Palladium(II)-promoted aziridination of olefins with bromamine T as the nitrogen transfer reagent

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The palladium(II)-promoted reaction of a variety of olefins and bromamine T, as the nitrogen atom transfer reagent, provided *N*-tosyl-2-substituted aziridines under mild conditions.

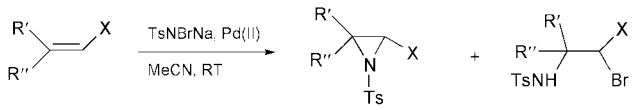
Aziridines have been shown to be valuable starting materials, for the synthesis of useful nitrogen containing compounds, due to the highly regio- and stereoselective ring opening reactions that they undergo.[1,2]

Recently two copper-catalysed aziridination methods for olefins have been reported. Whilst the first,[3] which involved the use of PhI=NTs, is of wide applicability, the second method that utilised chloramine T[4] or bromamine T,[5] as the nitrogen transfer agent, is limited to non-deactivated olefins. The aziridination procedure of Bäckvall[6] [olefins, Pd(II) and primary aliphatic amines] also suffers from a similar disadvantage.

We report herein our preliminary results, collected in Table 1, of a novel $PdCl_2$-assisted aziridination[7]† of olefins **1**, both simple and electron-deficient, by bromamine T.

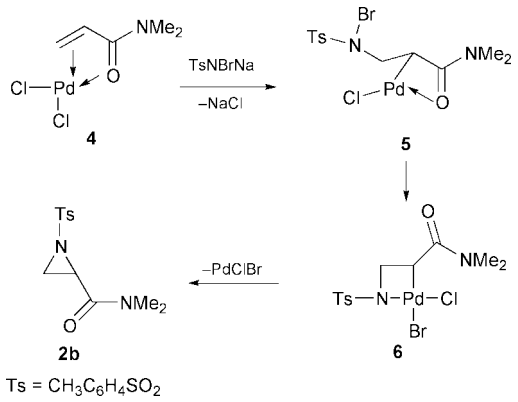
An examination of the Table shows that all olefins examined participate with varying degrees of efficiency. The electron deficient olefins in general react to give better yields of aziridines than the simple alkenes. Amongst the former class of compounds, *N*,*N*-dimethylacrylamide (**1b**) (entry 2) afforded the highest yield (81%) and phenylvinylsulfoxide (**1g**) (entry 7) the lowest (20%). Whilst methyl acrylate (**1a**) (entry 1) afforded the synthetically useful aziridine **2a**[8] in acceptable yield (60%), as the only isolable product, acrylonitrile (entry 4) however provided a mixture of bromosulfonamide **3d** and the aziridine **2d**[9] in almost equal amounts‡ (*ca.* 20%). A methyl substituent in the β-position **1c** (entry 3) completely inhibited the reaction possibly due to steric reasons. In contrast to styrene (**1i**) (entry 9) and cyclohexene (**1h**) (entry 8), which provided negligible yields of the corresponding heterocycles, allyl alcohol (**1j**) (entry 10), containing an additional metal coordinating centre (OH), afforded the expected product[10] in modest yield (40%). Although the exact nature of the palladium reagent involved in the reaction is not known, a possible mechanism is outlined in Scheme 1 for the substrate *N*,*N*-dimethylacrylamide. Thus, the initially formed π-complex **4** leads, on nucleophilic attack by TsNBrNa,[11] to the σ-alkylpalladium species **5**. Subsequent intramolecular oxidative addition would furnish the 4-member palladocycle Pd(IV) **6**, which collapses to the aziridine **2b**,[12] regenerating the Pd(II) salt. Organopalladium(IV) complexes are known[13] and have been occasionally invoked as intermediates in reactions of Pd(II) species with electrophiles.[14]

Table 1 Aziridination of olefins with bromamine T promoted by Pd(II) compounds



Entry	R″	R′	X	1	Reaction conditions[a]	Yield[b] of **2** (%)	Yield[b] of **3** (%)
1	H	H	COOMe	**a**	*A*	60	—
2	H	H	$CONMe_2$	**b**	*B*	81	12
3	Me	H	$CONMe_2$	**c**	*B*	—	—
4	H	H	CN	**d**	*A*	22	19
5	H	H	COMe	**e**	*C*	44	7
6	H	$CO(CH_2)_3$		**f**	*D*	33	—
7	H	H	SOPh	**g**	*D*	20	7
8	H	$(CH_2)_4$		**h**	*B*	2.5	—
9	H	H	Ph	**i**	*B*	—	—
10	H	H	CH_2OH	**j**	*B*	40	—

[a] *Method A*—Olefin (3 eq., 0.55 mmol), TsNBrNa (1.2 eq., 0.22 mmol), $Pd(MeCN)_2Cl_2$ (0.5 eq., 0.09 mmol); *Method B*—Olefin (1.2 eq., 0.22 mmol), TsNBrNa (1.5 eq., 0.27 mmol), $PdCl_2$ (0.2 eq., 0.04 mmol); *Method C*—Olefin (3 eq., 0.55 mmol), TsNBrNa (1.2 eq., 0.22 mmol), $PdCl_2$ (0.5 eq., 0.09 mmol); *Method D*—Olefin (3 eq., 0.55 mmol), TsNBrNa (1 eq., 0.18 mmol), $Pd(MeCN)_2Cl_2$ (0.5 eq., 0.09 mmol). [b]Isolated yield.



Scheme 1

In conclusion a mild one-pot procedure for the preparation of *N*-tosyl-2-substituted aziridines§ is reported. Further experiments to define the palladium species involved in the process and the stereochemical aspects of the reaction are in progress.

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Notes and references

† No significant aziridination occurred in the absence of $PdCl_2$.

‡ It is likely that the bromosulfonamides are formed from the initially produced aziridines undergoing nucleophilic ring opening with bromide ion. A blank experiment performed with pure **2d** and NaBr in CH_3CN did indeed afford **3d** in excellent yield. Compound **3d** in CH_3CN on treatment with NaH furnished **2d** in 64% yield.

§ All spectral data were in accord with the structures assigned. *Selected data for* **2f**: δ_H (400 MHz, $CDCl_3$) 7.81 (2H, d, *J* 8.2, ArH_{2+6}), 7.35 (2H, d, *J* 8.2, ArH_{3+5}), 3.46 (1H, d, *J* 6.5, H_2), 3.15 (1H, d, *J* 6.5, H_3), 2.45 (3H, s, ArCH_3), 2.20–2.16 (1H, m), 2.07–1.99 (1H, m), 1.94–1.84 (2H, m), 1.70–1.54 (2H, m); δ_C (100 MHz, $CDCl_3$) 200.8 (CO), 144.9 (ArC_4), 135.2 (ArC_1), 129.9 (ArC_{3+5}), 128.0 (ArC_{2+6}), 44.12 (C_2), 41.23 (C_3), 37.0 (C_6), 22.0 (C_4), 21.5 ($ArCH_3$), 17.61 (C_5); HR-EIMS calcd for $C_{13}H_{15}NO_3S$ (M^+) 265.076715,

found 265.07666. *Selected data for* **2g**: δ_H (400 MHz, $CDCl_3$) 7.75 (2H, d, *J* 8.0 Hz, ArH_{2+6}), 7.60–7.47 (5H, m, Ar*H*), 7.31 (2H, d, *J* 8.0 Hz, ArH_{3+5}), 3.82 (1H, dd, *J* 6.0, 3.7 Hz, H_2), 2.91 (1H, d, *J* 3.8 Hz, H_3), 2.79 (1H, d, *J* 6.4 Hz, H_3), 2.46 (3H, s, ArCH_3); δ_C (100 MHz, $CDCl_3$) 145.1 (ArC_4), 140.0 (ArC_1), 131.6 (ArC), 129.7 (ArC_{3+5}), 129.3 (ArC), 128.1 (ArC_{2+6}), 124.4 (ArC), 55.3 (C_2), 28.4 (C_3), 21.3 ($ArCH_3$); HR-EIMS calcd for $C_{14}H_{15}NS_2O_3$ (MH^+) 322.056610, found 322.05693.

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