Highlight Review

Azide Compounds: Nitrogen Sources for Atom-efficient and Ecologically Benign Nitrogen-atom-transfer Reactions

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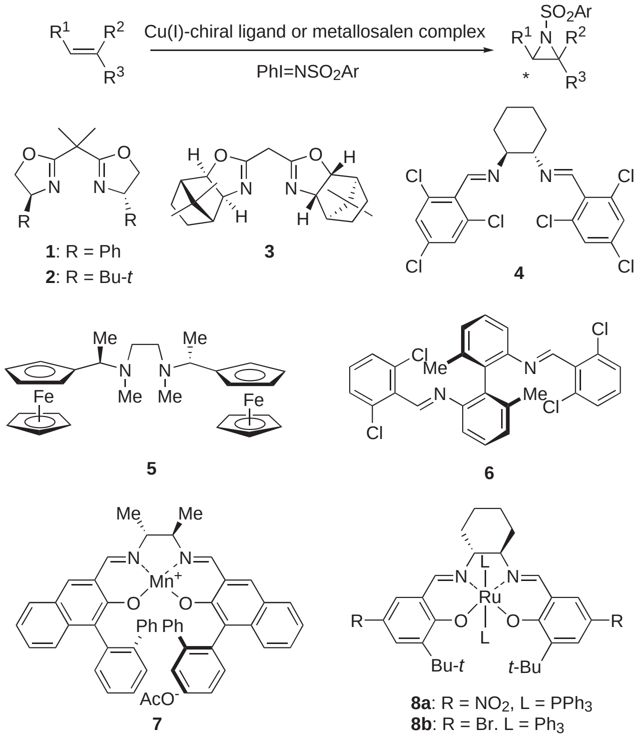
Abstract

Azide compounds that are readily available and easily manageable, are desirable nitrogen sources for nitrogen-atom-transfer reactions such as aziridination and sulfimidation, in terms of atom-efficiency and ecological benignity. Recent development of catalysts has allowed some of these reactions to be carried out in a highly stereocontrolled manner under mild reaction conditions. This article describes recent progress in such nitrogen-atom-transfer reactions.

♦ 1. Introduction

Organic compounds consist mainly of carbon, hydrogen, oxygen, and nitrogen atoms and, for organic synthesis, introduction of nitrogen functional groups is as important as that of oxygen functional groups. Although reactions for introducing these functional groups include isoelectronic activated species and their reaction patterns are analogous (e.g., aziridination vs epoxidation and sulfimidation vs sulfoxidation), nitrogen-atom-transfer reactions have been studied far less frequently.[1] This is partly due to scarcity of appropriate nitrogen sources, as opposed to oxidants that are available in a wide variety of forms. Thus, there have been many excellent methods developed for oxidation in terms of stereoselectivity, mildness of reaction conditions, atom-efficiency and ecological benignity; however, the number of nitrogen-atom-transfer reactions satisfying such terms has been very limited.

In 1983, Groves and Takahashi reported that irradiation of Mn(porphyrin)(azide) complex gave a nitrido–Mn species that underwent aziridination by treatment with trifluoroacetic anhydride in the presence of olefins, via an *N*-trifluoroacetylnitrenoid species.[2] Later, nitrido–Mn(salen) complex was also reported to undergo aziridination under similar reaction conditions.[3] Furthermore, its asymmetric version was reported by using a chiral nitrido–Mn(salen) complex.[4] Use of trifluoroacetic acid in place of anhydride gave non-*N*-protected aziridine.[5] All these reactions need use of a stoichiometric amount of the nitrido–Mn species.



Scheme 1.

On the other hand, Mansuy et al. demonstrated that [*N*-(*p*-toluenesulfonyl)imino]phenyliodinane, PhI=NTs, could convert Fe- and Mn(porphyrin) complexes into the corresponding *N*-(*p*-toluenesulfonyl)nitrenoid species and its use as nitrogen sources enabled catalytic aziridination and allylic C–H amination, depending on the olefin used.[6] Subsequently to this, Evans et al. reported that various Cu(I) and Cu(II) complexes also catalyzed aziridination or C–H amination using PhI=NTs as the nitrogen source.[7] An asymmetric version of aziridination was achieved by using a Cu(I) complex bearing chiral bis(oxazoline) ligand **1** as catalyst (Scheme 1).[8] Since then, many dinitrogen ligands (**2**–**6**) have been introduced and the scope of copper-mediated asymmetric aziridination has been expanded.[9] High enantioselectivity has been achieved by using a chiral ligand suitable for substrate.[9,10] It is noteworthy that aziridination using **5** can be applied to nonconjugated olefins,[9e] though good substrates for most of the above aziridination reactions are conjugated olefins (R^1 = aryl, alkynyl, ester, etc.). Mn(salen) complexes that are excellent catalysts for asymmetric epoxidation[10] also catalyzed aziridination in the presence of $PhI{=}NSO_2Ar$[11] and complex **7** has been reported to show high enantioselectivity in the aziridination of styrene derivatives.[11c] Ru(salen) complexes **8** were also reported to catalyze aziridination of olefins and amidation of silyl enol ether with high enantioselectivity.[12] An Mn(porphyrin) complex has also been reported to catalyze azi-

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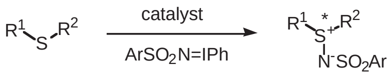
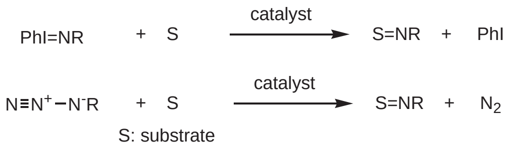
ridination, albeit with moderate enantioselectivity.[13] Some of the complexes used as the catalyst for aziridination can be used as catalyst for sulfimidation using ArSO$_2$N=IPh (Scheme 2).



Scheme 2.

Asymmetric sulfimidation was for the first time reported by using copper–bis(oxazoline) **1** complex as catalyst.[14] Subsequently to this, Mn(salen) complexes were reported to catalyze sulfimidation with high enantioselectivity.[15,16]

Use of PhI=NSO$_2$Ar as the nitrogen source, however, causes two problems from synthetic and ecological points of view: i) formation of coproduct, PhI, deteriorates the atom economy of nitrogen-atom transfer; and ii) awkward removal of the arylsulfonyl group in the product narrows their synthetic application. In connection with the second issue, Fukuyama et al. have reported that *o*- and *p*-nitrobenzenesulfonyl (Ns) groups can be removed under mild conditions[17] and it is noteworthy that copper-exchanged zeolite Y pretreated with **1** promotes highly enantioselective aziridination of styrene using PhI=NNs as the nitrogen source.[9h] On the other hand, azide compounds are ideal nitrogen sources to resolve the first issue, because they generate only innocuous nitrogen upon their decomposition (Scheme 3). Furthermore, as various azide compounds are available, the study on their use as nitrogen sources was also expected to give a clue for resolving the second issue. Thus, much effort has been directed toward development of asymmetric nitrogen-atom-transfer reactions using them and significant advancements have been made in this field, which are summarized in this article briefly.

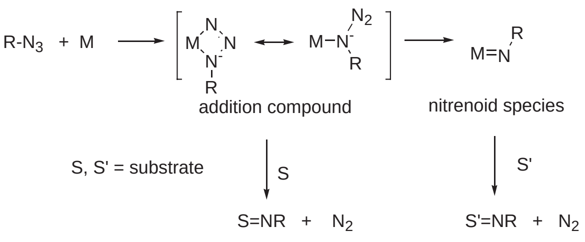


Scheme 3.

♦ 2. Azide Compounds as Nitrogen Sources

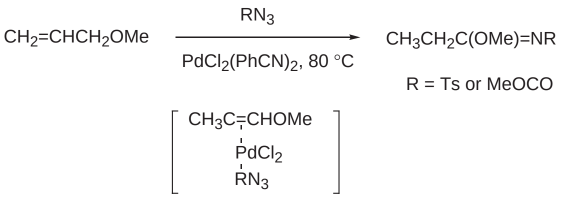
2.1 Seminal Studies on Nitrogen-atom Transfer Reactions Using Azide Compounds

It is well known that azide compounds decompose to produce the corresponding nitrenes under thermal or photo-irradiated conditions.[18] (Caution!)[19] In the presence of transition metal complexes, it has been reported that azide compounds give the corresponding metal–azide addition compounds or metal–nitrenoid species, depending on the reaction conditions and the nature of the substrates used (Scheme 4).[18,20,21] The seminal studies have disclosed that both active species can undergo synthetically useful nitrogen-atom-transfer reactions such as aziridination, C–H amination, sulfimidation, and imination of sulfoxides and it is important to note that the two species may react differently, depending on the substrate used. For example, heating a mixture of *p*-toluenesulfonyl azide and cyclohexene in the presence of copper powder at 84 °C gives a triazoline derivative via an azide–copper adduct and aziridine and allylic amine derivatives via a copper–nitrenoid species.[20] Furthermore, behavior of these active species may vary with the substrates used: in the presence of a Co(II)- or Ru(II)(porphyrin) complex, *p*-nitrophenylazide reacts with cyclohexene at reflux to give the corresponding allylic amine, while it reacts with cyclooctene to give the corresponding aziridine.[22] Recently, a Co(II)(porphyrin) complex has also been reported to catalyze benzylic C–H amination at reflux of benzene.[23] An azide–Co(II)(porphyrin) adduct has been postulated to participate in this amination.



Scheme 4.

It has been reported that, in some transition-metal-catalyzed nitrogen-atom-transfer reactions, another transition metal-catalyzed reaction occurs simultaneously and the combination of these reactions enables a unique conversion: treatment of allylic ethers with an azide in the presence of Pd(II) complex at 80 °C gives the corresponding N-substituted imino ethers via Pd-mediated olefin migration and subsequent decomposition of the resulting ternary enol ether–Pd–azide intermediate into an triazoline derivative that is converted into the imino ether (Scheme 5).[24]

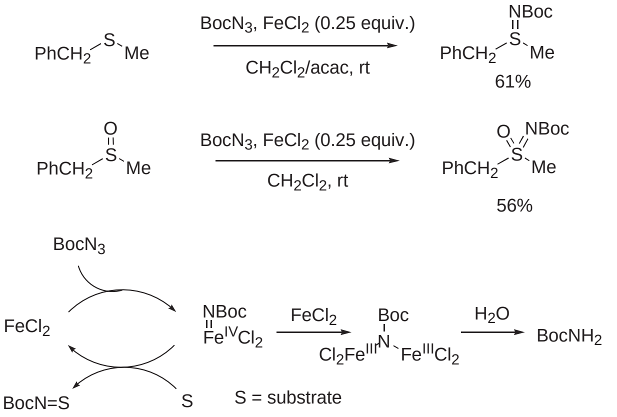


Scheme 5.

In the presence of copper powder, *p*-toluenesulfonyl azide reacts with dialkyl sulfides and sulfoxides at reflux of methanol to give the corresponding sulfimides and sulfoximines, respectively.[25] The latter reaction has been found to be stereospecific. Although harsh reaction conditions have been used in these seminal studies on nitrogen atom transfer using azide compounds, the results showed the potentiality of azide compounds as ecologically benign precursors and it has been expected that, if high selectivity and mild reaction conditions can be realized in the nitrogen-atom transfer, the reaction should become not only atom-efficient and ecologically benign but also synthetically useful. However, it should be noted that there was an uninvestigated issue in these seminal studies: the N-substituent of the azide compound becomes the N-protecting group of the nitrogen atom in the product and it is important that the protecting group is labile enough to be removed under mild conditions.

2.2 Sulfimidation Using Azide Compounds

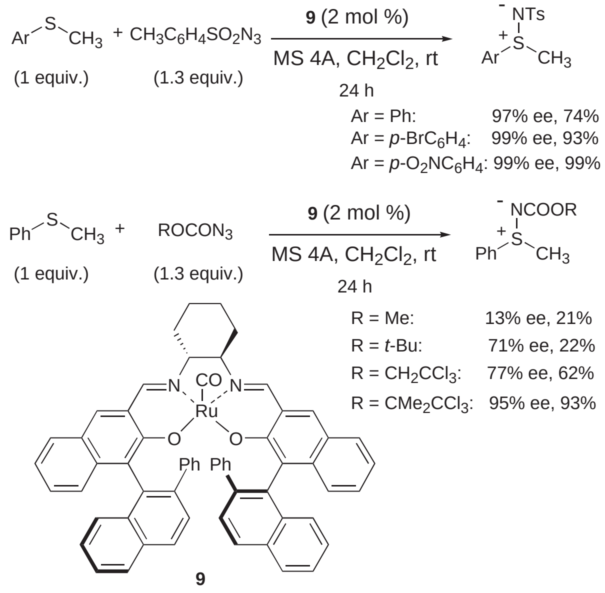
The *t*-butyloxycarbonyl (Boc) group has been widely used as a protecting group of various amino groups, because it can be cleaved under mild acidic conditions. Although reactivities of azides are in the order of $N_3SO_2R > N_3CO_2R > N_3R$,[24] Bach and co-worker reported that imidation of sulfides with $BocN_3$ could be catalyzed by 10–20 mol % of $FeCl_2$ in the presence of acetylacetone (acac) that stabilized the iron salt (Scheme 6).[26] Other metal salts such as $Fe(SO_4)_2$, $FeCl_3$, $RuCl_3$, $Rh_2(OAc)_4$, $Co(OAc)_2$, and CuCl were proved to be less effective.[26b] Imidation of sulfoxides with $BocN_3$ was also promoted stereospecifically in dichloromethane by $FeCl_2$. In the latter reaction, an excess of sulfoxide was used to complete the reaction. For these reactions, a nitrenoid–Fe(IV) species has been postulated to be an intermediate that is attacked by sulfides or sulfoxides to give the corresponding products. However, when the substrate attacked the intermediate slowly, solvated $FeCl_2$ attacked it competitively to yield a (μ-nitrenoid)Fe(III) complex that is catalytically inactive and gives $BocNH_2$ upon hydrolysis. Thus, excessive use of $FeCl_2$ might cause reduction of chemical yield.



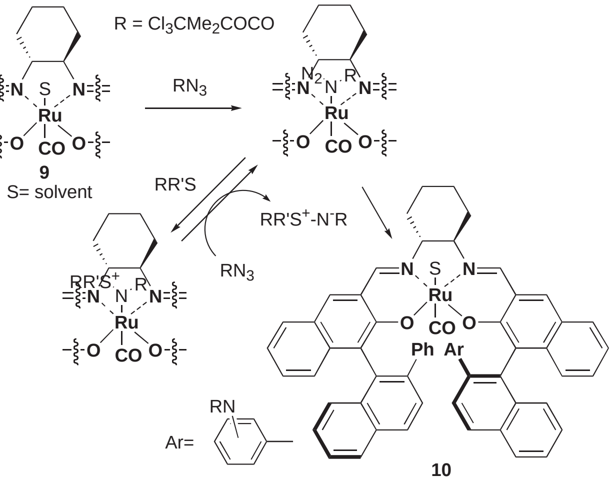
Scheme 6.

Recently, Katsuki and co-workers reported that Ru(salen) complex **9** catalyzed imidation of alkyl aryl sulfides using arylsulfonyl azides at room temperature in a highly enantioselective manner, irrespective of the presence or the absence of a functional group in the sulfides (93–99% ee) (Scheme 7).[27] Use of stoichiometric sulfides was essential for obtaining good chemical yields, because an excess amount of sulfide hindered the imidation probably owing to its coordination to the ruthenium ion. Imidation of dialkyl sulfide such as benzyl methyl sulfide was slow and less selective (66% ee). On the other hand, imidation of methyl phenyl sulfide with $BocN_3$ was slow and moderately enantioselective (71% ee).

However, since an active species involved in metal-mediated nitrogen-atom-transfer reactions is electrophilic, it was expected that the steric and electronic natures of the alkyl group of alkoxycarbonyl azides would affect reaction rate and enantioselectivity.[28] Indeed, Tamura and Katsuki et al. reported that enantioselectivity and chemical yield were improved remarkably, as steric bulkiness and electron-withdrawing ability of the alkyl group were increased and highly enantioselective sulfimidation was realized, when bulky 2,2,2-trichloro-1,1-dimethylethoxycarbonyl azide was used as the precursor (Scheme 7). It is noteworthy that the 2,2,2-trichloro-1,1-dimethylethoxycarbonyl group can be removed under mild reductive conditions. This imidation proceeded smoothly but, after the sulfide was completely consumed, the catalyst lost its activity. A spectroscopic study of stoichiometric reaction between complex **9** and 2,2,2-trichloro-1,1-dimethylethoxycarbonyl azide has disclosed that the active species for this reaction is an additive compound which undergoes intramolecular C–H amination to give a catalytically inactive Ru(salen) complex **10** (Scheme 8).[29] This knowledge provided a basis for the construction of a robust Ru(salen) complex (vide infra).

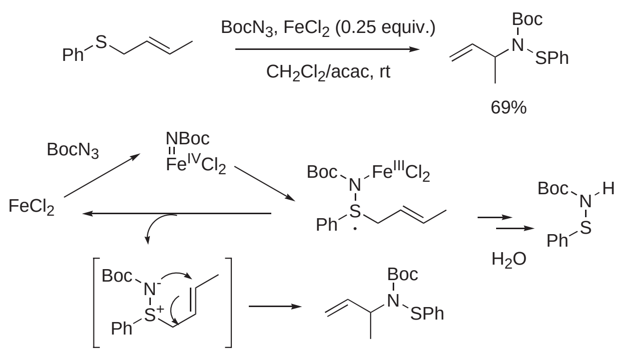


Scheme 7.



Scheme 8.

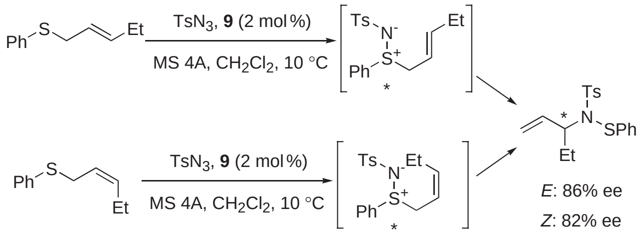
When the imidation is applied to allylic sulfides, the resulting allylic sulfimides undergo [2,3]sigmatropic rearrangement to give allylic sulfonamides. An asymmetric version of this reaction has been reported by using a combination of TsN=IPh and Cu–bis(oxazoline) complex (up to 71% ee).[14b] Bach and co-worker reported that the reaction between allylic sulfides



Scheme 9.

and $BocN_3$ gave the corresponding allylic sulfonamides (Scheme 9).[30]

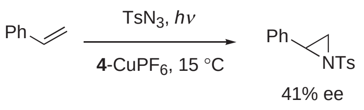
Interestingly, it has been postulated that the nitrene transfer from an Fe(IV)–nitrenoid species to sulfide is not a two-electron process but occurs via an Fe(III) species, based on the fact that *N*-Bocbenzenesulfenamide is formed as the by-product.[30] Reaction of propargyl sulfides under similar conditions using $dppeFeCl_2$ gives the corresponding *N*-allenylsulfenimides.[31] Katsuki and Murakami reported that imidation of allylic sulfides using *p*-toluenesulfonyl azide in the presence of complex **9** proceeded with high enantioselectivity (up to 86% ee) (Scheme 10).[32] It was assumed that the ruthenium complex did not participate in the [2,3]sigmatropic rearrangement step and the stereochemistry of the rearrangement should be controlled spontaneously, depending on the substitution pattern of substrates. Thus, *E*- and *Z*-allylic sulfides gave the same product of similar enantiomeric excess, because the transition states for the rearrangements of *E*- and *Z*-substrates differ from each other.



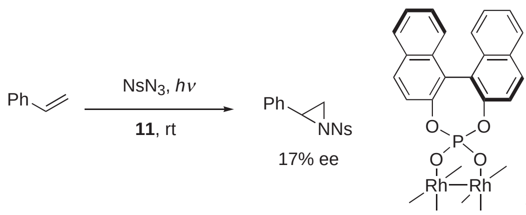
Scheme 10.

2.3 Aziridination Using Azide Compounds

Azides decompose upon irradiation of UV light and the resulting nitrenes can react with a metal complex to give the corresponding metal–nitrenoid species that undergo aziridination. Thus, if an appropriate chiral metal complex is used as nitrene scavenger, asymmetric aziridination using azide should be realized. Indeed, Jacobsen and co-workers reported that irradiation of a mixture of styrene, toluenesulfonyl azide, and complex **4** promoted asymmetric aziridination to give the corresponding aziridine of 41% ee (Scheme 11).[9c] Mueller and co-workers also reported asymmetric aziridination using *p*-nitrobenzenesulfonyl azide (*p*-NsN_3) in the presence of Rh complex **11** under irradiation, though enantioselectivity was modest (Scheme 12).[33]



Scheme 11.



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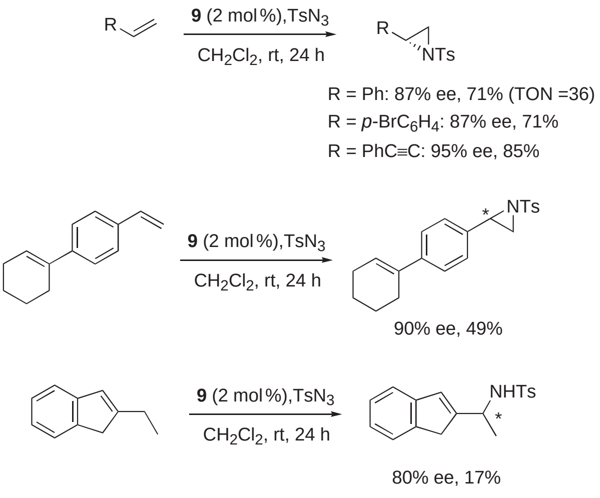
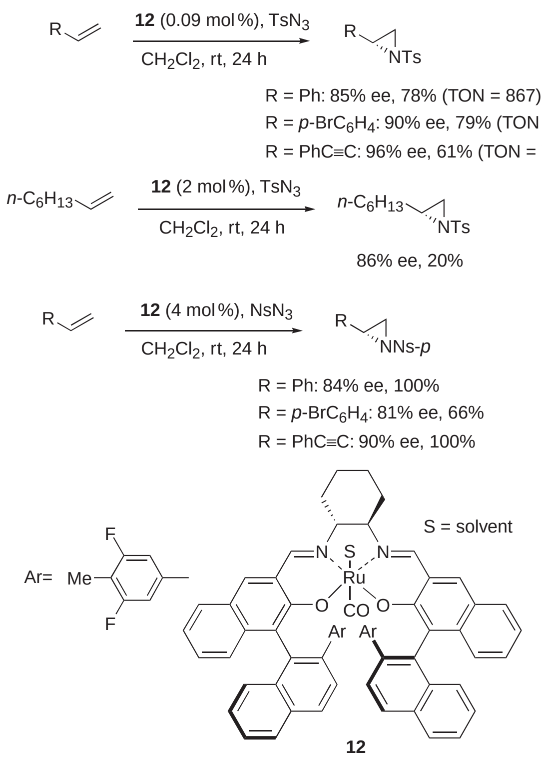
Scheme 12.

Katsuki and co-workers reported that complex **9** catalyzed aziridination of styrene derivatives with high enantioselectivity at room temperature without irradiation (Scheme 13).[34] The reaction site provided by complex **9** seems limited in space and this agrees with the fact that the terminal olefin was aziridinated in preference to the tri-substituted olefin, though the former is less nucleophilic than the latter. Olefins having an *E*-substituent underwent allylic C–H amination under the conditions. However, the turnover number of complex **9** was moderate (TON = 36), probably because the intramolecular C–H amination observed in the sulfimidation decomposed **9** at a certain rate during the reaction (vide supra).



Scheme 13.

In order to suppress the undesired intramolecular C–H amination, fluorinated complex **12** was synthesized and used as catalyst for aziridination (Scheme 14).[35] Indeed, complex **12** showed TON as high as 867 without diminishing enantioselectivity (85% ee). It is noteworthy that complex **12** also catalyzed aziridination of 1-octene, a nonconjugated olefin, with high enantioselectivity of 86% ee, albeit with moderate TON. It is another advantage that use of complex **12** also allowed aziridination using *p*-NsN_3: The reactions using *p*-NsN_3 with 4 mol % of **12** gave the corresponding aziridines in good yields, albeit with somewhat reduced selectivity. Their recent study further disclosed that a complex possessing a chloro-substituent instead of a fluoro-substituent allowed use of not only *p*-NsN_3 but also 2-(trimethylsilyl)ethanesulfonyl azide ($SESN_3$), SES



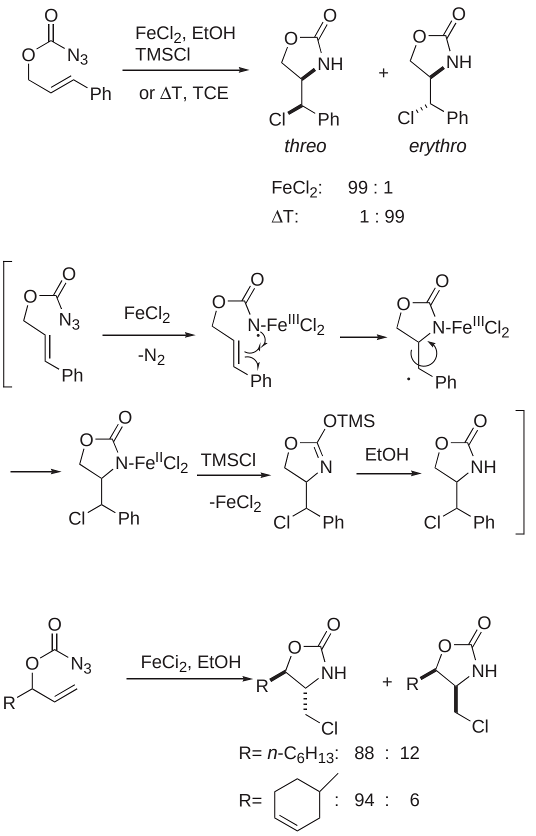
Scheme 14.

of which is a labile group, with high TON (aziridination of styrene: 81% ee and TON = 700 for p-NsN$_3$, 91% ee and TON = 260 for SESN$_3$).[36]

2.4 Intramolecular Aminochlorination of Alkenyloxycarbonyl Azide Compounds

Bach and co-workers reported that intramolecular aminochlorination occurred diastereoselectively, when alkenyloxycarbonyl azides were treated with FeCl$_2$. Although this cyclization needed an almost stoichiometric amount of FeCl$_2$, the reaction could be carried out catalytically in the presence of trimethylsilyl chloride (Scheme 15).[37] It is noteworthy that this cyclization gave *threo*-4-(chloromethyl)oxazolidinones as the major product, while the cyclization under thermal conditions in 1,1,2,2-tetrachloroethane (TCE) gave the erythro-isomer exclusively. If the reaction proceeds via aziridination and subsequent nucleophilic ring-opening, stereochemistry of the product should be erythro. In the thermal cyclization, it is known that an aziridine is formed as the intermediate and it undergoes the ring-opening caused by HCl that is formed upon heating of TCE. Based on these results, it has been proposed that Fe^{II}-mediated cyclization proceeds through a radical intermediate. This agrees with the proposal that imidation of allylic sulfides includes an Fe(III) species (vide supra).

In summary, recent studies described here clearly demonstrated the high potentiality of azide compounds as nitrogen sources for achieving highly stereoselective, atom-efficient, and ecologically benign nitrogen-atom-transfer reactions. Although high enantioselectivity and TON of catalyst have been obtained in some sulfimidation and aziridination using azide compounds under mild conditions, further expansion of the scopes of the reactions has been required. It is noteworthy that the selectivity and the rate of nitrogen-atom-transfer reactions have been found to depend on the nature of the catalyst and nitrogen sources. Since metal complexes and azide compounds used for the previous studies are limited in number and new complexes and azides can be introduced readily, it appears quite certain that further progress will be made shortly in this field of chemistry and asymmetric nitrogen-atom-transfer using azide compounds will become a standard method for introducing nitrogen functional groups in an enantioselective manner.



Scheme 15.

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