# Formation of Aziridines in the Oxidation of β-Aminoalkylpalladium Complexes by Bromine. Aziridination of Olefins

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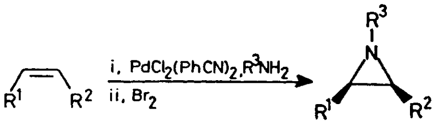
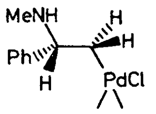
*Summary* Palladium-promoted amination of olefins, using primary amines followed by oxidation by bromine, results in the formation of *N*-substituted aziridines.

We have recently observed that palladium-promoted oxyamination[1] and diamination[1,2] of olefins take place at low temperature. These reactions are stereospecific and are achieved by aminopalladation[3] of the olefin followed by oxidation of the organometallic adduct in the presence of added nucleophile. During the course of these studies we observed that formation of aziridines takes place with primary amines, when bromine is used as an oxidant. We now report on this reaction [equation (1)], which involves an intramolecular replacement of palladium and permits transformation of an olefin into the corresponding aziridine.

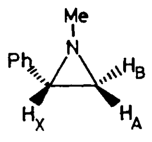


(1)

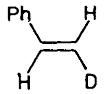
Aminopalladation[3] of styrene with methylamine at $-50$ °C gave the $\sigma$-bonded complex (**1**) which, on subsequent bromination, afforded the aziridine (**2**) identified by its n.m.r. spectrum[4] [($CCl_4$, $Me_4Si$) $\delta_A$ 1·34, $\delta_B$ 1·58, and $\delta_X$ 2·02; $J_{AX}$ 6·4, $J_{BX}$ 3·2, and $J_{AB}$ 1·3 Hz]. Other olefins, for example dec-1-ene and oct-2-enes, were also shown to undergo the aziridination reaction. Thus dec-1-ene gave the corresponding *N*-methylaziridine in an isolated yield of 43%.



(1)



(2)



(3)

As shown by reaction with the specifically deuteriated styrene (**3**),† there is a preference for formation of the

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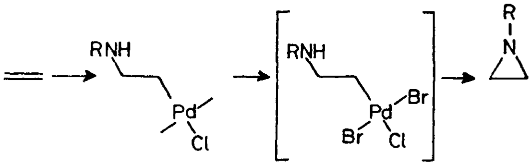
† Prepared by hydroalumination of phenylacetylene followed by $D_2O$ quenching (G. Wilke and H. Müller, *Annalen*, 1958, **618**, 267). Unchanged phenylacetylene was removed by treatment with CuCl–$NH_3$. In this way $\beta$-deuteriostyrene with a *trans*:*cis* ratio of 88:12 was obtained.

aziridine isomer (**2**; $H_A = D$) with the same geometry as the starting olefin. N.m.r. analysis of the aziridine product indicated the ratio of overall *cis* : *trans* addition to be **4** : 1.‡



(4)

Scheme

The formation of the main isomer (**2**; $H_A = D$) is consistent with a *trans*-aminopalladation[5] followed by an oxidative internal replacement of palladium by nitrogen with inversion of configuration at carbon (Scheme). A palladium(IV) intermediate (**4**) is possible and has been suggested previously in the oxidative cleavage of palladium–carbon bonds.[1,6] The inversion at carbon found here for the oxidative cleavage by bromine is in accordance with results from other oxidative cleavages of palladium–carbon bonds in the presence of free nucleophile.[1,6,7]

A few methods for transforming an olefin into an aziridine are known[8] but they suffer from lack of either generality or simplicity. The procedure presented here appears promising and further work along these lines is in progress.

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‡ Isolation of unchanged $\beta$-deuteriostyrene and subsequent n.m.r. analysis showed that the extent of isomerisation was <2% and thus cannot account for the partial loss of stereospecificity.

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[6] P. K. Wong and J. K. Stille, *J. Organometallic Chem.*, 1974, **70**, 121.

[7] P. M. Henry, *J. Org. Chem.*, 1974, **39**, 3871; *Adv. Organometallic Chem.*, 1975, **13**, 363; J. E. Bäckvall, *Tetrahedron Letters*, 1977, 467.

[8] O. C. Dermer and G. E. Ham, 'Ethylenimine and other aziridines,' Academic Press, New York and London, 1969; H. Wenker, *J. Amer. Chem. Soc.*, 1935, **57**, 2328; W. Lwowski and T. W. Mattingly, *ibid.*, 1965, **87**, 1947; A. Hassner, G. J. Matthews, and F. W. Fowler, *ibid.*, 1969, **91**, 5046.