Taming Tethered Nitreniums for Alkene Functionalization Reactions

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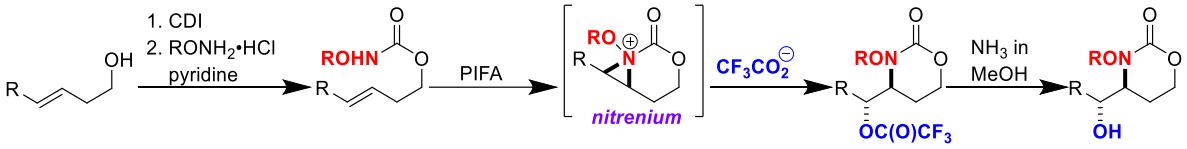


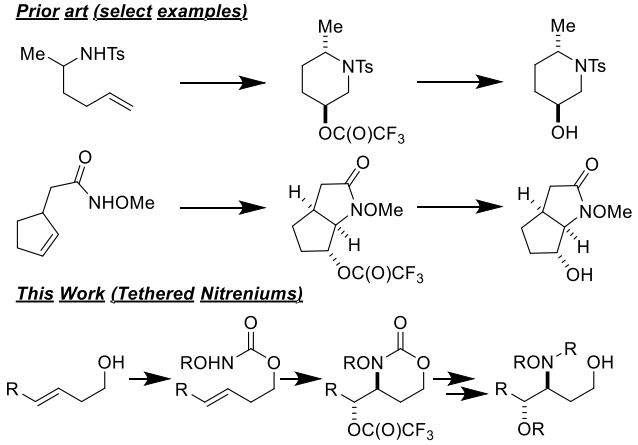
regioselective, stereospecific, metal-free amino-hydroxylation of alkenes

ABSTRACT: Here, we present the first examples of amino-trifluoroacetoxylations of alkenes using *N*-alkoxy carbamate tethers. The trifluoroacetate group can be conveniently removed from the product by treatment with a solution of NH_3 in MeOH. Hypervalent iodine oxidants mediate this transformation, providing a "green" alternative to existing intramolecular amino-hydroxylation protocols which use toxic metals such as osmium. In all cases examined, the reaction is regioselective and stereospecific, with the geometry of the starting alkene controlling the diastereomeric outcome. By analogy to prior art and from our own observations, we posit that a transient nitrenium species serves as a key intermediate in this transformation.

Given the enormous interest in intramolecular alkene functionalization reactions with tethered nitrenes,[1-17] we were surprised to find very few reports with tethered nitreniums,[18-20] their isoelectronic relatives.[21] Nitreniums themselves have been explored in synthetic organic chemistry since the 1960s, arguably starting with the work of Gassman and co-workers.[22] The advent of heteroatom stabilized nitrenium ions allowed for an explosion in synthetic protocols utilizing these species for alkene, alkyne, and arene functionalization reactions.[23-26] We were intrigued that although many alkene functionalization reactions with nitreniums have been developed, almost all employ amines or amides (**Scheme 1**).[27-37] Our laboratory has a programmatic focus on developing alkene functionalization reactions with tethers that can be attached to ubiquitous functional groups such as alcohols and amines and then removed post-reaction.[38-47] Such versatile reactions greatly expand the substrate scope of and employable contexts for intramolecular alkene functionalizations. Here, we describe the first examples of amino-trifluoroacetoxylations of alkenes using *N*-alkoxy carbamate tethers. The trifluoroacetate group can be excised from the product upon mild treatment with a solution of NH_3 in MeOH. Hypervalent iodine oxidants mediate this transformation, providing a "green", metal-free alternative to existing intramolecular amino-hydroxylation protocols which use toxic metals such as osmium.[48, 49] Based on prior art and our own observations, we hypothesize that the formation of a transient nitrenium is a key step in our optimized protocol.

We began reaction exploration with (E)-hex-2-en-1-yl methoxycarbamate, prepared in an excellent yield from commercially available *trans*-2-hexen-1-ol (**Table 1**)

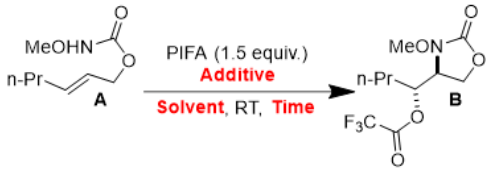
Scheme 1. Existing reports of intramolecular alkene functionalization reactions with nitreniums have employed amines or amides. We present the first examples of using "tethered" nitreniums with removable auxiliaries attached to alcohols.



using a two-step protocol (1. 1,1'-carbonyldiimidazole (CDI), CH_2Cl_2 2. $MeONH_2$•HCl, pyridine).[16] Stirring substrate with 1.5 equivalents of [bis(trifluoroacetoxy)]iodobenzene (PIFA) gave desired product in a 41% yield (**Table 1**, **Entry 1**). Decreasing the reaction concentration from 0.1 M to 0.05 M or 0.033 M improved the yield of product (**Table 1**, **Entries 2 – 3**), mirroring what we have observed in our laboratory's I(III)- promoted alkene disulfonoxylation.[50] Further dilution, however, did not help reaction performance (**Table 1**, **Entries 4 – 5**). In related prior work with *N*-methoxy amides,[36, 37] the authors reported a dramatic, positive effect on yield with the addition of trifluoroacetic acid. In contrast, with our *N*-methoxy carbamates, we saw no improvement with either acid or base additives (**Table 1**, **Entries 6 – 7**). Switching solvents from CH_2Cl_2 to $C_2H_4Cl_2$, $CHCl_3$, or $PhCF_3$

was deleterious to reaction performance (**Table 1**, **Entries 8 – 10**). For this substrate, the use of [bis(trifluoroacetoxy)iodo]pentafluorobenzene (5F-PIFA) led to a diminished product yield (**Table 1**, **Entry 11**), but we found that this was not a general trend across all substrates tested (*vide infra*).

Table 1. Reaction Optimization.

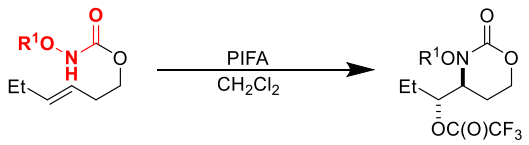


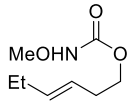
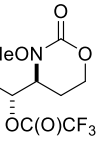
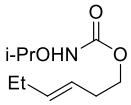
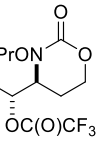
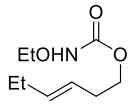
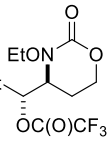
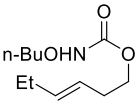
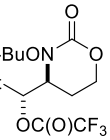
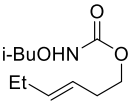
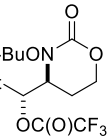
	Solvent	Additive	Time	Concn[a]	Yield[b]
1	CH_2Cl_2	None	4 h	0.1 M	41%
2	CH_2Cl_2	None	4 h	0.05 M	54%
3	**CH_2Cl_2**	**None**	**19 h**	**0.033 M**	**64%**
4	CH_2Cl_2	None	19 h	0.025 M	58%
5	CH_2Cl_2	None	19 h	0.017 M	60%
6	CH_2Cl_2	CF_3CO_2H	19 h	0.033 M	54%
7	CH_2Cl_2	$NaHCO_3$	19 h	0.033 M	48%
8	DCE[c]	None	19 h	0.033 M	54%
9	$CHCl_3$	None	19 h	0.033 M	43%
10	$PhCF_3$	None	19 h	0.033 M	33%
11[d]	CH_2Cl_2	None	19 h	0.033 M	56%[e]

[a] concn = reaction concentration
[b] Estimated by ^{1}H NMR integration against an internal standard; relative configuration of product is shown.
[c] DCE = 1,2-dichloroethane
[d] [Bis(trifluoroacetoxy)iodo]pentafluorobenzene (5F-PIFA) used in place of [Bis(trifluoroacetoxy)iodo]benzene (PIFA)
[e] isolated yield

We next wished to explore the scope of carbamate tethers (**Scheme 2**). We found that in addition to *N*-methoxy carbamates, *N*-ethoxy, *N*-isopropoxy, *N*-n-butoxy, and *N*-isobutoxy tethers were all very competent in delivering product (**Scheme 2**, **Entries 1 – 5**). We hypothesize that the increase in steric bulk with the *N*-isopropoxy tether caused a slight diminution in product formation (**Scheme 2**, **Entry 2**). In all cases, the formation of a single diastereomer was observed (within the limits of ^{1}H NMR detection), increasing the utility of this method. A crystal structure of product **2** (**CCDC: 2363976**) allowed assignment of the relative stereochemistry of the two newly formed stereocenters, and the relative configurations of other products have been assigned by analogy. Not all tethers were useful for this reaction (**Scheme 2**, **Poor Performers**). In some cases, we hypothesize that steric bulk precluded reactivity (**Scheme 2**, **Substrates 11** and **13**). In others, side reactions led to complex product mixtures (**Scheme 2**, **Substrates 12** and **16**). We have also shown that tethers bearing an *N*-alkoxy substituent were necessary for product formation. With *N*-alkyl carbamates or *N*-hydroxy carbamates, there was little to no

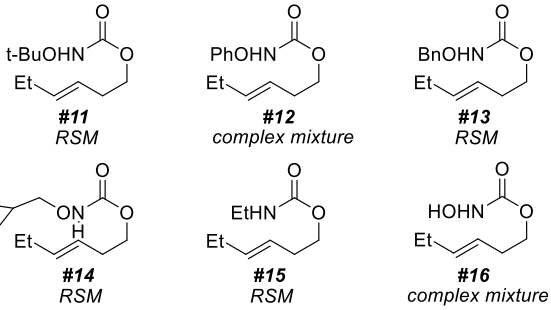
Scheme 2. Structure-Reactivity Relationship with Nitrenium Tethers.



Entry	Substrate	Product	Isolated Yield	
1			*(#1, #2)*[a]	85% *[X-ray]*
2			*(#3, #4)*	75%
3			*(#5, #6)*	90%
4			*(#7, #8)*	92%
5			*(#9, #10)*	87%

[a] (Substrate number, Product number)

Poor Performers

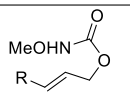
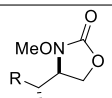
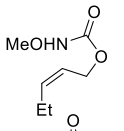
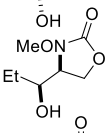
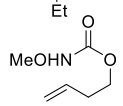
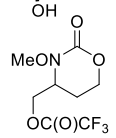
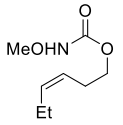
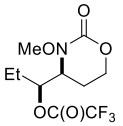
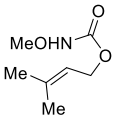
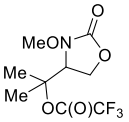
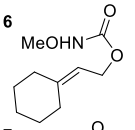
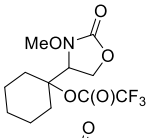
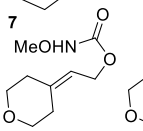
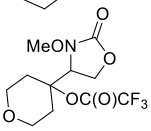
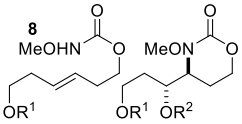
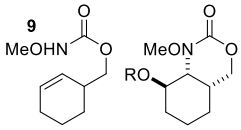
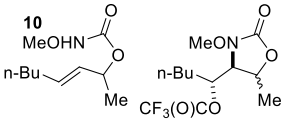
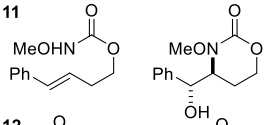
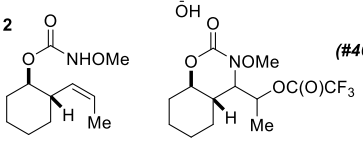
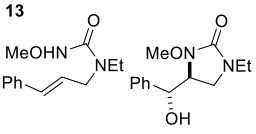


RSM = recovered starting material

desired product formation (**Scheme 2**, **Substrates 15** and **16**).

Our optimized protocol was compatible with a variety of substrates (**Scheme 3**). *Cis*-di-substituted alkenes, *trans*-di-substituted alkenes, and tri-substituted alkenes all reacted well. In general, homoallylic carbamates gave better yields than analogous allylic ones. Terminal alkenes could be functionalized, but the products were unstable to purification (**Scheme 3**, **Entry 3**). Several functional groups were tolerated, including alkyl ethers, benzylic ethers, tosylates, and TBS ethers (**Scheme 3**, **Entries 7** and **8**). Stereoarrays could be assembled in one pot with good to excellent diastereoselectivities (**Scheme 3**, **Entries 9, 10,** and **12**). In addition to carbamate tethers, we were pleased to see excellent reactivity with substrates bearing urea tethers (**Scheme 3**, **Entry 13**).

Scheme 3. Alkene scope and functional group compatibility.

Entry	Substrate	Product	Isolated Yield
1		 R = n-Pr *(#17, #18)*[a] R = Ph *(#19, #20)*	55% 60%
2		 *(#21, #22)*	40%
3		 *(#23, #24)*	51%[b]
4		 *(#25, #26)*	86%
5		 *(#27, #28)*	68%
6		 *(#29, #30)*	40%
7		 *(#31, #32)*	39%
8		R^1 = Bn, R^2 = TFA *(#33, #34)* 65% R^1 = TBS, R^2 = TFA *(#35, #36)* 55% R^1 = Ts, R^2 = H *(#37, #38)* 58%	
9		R = C(O)CF$_3$ *(#39, #40)* 71%[b] (39%[c]) R = H *(#39, #41)* 47% *dr = >20:1*[d]	
10		*(#42, #43)* 52% *dr = 3:1*	
11		*(#44, #45)* 63%	
12		*(#46, #47)* 72% *dr = >20:1*[e]	
13		*(#48, #49)* 89%	

[a] (Substrate number, Product number); conditions: PIFA or 5F-PIFA (1.5 equiv.) in CH_2Cl_2 and, for alcohol products, treatment with NH_3 in MeOH (5 equiv.)

[b] Estimated by ^{1}H NMR integration against an internal standard due to product decomposition during purification

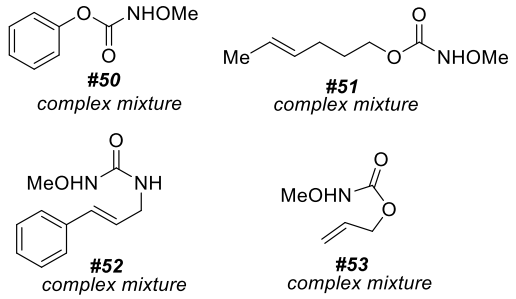
[c] isolated yield

[d] relative stereochemistry assigned from nOe data

[e] relative stereochemistry unassigned

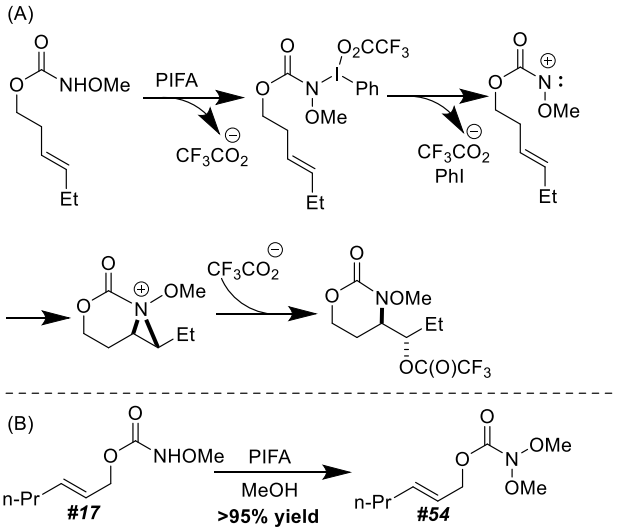
Some examples of poorly performing substrates are shown in **Scheme 4.** With our current protocol, we have seen no evidence of arene functionalization (**Scheme 4**, **Substrate 50**). In addition, while allylic and homoallylic carbamates fared well (**Scheme 2** and **Scheme 3**), carbamates with more remote double bonds (**Scheme 4**, **Substrate 51**) failed to react productively. With urea **52** (**Scheme 4**), the presence of an additional activated N-H likely led to a complex product mixture.

Scheme 4. Poor Performers.



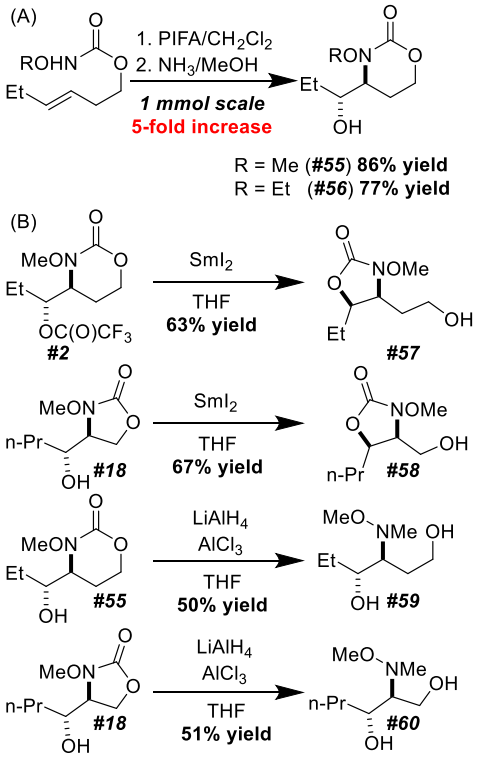
Given the high diastereoselectivity and predictable stereochemical outcome across all substrates tested and by analogy to prior art, [21] we propose that our reaction follows the mechanism depicted in **Scheme 5A**. A transient nitrenium is formed from the oxidation of the *N*-alkoxy carbamate by an I(III) species. This electrophilic nitrenium attacks the pendant olefin to form a transient bicyclic aziridinium ion. This aziridinium ion is ring-opened in an *exo*-selective, S_N2 reaction with $CF_3CO_2^-$. During the solvent-screen portion of the reaction optimization, we observed the quantitative formation of (E)-hex-2-en-1-yl dimethoxycarbamate (**Compound 54**) when (E)-hex-2-en-1-yl methoxycarbamate was reacted with PIFA in MeOH (**Scheme 5B**). With this reaction, we posit that the nitrenium intermediate was rapidly trapped by solvent.

Scheme 5. (A) Putative reaction mechanism. (B) Indirect evidence of nitrenium formation.



The scale of our reaction could be increased from 0.2 mmol to 1 mmol without loss of yield or selectivity (**Scheme 6A**). The products were amenable to further transformations. Upon treatment with SmI_2, a very interesting and unexpected carbamate transposition occurred with both trifluoroacetate **2** and oxazolidinone **18** (**Scheme 6B**). With substrates **55** and **18**, the carbamate could be excised with $LiAlH_4/AlCl_3$,[51] allowing for the preparation of linear amino-alcohols.

Scheme 6. (A) Scale up. (B) Applications.



In summary, we have developed a convenient alkene amino-hydroxylation mediated by commercial hypervalent I(III) oxidants. To our knowledge, this is the first study which explores the synthetic utility of nitreniums generated *in situ* using carbamate tethers. Across a range of substrates, the reaction is predictably regioselective and diastereoselective. Given the importance of toxic-metal free protocols for alkene functionalization reactions, we expect this technology to be welcomed by academic and industrial chemists.

ASSOCIATED CONTENT

Supporting Information.
Additional experimental details including reaction procedures, X-ray crystallographic data, and NMR spectra.

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