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PALLADIUM COMPLEX CATALYZED REACTIONS OF CONJUGATED DIENES
I. REACTION OF BUTADIENE WITH ALDEHYDES

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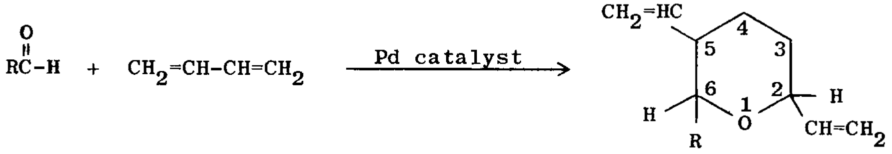
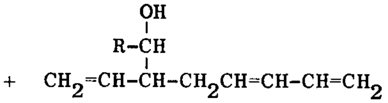
Recently several reports have appeared concerning the reactions of butadiene with nucleophiles catalyzed by soluble palladium complexes (1-4). These reactions have resulted in dimerization of the butadiene along with predominantly terminal addition of the nucleophile to yield octadienyl ethers, amines, esters, or C-alkadienylated β-diketones or β-keto esters.

We wish to report a novel Palladium catalyzed telomerization of butadiene with aldehydes to give the previously unknown products, I and II.



I

a. R = CH_3
b. R = H



$$+\ CH_2=CH-\underset{|}{\overset{\overset{OH}{|}}{\underset{}{\overset{R-CH}{|}}}}CH-CH_2CH=CH-CH=CH_2$$

II

a. R = CH_3
b. R = H

Reaction of acetaldehyde with butadiene at 25° for 60 hours in the presence of palladium acetylacetonate and triphenylphosphine gave 2,5-divinyl-6-methyl-tetrahydropyran, Ia, and 1,5,7-octatrien-3-ylmethylcarbinol, IIa. These compounds can be selectively produced by varying the triphenylphosphine: palladium acetylacetonate (P:Pd) ratio. Generally the reaction is conducted using 0.5-2.0 mmoles of palladium per mole of butadiene (5).

When the reaction of butadiene and acetaldehyde was run using a 4:1 P:Pd ratio, Ia (bp 95°/50 mm) was the predominant product in 70% yield. The nmr spectrum [δ1.1 ppm, d, J = 6.3 cps $-CH_3$(3H); 1.5, m, $-CH_2-$(4H); 2.0, m, -C-C-H (1H); 3.2, m, O-C-H (1H); 3.7, m, =C-CH-O (1H); 5.0, m, $=CH_2$ (4H); 5.6 =CH (2H).] was consistent with the proposed structure, indicating the presence of two non-equivalent vinyl groups by the unusual complexity in that region as well as the area distribution. The methyl group absorbs as a pair of doublets between 1.0 and 1.2 ppm probably signifying the existence of conformational isomers (6). The infrared spectrum [cyclic C-O-C 8.95μ and 9.2μ; =CH and $=CH_2$ 6.1μ, 10.1μ, and 11.0μ] is also consistent with this structure.

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 79.04; H, 10.39.

When the reaction was run using a 1:1 P:Pd ratio, IIa (bp 100°/20 mm) was produced in high yield (70%). The location of double bonds at the 1, 5, and 7 positions was clearly indicated from the nmr spectrum [δ1.1 ppm, d, J = 6.5 cps $-CH_3$ (3H); 2.2, m, =CCH (3H); 3.0, s, O-H (1H); 3.7, m, O-C-H (1H); 5.1, m, $=CH_2$ (4H); 6.0, m, =CH (4H).]. The wide range of low field absorption and the area distribution of the peaks indicated a conjugated system and the presence of two vinyl groups. The other spectral data [u.v.: λ_{max} 227 mμ ϵ = 22,800; infrared: 3.0μ -OH, 10.1 and 11.0μ $CH_2=$ and =CH] was consistent with the proposed structure.

Anal. Calcd. for $C_{10}H_{16}O$: C, 78.89; H, 10.59. Found: C, 79.05; H, 10.45.

Intermediate levels of P:Pd ratios were used and gave mixtures of Ia and IIa. In all cases some linear butadiene dimerization to 1,3,7-octatriene was observed.

Formaldehyde, as formalin, also reacted with butadiene under these conditions to give 2,5-divinyltetrahydropyran, IIb (bp 173°) in good yield (70-80%). The nmr spectrum [δ1.6 ppm, m, $-CH_2-$ (4H); 2.2, m, =C-C-H (1H); 3.1, t, J = 11.0 cps, O-C-H (axial) (1H); 3.7, m, O-C-H (equatorial) and O-CH-C= (2H); 5.0, m, $=CH_2$ (4H); 5.6, m, =CH (2H).] was consistent with the proposed structure. Confirmation of the assignment of the δ3.1 signal to one of the methylene hydrogens on position 6 was confirmed by a double resonance experiment. The original triplet collapsed to a doublet when the methine proton at position 5 was irradiated. This was also accompanied by the expected simplification of the δ3.7 signal, corroborating the fact that the equatorial proton of position 6 absorbed there. The infrared spectrum [C-O-C 9.2-9.3μ; $=CH$ and $=CH_2$ 10.1μ and 11.0μ] was also consistent with the proposed structure (7).

Anal. Calcd. for $C_9H_{14}O$: C, 78.21; H, 10.21. Found: C, 77.98; H, 9.92.

Compound Ib was hydrogenated, taking up two moles of hydrogen, to yield 2,5-diethyltetrahydropyran. The nmr spectrum [δ1.0 ppm $-CH_3$, 1.5 $-CH_2-$, 1.9 C-CH (15H); 3.0, m, $O-\overset{H}{C}-C_2H_5$ and O-C-H (axial) (2H); 3.7, m, O-C-H (equatorial) (1H)] indicated an upfield shift of the axial hydrogen on the 2-position and the methine hydrogen on the 5-position, both due to removing the double bonds.

Anal. Calcd. for $C_9H_{18}O$: C, 76.00; H, 12.75. Found: C, 75.91; H, 12.67.

Thus far no compound IIb has been isolated although a number of higher boiling components have been observed in varying yields. The structures of these compounds will be discussed later in a full paper.

The rate of reaction of both formaldehyde and acetaldehyde with butadiene can be dramatically increased by the use of appropriate solvents. For example, acetaldehyde and butadiene were reacted at 80° for 2 hours in ethanol using a 4:1 P:Pd ratio to give a 6% yield of IIa and a 74% yield of Ia. A similar reaction in isopropanol for 3 hours using a 1:1 P:Pd ratio gave 75% of IIa and 8% of Ia. There was no reaction of the alcohol solvent to yield octadienyl ethers even though alcohols are known to react with butadiene using this and other palladium catalyst systems (1).

To see if IIa was an intermediate in the formation of Ia, IIa was heated with palladium acetylacetonate and triphenylphosphine (4:1 P:Pd ratio). After 4 hours at 100°, only 17% conversion to Ia had occurred. In the presence of ethanol, a similar result was obtained. In another experiment, a crude reaction product from a 1:1 P:Pd catalyzed reaction of butadiene and acetaldehyde in ethanol (containing IIa and Ia in a 70:30 mole ratio) was treated with enough triphenylphosphine to give a 4:1 P:Pd ratio. On further heating at 100° for 4 hours, no change occurred in the relative quantities of IIa and Ia. These results indicate that IIa is probably not formed from Ia, although both may be formed from a common intermediate.

The reaction of formaldehyde with butadiene was accelerated by the addition of tertiary amines but was not affected by the use of alcohol beyond that already present in the commercial formalin solution. Butadiene and formaldehyde were reacted at 80° in the presence of triethylamine or N-methylmorpholine and palladium catalyst to yield 75-80% of Ib within 1-4 hours. Interestingly, the reaction of butadiene with acetaldehyde is not aided by the presence of tertiary amines. Both the amine and alcohol solvents are normally used in about 0.5:1 mole ratio to the butadiene.

The increased rate achieved when using solvents is in part due to the higher temperature which can be used. In the absence of solvent, reaction temperatures of 60-80° lead to increased formation of by-products such as 1,3,7-octatriene. The nature of these solvent effects is not clearly understood and the phenomenon is under study. Further extensions of our work with aldehydes as well as the possible mechanism of this reaction will be published as soon as it is completed.

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5. All reactions were run in a nitrogen atmosphere. All solvents were nitrogen purged before use.
6. VPC analyses indicate the presence of four stereoisomers, but they could not be separated by distillation or preparative-scale VPC.
7. Two steroisomers are indicated by VPC but cannot be separated.