Molybdenum-catalysed Allylic Amination†

Anurag Srivastava, You-an Ma, Ratnadevi Pankayatselvan, Warren Dinges and Kenneth M. Nicholas*
Department of Chemistry and Biochemistry, University of Oklahoma, Norman, OK 73019, USA

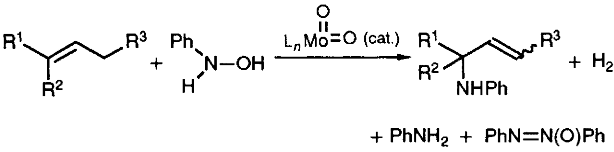
Dioxomolybdenum(VI) complexes including $MoO_2(dipic)(HMPA)$ **2a** and $MoO_2(dedtc)_2$ **2b** (dipic = 2,6-pyridinedicarboxylate; HMPA = hexamethylphosphoramide; dedtc = *N*,*N*-diethyl dithiocarbamate) catalyse the allylic amination of alkenes by phenyl hydroxylamine; the reactions are characterized by a high degree of regioselectivity resulting from double bond migration.

The direct, selective functionalization of hydrocarbons remains a continuing challenge for synthetic chemists. Although practical processes currently exist for the synthesis of oxygenated compounds by allylic oxidation,[1] methods for the production of corresponding organonitrogen compounds are few, with stoichiometric reactions of imido compounds (RN=X=NR; X = S,[2] Se[3]) being the most familiar. Possibly related is a recently reported Mn-catalysed allylic amination by PhINTs (Ts = toluene-*p*-sulfonyl).[4] An early report by Sharpless[5] noted the stoichiometric imido-transfer reactions of molybdooxoaziridine (alt. nitrosoarene) complexes [$MoL_n(\eta^2\text{-RNO})$, **1**] with a few alkenes, producing allylic amines. We report herein a new catalytic reaction, based on this chemistry, which results in the regioselective allylic amination of alkenes by hydroxylamines [eqn. (1)].

Our initial experiments confirmed the generality of stoichiometric alkene amination by nitrosobenzene complex **1a**

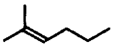
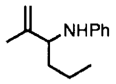
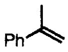
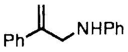
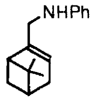
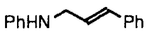
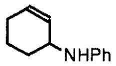
---

† Patent pending.



(1)

Table 1 Amination of alkenes by PhNHOH catalysed by MoO_2(dipic)(HMPA)[a]

Alkene	Allyl amine[b]	Yield (%)[c]
		52
		42
		26
		11
		4

[a] All reactions conducted in dioxane at 100 °C for 8 h. [b] Only isomer detected by ^{1}H NMR spectroscopy. [c] GC yield with naphthalene as internal standard.

(L = dipic = 2,6-pyridinedicarboxylate). Thus, heating **1a** (100 °C, dioxane) with cyclohexene, cycloheptene, 2-methylhex-2-ene and oct-1-ene produced the corresponding allylamines (30–70% yield‡) and MoO_2(dipic)(HMPA) (HMPA = hexamethylphosphoramide) along with small to moderate amounts of aniline (*ca.* 10%) and azoxybenzene (*ca.* 20%); only one regioisomer was detected in each case by ^{1}H NMR spectroscopy (see below).

Since nitrosobenzene complexes **1** can be produced by the reaction of MoO_2L(HMPA) with PhNHOH,[5] we reasoned that the latter complexes could serve as catalysts for the amination of alkenes by hydroxylamines. In fact slow addition of phenyl hydroxylamine to a refluxing dioxane solution of various alkenes containing 1–10 mol% of MoO_2(dipic)(HMPA) **2a** or $MoO_2(dedtc)_2$ (dedtc = *N*,*N*-diethyl dithiocarbamate) **2b**[5] produces the desired allyl amine along with varying amounts of aniline (10–30%) and azoxybenzene (10–20%).§ A summary of representative results with **2a** as the catalyst is given in Table 1. Key features of the reactions are: (*i*) yields (unoptimized) of allyl amines range from moderate to modest depending on the alkene structure; (*ii*) best results are obtained with trisubstituted or 1,1-disubstituted alkenes and (*iii*) single regioisomers are produced, the result of double bond transposition. This selectivity complements that generally observed with aminations by $(TolN)_2X$ (Tol = tolyl) (X = S, Se), namely retention of double bond position,[2,3] and produces allyl amines directly without the necessity of a subsequent *N*-deprotection step. Although the yields of allyl amine are presently only fair, the ready availability of the aminating agent and the recyclability of the byproducts combine to make the present method an attractive one compared to other less direct ones.

Control experiments have revealed that aniline and azoxybenzene are derived both from competing thermal self condensation of the hydroxylamine[5] as well as from decomposition of the intermediate MoO(dipic)(HMPA)(η^2-RNO) (**1**). The latter process appears to have little precedent in the chemistry of *C*-nitroso complexes.[6] Thermal reactions conducted in [$^2H_8$]dioxane produced only $PhNH_2$, showing that aniline is not derived from the reaction of free phenyl nitrene with solvent.

Although detailed mechanistic information on the catalytic amination is not yet available, we note that the nitrosobenzene complexes MoOL(η^2-PhNO) **1** can be detected (IR, UV–VIS, isolation) in the reactions. Furthermore, the greater reactivity of the more substituted alkene and the regioselective C=C transposition suggests that the key C–N bond-forming step may involve an ene reaction between the alkene and PhN=O.[7] That free PhNO is generated under the reaction conditions is supported by the fact that MoO(dipic)(η^2-PhNO) undergoes exchange of the nitrosoarene ligand when heated with *o*-MeC_6H_4NO in dioxane. The role of molybdenum thus may be to serve as a redox catalyst with $Mo^{VI}O_2L$ oxidizing the hydroxylamine to nitrosoarene and $Mo^{IV}OL$ reducing the allyl hydroxylamine (from the ene reaction) to amine.

The present results demonstrate the feasibility of effecting catalytic allylic amination of alkenes by hydroxylamines with a high degree of regiocontrol. Studies are underway to improve the efficiency of the catalytic amination process through systematic variation of catalyst structure and reaction conditions, to extend its scope, and to elucidate further its mechanism.

We are grateful for partial support provided by the National Institutes of Health (GM34799) and for helpful discussions with K. B. Sharpless and F. Mares.

Received, 25th February 1992; Com. 2/00999D

---

‡ All new compounds have been characterized by IR, ^{1}H NMR and mass spectrometry.

§ *Representative procedure*: a solution of phenyl hydroxylamine (3.0 mmol) in 15 ml of dioxane is added dropwise over 5 h to a refluxing dioxane solution (15 ml) containing 5–10 equiv. of alkene and 10 mol% of **2a** under nitrogen. After an additional 3 h, the product allyl amine was isolated by solvent evaporation and flash chromatography over silica or by extraction into HCl (1 mol dm^{-3}), neutralization with Na_2CO_3, extraction into diethyl ether, and distillation.

References

1 SeO_2: N. Rabjohn, *Org. React*, 1976, **24**, 261; M. A. Umbreit and K. B. Sharpless, *J. Am. Chem. Soc.*, 1977, **99**, 5536; Bu^tO_2H–$Cu^{I,II}$: D. J. Rawlinson and G. Sosnovsky, *Synthesis*, 1972, 1; C. Walling and A. Zavitsas, *J. Am. Chem. Soc.*, 1963, **85**, 2084; A. L. J. Beckwith and A. Zavitsas, *J. Am. Chem. Soc.*, 1986, **108**, 8230; MnO_2 or Bu^tO_2H–Pd^{II}: A. Heumann and B. Akermark, *Angew. Chem., Int. Ed. Eng.*, 1984, **23**, 453; S. Hansson, A. Heumann, T. Rein and B. Akermark, *J. Org. Chem.*, 1990, **55**, 975; J. E. McMurry and P. Kocovsky, *Tetrahedron Lett.*, 1984, **25**, 4187; S. Uemura, S. Fukuzawa, A. Toshimitsu and M. Okano, *Tetrahedron Lett.*, 1982, **23**, 87.
2 K. B. Sharpless and T. Hori, *J. Org. Chem.*, 1976, **41**, 176; G. Kresze, H. Braxmeier and H. Munsterer, *Org. Synth.*, 1987, **65**, 159.
3 K. B. Sharpless, T. Hori, L. K. Truesdale and C. O. Dietrich, *J. Am. Chem. Soc.*, 1976, **98**, 269.
4 D. Mansuy, *Pure Appl. Chem.*, 1990, **62**, 741.
5 L. S. Liebeskind, K. B. Sharpless, R. D. Wilson and J. A. Ibers, *J. Am. Chem. Soc.*, 1978, **100**, 7061.
6 M. Cameron, B. G. Gowenlock and G. Vasapollo, *Chem. Soc. Rev.*, 1990, **19**, 355.
7 R. E. Banks, R. N. Hazeldine and P. J. Miller, *Tetrahedron Lett.*, 1970, 4417; W. Motherwell and J. S. Roberts, *J. Chem. Soc., Chem. Commun.*, 1972, 328; G. T. Knight, *J. Chem. Soc., Chem. Commun.*, 1970, 1016; G. E. Keck, R. R. Webb and J. B. Yates, *Tetrahedron*, 1981, **37**, 4007.