Palladium Catalysed Intra- and Inter-molecular Coupling of Vinyl Halides. Regiospecific Formation of 1,3-Dienes

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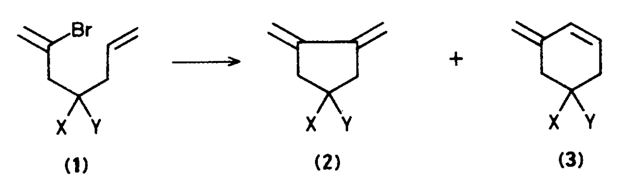
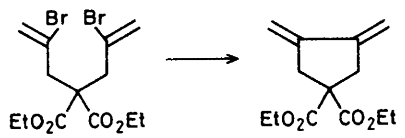
Palladium catalysed coupling of vinyl bromides proceeds in good yield under mild conditions provided sufficient triarylphosphine and potassium carbonate are present to regenerate the active palladium(0) species; double bond isomerisation is not observed under these conditions.

We have recently shown that 2-bromo-1,6-dienes (**1**) react with $Pd(OAc)_2$, $Pd(PPh_3)_4$, or $RhCl(PPh_3)_3$ in boiling acetonitrile in the presence of potassium carbonate to give a mixture of cyclic dienes (**2**) and (**3**) usually in good yield.[1] 2-Bromo-1,7-dienes cyclise regiospecifically to give six-membered rings. The ratio of (**2**) to (**3**) is sensitive to the metal catalyst employed and good selectivity for (**2**) or (**3**) can often be achieved. However, the problem of regioselectivity of the coupling process would be circumvented if a process for the catalytic coupling of vinyl halides was developed. This type of chemistry has been previously exemplified by the Ullman reaction (copper) and by related biaryl syntheses that employ nickel[2] or cobalt.[3] A few examples of Pd^0 and Pt^0 complexes effecting aryl–aryl coupling of aryl halides have also been reported.[4] We now have preliminary experiments to hand which suggest a novel solution to the problem of catalytically coupling vinyl bromides.

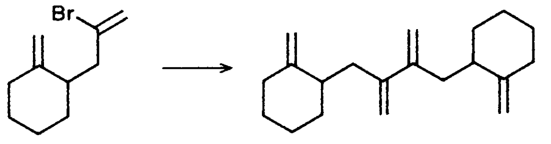
The 2,6-dibromohepta-1,6-diene (**4**) is catalytically cyclised



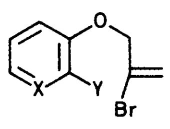
(1) (2) (3)



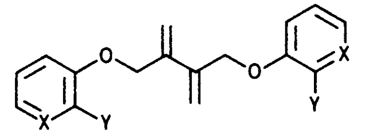
(4) (5)



(6) (7)



(8)

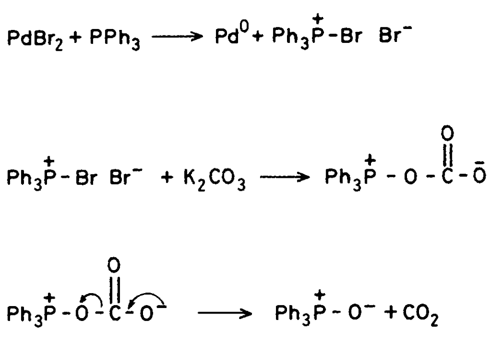


(9)

a; X = CH, Y = H
b; X = CH, Y = Br
c; X = N, Y = Br

(MeCN; 80 °C) to give (**5**) by 5 mole % palladium acetate in the presence of triarylphosphine (1.25 mol. equiv.), and potassium carbonate (7.5 mol. equiv.). A brief survey of the efficacy of the phosphine showed good yields (*ca.* 90%) of (**5**) with PPh_3 and $P(p\text{-}MeOC_6H_4)_3$ after 1.25 h whilst $Ph_2PCH_2CH_2PPh_2$ (diphos) and PBu_3 gave substantially lower yields (12 and 50% respectively). Replacing palladium acetate by $Pd(PPh_3)_4$ and by $RhCl(PPh_3)_3$ resulted in lower yields of (**5**).†

Several other substrates have been investigated including (**6**) for which an intramolecular 5-*endo trig* process is potentially in competition with an intermolecular dimerisation process. The sole product (90%) is (**7**) using 5 mole % palladium acetate, triphenylphosphine (0.5 mol. equiv.), and potassium carbonate (2.5 mol. equiv.) The greater reactivity of vinyl bromides compared to aryl bromides is illustrated by the intermolecular coupling of (**8a**—**c**) to give (**9a**—**c**) in moderate yield (31—55%), and slow coupling (80 h; 115 °C) of iodobenzene to give biphenyl (48%). No intramolecular coupling products were isolated from the reactions of (**8a**—**c**).

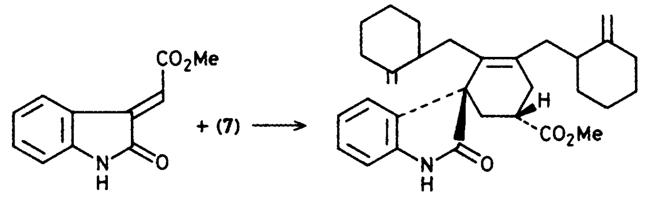


$$PdBr_2 + PPh_3 \longrightarrow Pd^0 + Ph_3\overset{+}{P}\text{-}Br\ Br^-$$

$$Ph_3\overset{+}{P}\text{-}Br\ Br^- + K_2CO_3 \longrightarrow Ph_3\overset{+}{P}\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}\bar{O}$$

$$Ph_3\overset{+}{P}\text{-}O\text{-}\overset{\overset{O}{\|}}{C}\text{-}O^- \longrightarrow Ph_3\overset{+}{P}\text{-}O^- + CO_2$$

Scheme 1



(10) (11)

The success of the catalytic coupling of vinyl bromides depends on the presence of sufficient triarylphosphine and potassium carbonate to regenerate a catalytically active Pd^0 species according to Scheme 1.

As expected the conjugated dienes (**5**) and (**7**) undergo Diels–Alder reactions under mild conditions as illustrated by the reaction of (**7**) with (**10**) (48 h; 80 °C) to give (**11**) (90%).

The catalytic coupling of vinyl bromide provides new regiospecific methodology for the creation of conjugated dienes with potential for Diels–Alder reactions. No double bond isomerisation was observed in these coupling processes.

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† All new compounds reported have microanalytical and spectroscopic data in accord with their structures.