The Synthesis of βγ-Unsaturated Esters from Conjugated Dienes

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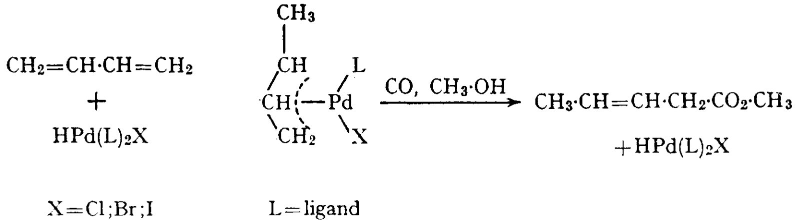
THE synthesis of ethyl pent-3-enoate from butadiene, carbon monoxide, and ethanol by using palladium chloride as catalyst has been reported briefly.[1] In the course of similar studies in these laboratories[2,3] we had found that the yield of methyl pent-3-enoate from butadiene, carbon monoxide, and methanol was markedly dependent on the nature of the palladium catalyst used.

With sodium chloropalladite or sodium bromopalladite as catalysts, at 70° and 1000 atm. of carbon monoxide, a 1—2% yield* of methyl pent-3-enoate was obtained in 3 hr., corresponding to 0·6 moles of ester per g.-atom of palladium present. However, when sodium iodopalladite was used a 35—40% yield was obtained and the reaction was catalytic on palladium giving 9—11 moles of ester per g. atom of palladium. Above 70° the catalyst partially decomposed to give palladium metal. Catalyst decomposition was prevented by adding a ligand, such as tributylphosphine, to the reaction mixture. With ligand-modified catalysts the optimum temperature was found to be 150°, and, at this temperature, the yields and catalytic activity were higher than those attained with the palladite catalysts at 70°. The yield and catalytic activity were still dependent on the halide present. Thus the dihalogenobis(tributylphosphine)palladium(II) complexes, $(Bu_3P)_2PdX_2$, gave, when X = Cl, a 20% yield of methyl pent-3-enoate and 21 moles of ester per g.-atom of palladium; when X = Br, 64% and 54 moles; and with X = I, 68% and 61 moles.

The bridged palladium complexes were found to be the best catalysts. The dihalogenobis(tributylphosphine)-μ-dihalogenodipalladium(II) complexes, $(Bu_3P)_2PdX_2$, gave, when X = Cl, a 56% yield and 49 moles of ester per g.-atom Pd of palladium; when X = Br, 73% and 67 moles; and when X = I, 71% yield and 60 moles. Catalyst concentrations of 1—2% of the complex in methanol were employed. Methyl pent-4-enoate (1%) and 4-vinylcyclohexene in 1—2% yield were also formed in this reaction.

The reaction occurs with other conjugated dienes, and the main products from the carbonylation of some dienes with the sodium iodopalladite catalyst are given. Penta-1,3-diene gave methyl 2-methylpent-3-enoate (34%), cyclopentadiene



* All yields are based on the diene charged to the reaction mixture.

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[1] J. Tsuji, J. Kiji, and S. Hosaka, *Tetrahedron Letters*, 1964, 605.
[2] W. T. Dent, R. Long, and G. H. Whitfield, *J. Chem. Soc.*, 1964, 1588.
[3] R. Long and G. H. Whitfield, *J. Chem. Soc.*, 1964, 1852.

gave methyl cyclopent-2-ene-1-carboxylate (73%), and 2,3-dimethylbuta-1,3-diene gave methyl 3,4-dimethylpent-3-enoate in 50% yield. Isoprene gave three products, methyl 3-methylpent-3-enoate (15% yield), methyl 4-methylpent-3-enoate (38%), and methyl 4-methylpent-4-enoate (10%). 2,5-Dimethylhexa-2,4-diene did not react. The products were identified by elemental analysis, molecular weight determination, and n.m.r. and infrared spectra.

The above evidence suggests that this is a general reaction for the synthesis of $\beta\gamma$-unsaturated esters from conjugated dienes. There are a number of possible mechanisms for this reaction, but, at present, we favour the formation of a palladium hydride species by reaction of the palladium salt with the alcohol,[4] followed by the sequence of reactions shown. The carbonylation of di-μ-chlorodi-π-crotyldipalladium(II) to give pent-3-enoic acid has been described,[3] and we have shown that the complex reacts with carbon monoxide and methanol to give methyl pent-3-enoate in 55% yield.

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[4] J. Chatt, L. A. Duncanson, and B. L. Shaw, *Chem. and Ind.*, 1958, 859; J. Chatt and B. L. Shaw, *Chem and Ind.*, 1960, 931.