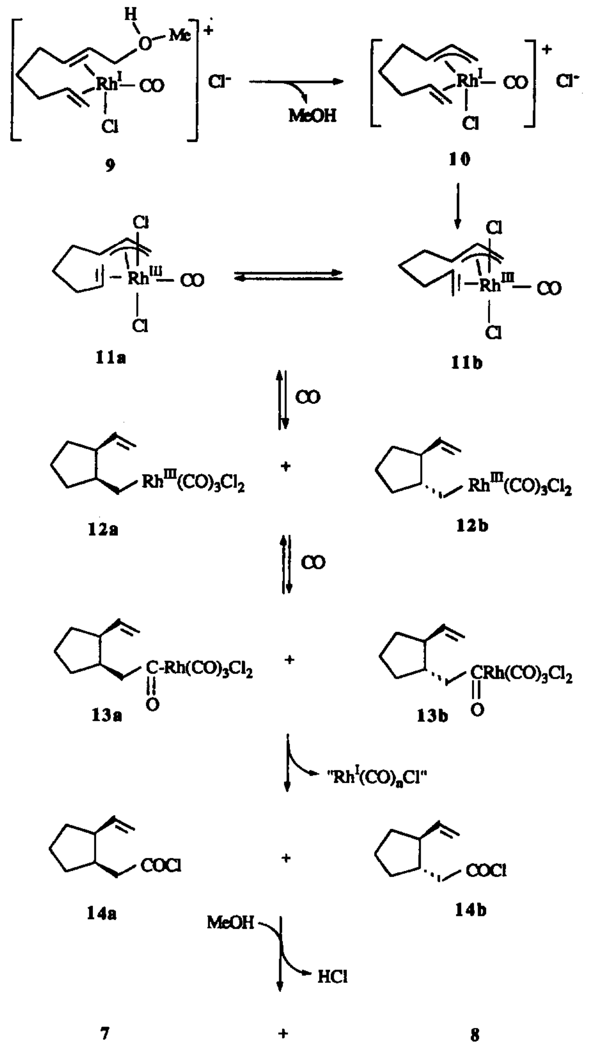
High selectivity for **7** and **8** is strongly dependent on the carbon monoxide pressure. Stoichiometric carbonylation to **7** occurs with $[Rh_2(CO)_4Cl_2]$ without added CO. Increase in CO pressure leads to larger amounts of the linear ester, **2a**. Surprisingly, the selectivity for cyclic products increases with temperature. The best compromise conditions were found to be 100°C and 15 bar CO.

The negative effect of an excess of CO is further supported by the effect of phosphorus donors. Addition of 1 eq. of PBu^n_3, PPh_3 or $P(OPh)_3$ favours the formation of **2a** (50, 65 or 68% selectivity, respectively) at the expense of **7** (15, 17.5 or 14%, respectively) and **8** (35, 17.5 or 18%, respectively).

Toluene and higher boiling aromatic hydrocarbons are the best solvents. The reaction is inhibited by good donor solvents such as dimethylacetamide (DMAC). With acetic acid, the ester yield is low but the *cis*-vinyl ester is formed preferentially. This should be compared with the observation of Yamamoto and Mikami who claim that acetic acid plays an important role in the cyclization-carbonylation process (reaction 1) [4]. Indeed the acetate ligand may have a specific function,

TABLE 1. Carbonylation of the mixture of allylethers **1a**-1, **1a**-2 (92 : 8) in the presence of rhodium catalysts (reaction conditions: [Rh] = 1 mmol; [Substrates] = 50 mmol; Solvent: 8 ml; Stirring: 500 r.p.m.)

Run	Solvent	Catalyst precursor	Additive (mmol)	Time (h)	Temperature (°C)	Pressure CO (bar)	Conversion (%)	Ester yield (%)	Ester selectivities %		
									2a	**7**	**8**
1	PhMe	$[Rh_2(CO)_4Cl_2]$	–	24	100	30	20	0	0	0	0
2	PhMe	$[Rh_2(CO)_4Cl_2]$	HCl(5)	24	100	30	36	19	25	38	37
3	PhMe	$RhCl_3 \cdot 3H_2O$	–	24	100	15	43	21	14	48	37
4	PhMe	$RhCl_3 \cdot 3H_2O$	–	4	100	15	30	11	14	52	34
5	PhMe	$RhCl_3 \cdot 3H_2O$	HCl(5)	24	100	15	86	48	6	52	42
6	PhMe	$RhCl_3 \cdot 3H_2O$	HCl(10)	24	100	15	96	56	3	54	43
7	PhMe	$RhCl_3 \cdot 3H_2O$	HCl(10)	4	100	15	84	46	4	55	41
8	PhMe	$RhCl_3 \cdot 3H_2O$	Bu_4NCl(5)	24	100	15	0	–	–	–	–
9	PhMe	$RhCl_3 \cdot 3H_2O$	HCl(5)	24	100	0	80	0	–	–	–
10	PhMe	$[Rh_2(CO)_4Cl_2]$	HCl(5)	24	100	0	90	2	–	–	–
11	PhMe	$RhCl_3 \cdot 3H_2O$	HCl(5)	24	100	30	79	49	24	38	38
12	PhMe	$RhCl_3 \cdot 3H_2O$	HCl(5)	24	100	5	81	41	2	66	32
13	PhMe	$RhCl_3 \cdot 3H_2O$	HCl(5)	24	100	45	75	51	37	30	33
14	PhMe	$RhCl_3 \cdot 3H_2O$	HCl(5)	24	80	15	60	32	15	43	42
15	PhMe	$RhCl_3 \cdot 3H_2O$	HCl(5)	24	90	15	81	46	11	47	42
16	PhMe	$RhCl_3 \cdot 3H_2O$	HCl(5)	24	120	15	71	39	4	56	40
17	MeCN	$RhCl_3 \cdot 3H_2O$	HCl(3)	24	100	15	21	5	10	40	40
18	DMAC	$RhCl_3 \cdot 3H_2O$	HCl(5)	24	100	15	0	–	–	–	–
19	MeOH	$RhCl_3 \cdot 3H_2O$	HCl(5)	24	100	15	25	8	49	21	30
20	AcOH	$RhCl_3 \cdot 3H_2O$	–	24	100	15	54	12	5	84	11
21	AcOH	$RhCl_3 \cdot 3H_2O$	–	4	100	15	42	6	5	62	33
22	AcOH	$RhCl_3 \cdot 3H_2O$	HCl(10)	4	100	15	87	25	4	64	32
23	PhMe	$[Rh_2(OAc)_4]$	HCl(5)	24	100	15	78	39	0	59	41
24	PhMe	$[Rh_2(OAc)_4]$	HBF_4(1)	24	100	15	28	0	0	0	0
25	PhMe	$[Rh_2(OAc)_4]$	–	24	100	15	20	0	0	0	0
26	PhMe	$[Rh_2(OAc)_4]$	–	4	100	15	7	0	0	0	0
27	AcOH	$[Rh_2(OAc)_4]$	–	4	100	15	5	0	0	0	0
28	AcOH	$[Rh_2(OAc)_4]$	HCl(10)	4	100	15	65	26	2	64	34



Scheme 1.

as suggested by the use of $[Rh_2(OAc)_4]$ which catalyzes the formation of **7** and **8** only.

On the basis of these results, we suggest that, as in the case of palladium, HCl is necessary for the protonation of the ether oxygen, thus providing the driving force for the C-O bond breaking process which leads an η^3-allyl intermediate **10** similar to **3** (Scheme 1). Since BF_4^- apparently exercises no stabilizing effect, **10** rearranges into the neutral complexes **11**. Two conformations are available for **11** which will dictate the formation of **7** or **8**. Dreiding models show that there is no preferred conformation for the intermediate **11** if one assumes a *trans* configuration of the chlorides. Coupling of allyl and vinyl ligands has a precedent in the case of rhodium chemistry [7] and provides the alkyl rhodium(III) species **12** which undergoes migratory CO insertion leading to **13**. The cyclocarbonylation reaction does not occur without chloride when using $[Rh_2(OAc)_4]$. We therefore propose the formation of acid chloride **14**, which is more reasonable in an acidic medium. A similar reaction pathway has been observed with palladium [2,8]. Moreover, generation of acetyl iodide from acylrhodium(III) has been proposed [9], and formation of carboxylic acid halides has been recently demonstrated for d^6 Pt^{IV} and Pd^{IV} complexes [10].

Further work is in progress to understand the origin of the differing behaviour of palladium and rhodium catalysts, and to extend the scope of this cyclization–carbonylation process.

Acknowledgements

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