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PALLADIUM COMPLEX CATALYZED REACTIONS OF CONJUGATED DIENES. II SOLVENT AND LIGAND EFFECTS ON THE REACTION OF BUTADIENE WITH ACETIC ACID

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The palladium complex catalyzed reaction of butadiene with carboxylic acids to octadienyl esters has been reported(1,2). However, these reactions do not generally give high yields of octadienyl esters. They are slow and are accompanied by the formation of 1,3,7-octatriene and butenyl esters. We wish to report a facile synthesis of octadienyl esters and octadienyl amines which has resulted from our study of ligand effects on the palladium catalyzed telomerization of butadiene with acetic acid. The reaction rates have been increased by orders of magnitude, yields and efficiencies have been raised to near quantitative, and some control of octadienyl isomer distribution is possible.

Ι

 $2CH_2=CH-CH=CH_2 + HOAc \xrightarrow{Pd cat} CH_2=CH-(CH_2)_3-CH=CH-CH_2OAc + CH_2OAc + CH_2OAc$

$$CH_2 = CH - (CH_2)_3 - CH - CH = CH_2 + III$$

$$CH_3 - CH = CH - CH_2OAc + IIII$$

$$CH_3 - CH = CH - CH_2OAc + IIII$$

$$CH_2 = CH - CH - CH_3 + CH_2 = CH - CH = CH - (CH_2)_2 - CH = CH_2$$

$$IV \qquad V$$

The reaction of acetic acid with butadiene using palladium acetylacetonate and triphenylphosphine as catalyst (\emptyset_3 P/Pd ratio = 1:1) gave a 45% conversion of butadiene after 20 hours at 90°(3). About 50% of the product was 2,7-octadien-1-yl acetate I, 15% 1,7-octadien-3-yl acetate II, 15% butenyl acetates III and IV, and 20% 1,3,7-octatriene V. Use of triphenylphosphite as the ligand in place of triphenylphosphine gave generally the same results.

When the same reaction was carried out in the presence of molar quantities of tertiary amines, a remarkable increase in the rate of the reaction was observed and an increased efficiency to the octadienyl acetates was obtained. For example, the reaction of butadiene (4.0 moles) and acetic acid (4.0 moles) in the presence of 2-(N,N-dimethylamino)ethanol (4.0 moles) palladium acetylacetonate (3.0 mmoles) and triphenylphosphine (3.0 mmoles) gave essentially a complete conversion of butadiene after 2 hours at 90°. A 71% yield of I, 21% yield of II, and 8% yield of V were realized. No butenyl esters were observed. Various other tertiary amines such as triethylamine, N-methylmorpholine, N,N,N',N'-tetramethyl-1,3-butanediamine, and triethylenediamine affected the reaction the same manner.

The effect of the $\emptyset_3^{P/Pd}$ ratio on the reaction was studied using 2-(N,Ndiethylamino)ethanol as solvent. Varying the $\emptyset_3^{P/Pd}$ ratio from 0.5/1 to 4/1 had little influence on the rate of the reaction, but the ratio of I:II in the reaction mixture changed from 83:17 to 68:32.

A greater change in the I:II ratio was obtained when phosphites were used as the ligand. When a 1:1 ratio of triphenylphosphite to palladium acetylacetonate was used in a reaction of butadiene with acetic acid at 50° in the presence of 2-(N,N-dimethylamino)ethanol a 75% conversion of butadiene was obtained in 0.5 hour. The efficiency to octadienyl acetates was 93% and the ratio was 92:8. Only 5% of V was obtained.

The use of trimethylolpropanephosphite(4), VI, as the ligand completely eliminated the formation of V and gave high yields of I. For example, butadiene (8.0 moles), acetic acid (4.0 moles), N,N,N',N'-tetramethyl-1,3-butanediamine (1.0 mole), palladium acetylacetonate (4.0 mmoles) and VI (4.0 mmoles) gave an 81% yield of I and a 9% yield of II after 2 hours at 50° .

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Other solvents have been examined such as dioxane, acetonitrile, dibutyl CARBITOL, acetophenone, and benzonitrile. The oxygen containing solvents did not increase the rate of reaction relative to the solvent free system but did eliminate the formation of butenyl acetates. The nitriles decreased the rate and directed the reaction to produce primarily compound V.

All products reported were isolated and found to have identical nmr and infrared spectra with those of authentic samples.

The variation in the ratio of I to II has been shown to be due to the formation of I in a kinetically controlled reaction followed by isomerization of I to II. Analyses of the reaction mixture with palladium-triphenylphosphine catalyst in tertiary amine solvent showed that the ratio of I to II fell as the reaction progressed. In addition, the equilibrium value of 70% of I at 100°C was reached in 0.5 hour starting from either pure I or pure II. Triphenylphosphite or VI containing catalysts took 24 hours to reach the equilibrium value. While palladium catalyzed double bond isomerizations are well known(5), this is the first example of a facile allylic functional group isomerization using palladium as catalyst.

When a secondary or primary amine was used to promote this reaction only traces of octadienyl acetates were observed and the corresponding octadienyl amines were obtained in high yield. For example, butadiene (0.10 mole), diethylamine (0.10 mole), acetic acid (0.10 mole), palladium acetylacetonate (0.25 mmole) and triphenylphosphine (0.25 mmole) were reacted at 85° for 0.5 hour to give N,N-diethyl-2,7-octadien-1-ylamine, VII, in greater than 90% yield. A similar reaction without acetic acid present gave only a 50% conversion of butadiene after 20 hours at 95°.

 $2CH_2=CH-CH=CH_2 + CH_3CO_2H + (C_2H_5)_2NH \xrightarrow{Pd(AcAc)_2} CH_2=CH-(CH_2)_3-CH=CH-CH_2-N \underbrace{C_2H_5}_{C_2H_5}$

The structure of VII was evident from its nmr [0.96 ppm, t, J = 7.0 cps]N-C-CH₃ (6H); 1.50, m, -C-CH₂-C (2H); 2.00, m, =C-CH₂ (4H); 2.43, q, J = 7.0 cps N-CH₂- (4H); 2.96, d, J = 4.5 cps =C-CH₂-N (2H); 5.0, m, =CH₂ (2H); 5.5, m, =CH (3H)] and infrared spectra $[CH_2 = CH, 10.1 \text{ and } 11.0\mu \text{ and trans } CH=CH- 10.3\mu].$ Analyzed for C₁₂H₂₃N: %C, 79.39; H, 12.66; N, 7.49.

Compound VII is probably produced from rapid reaction of the diethylamine with octadienyl acetate as it is formed rather than direct telomerization. 2,7-Octadienyl acetate (0.05 mole), diethylamine (0.05 mole), palladium acetyl-acetonate (0.25 mmole) and triphenylphosphine (0.25 mmole) were reacted at 50° for 0.5 hour to yield VII (95%) to illustrate this novel reaction. This reaction has been independently discovered by other workers and was recently reported in the patent literature(6).

$$I + (C_2H_5)_2NH \xrightarrow{Pd(AcAc)_2} VII$$

Further work is under way on this palladium complex catalyzed functional group exchange reaction. Amplification of the functional group exchange work is given in the next paper. Extensions of this work including detailed studies of ligand effects on the kinetics of the telomerization reactions and further isomerization data will be published as soon as it is completed.

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