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Molecular Sieves Promoted Regioselective Ring Opening of *N*-Tosylaziridines Catalyzed by Imidochromium Complexes

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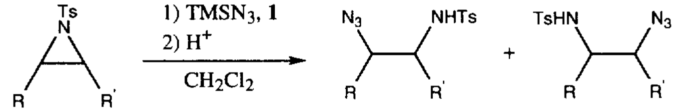
Abstract: $Cr(NBu^t)Cl_3(dme)$ catalyzes ring-opening of *N*-tosylaziridines with trimethylsilyl azide; the yield and selectivity of which was found to be enhanced by molecular sieves.

Organoimidometal (M=NR) complexes have attracted much attention due to their applications to olefin metathesis and metathesis polymerization of cyclic olefins.[1] Previously we reported that high-valent *t*-butylimido complexes of Group VI transition metals are capable of catalyzing nucleophilic ring-opening of epoxides in good regioselectivities, demonstrating that this new class of catalysts are potentially useful in organic synthesis.[2] Also of synthetic interest is the ring-opening of aziridines with *N*-nucleophiles to give biologically important vicinal diamines.[3] Recently, Yamamoto and coworkers reported the synthesis of vicinal diamines via Yb(III)-mediated aminolysis of aziridines.[4] Herein we describe the Cr-catalyzed azidolysis of *N*-tosylaziridines and the unexpected regioselectivity enhancement by molecular sieves.



Scheme 1

Table 1 summarizes the results of catalytic ring-opening of *N*-tosylaziridines with trimethylsilyl azide ($TMSN_3$). Typically, addition of 3 equiv of $TMSN_3$ to a mixture of styrene *N*-tosylaziridine and 10 mol% of $Cr(NBu^t)Cl_3(dme)$ **1** (dme = 1,2-dimethoxyethane) followed by silica gel chromatography led to the isolation of a 1:1 mixture of the azido products in 40% yield (Scheme 1). The yield was found to increase with the catalyst loading, e.g. the yield rises from 27 to 67% as the loading of **1** increases from 5 to 20 mol%. **1** also promote the azidolysis of aliphatic aziridines such as cyclohexene*N*-tosylaziridine and 1-hexene *N*-tosylaziridine (entries 8 and 10). For the ring-opening of the latter aziridine, a ca. 1:1 mixture of 1- and 2-azido products were isolated. The bisimido-Cr(VI) complex $Cr(NBu^t)_2Cl_2$ (**2**)[6] was found to be less active than **1** in catalyzing the ring-opening reaction (entry 6).

Remarkably, addition of molecular sieves to the reaction mixture improves both the yield and the regioselectivity of the aziridine ring opening. Therefore reaction of styrene *N*-tosylaziridine with $TMSN_3$ and 10 mol% of **1** in the presence of 2 equiv of 4Å molecular sieves[7] afforded the 1- and 2- azido products in 86% yield (not optimized) and with selectivity of ca. 1:40 (entry 3). Preliminary results showed that the selectivity was rather insensitive to the amount of molecular sieves added. However, no reaction was observed when the imido-Cr complex was omitted (entry 7), indicating that molecular sieves itself is not a catalyst. Similarly, azidolysis of 1-hexene *N*-tosylaziridine with molecular sieves afforded the 1- and 2-azido products in 32% yield and with a ratio of 2.1:1 (entry 9). Furthermore, molecular sieves was also found to promote the regioselectivity of epoxide ring opening with **1**. For example, azidolysis of styrene oxide with **1** and molecular sieves gave the 1- and 2-azido products in a ratio of 1:7 (c.f. the ratio of 1:2 in the absense of molecular sieves[2]). It seems unlikely that molecular sieves merely acts as a water scavenger, as in the Sharpless epoxidation,[8] because both partially hydrated[9] and very dry[10] molecular sieves enhance the selectivity of the ring-opening reaction similarly. Although the underlying mechanism is not clear, molecular-sieves-controlled stereoselective reactions are not without precedent.[11]

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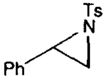
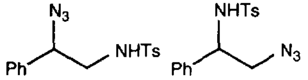
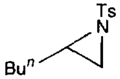
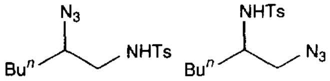
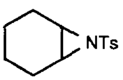
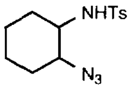
Table 1. Catalytic Ring-Opening of *N*-Tosylaziridines

entry	catalyst	substrate	products (%yield)	substrate recovered(%)	time(d)
					
1	**1** (5 mol %)		2:1 (27)	51	2
2	**1** (10 mol%)		1:1 (40)	48	2
3	**1** (10 mol%) + MS[c]		40:1 (86)	14	2
4	**1** (20 mol%)		4:3 (67)	33	2
5	**1** (20 mol%) + MS[c]		19:1 (97)	trace	2
6	**2** (20 mol%)		2:1 (29)	66	2
7	MS only		(0)	89	2
					
8	**1** (40 mol%)		1:1.1 (18)	60	9
9	**1** (40 mol%) + MS[c]		1:2.1 (32)	45	7
10	**1** (40 mol%)		 (60)	37	7

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[a] Typical experimental procedure : a mixture of aziridine (0.73 mmol), catalyst, and TMSN$_3$ (2.19 mmol) in CH$_2$Cl$_2$ (5 mL) was stirred under nitrogen at ambient temperature. The reaction mixture was then concentrated and the products were obtained as an inseparable mixture by silica gel column chromatography (eluent : 30% Et$_2$O/hexane). [b] Ratio determined by ^{1}H NMR spectroscopy. [c] 2 equivalents (by weight); the molecular sieves were filtered off through a celite pad before the above workup procedure was carried out.
[d] see ref. 2.

REFERENCES AND NOTES

1. (a) Schrock, R. R. *Acc. Chem. Res.*, **1991**, *23*, 158. (b) Schrock, R. R. *Pure Appl. Chem.* **1994**, *66*, 1447.
2 Leung, W.-H.; Chow, E. K. F.; Wu, M.-C.; Kum, P. W. Y.; Yeung, L.-L. *Tetrahedron Lett.* **1995**, *36*, 107.
3. Reets, M. T.; Jaeger, R.; Drewlies, R.; Hübel, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 103 and references cited therein.
4. Meguro, M.; Asao, N.; Yamamoto, Y. *Tetrahedron Lett.* **1994**, *35*, 7395.
5. Leung, W.-H.; Danopolous, A. A.; Wilkinson, G.; Hussain-Bates, B.; Hursthouse, M. B. *J. Chem. Soc., Dalton Trans.* **1991**, 2051.
6. Danopolous, A. A.; Leung, W.-H.; Wilkinson, G.; Hussain-Bates, B.; Hursthouse, M. B. *Polyhedron* **1990**, *9*, 2625.
7. Activated powder, Aldrich. The isolated yields of reactions with molecular sieves were found to vary (within 15%) presumably due to adsorption of the products by molecular sieves.
8. (a) Gao, Y.; Hanson, R. M.; Klunder, J. M.; Ko, S. Y.; Masamune, H.; Sharpless, K. B. *J. Am. Chem. Soc.* **1987**, *109*, 5765. (b) Hanson, R. M., Sharpless, K. B. *J. Org. Chem.* **1986**, *51*, 1922.
9. Exposed to air for one day.
10 Dried at 150°C, 0.01 mmHg for 10 hours.
11. Tottie, L.; Baeckström, P.; Moberg, C.; Tegenfeldt, J.; Heumann, A. *J. Org. Chem.* **1992**, *57*, 6579 and the references therein.

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