Palladium(II)-catalysed Formation of Indoles from 2,2-Diphenyl-2*H*-azirines

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Summary Treatment of four 2,2-diphenyl-2*H*-azirines with a catalytic amount of dichlorobis(benzonitrile)-palladium(II) at room temperature gave the same indoles as were obtained by heating the 2*H*-azirines, *via* dichlorobis-(2*H*-azirine)palladium(II) complexes.

There has been much interest in the transition metal-catalysed ring opening of strained ring systems.[1] Recently, Alper *et al.*[2] and we[3] reported reactions of 3-aryl-2*H*-azirines in the presence of transition-metal compounds to give several types of dimerisation products. In connection with those studies, we expected that transition metal (*e.g.* Pd) compounds could catalyse the intramolecular rearrangement of 2-aryl-2*H*-azirines to give indole derivatives, since the azirines were known to undergo thermal rearrangement.[4]

We have found that dichlorobis(benzonitrile)palladium(II) acts as an excellent catalyst for the conversion of 2*H*-azirines into indoles. Thus, reactions of 0·3 mmol of the 2,2-diphenyl-2*H*-azirines (**1a**—**c**) with 0·015 mmol of Pd^{II} in 100 ml of benzene at 30 °C followed by washing with 2N-aqueous ammonia and the usual work up gave the indoles (**3a**—**c**) quantitatively. Thermal reactions of these azirines gave the same indoles. The results (Table 1) show a large rate-enhancing effect of Pd^{II} in indole formation.

Table 1. Half lives for the Pd^{II}-catalysed and non-catalysed formation of indoles (**3**) from 2,2-diphenyl-2*H*-azirines (**1**).

		Non-catalysed		
Azirine	Catalysed[a] $t_{1/2}$/min	Solv.	Temp./°C	$t_{1/2}$/min
(**1a**)	<3	C_6H_6	80	18
(**1b**)	360	Decalin	170	53
(**1c**)	4200	Decalin	170	720

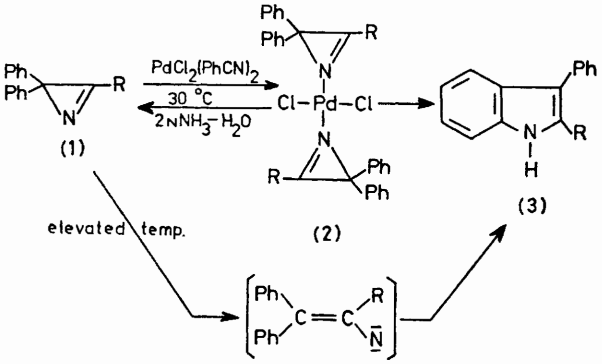
[a] All catalysed reactions at 30 °C in C_6H_6, with 0·05 mol. equiv. of Pd^{II} and concentration of azirine adjusted to 3 mM.

Although the mechanism of the Pd^{II}-catalysed indole formation is not clear at this stage, we assume intervention of Pd^{II} complexes. In fact, we have obtained such complexes, (**2c**) and (**2d**), as yellow precipitates, in the reactions of (**1c**) and (**1d**) with 0·5 mol. equiv. of Pd^{II} in benzene for 2 h at ambient temperature (Table 2). The recovery of the 2*H*-azirines upon treatment of (**2c**) and (**2d**) with 2N-aqueous ammonia and elemental analysis of (**2d**) showed that compounds (**2**) are 2 : 1 complexes of the 2*H*-azirines and $PdCl_2$.† The quantitative formation of indoles upon stirring a suspension of compounds (**2**) in benzene at room temperature showed the above assumption to be correct.

Table 2. Yields and physical properties of dichlorobis(2*H*-azirine)palladium(II) complexes (**2**).

			$\nu_{C=N}$/cm^{-1}	
Complex	Yield (%)	M.p./°C	(**2**)	(**1**)
(**2b**)	21	101—102	1796	1765
(**2c**)	83	108—110	1766	1737
(**2d**)	89	134—135	1772	1735

In the reactions of (**1a**) and (**1b**) with 0·5 mol. equiv. of Pd^{II}, the solutions immediately turned red-brown and the indoles (**3a**) and (**3b**) were obtained after 2 h in 95 and 97% yields, respectively. However, the reaction of (**1b**) at −40 °C in toluene for 2 h gave (**2b**), but in low yield. Under the same conditions, (**1a**) failed to give (**2a**).



a; R = H
b; R = Me
c; R = Ph
d; R = *p*-MeC_6H_4

The reactivity sequence in the Pd^{II}-catalysed formation of indoles shows the same trend as that in the non-catalysed thermal reaction and depends on the substituent at the 3-position of the azirine ring (H>>Me>Ph). This indicates that ring opening by C–N bond fission is accelerated by Pd^{II} complex formation, since the thermal reaction has been shown to proceed by C–N bond fission.[4]

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† According to a personal communication from Professor A. Hassner, a *trans* square-planar structure, in which the nitrogen is co-ordinated to Pd^{II}, has been determined for dichlorobis(3-*p*-tolyl-2*H*-azirine)palladium(II) by *X*-ray crystallography.

[1] K. C. Bishop, III, *Chem. Rev.*, **1976**, **76**, 461.
[2] H. Alper and S. Wollowitz, *J. Amer. Chem. Soc.*, **1975**, **97**, 3541; H. Alper and J. E. Prickett, *J.C.S. Chem. Comm.*, 1976, 191, 483, 983.
[3] K. Hayashi, K. Isomura, and H. Taniguchi, *Chemistry Letters*, **1975**, 1011.
[4] K. Isomura, S. Kobayashi, and H. Taniguchi, *Tetrahedron Letters*, **1968**, 3499; K. Isomura, M. Okada, and H. Taniguchi, *ibid.*, **1969**, 4073; K. Isomura, T. Tanaka, and H. Taniguchi, *Chemistry Letters*, **1977**, 401.