# Influence of the acidity of the hydrogen undergoing β-elimination on the outcome of oligomerization and co-oligomerization processes of functionalized conjugated dienes in presence of palladium catalysts.

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Abstract:It is shown that the polarity of the functional groups and the presence of pseudo acidic hydrogens have a decisive influence on the oligomerization and cooligomerization of functionalized dienes in presence of palladium catalysts.

Oligomerization of conjugated dienes can be carried out under homogeneous conditions with a great variety of transition metal catalysts (1). The reactions involving Nickel or Palladium complexes as catalysts are particularly well documented. The difference in behaviour of both metal (obtention of cyclic derivatives with Nickel and linear products with Palladium) is generally assigned to the size of the metal (2), but is also likely to be due to the ease of β elimination which occurs when σ C-Pd bonds are involved (3), a process which is for instance decisive in the Heck reaction (4). We have recently shown that the presence of a polar functional group on the terminal carbon of a conjugated diene has a major influence on the dimerization process when nickel catalysts are used (6). In the present paper we report our results on the palladium catalyzed dimerization and codimerization with butadiene of methyl hexadien-3,5 oate 1 obtained by treatment of methyl sorbate with LDA (7). The presence of two fairly acidic hydrogens in α of the ester function was expected to facilitate the β elimination process. This is indeed the case. Whereas diene ester 1 in presence of nickel catalysts yields a complex mixture of six and eight membered ring esters , a rather unequivocal reaction is observed with palladium catalysts (1 mole %) which yields dimer 2 (8) :
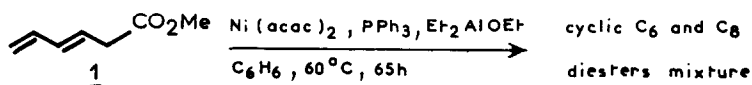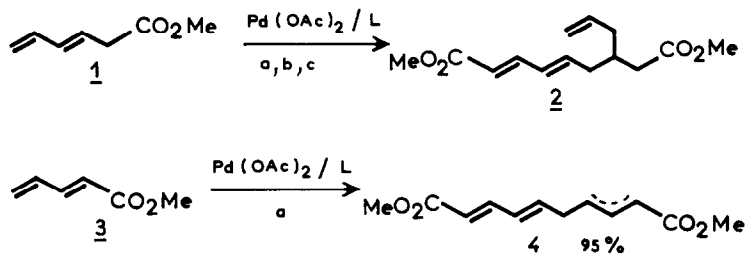
a:L=PPh3 (1.7 eq),iPrOH,60°C,17h,36%; b:L=P(o-tolyl)3 (2 eq),Me2CO, 70°C,17h,46%; c:L=P(o-tolyl)3 (2 eq),iPrOH,70°C,66h,63%

This result is in marked contrast with the one observed during the dimerization of **3** where exclusive tail-to-tail coupling yields **4**(8). Codimerization of **1** with butadiene yields a substituted 1,5 cyclooctadiene **5**(8) with nickel catalyst and a branched derivative **6**(8) with palladium catalyst (1 mole %) :
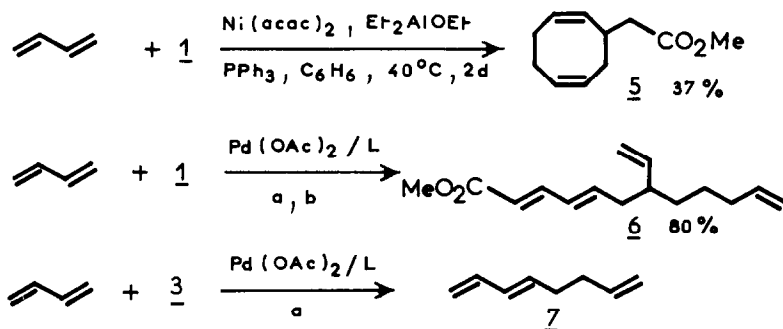

a:L=PPh3 (1 eq),CH3CN,60°C,22h,79%; b:L=Diphos. (1 eq), CH3CN,80°C, 18h, 81%.


1,3,7-octatriene **7** which can be prepared independently from butadiene (9), (or which is the only product formed when **3** is codimerized with butadiene), is not an intermediate in the formation of **6** from codimerization of **1** with butadiene.

In all these reactions involving palladium acetate as a catalyst, the active species is liganded palladium zero formed by the reduction of Pd (II) (3). We suggest that the oxidative coupling of the two units of functionalized diene **1** occurs tail-to-head i) because of the ease of

subsequent β elimination of α hydrogen in complex B ii) because of the more favourable polarity (10) which is induced in bis π-allylic intermediate B as compared to the one in A. Furthermore head-to-head oxidative coupling as in C is disfavoured for the lack of availaibility of electrons in the β position relative to the ester group. Finally the formation of D is a compromise between the relative stability and reactivity of the three possible intermediates A, B,and C. In B, the charge distribution favours a push-pull type mechanism (11) which is enhanced by the β elimination process.
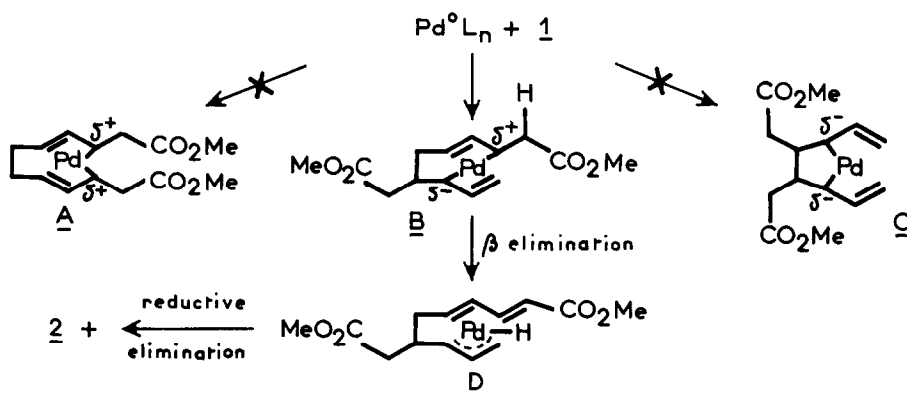
This interpretation is confirmed by the codimerization of 1 with butadiene yielding the intermediate E. Butadiene is definitely more reactive towards itself, an observation which is in agreement with the poor reactivity of functionalized diene 1. Complex E yields 1,3,7 octatriene 7 which does not further react with 1. Therefore functionalized diene 1 must insert in the carbon palladium bond of E so that to form F which readily undergoes an easy β elimination to G. The final derivative 6 is formed from G by reductive elimination.
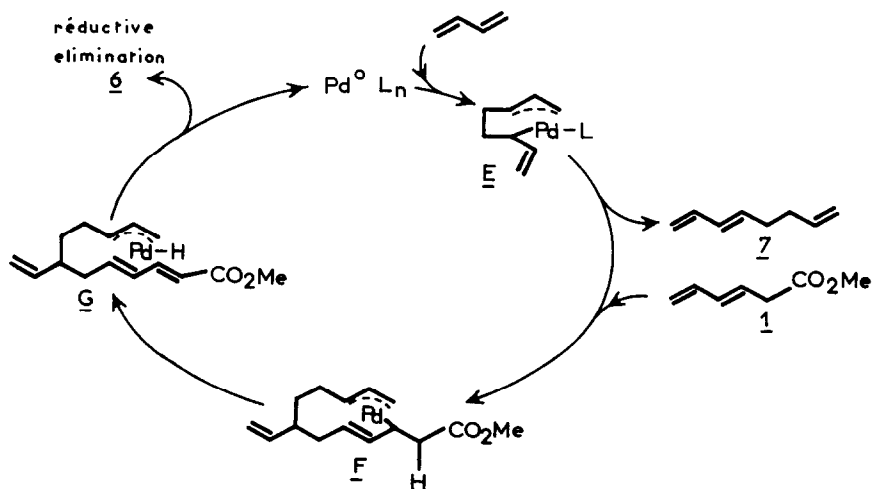
The present work clearly shows the influence of a polar group such as a methyl carboxylate on the reactivity of a conjugated diene in presence of nickel or palladium catalysts.In the latter case the polarity of the diene induced by the polar groups as well as the ease of β elimination have a decisive influence on the outcome of the oligomerization and cooligomerization processes.

References:

1 - W.Keim, A.Behr, and M.Roper, Comprehensive Organometallic Chemistry, 1982, 8, 371.

2 - G.Wilke, B.Bogdanovic, P.Heimbach, W.Keim, M.Kroner, W.Oberkirch, K.Tanaka, E.Steinrucke, D.Walter and H.Zimmermann, Angew.Chem.,1966, 78, 157.

3 - J.Tsuji, Advances in Organomet.Chemistry, 1979, 17, 141.

4 - R.F.Heck, Accounts Chem.Res., 1979, 12, 146.

5 - However, it has recently been shown that butadiene can be cyclodimerized with phosphine-free palladium catalysts :A.Goliaszewski and J.Schwartz, Organometallics, 1985, 4, 415.

6 - A.Tenaglia, P.Brun and B.Waegell, J.Organomet. Chem.1985,285,343.

7 - R.V.Stevens, R.E.Cherpeck, B.L.Harrison, J.Lai, and R.J.Lapalme,J.Amer.Chem.Soc., 1976, 98, 6317.

8 - 2 : IR (neat) : 2940, 2830, 1735, 1720, 1640, 1615, 1430, 1300,1250, 1200, 1135, 995, 910. 1H NMR (CCl4) :1,85-2,6 (m,7H), 3,56(s,3H), 3,63(s,3H), 4,7-4,9(m,2H), 4,95-6,25(m,3H), 5,64(d,1H, J =15Hz), 7,10(dd, 1H, J = 15, 10 Hz) 13C NMR(CDC13): 34.8 (d),37.2 (t), 38.0 (t), 38.2 (t), 51.37(q), 51.41(q), 117.3(t), 119.6(d), 130.6 (d),135.7 (d), 141.5 (d), 144.7(d), 165.5 (s), 173.2 (s).Anal. : Calcd for C14H2004 : C, 66.64 ; H, 7.98 . Found : C, 66.42; H, 7.91.

4 : IR (neat) : 3015, 2995, 2945, 1735, 1720, 1640, 1615, 1430,1265, 1165, 995, 970, 865. 1H NMR (CDC13) : 2.8-3.15 (m,4H), 3.6(s,3H), 3.65(s,3H), 5.4-6.2 (m,4H), 5.84(d,1H, J = 16 Hz), 7.3(dd, J = 15, 11Hz). Anal. : Calcd for C12H1604 : C, 64.32; ; H, 7.19 . Found : C, 64.39 ; H, 7.23

5 : IR (neat) : 3005, 2910, 2840, 1735, 1640, 1430, 1260, 1155,990, 960, 905. 1H NMR (CDC13) : 1.8-3.2 (m, 9H), 3.6 (s, 3H),5.15-5.75 (m, 4H). 13C NMR(CDC13) : 27.2(t), 28.0(t), 33.9(t), 36.6(d), 41.2(t), 51.55(q), 127.4(d), 128.5(d), 129.2(d), 131.9(d),173.0(s)

6 : IR (neat) : 3075, 2920, 1720, 1640, 1430, 1305, 1265, 1185,1165, 990, 905. 1H NMR (CDC13) : 2.2-2.5 (m,9H), 3.66(s, 3H),4.65-6.2(m, 9H), 7.4(dd, 1H, J = 15, 11 Hz). 13C NMR (CDC1)3 : 22.5(t), 33.6(t), 33.8(t), 33.9(t), 44.0(d), 51.4(q), 114.5(t),115.1(t), 121.0(d), 127.2(d), 138.7(d), 139.6(d), 139.7(d), 141.8(d), 167.6(s). Anal. Calcd for C15H2202 : C, 76.88 ; H, 9.46. Found : C, 76.90 ; H, 9.53.

9 - E.J.Smutny, J.Amer.Chem.Soc., 1967, 89 , 6793.

10- J.R Jones, J. Chem. Soc. (C), 1971,p.1117.

11- A.Tenaglia, These d'Etat, Université d'Aix-Marseille III, 1984