Tetrahedron Letters, Vol. 34, No. 19, pp. 3163-3164, 1993
Printed in Great Britain

0040-4039/93 $6.00 + .00
Pergamon Press Ltd

Palladium Catalysed Cascade Cyclisation - Cyanide Ion Capture.

Ronald Grigg,* Vijayaratnam Santhakumar and Visuvanathar Sridharan.

School of Chemistry, Leeds University, Leeds LS2 9JT

Abstract: A range of δ- and ω-alkenyl aryl- and vinyl- halides undergo palladium catalysed cyclisation with subsequent transfer of cyanide ion in the presence of potassium cyanide (1.2mol) and 10mol % 18-crown-6.

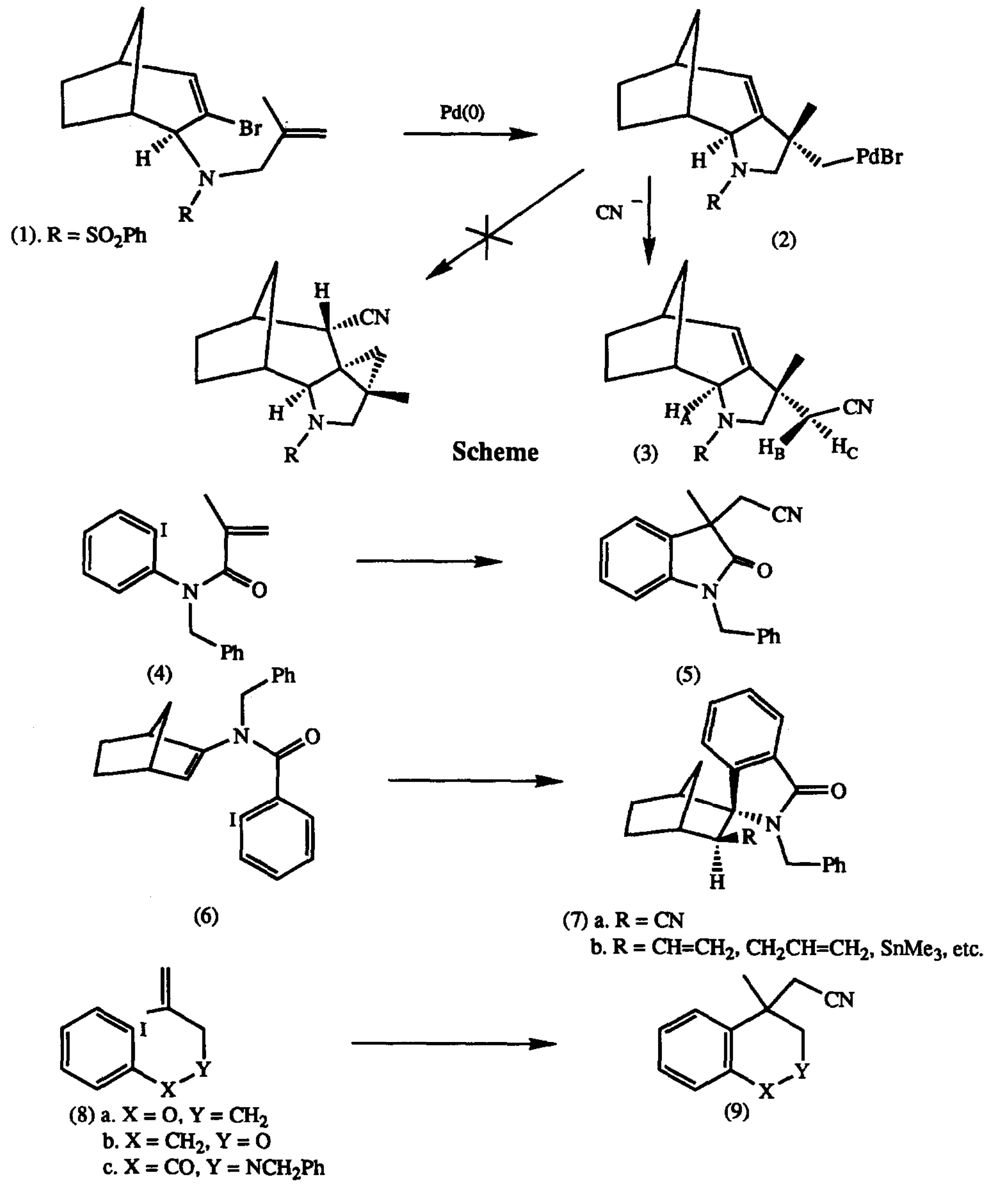
Recently we have been developing a new, synthetically powerful, catalytic cascade cyclisation - anion capture process.[1,2] The (poly) cyclisation phase is terminated by capture of the organopalladium (II) intermediate by a wide variety of "capping" agents including anionic (H^-, OAc^-, $PhSO_2^-$, $(RO_2C)_2CH^-$), neutral (amines, CO/MeOH, acrylates), and organometallic [RM, M=Sn(IV), B(III), Zn(II)] species. The recent reports of palladium catalysed cyanation of allylic substrates[3] and Torii's elegant work on diastereofacial- and enantio-selective cyanation of norbornenes[4] prompts us to record our results on catalytic cyclisation with cyanide capture. The vinyl bromide (1) undergoes regio- and stereo-specific 5-exo trig cyclisation (C_6H_6, 80°C, 12h) with cyanide capture to afford (3) (68%) (Scheme). The organopalladium (II) intermediate (2) could conceptually undergo a 3-exo trig cyclisation with cyanide capture. However, no cyclopropyl products are observed although we have shown that (2) does undergo competitive direct hydride ion capture and 3-exo trig cyclisation with hydride ion capture in the presence of thallium(I) acetate.[5] In the absence of TlOAc no cyclopropyl products are formed, only the product of direct hydride capture from (2).[5]. The catalyst-cyanide system employed in all the examples described in this paper comprises 10mol % palladium acetate, 20mol % triphenylphosphine, 10mol % 18-crown-6 and potassium cyanide (1.2mol). The stereochemistry of (3) was established by n.O.e. studies in C_6D_6. In particular irradiation of H_A (δ 3.3) effected enhancement on a proton signal at δ 1.1 (5%). The methylene protons H_B and H_C give rise to an AB system at δ 1.1 and 0.97.

The aryl iodide (4) is similarly (C_6H_6, 80°C, 12h) cyclised to (5) (62%) whilst the norbornene enamide (6) gives (7a) (50%). The stereochemistry of (7a) accords with that established previously for a wide range of products (7b) arising from cyclisation of (6) with transfer of groups from Sn(IV).[6]

A series of 6-exo trig cyclisations with cyanide ion capture have also been carried out. Thus (8a) cyclises (toluene, 110°C, 18h) to (9a) (62%) and (8b) gives (9b) (58%) under the same conditions using the standard palladium catalyst system. Amide (8c) also undergoes a 6-exo trig cyclisation (C_6H_6, 80°C, 12h) to give (9c) (45%).

References.

1. Burns, B., Grigg, R., Santhakumar, V., Sridharan, V., Stevenson, P., and Worakun, T., *Tetrahedron*, 1992, **48**, 7297-7320, and references therein.
2. Grigg, R., Kennewell, P., and Teasdale, A., *Tetrahedron Lett.*, 1992, **33**, 7789-7792.
3. Tsuji, Y., Yamada, N., and Tanaka, S., *J.Org.Chem.*, 1993, **58**, 16-17.



Scheme

---

4. Torii, S., Okumoto, H., Ozaki, H., Nakayasu, S., and Kotani, T., *Tetrahedron Lett.*, 1990, **31**, 5319-5322, Torii, S., Okumoto, H., Ozaki, H., Nakayasu, S., Tadokoro, T., and Kotani, T., *Tetrahedron Lett.*, 1992, **33**, 3499-3502.
5. Grigg, R., and Sridharan, V., *Tetrahedron Lett.*, 1992, **33**, 7965-7968.
6. Burns, B., Grigg, R., Ratananukul, P., Sridharan, V., Stevenson, P., Sukirthalingam, S., and Worakun, T., *Tetrahedron Lett.*, 1988, **29**, 5565-5568.

(Received in UK 25 February 1993)