The Palladium-catalysed Carbonylation–Dimerization of Butadiene

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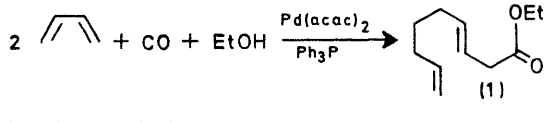
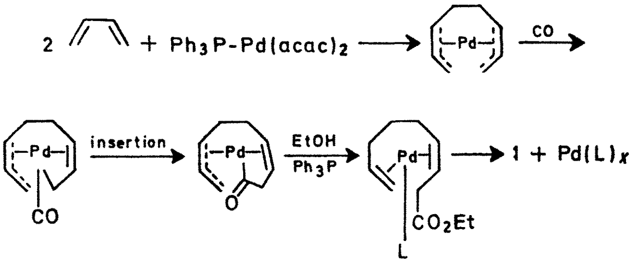
Summary A palladium complex catalysts prepared *in situ* from palladium acetylacetonate and triphenylphosphine is catalytically active for the production of ethyl nona-3,8-dienoate from butadiene, ethanol, and carbon monoxide.

Recent reports[1,2] indicate that palladium catalysts are effective in the carbonylation of dienes. Palladium chloride[1]-catalysed carbonylation of piperylene in ethanol gives ethyl 2-methylpent-3-enoate and the low temperature palladium-catalysed carbonylation of butadiene gives ethyl pent-3-enoate in 71·5% yield. The better catalyst, which was sufficiently active to catalyse carbonylations below 100 °C, was found to be $[Ph_3P]_2PdCl_2$. In general, Pd^0 compounds were found to be inactive in the absence of HCl.

We now report that halogen-free palladium complex catalysts, *e.g.* $Pd(acac)_2$, [(acac) = acetylacetonate] generated *in situ* are capable of catalysing a one-step carbonylation–dimerization of butadiene in ethanol at 80°. The reaction leads directly to ethyl nona-3,8-dienoate (**1**), equation (1).



In a typical run butadiene (3 mols), ethanol (6 mols), palladium acetylacetonate (4 mmol), and triphenylphosphine (8 mmols) were heated to 75—80° in presence of CO (80 lb. in.$^{-2}$) in a Chemco glass reactor for *ca.* 4 h with repressurization as necessary. No decline in CO consumption was observed during this time. After "weathering," g.l.c. analysis revealed that two types of products were produced in the ratio *ca.* 2·4 : 1. The first is a mixture of the ethoxyoctadienes (**2**) and (**3**), products recently reported from the palladium-catalysed reaction of butadiene with ethanol.[3]† The second higher boiling product (23 g) (**1**) was isolated by preparative g.l.p.c. (20% Se-30 on Chromosorb P) and identified spectroscopically; n.m.r. δ



Scheme

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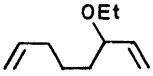
† The presence of CO greatly diminishes the rate of formation of these products. Typically, the same catalyst in the absence of CO is sufficiently active to complete the formation of (**2**) and (**3**) in a few minutes.

(CCl_4) 1·22 (t) overlapped with m at 1·51 (5H total), 2·0 (4H, m), 2·9 (2H, m), 4·02 (2H, q), and olefinic pattern from 5·65 to 6·0 p.p.m. (5H); mass spectrum, *m/e* 182 (M^+).


(**2**)


(**3**)

Significantly, this catalyst system is inactive for the carbonylation of 1-ethoxy-octa-2,7-diene (**2**), although a catalyst[2] composed of $PdCl_2$–Ph_3P (1 : 2) was moderately active for the carbonylation of (**2**). When (**2**) was heated with the catalyst at 100° under 1000 lb. in.$^{-2}$ CO for 20 h a 38% yield of (**1**) was obtained. These results suggest that butadiene must be present to co-ordinate with the catalyst for the reaction to proceed (see Scheme) and (**1**) is not produced by a secondary reaction from (**2**). A less likely, but alternative mechanism involves the 1,4-addition of the species –Pd–(C : O)–OEt to butadiene to give a π-allyl complex followed by insertion of a second butadiene.[4] The scope of this reaction is now being studied.

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[1] C. Bordenca and W. E. Marsico, *Tetrahedron Letters*, 1967, 1541.

[2] K. Bittler, N. V. Kutepow, D. Neubauer, and H. Reis, *Angew. Chem. Internat. Edn.*, 1968, **7**, 329 and references therein.

[3] S. Takahashi, T. Shibano, N. Hagihara, *Bull. Chem. Soc., Japan*, 1968, **41**, 454.; E. J. Smutny, *J. Amer. Chem. Soc.*, 1967, **89**, 6793; W. E. Walker, R. M. Manyik, K. E. Atkins, and M. L. Farmer, *Tetrahedron Letters*, 1970, 3817.

[4] *E.g.* Heck (see *J. Amer. Chem. Soc.*, 1968, **90**, 5542) reports the addition of alkyl and arylpalladium chlorides to conjugated dienes, although even in the presence of excess of diene no oligomeric products were obtained.