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PALLADIUM CATALYSED TANDEM CYCLISATION-ANION CAPTURE PROCESSES INITIATED BY ALKYL- AND π-ALLYL-PALLADIUM SPECIES

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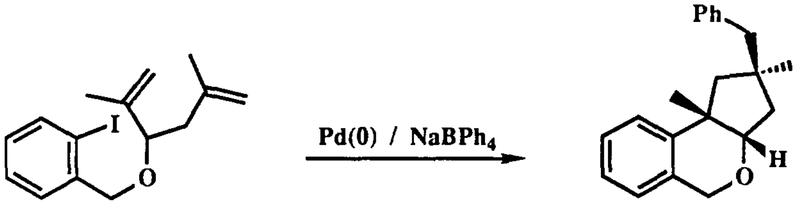
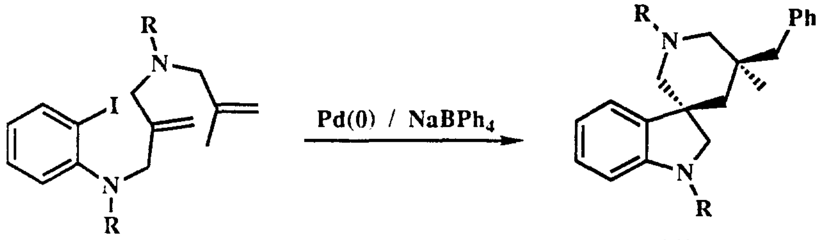
Abstract Palladium catalysed tandem cyclisation-anion capture processes initiated by oxidative addition of benzylic or allylic halides or acetates to Pd(0) occur regio- and stereo- specifically in good yield. Examples of "anion" capture involving formate (H^-), and organo- tin, -zinc, and -boron species are described.

Over the past few years we have been developing a general palladium catalysed tandem cyclisation-anion capture process that is flexible and synthetically powerful.[1,2] The concept has been extended to polycyclisation-anion capture processes[3] and, in the cases studied thus far, these occur stereospecifically e.g. (1) → (2) and (3) → (4)[3]. More recently we showed that addition of Tl(1) salts is advantageous in certain cases in that they can promote cyclisation-anion capture at the expense of the unwanted direct capture process.[4]



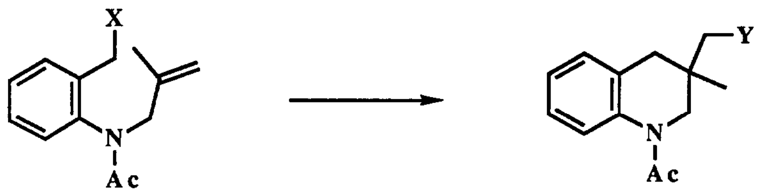
(1) (2)



(3) (4)

In our previous work the catalytic tandem process was initiated by oxidative addition of aryl or vinyl halides to a Pd(0) species generated *in situ*. We now report catalytic tandem processes that are initiated by oxidative addition of benzylic or allylic halides or acetates to Pd(0).

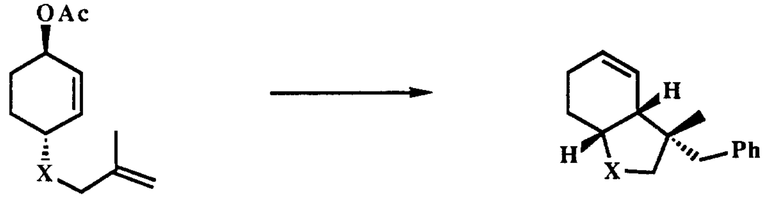
The benzylic halide (5) reacts (anisole, 90°C, 9h) with sodium tetraphenylborate (1.1 mol) in the presence of Pd(0)[5] to give (6a) (69%). An analogous palladium catalysed reaction (MeCN, 80°C, 4-6h) of (5) with sodium formate (1.1 mol, hydride ion source) afforded (6b) (54%). In this latter case tetraethylammonium chloride (1 mol) was added to promote the reaction.[6]



(5) X=1:1 mixture of Cl and Br

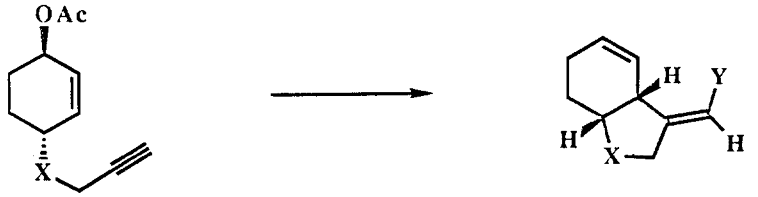
(6)a. Y=Ph
b. Y=H

The seminal work of Oppolzer on metallo-ene reactions[7] augered well for the incorporation of π-allyl species as initiators in our tandem cyclisation-anion capture processes. This promise was amply fullfilled by experimentation. Thus (7a) and (7b) react stereospecifically (anisole, 60°C, 1.5-3h) with sodium tetraphenylborate (1.1 mol) in the presence of Pd(0)[5] to give (8a) (90%) and (8b) (80%) respectively.[8]



(7) a. $X=C(CO_2Me)_2$
b. $X=NSO_2Ph$

(8) a. $X=C(CO_2Me)_2$
b. $X=NSO_2Ph$

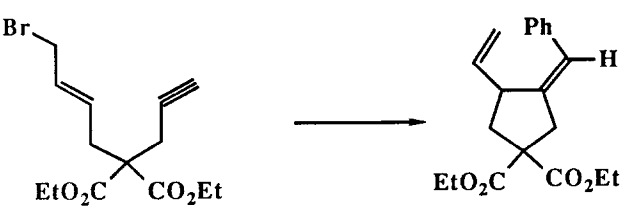


(9) a. $X=C(CO_2Et)_2$
b. $X=NSO_2Ph$

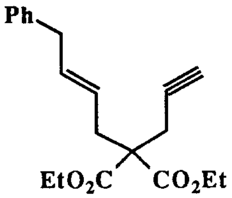
(10) a. $X=C(CO_2Et)_2$, Y=Ph
b. $X=NSO_2Ph$, Y=H
c. $X=NSO_2Ph$, $Y=CH_2CH=CH_2$

The Pd(0) catalysed reaction (anisole, 60°C, 1h) of (9a) with sodium tetraphenylborate (1.1mol) is stereospecific and affords (10a) (67%). The analogous reaction of (9a) with PhZnCl affords (10a) in a somewhat lower yield (57%). The nitrogen analogue (9b) reacts (DMF, 100°C, 12h) with sodium formate to give (10b) (50%). Transfer of functionality from tin can also be achieved. Thus (9b) reacts (THF, 60°C, 24h) with allyl tributyl tin in the presence of Pd(0) to give (10c) (42%).

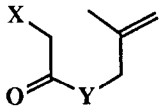
A potential problem with the cyclisation-anion capture methodology is that the direct capture rate may be faster than the rate of cyclisation. This is not normally a problem. However, the allylic bromide (11) shows interesting behaviour in this respect. Thus cyclisation (anisole, 60°C, 2h) in the presence of sodium tetraphenyl borate (1.1 mol) affords (12) (31%), whilst reaction (ether-THF, 60°C, 2h) of (11) with phenyl zinc chloride (3 mol) affords (13) (40%). Attempts to effect cyclisation-anion capture on (14a and b) have so far been unsuccessful.



(11) (12)



(13)



(14) a. X=Cl, Br, I; Y=O
b. X=Cl, Br, I; Y=NSO_2Ph

Further work on these and related processes are in hand. We thank SERC and Leeds University for support.

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2 For other applications of this chemistry see: Negishi, E.-I., Noda, Y., Lamaty, F., and Vawter, E.J., *Tetrahedron Letters,* 1990, 31. 4393-4396; Wang, R.-T., Chou, F.-L., and Luo, F.-T., *J. Org.*

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4 Grigg, R.; Loganathan, V., Sukirthalingam, S., and Sridharan, V., *Tetrahedron Letters,* 1990, 31, 6573-6576; see also: Grigg, R.; Loganathan, V., Santhakumar, V., Sridharan, V., and Teasdale, A., *ibid,* 1991, 32, 687-690.

5 All reactions described in this paper utilised 10mol% palladium acetate and 20mol% triphenylphosphine as the catalyst system.

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7 Oppolzer, W.; Keller, T.H., Bedoya-Zurita, M., and Stove, C., *Tetrahedron Letters,* 1989, 30, 5883-5886; Oppolzer, W.; Birkinshaw, T.N., and Bernadinelli, G., *ibid,* 1990, 31, 6995-6998 and references therein.

8 The stereochemistry of (8a), (8b), (10a-c), and (12) was established from n.O.e. data.

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