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Carbonylation Reaction of Isoprene Catalyzed by Palladium(II) Acetate and Triphenylphosphine

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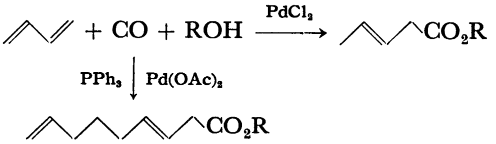
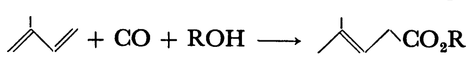
Synopsis. The carbonylation reaction of isoprene in alcohol catalyzed by palladium(II) acetate and triphenylphosphine gave 4-methyl-3-pentenoate selectively in a moderate yield. Unlike butadiene, no dimerization-carbonylation of isoprene to give C_{11} esters took place.

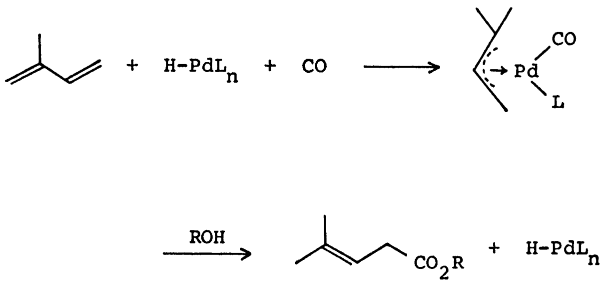
Palladium catalyzed carbonylation of butadiene in alcohol proceeds in two ways depending on the catalytic species. When palladium(II) chloride is used as the catalyst, 3-pentenoate is obtained selectively.[1] On the other hand, when halogen free palladium compounds such as palladium(II) acetate or palladium(II) acetylacetonate are used with triphenylphosphine as the catalyst, the dimerization-carbonylation occurs to give 3,8-nonadienoate exclusively.[2] Carbonylation of isoprene catalyzed by palladium(II) chloride in ethanol gave ethyl 4-methyl-3-pentenoate as the main product.[2]



In this paper we report on the carbonylation reaction of isoprene in alcohol which we carried out with use of palladium(II) acetate and triphenylphosphine as the catalyst, expecting the formation of C_{11} esters by the dimerization-carbonylation of isoprene. However, no dimerization took place, the product being a C_6 ester. The C_6 ester was a single compound with no contamination of isomeric C_6 esters. The structure of the ester was determined to be 4-methyl-3-pentenoate based on spectral data. The carbonylation of isoprene proceeded much slower than that of butadiene under the same reaction conditions, taking roughly three times longer a period than that of butadiene. The structure of alcohols used as the reactant and solvent showed crucial effect on the carbonylation. As observed in the carbonylation of butadiene catalyzed by palladium(II) acetate, methanol was not a good solvent, hardly any carbonylation taking place in methanol. In ethanol, the ethyl ester was obtained after 60 h in 37% yield by using 1 mol % of the catalyst. *t*-Butyl alcohol seems to be an effective reactant and *t*-butyl 4-methyl-3-pentenoate was obtained as the sole product in 50% yield with 0.45 mol % of palladium(II) acetate. The ratio of palladium(II) acetate to triphenylphosphine is also an important factor, the ratio of 1:6—7 giving the best result. With a lower ratio, palladium metal precipitated during the course of reaction. The reaction was carried out at 115 °C. A reaction temperature higher than 130 °C resulted in the decomposition of the catalyst into black palladium metal, no carbonylation taking place above this temperature.



The selective formation of 4-methyl-3-pentenoate can be explained by the following mechanism. At first the π-allyl complex is formed by the reaction of isoprene with palladium–hydride species. The selective attack of carbon monoxide at the unsubstituted side of the π-allylic complex then follows to give 4-methyl-3 pentenoate. Usually the reaction of isoprene with nucleophiles catalyzed by palladium(II) acetate and triphenylphosphine leads to the formation of a mixture of various substituted head-tail and tail-tail dimers.[3-6] It is interesting that in the carbonylation only one π-allylic complex is formed selectively, which is attacked by carbon monoxide, but not by another isoprene to lead to the dimer formation.



Experimental

A typical carbonylation reaction in *t*-butyl alcohol was carried out in the following way. A mixture of isoprene (2.72 g, 40 mmol), palladium(II) acetate (40 mg, 0.178 mmol, 0.45 mol% based on isoprene), triphenylphosphine (327 mg, 1.245 mmol) and *t*-butyl alcohol (10 ml) was put in a glass cylinder placed in a 50-ml autoclave and then carbon monoxide was introduced until the pressure reached 30 atm. The autoclave was placed in an oil bath kept at 120 °C and stirred with a magnetic stirrer. Gas absorption took place slowly. Gas chromatographic analysis of the reaction mixture showed the exclusive formation of 4-methyl-3-pentenoate and the presence of a very small amount of by-products. After 48 h, the product was subjected to distillation to give 3.40 g (50%) of *t*-butyl 4-methyl-3-pentenoate at 76—78 °C/19 Torr. NMR (CCl_4); 5.25 (m, 1, olefinic), 2.83 (d, 2, $J=7$ Hz, $-CH_2-CO$), 1.75, 1.64 (s, s, 6, $2CH_3$), 1.4 ppm (s, 9, *t*-Bu), IR (neat); 1715 cm^{-1}.

Similarly the ethyl ester (1.60 g, 37.6%) was obtained by the reaction of isoprene (1.98 g, 30 mmol) in ethanol (10 ml) with use of palladium(II) acetate (67 mg, 0.3 mmol) and triphenylphosphine (393 mg, 1.5 mmol) at 115 °C for 60 h. Bp 62—63 °C/18 Torr.

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