

## THE PALLADIUM-CATALYSED REACTION OF BUTADIENE WITH ACETIC ACID IN THE PRESENCE OF PHOSPHITES\*

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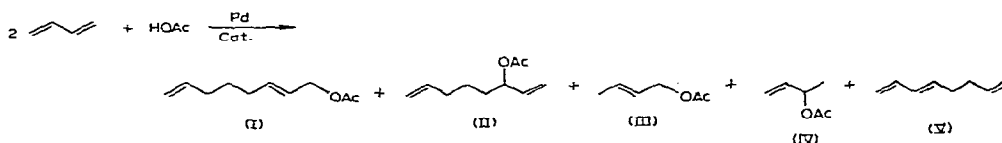
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### SUMMARY

The palladium-catalysed co-oligomerisation of butadiene with acetic acid in the presence of various phosphites has been studied. It has been found that the use of *ortho*-alkyl or *ortho*-aryl substituted triaryl phosphites as ligands enables almost quantitative yields of acetoxyoctadienes to be obtained. Furthermore a significant degree of control of isomer ratios can be achieved.

### INTRODUCTION

Recently a number of publications and patents dealing with the palladium-catalysed reaction of butadiene and acetic acid have appeared<sup>1-4</sup>. In general the reaction leads to the formation of the acetoxyoctadienes (I) and (II), but these are accompanied by the butenyl acetates (III) and (IV) and 1,3,7-octatriene (V). The yield of (I) and (II) is often low and the ratio of (I)/(II) is generally of the order 2-3/1.



An improvement of the general procedure has been described<sup>3</sup> in which the reaction was carried out with a palladium acetylacetonate catalyst to give largely (I). A phosphine (PPh<sub>3</sub>) or phosphite [EtC(CH<sub>2</sub>O)<sub>3</sub>P] was necessary as ligand, and the reaction was strongly promoted by using molar quantities of tertiary amines such as Me<sub>2</sub>NCH<sub>2</sub>CH<sub>2</sub>OH. High yields of (I) + (II) were claimed, and some control of the ratio of (I)/(II) was possible. It was further demonstrated that (II) was formed from (I) by a palladium-catalysed isomerisation.

We now report that when the reaction of butadiene with acetic acid is carried out in the presence of certain *ortho*-substituted triaryl phosphites, quantitative or almost quantitative yields of (I) + (II) are obtained. Furthermore, extremely high selectivity for the formation of (I) under very mild conditions is possible.

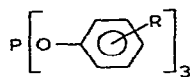
\* Dedicated to Dr. Wily Manchot on the occasion of his 65th birthday.

## RESULTS AND DISCUSSION

The effects of various ligands upon the reaction between butadiene and acetic acid are shown in Table 1. From the results it can be seen that replacement of an *ortho*-hydrogen on each phenyl ring in triphenyl phosphite by an alkyl or an aryl group causes a large increase in product yield, and an increase in the ratio of (I)/(II). Comparing the results obtained at 90° with *para*-C<sub>6</sub>H<sub>5</sub>, -CH<sub>3</sub>, -Cl and -F substituents, it is clear that an electronic effect is operative, with activating groups favouring the reaction. However, it is also evident from a comparison of the results obtained with *o*- and *p*-methyl and -phenyl derivatives that a steric effect is also important. It should be noted that the acceptor ability of the *o*- and *p*-phenyl (and presumably the *o*- and *p*-methyl) triphenyl phosphites has been shown to be identical by measurement of the CO stretching frequencies in the complexes Ni(CO)<sub>2</sub>(L)<sub>2</sub>.<sup>5</sup>

TABLE 1

REACTION<sup>a</sup> OF BUTADIENE WITH ACETIC ACID, CATALYSED BY Pd(Acac)<sub>2</sub> + LIGAND

Ligand 	Reaction temp. 90°		Reaction temp. 50°	
	Yield of (I) + (II)	Ratio (I)/(II)	Yield of (I) + (II)	Ratio (I)/(II)
H	15	3.8/1	5	11.0/1
<i>o</i> -CH <sub>3</sub>	87	7.0/1	97	12.7/1
<i>o</i> -C <sub>6</sub> H <sub>5</sub>	78	14.6/1	93	12.0/1
<i>m</i> -CH <sub>3</sub>	27	4.3/1		
<i>p</i> -CH <sub>3</sub>	43	5.1/1	4	2.9/1
<i>p</i> -C <sub>6</sub> H <sub>5</sub>	0			
<i>o</i> -Cl	27	3.1/1	0	4.0/1
<i>p</i> -Cl	6	3.4/1	9	4.0/1
<i>p</i> -F	19	5.8/1		
<i>o</i> -OCH <sub>3</sub>	17	2.2/1		

<sup>a</sup> Reaction conditions: 1 g Pd(Acac)<sub>2</sub>; mole ratio Pd/ligand = 1/1; 4.0 g NaOAc, 30 g HOAc and 54 g C<sub>4</sub>H<sub>6</sub>. Reaction time: 2 h.

The marked superiority of these *ortho*-substituted triaryl phosphites to triphenylphosphine is clearly shown by the results obtained at 50°. For example, use of triphenylphosphine (Pd/PPh<sub>3</sub> = 1/1) and a reaction time of 0.5 h resulted in a 20% yield of (I) + (II) in a ratio of 1.2/1. The corresponding experiment using tris(*o*-methylphenyl) phosphite gave a 97% yield of (I) + (II) with an isomer ratio of 12.7/1. Similar results were obtained with the *o*-phenyl derivative (Table 1). At even lower temperatures it was found that the ratio of (I)/(II) improved dramatically. At 25° for 2 h, using tris(*o*-methylphenyl) phosphite gave (I) + (II) in 88% yield with an isomer ratio (I)/(II) of 28/1.

We have also found that the presence of additional acetate ions (added as NaOAc) favours high isomer ratio (I)/(II). For example, experiments carried out at 50° show that the isomer ratio (I)/(II) is ca. 3 times higher when the reaction is carried out in the presence of sodium acetate (Pd/NaOAc = 1/1.5). The use of larger quantities of sodium acetate, up to 100 moles per mole of palladium, had no further effect.

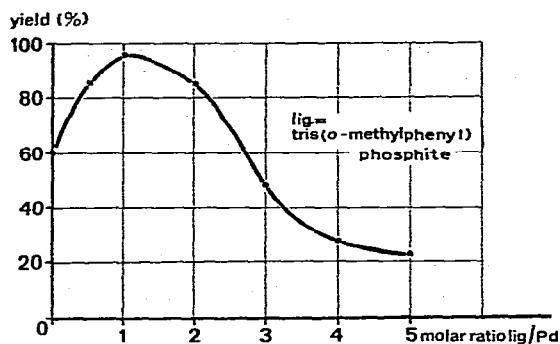


Fig. 1. Variation in yield of acetoxyoctadienes as function of ligand concentration (30 min at 50°).

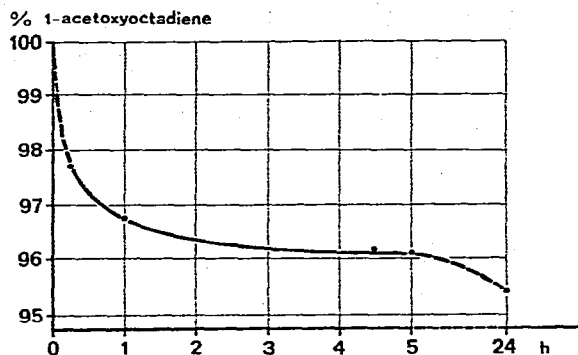
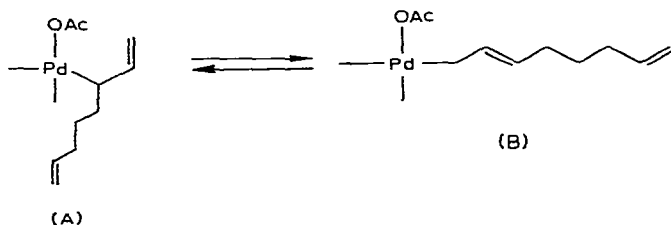


Fig. 2. Variation in isomer content as function of time (at 50°).

As shown in Fig. 1 the yield of (I) + (II) increases sharply upon addition of 1 equivalent of ligand per equivalent of palladium. As further quantities of ligand are added, the yield of (I) + (II) decreases sharply. This suggests that the excess ligand is occupying a second coordination site on the palladium, thus blocking coordination of a second butadiene molecule to the palladium, which is a necessary step before dimerisation can occur.

We have confirmed that (II) is formed during the reaction by a palladium catalysed isomerisation of (I) (Fig. 2). We have studied this isomerisation further by using pure (I) in the presence of palladium complexes and ligand. After 12 h at 90°, using  $\text{Pd}(\text{Acac})_2 + \text{PPh}_3$  (1/1) we found an isomer ratio (I)/(II) of 3.9/1. A comparable experiment using tris(*o*-methylphenyl) phosphite gave an isomer ratio of 17/1. This indicates that the high ratios of (I)/(II) found using tris-*ortho*-substituted triphenyl phosphite derivatives is due to the slowness of the isomerisation reaction, probably involving the following equilibrium:



Isomer (A) would be expected to be unstable relative to (B) in the presence of bulky ligands.

In the absence of kinetic evidence we are unable to suggest a detailed mechanism for the overall reaction. However we have shown, by using Pd on charcoal and other palladium salts such as  $\text{K}_2[\text{Pd}(\text{C}_2\text{O}_4)_2]$ , that the yields and isomer ratios are similar to those found when  $\text{Pd}(\text{Acac})_2$  is used. This suggests that the ligands\* in the starting material are not attached to the active catalyst. Possibly a palladium-hydride complex

\* Bound to the palladium.

is formed by oxidative addition of HOAc to a Pd<sup>0</sup> species. Step-wise addition of two butadiene molecules followed by elimination of (I) would then regenerate the catalyst. This mechanism would explain the observation that the reaction of butadiene with CH<sub>3</sub>OD gives 1-methoxy-6-deutero-2,7-octadiene<sup>6</sup>.

#### EXPERIMENTAL

A typical reaction was carried out as follows:

An autoclave of 250 ml capacity was charged with 1 g Pd(Acac)<sub>2</sub>, 1.2 g P(O-*o*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>)<sub>3</sub> and 30 ml of acetic acid. The autoclave was then evacuated and 54 g of butadiene drawn in. The mixture was kept at 50° for ½ h and then allowed to cool to room temperature. The unreacted acetic acid was removed by washing with water, the organic layer dried over MgSO<sub>4</sub>, and the solution was distilled under reduced pressure. The fraction boiling between 80–110°/15 mmHg was collected and analysed by GLC. A total of 81.5 g of (I) + (II) was obtained, with an isomer ratio (I)/(II) of 12.7/1.

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