Novel Palladium-catalysed Cyclodimerization of Butadiene in the Presence of Carbon Dioxide and Water

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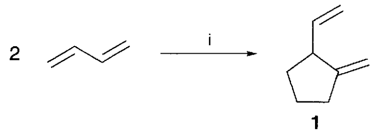
The first example is reported of a palladium-catalysed cyclodimerization of butadiene to 2-vinylmethylenecyclopentane occurring in catalytic turnovers and yields far superior to the nickel-based systems, which are claimed to be specific for cyclodimerization reactions.

During studies aimed at developing an understanding of the factors affecting the telomerization of butadiene with water in the presence of CO_2, we unexpectedly found that, under certain conditions, 2-vinylmethylenecyclopentane **1** can be formed in high yield and selectivity, according to Scheme 1. This result appears rather unusual in palladium–diene chemistry where, on the other hand, it is well known that CO_2 displays an activating effect both in butadiene dimerization to linear octatrienes[1] and in its telomerization with water to afford octa-2,7-dien-1-ol and octa-1,7-dien-3-ol.[2] Besides these results, and despite a variety of examples of catalysed palladium–ene reactions,[3] there have been as yet no reports of palladium-catalysed cyclodimerization of butadiene. Moreover, palladium is reported to be ineffective towards cyclodimerization of 1,3-dienes,[4] where nickel-based complexes are the catalysts of choice.[5]

However, the presence of phosphorus-based ligands such as triaryl phosphines allows the isolation of **1** in moderate to good yield and selectivity, provided that CO_2 and H_2O are present. Table 1 reports the results obtained with Ph_3P and (*o*-tolyl)$_3$P as ligands.† Yields as high as 52% were obtained with (*o*-tolyl)$_3$P at 90 °C. Under these conditions, a catalytic efficiency corresponding to 420 mol per mol of palladium was achieved. When nickel was used as the catalyst, the literature reports catalytic efficiencies not higher than 80 mol per mol of nickel.[5]



Scheme 1 *Reagents and conditions*: i, $Pd(O)L_n$, CO_2,H_2O; L = Ph_3P, (*o*-tolyl)$_3$P

Table 1 Effect of several variables on the palladium-catalysed cyclodimerization of butadiene[a]

Run	L[b]	*t*/h	*T*/°C	Products Yield (%) (Selectivity (%)) **1**	**4 + 5**	**2 + 3**
1	Ph_3P	6	70	2 (8)	4 (17)	18 (75)
2	Ph_3P	6	90	15 (21)	13 (19)	42 (60)
3	Ph_3P	6	110	25 (40)	21 (33)	17 (27)
4	Ph_3P	3	90	5 (12)	7 (17)	30 (71)
5	Ph_3P	16	90	26 (37)	15 (21)	29 (42)
6	Ph_3P	72	90	39 (56)	16 (23)	2 (3)[c]
7	(*o*-tolyl)$_3$P	6	70	1 (5)	2 (2)	27 (93)
8	(*o*-tolyl)$_3$P	6	90	10 (16)	6 (10)	45 (74)
9	(*o*-tolyl)$_3$P	6	110	36 (58)	15 (27)	9 (15)
10	(*o*-tolyl)$_3$P	3	90	5 (9)	4 (9)	42 (82)
11	(*o*-tolyl)$_3$P	16	90	27 (43)	10 (7)	25 (40)
12	(*o*-tolyl)$_3$P	72	90	52 (87)	6 (10)	2 (3)

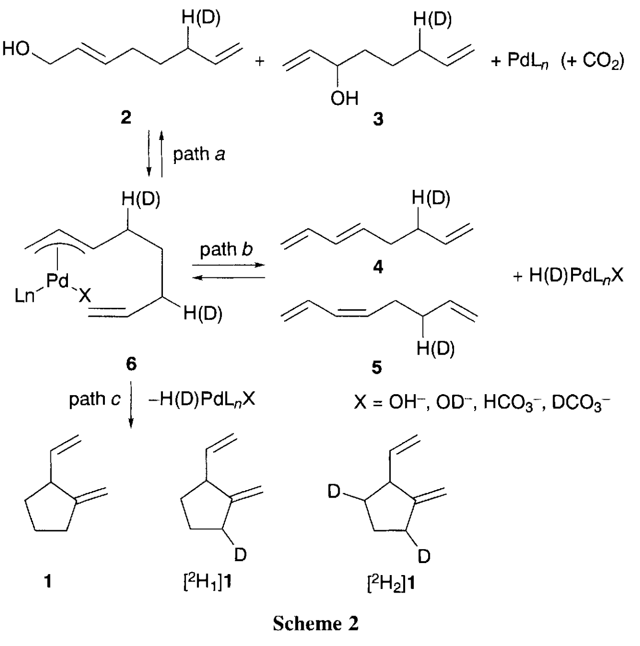
[a] See footnote for experimental conditions. [b] Molar ratio $Ph_3P:Pd = 5:1$, (*o*-tolyl)$_3$P : Pd = 12 : 1. [c] 13% of ether byproducts $(C_8H_{13})_2O$, formally obtained by addition of **2** and/or **3** to **4** and/or **5**, were observed.

On comparing the results obtained with the two ligands, it can be seen that in the former case a relatively low ligand : palladium ratio is required to increase selectivity to **1**, whereas a high ratio is needed in the latter case (5 : 1 and 12 : 1, respectively). The deposition of metallic palladium at low P : Pd molar ratios when using (*o*-toly)$_3$P suggests that in this case the oxidation of the coordinated ligand to the corresponding phosphine oxide by CO_2 occurs extensively.[6]

At lower temperatures octa-2,7-dien-1-ol **2** and octa-1,7-dien-3-ol **3** are the major products (runs 1 and 7). Increasing the reaction temperature lowers the selectivity towards alcohols, a mixture of **1** and *E*- and *Z*-octa-1,3,7-triene (**4** and **5**, respectively) being formed (runs 1–3 and 7–9). Moreover, the use of (*o*-tolyl)$_3$P as ligand causes an increase in the selectivity towards **1**.

The change in product distribution with time (runs 2, 4–6 and 8, 10–12) indicates good selectivity towards **1** for long reaction times (run 6 and 12). At relatively short reaction times, **2** and **3** appear to be the primary products, which are subsequently converted to a mixture of **1**, **4** and **5**, with **1** eventually being obtained in good selectivity (run 12).

The same intermediate **6** (Scheme 2) should be involved in alcohol formation[7] (path *a*), triene formation (path *b*) and palladium–ene reaction[3] (path *c*). This hypothesis is supported by experiments carried out using D_2O with (*o*-tolyl)$_3$P as ligand on palladium, monodeuteriated $[^2H_1]$**1** and bisdeuteriated $[^2H_2]$**1** were obtained in a 60 : 40 molar ratio. The presence of the bisdeuteriated product is indicative of the fact that monodeuteriated trienes **4** and **5** can react with the palladium deuteride formed according to path *b*, to give rise to bis-



Scheme 2

deuteriated **6** from which $[^2H_2]$**1** is obtained. Compound $[^2H_1]$**1** arises through path *c* from monodeuteriated **6** formed either directly from butadiene and D_2O[7] or from monodeuteriated alcohols **2** and **3** through reversible path *a*.

Further work is in progress to clarify the mechanistic aspect of the reaction, and to investigate the effect of CO_2, which appears to favour both the addition of palladium hydrides to trienes and the reversibility of path *a*.

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Footnote

† Typical procedure: to a deaerated mixture of acetonitrile (11 ml) and water (2.8 ml) was added the phosphorus ligand [0.37 mmol PPh_3 or 0.89 mmol $(o\text{-tolyl})_3P$]. The resulting solution was siphoned into a 100 ml autoclave containing 0.074 mmol of $Pd(acac)_2$ under an inert atmosphere. Butadiene (1200 ml, 0.059 mol) was charged into the autoclave precooled at −30 °C. After raising the temperature to 25 °C, the apparatus was pressurized with 3 atm CO_2 and put into a thermostated bath (±1 °C) and stirred magnetically for the given time (Table 1). Finally, CO_2 and the excess of butadiene were vented, the mixture diluted with CH_2Cl_2, and the solution analysed by GC after the addition of *n*-dodecane as internal standard.

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