Molybdenum-catalysed allylic amination of alkenes by arylamine–Bu^{t}OOH

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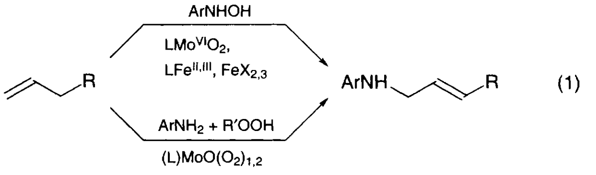
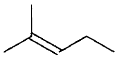
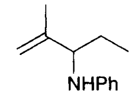
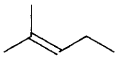
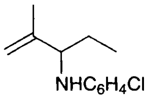
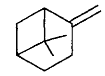
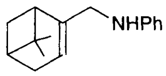
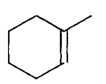
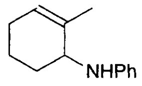
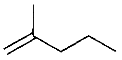
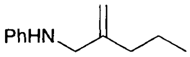
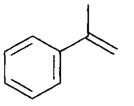
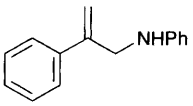
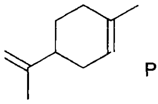
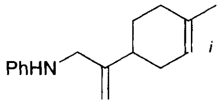
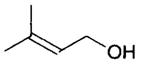
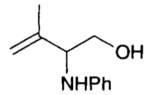
Molybdenum peroxo complexes catalyse the regioselective allylic amination of alkenes by aryl amines with *tert*-butyl hydroperoxide as oxidant.

The selective functionalization of hydrocarbons continues to be a central goal of synthetic chemistry. Although the oxidation of alkenes provides several important industrial and laboratory processes for the preparation of oxygenated compounds,[1] the direct synthesis of organonitrogen compounds from unsaturated hydrocarbons, though very attractive, is largely unrealized.[2] Stimulated by early reports by Sharpless *et al.* and Mares *et al.* of stoichiometric allylic amination of alkenes and acetylenes by LMoO(η^2-RNO) complexes,[3] we and others have recently found that LMo^{VI}O$_2$[4] and Fe^{II,III} complexes[5] and salts[6] catalyse the amination of alkenes by *N*-arylhydroxylamines [eqn. (1)]. These reactions are highly regioselective (*i.e.* with C=C transposition), derived from the involvement of free ArNO as the active aminating agent, except in the catalysis by iron salts. A substantial improvement in the synthetic utility of allylic amination would be realized if the more readily available (and more stable) amines could be used directly as aminating agents. Recent reports of selective amine oxidations by hydrogen peroxide catalysed by peroxomolybdenum complexes[7] prompted us to examine the prospects for effecting direct allylic aminations employing arylamines as aminating agents, hydroperoxide oxidants and peroxomolybdenum complexes as catalyst [eqn. (1)].



(1)

Table 1 Molybdenum-catalysed allylic amination by aryl amines

Run	Alkene	Product	Oxidant	Catalyst	Solvent	TON (24 h)[a]	N-Selectivity (%)[b]
1			Bu^{t}OOH[c]	1[d]	dioxane	8.0	66
2			Bu^{t}OOH	2[e]	dioxane–CH$_2$Cl$_2$	1.9	81
3			Bu^{t}OOH	1	dioxane–CH$_2$Cl$_2$	13.3	91
4			H$_2$O$_2$[f]	1	dioxane–CH$_2$Cl$_2$	1.6	72
5		 [g]	Bu^{t}OOH	1	dioxane–CH$_2$Cl$_2$	2.4	84
6			Bu^{t}OOH	1	dioxane–CH$_2$Cl$_2$	9.2	88
7			Bu^{t}OOH	1	dioxane–CH$_2$Cl$_2$	3.2	64
8		 [h]	Bu^{t}OOH	1	dioxane–CH$_2$Cl$_2$	5.0	92
9			Bu^{t}OOH	1	dioxane–CH$_2$Cl$_2$	0	—
10		 [i]	Bu^{t}OOH	1	dioxane–CH$_2$Cl$_2$	2.5	51
11			Bu^{t}OOH	1	dioxane–CH$_2$Cl$_2$	3.5	60

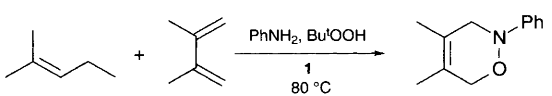
[a] Moles of allyl amine/moles of catalyst (by GC). [b] Moles of allyl amine/total moles of organonitrogen products (by GC). [c] 90% in H$_2$O–Bu^{t}OH. [d] (dipic)(HMPA)MoO(O$_2$). [e] Me$_4$N[(HMPA)MoO(O$_2$)$_2$]. [f] 30% in H$_2$O. [g] Reactant: *p*-ClC$_6$H$_4$NH$_2$. [h] Plus 5–10% of regio-isomer. [i] Plus 33% of the 2-amino (ring attack) isomer.

Slow, simultaneous addition of aniline (3 mmol) and *tert*-butyl hydroperoxide (9.0 mmol) in dioxane or dioxane–CH_2Cl_2 to a heated (70–80 °C) dioxane solution containing excess alkene and 2 mol% of (dipic)(HMPA)Mo(O)(O_2)[7a] (**1**) (dipic = pyridine-2,6-dicarboxylate) produced the corresponding *N*-phenyl-*N*-allylamines with moderate turnover numbers (TON) and fair to moderate yields, accompanied by azo- and azoxy-benzene and polyaniline (Table 1).[8] As found for aminations by *N*-arylhydroxylamines,[4–6] the best yields were obtained with more highly substituted alkenes. Moreover, a single regioisomer (that resulting from C=C transposition) was produced from substrates with unsymmetrical double bonds; this selectivity complements that generally observed from stoichiometric amination by $(TolN)_2X$ (Tol = tolyl, X = S, Se).[2d] Since **1** is a proven catalyst for alkene epoxidation by Bu^tOOH,[9] it is remarkable that allylamine was the only alkene-derived product detected in most cases (except with α-methylstyrene). Interestingly, 30% H_2O_2 was less effective as a coreactant (runs 3,4) despite having greater efficacy than Bu^tOOH in the oxidations of arylamines to nitrosoarenes catalysed by **1**.[7a] Diperoxo complex $[Me_4N](HMPA)MoO(O_2)_2]$[10] (**2**) was less active than **1** (runs 2,3). Although extensive optimization studies have not been performed, use of a CH_2Cl_2–dioxane mixed solvent system noticeably improved the conversion and the selectivity for allylamine (*c.f.* runs 1,3). The turnover number and selectivity were somewhat diminished with *p*-chloroaniline as the aminating agent (run 5). Modestly chemoselective amination of the acyclic disubstituted double bond of limonene (run 10) and selective amination of 3-methylbut-2-en-1-ol (run 11) is also noteworthy. Because of non-productive oxidation of aniline to polyaniline, preparatively useful conversions to allylamines are best effected using excess amine–Bu^tOOH. For example, treatment of 2-methylpent-2-ene with 8 equiv. of $PhNH_2$–Bu^tOOH (5 mol% **1**) produced the corresponding allylamine in 65% yield based on the alkene.

While mechanistic details of the catalysis are presently under investigation, we note that the reaction of aniline with (dipic)$MoO(O_2)$ is known to rapidly produce the *C*-nitroso complex (dipic)$MoO(\eta^2$-RNO)[5] [eqn. (2)]. Trapping experiments, conducted on stoichiometric aminations by this complex[4b] and on the present catalytic amination reaction, point to the intermediacy of free nitrosobenzene [eqn. (3)]. Thus, the reaction of aniline–Bu^tOOH (10% **1**, 80 °C, dioxane) with 1 : 1 2–methylpent-2-ene and 2,3-dimethylbutadiene, an effective trapping agent for PhNO,[4b] exclusively produced the Diels–Alder adduct **3** derived from PhNO [eqn. (4)]. The latter (in the absence of diene) can react with alkenes as an enophile, producing (regioselectively)[11] an *N*-allylhydroxylamine [eqn. (5)] which, in turn, can be reduced (by Mo^{IV}[4] or *via* disproportionation) to the product allylamine [eqn. (6)].

$$\text{(dipic)MoO(O}_2\text{)} + \text{ArNH}_2 \longrightarrow \text{(dipic)MoO(}\eta^2\text{-ArNO)} + \text{H}_2\text{O} \qquad (2)$$

$$\text{(dipic)MoO(}\eta^2\text{-ArNO)} \longrightarrow \text{(dipic)Mo}^{IV}\text{O} + \text{ArNO} \qquad (3)$$



3 only

(4)

$$\text{ArNO} + \text{alkene} \longrightarrow \text{allyl-N(OH)Ar} \qquad (5)$$

$$\text{allyl-N(OH)Ar} \xrightarrow{\text{reduce}} \text{allyl-NHPh} \qquad (6)$$

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