## The Palladium Complex-catalysed Synthesis of Octadienols from Butadiene and Water

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Summary Butadiene and water react in the presence of palladium complex catalysts and carbon dioxide to give high yields of octadienols.

THE palladium-catalysed reaction of butadiene with alcohols,<sup>1</sup> phenols, <sup>2</sup> and carboxylic acids<sup>1</sup> has been reported to yield octadienylated ethers and esters. The corresponding reaction with water has not been reported: the neat reaction between butadiene and water in the presence of palladium complexes is very slow and yields only octatrienes. When the reaction was run in the presence of solvents such as t-butyl alcohol, acetone, or acetonitrile, the reaction was still slow giving octa-1,3,7-triene as the major product, with a small amount of octadienols. We now report that the reaction of butadiene with water yields octa-2,7-dien-1-ol (I) as the major product when the palladium complex-catalysed reaction is carried out in the presence of carbon dioxide.



Table 1 shows the high yields of octadienols obtained in the carbon dioxide-assisted reaction in various solvents

## TABLE 1

Synthesis of octadienols from butadiene and watera

Temp.	Time	Products		(% yield)	
(°)	(h)	(I)	(II)	(III)	(IV)
85	4	65	19	4	4
90	<b>2</b>	69	7	13	10
<b>82</b>	3	56	4	6	6
	Temp. (°) 85 90 82	Temp. Time   (°) (h)   85 4   90 2   82 3	$\begin{array}{cccccccccccccccccccccccccccccccccccc$	Temp. Time Products   (°) (h) (I) (II)   85 4 65 19   90 2 69 7   82 3 56 4	$\begin{array}{cccccccccccccccccccccccccccccccccccc$

<sup>a</sup> All runs with 1.0 mol butadiene, 0.5 mol CO<sub>2</sub>, 2.0 mol H<sub>2</sub>O, 2mmol Pd(acac)<sub>2</sub>, and 6 mmol PPh<sub>3</sub>.

using catalysts formed in situ. Preformed palladium complexes such as (PPh<sub>3</sub>)<sub>4</sub>Pd and (PPh<sub>3</sub>)<sub>2</sub>PdCO<sub>3</sub> are also effective catalysts for the reaction. Carbon dioxide also assists this reaction at much lower levels. For example, when the t-butyl alcohol run (Table 1) was repeated using only 0.023 mol CO<sub>2</sub>, 43% (I), 7% (II), and 13% (III) were produced.

The structures of octa-2,7-dien-1-ol (I) and octa-1,7-dien-3-ol (II) were established by n.m.r., i.r., and elemental analyses.

Striking differences were noted between reactions run in t-butyl alcohol, acetone, and acetonitrile when higher triphenylphosphine: palladium acetylacetonate ratios were used for the in situ formation of the catalyst (Table 2).

## TABLE 2

## Octadienols: effects of high P: Pd ratios in various solvents

			Products (% yield)			
Solvent			(I)	(II)	(III)	
t-Butyl alcohol	••			traces		
Acetone	••		18	16	13	
Acetonitrile	••	••	<b>42</b>	5	2	

Conditions: Solvent 180 cc, butadiene 1.1 mol. CO, 0.16 mol. H<sub>2</sub>O 0.9 mol, Pd(acac)<sub>2</sub> 2.3 mmol, PPh<sub>3</sub> 13.0 mmol, 75° for 4 h.

A preliminary rationale of these differences is based on the ligand properties of the solvents. They are all weak ligands compared to triphenylphosphine but the stronger ones, acetonitrile and acetone, can by mass action compete with phosphine for the palladium. In effect, this lowers the "effective concentration" of the triphenylphosphine. Of the three solvents t-butyl alcohol is the weakest ligand, therefore the triphenylphosphine exerts its maximum "effective concentration" and the reaction rate is the slowest.

Octadienol can also readily be prepared in dioxan, dimethylacetamide, and pyridine using carbon dioxide. The reaction of water with butadiene in the absence of carbon dioxide has been examined in all of the solvents mentioned as well as in dimethyl sulphoxide and tetrahydrofuran. In no case does the rate approach that of the carbon dioxide-assisted reactions.

The role of carbon dioxide in this sequence is not clear. One possibility is the intermediacy of carbonate esters, although the rapid rate of reaction even at low levels of carbon dioxide make this unlikely. Bis(octa-2,7-dien-1-yl) carbonate was synthesized and could be observed by g.l.c. analysis. The bis-carbonate was not found in any significant quantity in any of the reaction mixtures, although its rate of hydrolysis under normal reaction conditions was slow enough that a build-up would have occurred during the synthesis of octadienol. A half ester is a possible intermediate which would not be observed by g.l.c. A recent report<sup>3</sup> regarding a novel effect of carbon dioxide on butadiene dimerization in the presence of transition-metal catalysts suggests that the effect could be directly on the catalyst. The fact that low levels of carbon dioxide enhance the reaction rate supports this possibility.

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