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Palladium Catalysed [4+2]-Cycloaddition Reactions of (2-Iodoaryl)allenes

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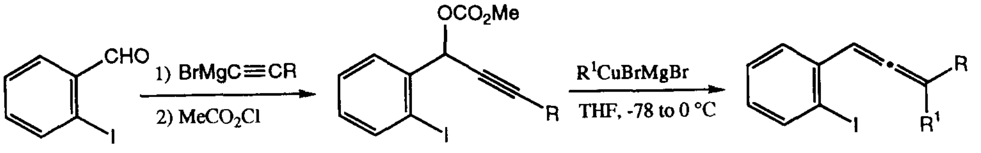
Abstract: (2-Iodoaryl)allenes are versatile 4C-components in palladium catalysed [4+2] cycloaddition reactions with norbornene, 2-aza-3-oxonorborn-5-ene, and allene acting as 2C-components. A variety of dihydronaphthalenes and naphthalenes are produced in excellent yield. Copyright © 1996 Elsevier Science Ltd

Recently we proposed a general scheme for palladium catalysed cycloadditions initiated by oxidative addition of Pd(0) and a suitable C-X bond (starter molecule).[1] We, and others, have provided a range of examples of such processes[2,3] but at present examples which generate carbocycles from allenic starter molecules are lacking. We now report examples of such processes.

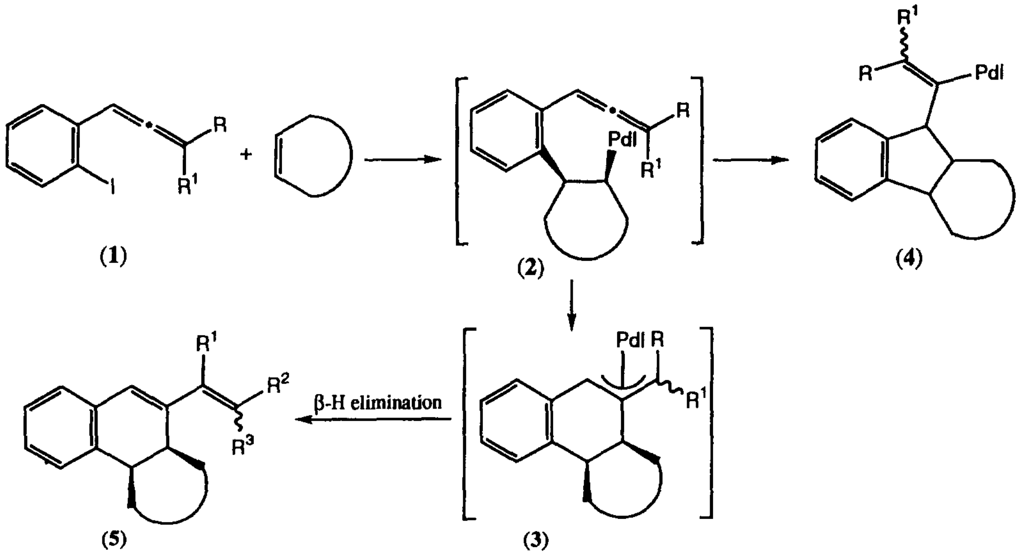
A series of (2-iodoaryl)allenes (1a-d) were prepared as outlined in Scheme 1 in overall yields of 70-80%



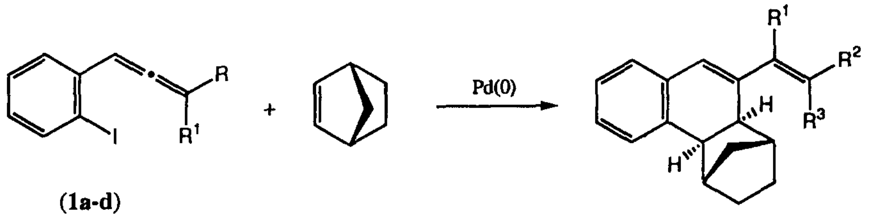
(1) **a**, R = Me, R^1 = Ph
b, R = c-Pentyl, R^1 = Ph
c, R = Me, R^1 = $C(Me)_2OTHP$
d, R = H, R^1 = $(CH_2)_5Me$

Scheme 1

A study of the [4+2] cycloaddition reactions of (1a-d) was initiated in which it was anticipated that (1a-d) would function as 4C-components (Scheme 2). Conceptually intermediate (2) could undergo cyclisation to (3) or (4). However, literature precedent indicates allenes undergo attack by Pd(II) species at the central carbon atom leading to (5) in the absence of overriding steric effects.[4,5]

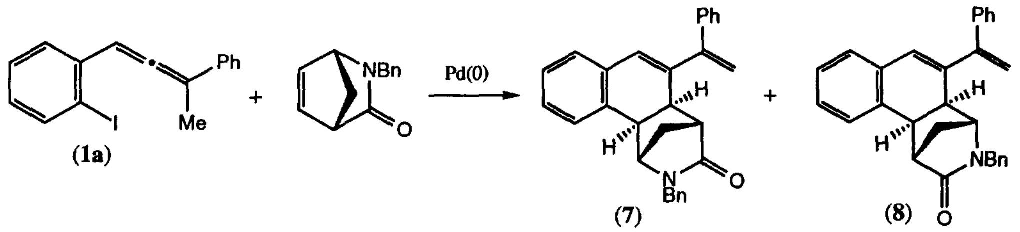


Scheme 2



(6)a, R^1 = Ph, R^2 = R^3 = H 96%
b, R^1 = Ph, R^2/R^3 = c-Pentyl 88%
c, R^1 = $C(Me)_2OTHP$, R^2 = R^3 = H 93%
d, R^1 = R^3 = H, R^2 = $(CH_2)_4Me$ 68%

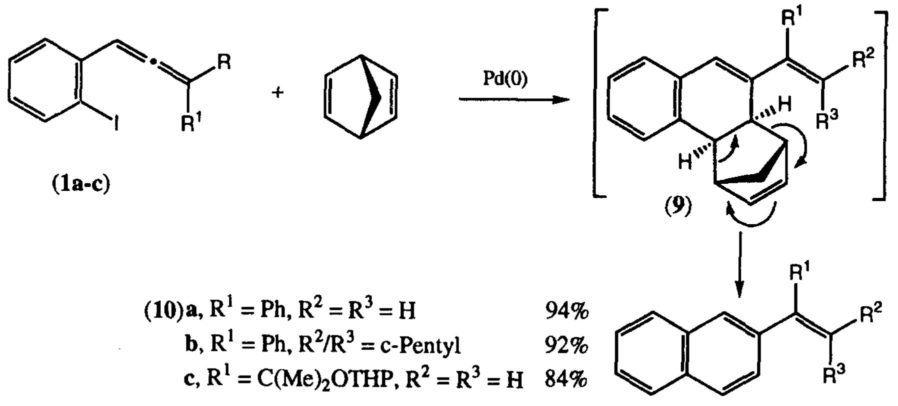
Allenes (1a-d) were reacted in boiling acetonitrile (15-20h) with norbornene (5eq) and a catalyst system comprising 10mol% $Pd(OAc)_2$, 20mol% PPh_3, K_2CO_3 (3-5eq) and $[Et_4N]Cl$ (1eq). Reaction occurred via (3) as outlined in Scheme 2 to furnish (6a-c) in 68-96% yield.[6]



7 : 8 = 1 : 1 (84%)

In an analogous reaction the azanorbornene (6) showed no regioselectivity in its reaction with (1a) and furnished a 1:1 mixture of (7) and (8) in 84% combined yield. The expected exo-stereochemistry exhibited by (5a-d), (7) and (8) was established from ^{1}H n.m.r. data (coupling constants and n.O.e.).

A second series of [4+2] cycloaddition reactions employing norbornadiene as the 2C- component was studied. Under analogous reaction conditions to those described above (1a-c) reacted with norbornadiene (5eq) to furnish naphthalenes (10a-c), via fragmentation of (9, arrows), in 84-92% yield.



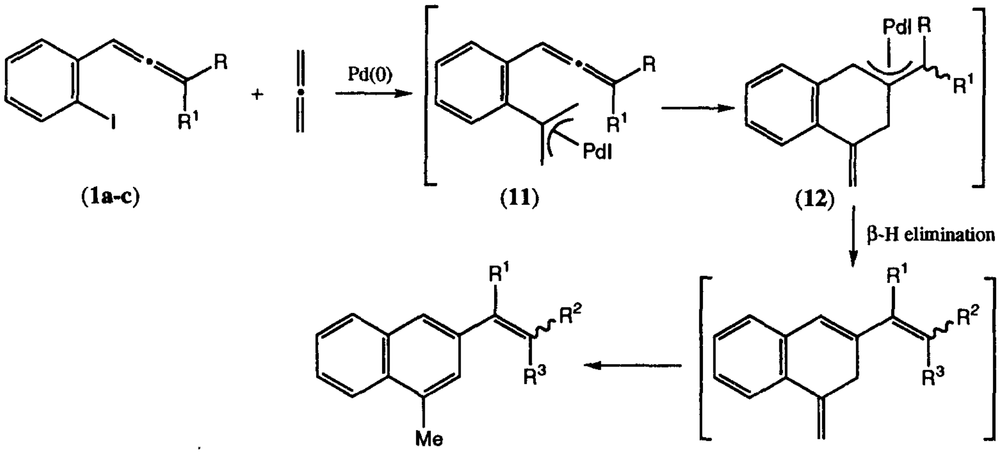
(1a-c)

(9)

(10)a, R^1 = Ph, R^2 = R^3 = H 94%
b, R^1 = Ph, R^2/R^3 = c-Pentyl 92%
c, R^1 = C(Me)$_2$OTHP, R^2 = R^3 = H 84%

The intermediate (9) was not detected under our reaction conditions. The facile nature of the retro-Diels-Alder reaction reflects the incipient aromaticity in the transition states leading from (9a-c) to (10a-c).[7]

A third series of [4+2] cycloaddition reactions employing allene (1atm) as the 2π-component have been evaluated. Thus (1a-c) react with allene as summarised in Scheme 3.



(1a-c)

(11)

(12)

(13)a, R^1 = Ph, R^2 = R^3 = H 83%
b, R^1 = Ph, R^2/R^3 = c-Pentyl 81%
c, R^1 = C(Me)$_2$OTHP, R^2 = R^3 = H 76%

Scheme 3

The initial addition of the ArPdI species to allene occurs at the central carbon atom generating the π-allylpalladium(II) species (11) which attacks the adjacent allene at the central carbon atom generating a new π-allyl species (12). β-Hydride elimination and isomerisation of the exocyclic double bond then furnishes naphthalenes (13a-c) in good yield.

The products of the above processes are potentially versatile intermediates for a range of subsequent chemistry and the utilisation of allenes as both starter species and acceptor species offers many further valuable synthetic opportunities. Work is continuing on evaluating these opportunities.

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6. All new compounds gave satisfactory microanalytical and spectroscopic data.
7. For other examples of retro-Diels-Alder reactions arising from the use of norbornadiene in palladium catalysed processes but occurring at much higher temperatures see: Liu, C.-H.; Li, C.-S.; Cheng, C.-H.; *Organometallics*, 1994, **13**, 18-20; An, Z.-W.; Catellani, M.; Chiusoli, G.P.; *Gazz. Chim. Ital.*, 1990, **120**, 383-385.
8. Reactions were carried out with stirring in a Schlenk tube since allene diffuses readily through an ordinary balloon.

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