Pure Appl. Chem., Vol. 78, No. 2, pp. 363–375, 2006.
doi:10.1351/pac200678020363

Catalytic activation of nitrogen derivatives with transition-metal complexes*

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Abstract: Studies regarding the transition-metal-catalyzed decomposition of nitrogen derivatives toward Curtius rearrangement and the formation of nitrenes which undergo C–H insertion and aziridination reactions are presented. These processes lead to the formation of C–N bond with a high level of selectivity and efficiency.

Keywords: Curtius rearrangement; nitrene; aziridination; C–H insertion; rhodium.

The activation of diazo compounds with transition-metal complexes derived from copper, rhodium, ruthenium, palladium, etc. [1] is a well-known process and had led to the development of efficient cyclopropanation [2], insertion [3], ylide formation [4], and olefination processes [5]. In most cases, metal carbenes are involved as intermediates. In the past years, we have disclosed a new methylenation process involving the activation of trimethylsilyldiazomethane with the Wilkinson's catalyst to generate the corresponding methylenetriphenylphosphorane, in the presence of triphenylphosphine and 2-propanol [6]. We have shown that the reaction pathway proceeded through nitrogen coordination of the diazo compound with the rhodium complex, rather than the formation of a metal carbene species (Fig. 1) [7].

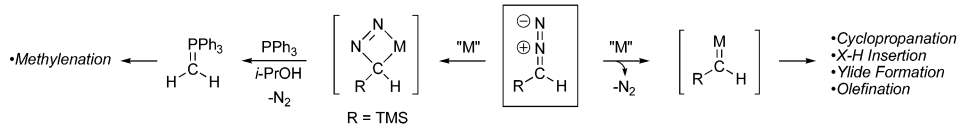

Fig. 1

More recently, we became interested in the activation of azide derivatives with transition-metal complexes. In contrast to the well-defined reactivity of diazo compounds with transition-metal complexes, examples of such reactions with azides are scarce [8]. We are interested to study the activation of acyl azides with transition-metal complexes toward Curtius rearrangement as well as for the formation of nitrene species, which could undergo aziridination and C–H insertion reactions (Fig. 2). Both processes involve the lost of nitrogen, similarly to the reaction with diazo compounds.

Pure Appl. Chem.* **78, 197–523. An issue of reviews and research papers based on lectures presented at the 13th IUPAC International Symposium on Organometallic Chemistry Directed Towards Organic Synthesis (OMCOS-13), Geneva, Switzerland, 17–21 July 2005.
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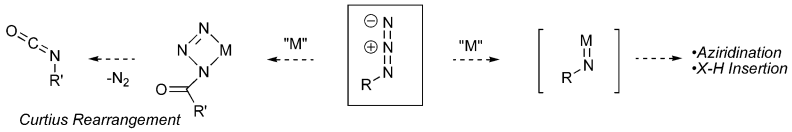
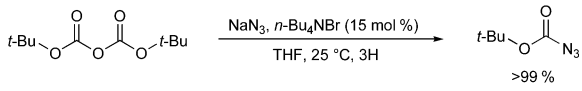


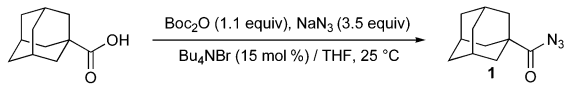
Fig. 2

The Curtius rearrangement is the formation of an isocyanate from the corresponding acyl azide [9]. The rearrangement is concerted and does not involve a nitrene species. The acyl azide is typically prepared from an activated derivative of the corresponding carboxylic acid [10–13]. Usually, the isocyanate is further reacted with a nucleophile, generally an alcohol to produce the corresponding carbamate. Diphenylphosphorazidate [14], which serves to activate the carboxylic acid and as a source of azide, is the most widely used reagent to perform the Curtius rearrangement [15]. Such a reagent allowed the direct conversion of carboxylic acids into carbamates. However, a number of drawbacks are associated with the use of this reagent including the high temperature and the difficulty to purify the desired product from the phosphorus residues [16]. These problems prompted us to study other reagents, which could also activate carboxylic acids and serve as an azide source while generating less harmful by-products.

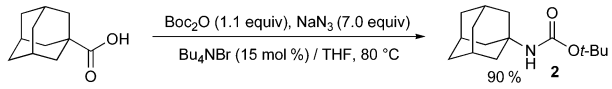
We turned our attention to the use of *tert*-butyl azidoformate, which could be reacted with carboxylate anions to form the corresponding mixed anhydride; this species will then be trapped by the azide anion to produce the desired acyl azide. In this case, the by-products are CO_2 and *tert*-butoxyde, the latter being reutilized while reacting with the isocyanate intermediate. Although the preparation of *tert*-butyl azidoformate has been disclosed in the literature [17], detonation has been reported during the final distillation under reduced pressure. We decided to devise a new procedure to generate in situ the desired reagent, avoiding the purification step. Indeed, the reaction between di-*tert*-butyl dicarbonate and sodium azide in the presence of tetrabutylammonium bromide led to a solution of *tert*-butyl azidoformate, as analyzed by GC–MS (eq. 1). Furthermore, addition of adamantyl carboxylic acid led to the formation of acyl azide **1**, which upon heating provided the corresponding Boc-carbamate **2** in 90 % yield (eqs. 2 and 3).



(1)



(2)



(3)

Presumably, *tert*-butyl azidoformate is generated from the reaction between di-*tert*-butyl dicarbonate and sodium azide together with sodium *tert*-butoxyde, which deprotonate the carboxylic acid leading to the carboxylate anion (Fig. 3).

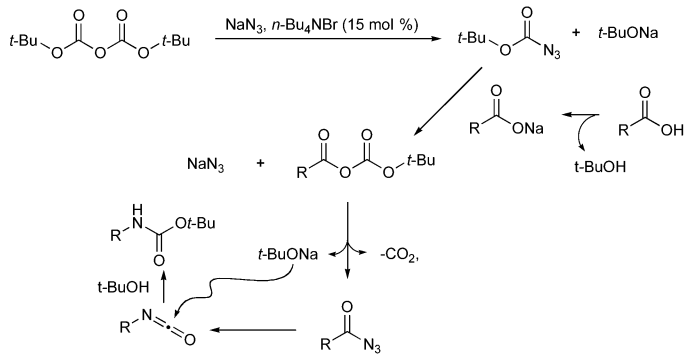
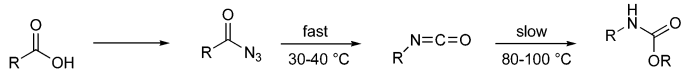


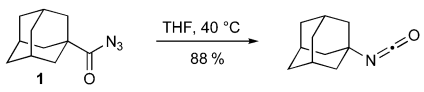
Fig. 3

The condensation with *tert*-butyl azidoformate formed the mixed anhydride, which further reacted with the azide anion to produce the acyl azide. Upon heating, the rearrangement occurs to produce the corresponding isocyanate, which condenses in situ with the by-product *tert*-butoxyde/*tert*-butanol to lead to the desired carbamate.

Before examining the effect of transition-metal complexes to promote the Curtius rearrangement, we decided to study the kinetics of this new one-pot process, which allows the direct conversion of carboxylic acids into Boc-protected amines. Surprisingly, we found that the slowest step was not the rearrangement itself, rather the addition of the nucleophile onto the isocyanate moiety. The rearrangement occurred at 30–40 °C for aliphatic acyl azides, whereas the formation of the carbamate from the isocyanate intermediate proceeded only at 80 °C (eq. 4). Indeed, we have observed the formation of the isocyanate from acyl azide **1** by heating a THF solution at 40 °C (eq. 5).



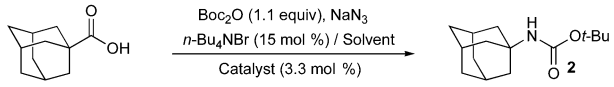
(4)



(5)

It is then not very surprising to find that a Lewis acid complex, such as zinc(II) triflate, was the best metal complex to catalyze this one-pot procedure to produce the desired carbamate **2** at 40 °C (Table 1). Other zinc metal complexes showed catalytic activity, although they are not as efficient as zinc(II) triflate (entries 1–5). The reaction required the use of 3.5 equiv of sodium azide and does not proceed at a temperature below 40 °C (entries 6 and 7). Furthermore, the reaction is very sensitive to solvent effect, and the reaction was ineffective when we switch from THF to DME or dioxane (entries 8 and 9).

Table 1 Zinc-catalyzed Curtius rearrangement: Optimization.

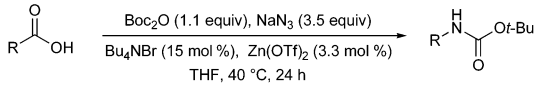


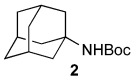
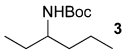
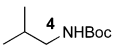
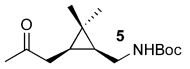
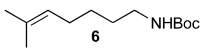
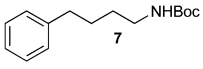
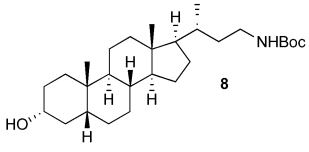
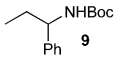
Entry	Catalyst	Conditions	Carbamate[a,b]
1	ZnF_2	NaN_3 (3.5 equiv) / THF, 40 °C	40 %
2	$ZnCl_2$	NaN_3 (3.5 equiv) / THF, 40 °C	60 %
3	$ZnBr_2$	NaN_3 (3.5 equiv) / THF, 40 °C	70 %
4	ZnI_2	NaN_3 (3.5 equiv) / THF, 40 °C	20 %
5	**$Zn(OTf)_2$**	**NaN_3 (3.5 equiv) / THF, 40 °C**	**≥95 %**
6	$Zn(OTf)_2$	NaN_3 (2.5 equiv) / THF, 40 °C	30 %
7	$Zn(OTf)_2$	NaN_3 (3.5 equiv) / THF, 30 °C	5 %
8	$Zn(OTf)_2$	NaN_3 (3.5 equiv) / DME, 40 °C	5 %
9	$Zn(OTf)_2$	NaN_3 (3.5 equiv) / Dioxane, 40 °C	20 %

[a] Conversion by GC-MS. [b] Acyl azide and isocyanate are the remaining products.

We have used our optimized reaction conditions to react a number of carboxylic acids. In the presence of 1.1 equiv of di-*tert*-butyl dicarbonate, 3.5 equiv of sodium azide, 15 mol % of tetrabutylammonium bromide, and 3.3 mol % of zinc(II) triflate in THF at 40 °C, a variety of carbamates were prepared in good to excellent yields, from tertiary, secondary, and primary carboxylic acids (Table 2). The reaction conditions are compatible with unprotected ketones and alcohols to lead to carbamates **5** and **8** in 68 and 72 % isolated yield (entries 4 and 7). 2-Phenylbutanoic acid led to the formation of carbamate **9** together with the corresponding *tert*-butyl ester, which probably resulted from the addition of the *tert*-butoxy moiety onto the corresponding ketene, generated from the elimination of hydrazoic acid (entry 8).

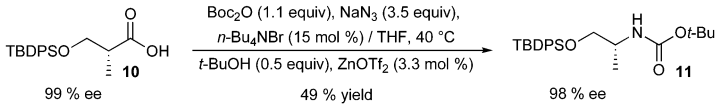
Table 2 Zinc-catalyzed Curtius rearrangement: Substrate scope.



Entry	Carbamate	Yield (%)[a]
1	 **2**	90
2	 **3**	94
3	 **4**	77
4	 **5**	68
5	 **6**	80
6	 **7**	57
7	 **8**	72
8	 **9**	58

[a] Isolated yields.

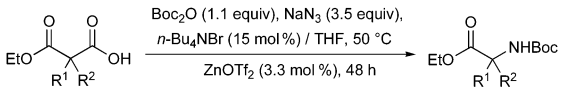
The Curtius rearrangement performed under these new reaction conditions proceeded with retention of configuration when starting from chiral enantioenriched α-substituted carboxylic acid **10**. However, under the standard reaction conditions described before, carbamate **11** was recovered with only 91 % ee (49 % yield), indicating an erosion of the enantiomeric excess during the process. *tert*-Butanol was added to decrease the basicity of the reaction mixture, and the desired product was obtained in same yield, but with almost no loss in the enantiomeric excess (eq. 6).

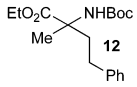
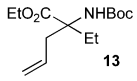
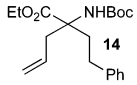


(6)

We have also synthesized protected α,α-disubstituted amino acids from the corresponding monoester malonic acid in good yields (Table 3). As the corresponding acyl azides are less reactive toward Curtius rearrangement, it was required to heat the reaction mixture at 50 °C for 48 h. No decarboxylation reaction of the substrate was observed.

Table 3 Zinc-catalyzed Curtius rearrangement: Synthesis of protected α,α-disubstituted amino acids.



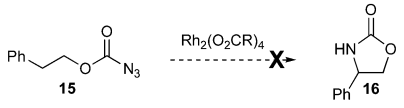
Entry	Carbamate	Yield (%)[a]
1	 **12**	75
2	 **13**	65
3	 **14**	60

[a] Isolated yields.

Our work on the Curtius rearrangement has provided a new one-pot process which allows the direct conversion of carboxylic acids into carbamates. Our initial investigation of the mechanism showed that the addition of *tert*-butanol onto the isocyanate is the slowest step of the sequence and is accelerated by adding a mixture of tetrabutylammonium bromide and zinc triflate (presumably through the formation of a zinc carbamoyl bromide species).

We were also interested in studying the formation of metal nitrene species from azides to undergo aziridination and C–H insertion reactions. As mentioned above, the activation of azides with transition-metal complexes to form metal nitrene species is scarce [8]. Conversely, free nitrenes are obtained from the thermal or photochemical decomposition of azides or via the base-mediated α-elimination of *N*-chloro and *N*-sulfonyloxy compounds [18]. However, nitrenes generated under such reaction conditions led typically to unselectivity and low yield [19]. To achieve highly efficient processes, metal nitrenes are typically produced by oxidation of the corresponding amine with hypervalent iodine reagents [20] in the presence of copper and rhodium catalysts [21]. Using such a strategy, highly efficient transition-metal-catalyzed aziridination of alkenes has been reported. [22,23]. More recently, rhodium-catalyzed intramolecular C–H insertion reactions have been reported using the oxidation of carbamates and sulfonylamines with hypervalent iodine reagents [24,25].

To pursue our investigation on the activation of azides with transition-metal complexes, we decided to study the decomposition of azidoformate **15** in the presence of various rhodium carboxylate complexes (eq. 7). The corresponding rhodium nitrene is known to produce oxazolidinone **16** through a C–H insertion reaction [25a]. However, no reaction was observed: azidoformate **15** was remarkably stable in the presence of various transition-metal complexes.



(7)

These results are quite surprising considering the analogy and the relative stability of azide and diazo derivatives (Fig. 4). It is indeed easier to thermally decompose an azide into a free nitrene than to form the free carbene from the corresponding diazo (the N=N bond is weaker than the C=N bond) [26].

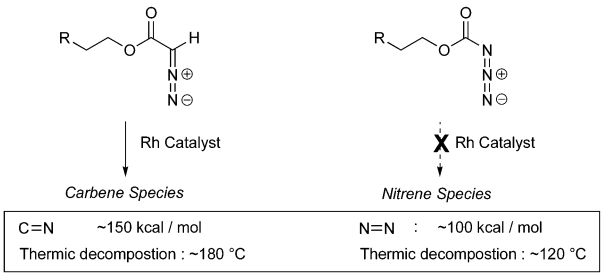


Fig. 4

We postulate that the coordination of the transition-metal complex with the azide moiety occurs at the terminal nitrogen rather than at the internal nitrogen, precluding to the expulsion of nitrogen (N_2) (Fig. 5). We rationalized to use a less coordinating leaving group than nitrogen (N_2) to favor the coordination at the internal nitrogen. Anions derived from alkoxycarbamate derivatives seem appealing and should be easily prepared through deprotonation reaction.

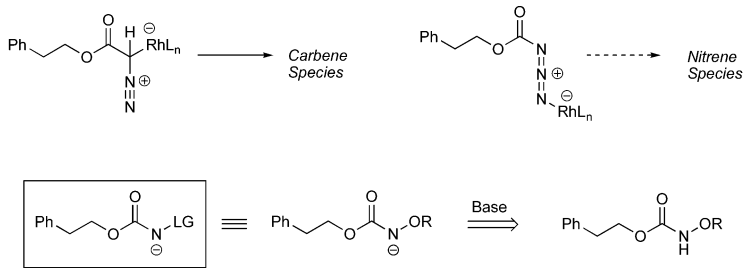
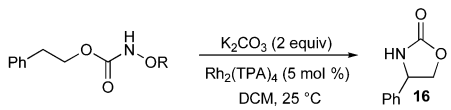


Fig. 5

We have tested a number of alkoxycarbamate derivatives into the rhodium-catalyzed C–H insertion reaction, using rhodium(II) triphenylacetate dimer as the catalyst and potassium carbonate as a base (Table 4).

Table 4 Rhodium-catalyzed C–H insertion reaction of nitrenes from various *N*-alkoxycarbamates.



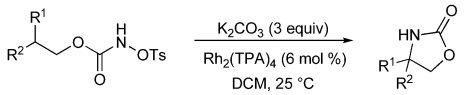
Entry	R	Conv. (Isolated yield)[a]
1	—CO_2Ph	≤5 %
2	—COMe	≤5 %
3	—CO*t*-Bu	≤5 %
4	—SO_2—C$_6$H$_4$—NO_2	15 %
5	—SO_2—C$_6$H$_4$—Me	≥95 % (83 %)
6	—SO_2—C$_6$H$_4$—Me	≥95 % (92 %)[b]

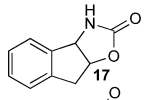
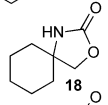
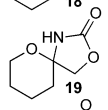
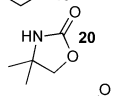
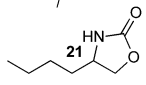
[a]Conv. determined by GC-MS. [b]$Rh_2(TPA)_4$ (6 mol %), K_2CO_3 (3 equiv)

Whereas the carboxycarbamates were found to be stable under these reaction conditions (entries 1–3), the formation of oxazolidinone **16** was observed with *N*-arenesulfonyloxycarbamates (entries 4 and 5) [27,28]. *N*-(*p*-Nitrophenyl)sulfonyloxycarbamate led mainly to the corresponding carbamate ($ROC(O)NH_2$) with only 15 % of the desired oxazolidinone **16** (entry 4). Conversely, high yields were observed with *N*-tosyloxycarbamates [*N*-(*p*-methylphenyl)sulonyloxycarbamates] and optimum isolated yields were achieved using 6 mol % of catalyst and 3 equiv of potassium carbonate in CH_2Cl_2 or dichloroethane (entries 5 and 6). Rhodium(II) triphenylacetate dimer proved to be a better catalyst than $Rh_2(OAc)_4$, probably due to a better solubility of the corresponding rhodium nitrene species in an organic solvent. No oxazolidinone **16** was formed in the absence of catalyst, and the base proved also essential, as only ~5 % conversion was achieved with only the rhodium catalyst. Potassium carbonate was the most convenient base, although other potassium bases such as potassium *t*-butoxyde were equally effective. However, sodium carbonate, sodium bicarbonate, and magnesium oxide led to the formation of oxazolidinone **16** in only 15–20 % conversion.

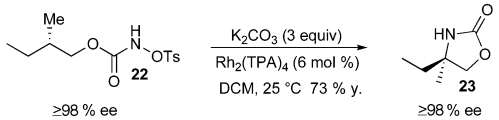
Various oxazolidinones were produced from *N*-tosyloxycarbamates in 64–87 % isolated yields after 6–7 h at room temperature (Table 5). The nitrene insertion proceeded efficiently in benzylic and tertiary C–H bonds (entries 1–4). Furthermore, oxazolidinone **21** resulting from the insertion of the nitrene species into a secondary C–H bond was isolated with 64 % yield (entry 5).

Table 5 Synthesis of oxazolidinones from *N*-tosyloxycarbamates.



Entry	Product	Isolated yield
1	 **17**	84 %
2	 **18**	84 %
3	 **19**	87 %
4	 **20**	71 %
5	 **21**	64 %

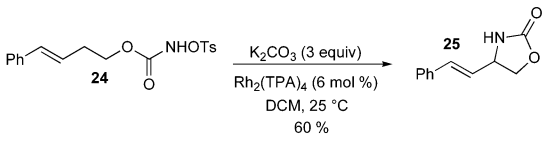
The C–N bond formation was stereospecific, as the rhodium-catalyzed insertion of chiral enantioenriched *N*-tosyloxycarbamate **22** occurred with retention of configuration, providing oxazolidinone **23** without racemization (eq. 8).



(8)

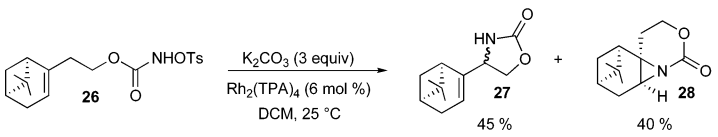
As nitrene species are known to perform aziridination reactions, the homoallylic *N*-tosyloxycarbamate **24** may in theory lead to both allylic C–H insertion and aziridination products. However, only

traces of the aziridination product were observed, and oxazolidinone **25** was isolated in 60 % yield (eq. 9).



(9)

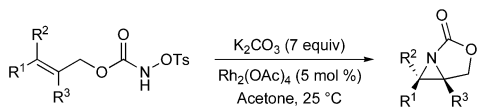
In sharp contrast, the decomposition of Nopol-derived *N*-tosyloxycarbamate **26** (containing a more electron-rich double bond) led to 45 % of C–H insertion product **27** as a mixture of diastereomers, and 40 % of aziridination product **28** as a single diastereomer (eq. 10).

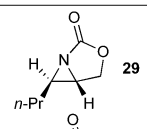
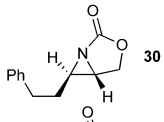
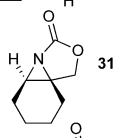
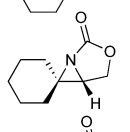
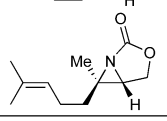


(10)

The reaction of allylic *N*-tosyloxycarbamates was chemoselective and led 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 in good yields (Table 6). The aziridination reaction is stereospecific as only one diastereomer was observed.

Table 6 Synthesis of aziridines from allylic *N*-tosyloxycarbamates.



Entry	Product	Isolated yield
1	 **29**	67 %
2	 **30**	74 %
3	 **31**	79 %
4	 **32**	79 %
5	 **33**	62 %

In conclusion, we have devised new transition-metal-catalyzed processes for the formation of C–N bonds via Curtius rearrangement, C–H insertion, and aziridination reactions, which result in high yields and selectivities.

ACKNOWLEDGMENTS

This research was supported by NSERC (Canada), the Canada Foundation for Innovation, Pfizer Inc., Boehringer Ingelheim (Canada) Ltée, Merck Frosst Canada, and the Université de Montréal. The authors thank Michel Couturier (Pfizer Inc., Groton) for helpful discussions and the Charette group (Université de Montréal) for the use of chiral columns. O. L. thanks the "Conseil général de la Guadeloupe" for a graduate fellowship. K. H. thanks NSERC (Canada) for a graduate scholarship.

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