Communication

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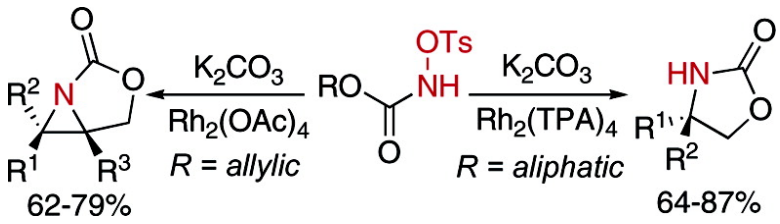

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N-Tosyloxycarbamates as a Source of Metal Nitrenes: Rhodium-Catalyzed C−H Insertion and Aziridination Reactions

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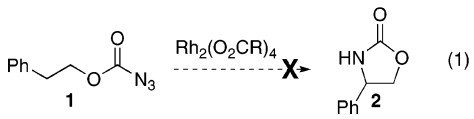
The activation of nitrogen derivatives with transition-metal complexes has attracted considerable attention in the past years.[1] For instance, metal carbenes have been efficiently obtained from transition-metal-catalyzed decomposition of diazo compounds[2] and led to numerous processes for C−C bond formation, including cyclopropanation,[3] C−H insertion,[4] and olefination reactions.[5] In contrast to the well-defined reactivity of diazo compounds with transition-metal complexes, activation of azide derivatives to produce nitrene metal species is not common, although both reactions involve the loss of nitrogen (N_2).[6] Indeed, nitrenes were initially produced via the thermal or photochemical decomposition of azides or via the base-mediated α-elimination of *N*-chloro and *N*-sulfonyloxy compounds.[7] Unselective and low yielding processes were typically observed with nitrenes generated under such reaction conditions.[8] Hypervalent oxidative iodine reagents[9] have led to improved yields and selectivities, thus efficient transition-metal-catalyzed aziridination[10] and C−H insertion reactions[1,11] of nitrene species have been reported.[12] However, one of the major drawbacks associated with the use of hypervalent iodine reagents is the generation of a stoichiometric amount of iodobenzene. In this communication, we present the first example of a rhodium-catalyzed decomposition of *N*-tosyloxycarbamates to produce nitrenes which undergo either C−H insertion or aziridination reactions with high yields and chemoselectivity.[13]

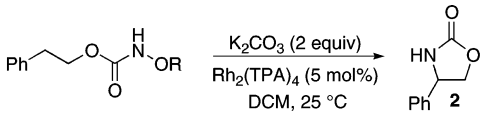
Our interest in the activation of nitrogen derivatives[14] prompted us to study the reaction of azide derivatives with transition-metal complexes to produce nitrenes that could undergo C−H insertion reactions. We first studied the decomposition of azidoformate **1** in the presence of various rhodium carboxylate complexes, as the corresponding rhodium nitrene has been shown to produce oxazolidinone **2** (eq 1).[1a] However, no reaction was observed under a variety of reaction conditions; azidoformate **1** was remarkably stable in the presence of various transition-metal complexes.[6,15]



(1)

Presumably, the coordination of the rhodium complex occurs at the terminal nitrogen of the azide moiety, precluding to the expulsion of nitrogen (N_2). We rationalized to replace the leaving group (N_2) with a less coordinating species, such as an ester or a sulfonate group. We prepared a number of alkoxycarbamate derivatives which were tested in the rhodium-catalyzed C−H insertion reaction, using rhodium(II) triphenylacetate dimer as the catalyst and potassium carbonate as a base (Table 1). Whereas the carboxycarbamates were found to be stable under these reaction conditions (entries 1−3), the formation of oxazolidinone **2** was observed with *N*-arenesulfonyloxycarbamates (entries 4 and 5). Low conversion was obtained with the *N*-(*p*-nitrophenyl)sulfonyloxycarbamate, which led mainly to the corresponding carbamate (ROC(O)NH_2) (entry 4). Conversely, high yields could be achieved with

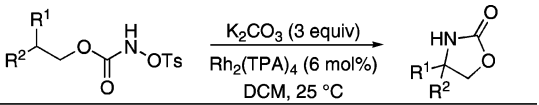
Table 1. Rhodium-Catalyzed C−H Insertion Reaction of Nitrenes from Various *N*-Alkoxycarbamates

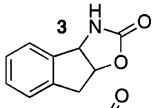
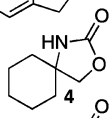
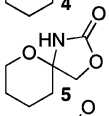
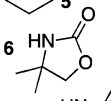
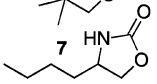


Entry	R	Conv. (Isolated yield)[a]
1	—CO_2Ph	≤5%
2	—COMe	≤5%
3	—CO*t*-Bu	≤5%
4	—SO_2—C$_6$H$_4$—NO_2	15%
5	—SO_2—C$_6$H$_4$—Me	≥95% (92%)[b]

[a] Conv. determined by GC-MS. [b] $Rh_2(TPA)_4$ (6 mol%), K_2CO_3 (3 equiv).

Table 2. Synthesis of Oxazolidinones from *N*-Tosyloxycarbamates



Entry	Product	Isolated yield
1	 **3**	84%
2	 **4**	84%
3	 **5**	87%
4	 **6**	71%
5	 **7**	64%

N-tosyloxycarbamates,[16] and optimum isolated yields were achieved using 6 mol % of catalyst and 3 equiv of K_2CO_3 in CH_2Cl_2 or dichloroethane (entry 5).[17] Rhodium(II) triphenylacetate dimer proved to be a better catalyst than $Rh_2(OAc)_4$, probably due to a better solubility of the rhodium nitrene species in an organic solvent. No oxazolidinone **2** was formed in the absence of catalyst, and the base also proved to be essential, as only ∼5% conversion was achieved with only the rhodium catalyst. K_2CO_3 was the most convenient base, although other potassium bases, such as *t*-BuOK, were equally effective.[18] These reaction conditions were compatible with various *N*-tosyloxycarbamates to produce oxazolidinones in 64−87% isolated yields after 6−7 h at room temperature (Table 2). The nitrene insertion proceeded efficiently in benzylic and tertiary C−H bonds (entries 1−4). Furthermore, oxazolidinone **7**, resulting from the insertion of the nitrene species into a secondary

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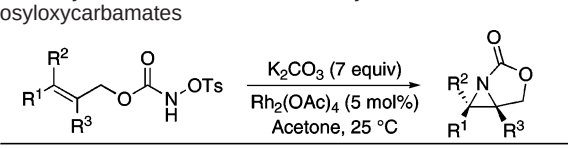
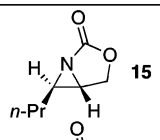
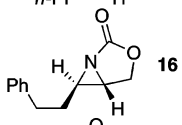
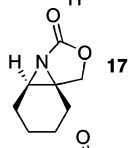
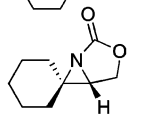
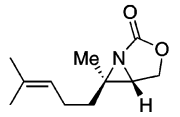
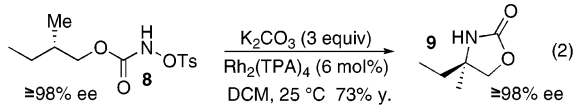
Table 3. Synthesis of Aziridines from Allylic *N*-Tosyloxycarbamates

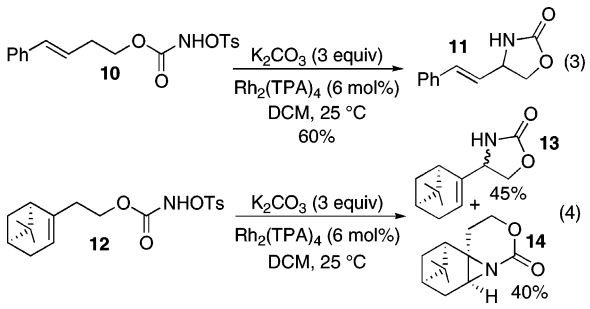


Entry	Product	Isolated yield
1	 **15**	67%
2	 **16**	74%
3	 **17**	79%
4	 **18**	79%
5	 **19**	62%

C−H bond, was isolated in 64% yield. The C−N bond formation was stereospecific, as the rhodium-catalyzed insertion of chiral enantioenriched *N*-tosyloxycarbamate **8** occurred with retention of configuration, providing oxazolidinone **9** without racemization (eq 2).



Nitrene species are also known to perform aziridination reactions, thus substrates derived from homoallylic alcohols may lead to both allylic C−H insertion or aziridination products.[9] However, only traces of the aziridination product was observed from **10**, and oxazolidinone **11** was isolated in 60% yield (eq 3). In contrast, the decomposition of Nopol-derived *N*-tosyloxycarbamate **12** (containing a more electron-rich double bond) led to 45% of C−H insertion product **13** as a mixture of diastereomers and 40% of aziridination product **14** as a single diastereomer (eq 4).[19] Conversely, the reaction of allylic *N*-tosyloxycarbamates is chemoselective and leads to aziridination products exclusively in the presence of 5 mol % of $Rh_2(OAc)_4$, an excess of K_2CO_3 in acetone.



A variety of aziridines, resulting from the intramolecular reaction of nitrene species generated from *N*-tosyloxycarbamates, were obtained under these reaction conditions with good yields (Table 3). The aziridination reaction is stereospecific, as only one diastereomer was observed. The aziridination reaction proceeded equally well with disubstituted (entries 1−2) and trisubstituted alkenes (entries 3−5).[20]

In conclusion, we have devised a new general process to convert *N*-tosyloxycarbamates into metal nitrene species which can undergo aziridination and C−H insertion reactions efficiently using rhodium catalysts. This very practical transition-metal-catalyzed process does not require the use of hypervalent iodine reagents and led to the desired products with high yields.

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Supporting Information Available: Characterization data for new compounds and experimental procedures. This material is available free of charge via the Internet at http://pubs.acs.org.

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(16) *N*-tosyloxycarbamates are very easily prepared via tosylation of *N*-hydroxycarbamates (see Supporting Information for details).
(17) Lower catalyst loading led to lower yields (5 mol %:83% yield of **2**).
(18) Low conversion was observed with Na_2CO_3, $NaHCO_3$, and MgO.
(19) For X-ray crystal structure, see Supporting Information.
(20) Both C−H insertion and aziridination reactions are not sensitive to water, and spectrograde solvent may be used.

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