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REVIEW ARTICLE OPEN ACCESS

AZA-HOFMANN REARRANGEMENT: A MINI REVIEW

***Pradip Debnath**

Department of Chemistry, Maharaja Bir Bikram College, Agartala, Tripura-799004, India

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****Corresponding author: Pradip Debnath***

ABSTRACT

The Hofmann rearrangement is a well-known method for the conversion of a primary amide into a primary amine with one less carbon atom. Classically, a mixture of halogen and a strong base is used as a reagent to perform the Hofmann rearrangement. In most cases, classical Hofmann rearrangement gave relatively poor yield and create enormous amount of waste products. Many modified version of Hofmann rearrangement has been developed to overcome the limitations associated with traditional Hofmann reaction. An important variant of Hofmann rearrangement is the aza-Hofmann arrangement in which amidines are used a starting materials instead of amides. This modification leads to the conversion of amidines to carbodiimide which on reaction with different nucleophiles such as carboxylates and amine lead to the corresponding amide or guanidine, respectively. In this article, hypervalent iodine mediated aza-Hofmann rearrangement of amidines has been described.

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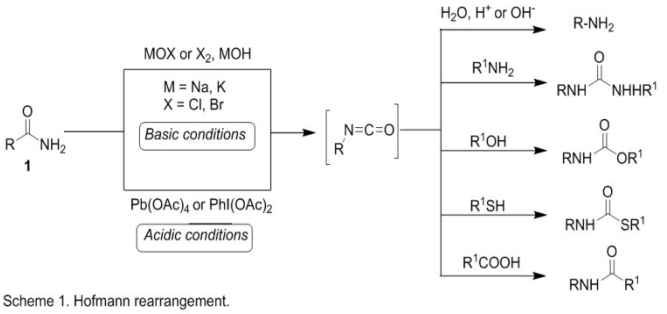
INTRODUCTION

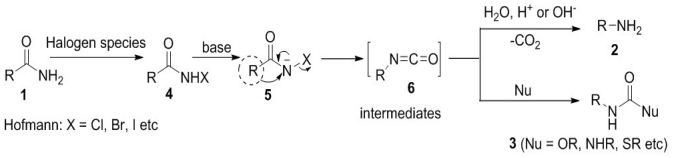
In the late 19th century, three similar reactions involving a stereospecific rearrangement of an alkyl or aryl group from a carbon atom to electron deficient nitrogen were discovered by Wilhelm Clemens Lossen (1838-1906) (Lossen, W. 1872), August Wilhelm von Hofmann (1818-1892) (Hofmann, A. W. 1981), and Julius Wilhelm Theodor Curtius (1857-1928) (Curtius, T. 1890). Among these, August Wilhelm von Hofmann discovered the conversion of primary amides to primary amines or their derivatives with one fewer carbon atom via a rearrangement reaction which is known as Hofmann rearrangement, named after his discovery (Hofmann, A. W. 1981). This rearrangement is an important tool for the preparation of primary amine from carboxylic acid derivative (Richter and Ulrich 1977, Aubé, et al. 2014). Traditionally, alkaline hypohalites or a mixture of halogen (like Br_2) and alkaline hydroxide (like NaOH) are used in aqueous solutions to perform the Hofmann rearrangement of amides. Initially, an *N*-haloamide is formedwhich undergoes rearrangement to form an isocyanate intermediate. This isocyanatehydrolysesto form amine with the release of CO_2. Carbamate products (Chaturvedi, D. 2012) are obtained from initial isocyanate when alcohols or alkoxides are used as nucleophiles (Fujisaki et al. 1988). For the molecules containing base sensitive functional group, the Hofmann reaction is carried out under mild acidic conditions. Many oxidizing agents such as lead tetraacetate, *N*-bromosuccinimide (NBS) or hypervalent iodine reagents have been developed to affect the Hofmann reaction under mild acidic reaction conditions (Scheme 1). Since the discovery, this classical reaction hadwidely used in synthetic organic chemistry.This reaction has been industrially valorized, and successfully applied in natural product and drugs synthesis. An important variant of Hofmann rearrangement is the aza-Hofmann arrangement in which amidines are used as starting materials instead of amides. This modification leads to the conversion of amidines to carbodiimide which on reaction with different nucleophiles such as carboxylate, thiocarboxylate and amine lead to the corresponding isourea, thiourea, secondary amide and guanidine. In this article, the hypervalent iodine mediated aza-Hofmann rearrangement of amidines to secondary amides, acetanilides, or guanidine has been described.



Scheme 1. Hofmann rearrangement.

General Mechanistic Aspects and Stereochemistry: Mechanistic studies on Hofmann rearrangement revealed that it is a concerted intramolecular rearrangement. The stereochemistry of the stereogenic centre retained during the rearrangement. The kinetic studies of the reaction revealed that it is first order reaction. The kinetic isotope effects (KIEs) also support the concerted mechanism (Imamoto etal. 1971). The reaction proceeds with the formation of a reactive N–X

amidate (where X is a halogen group) which undergoes rearrangement with the loss of X− group to afford the intermediate isocyanate **6**. This isocyanate on solvolysis in protic solvent lead to primary amine **2** with release of carbon dioxide or is attacked by with other nucleophiles to afford carbamates **3** (Nu = OR), ureas (Nu = NHR), or related compounds (Scheme 2). Isolation of isocyanates is also possible which makes this rearrangement more attractive in synthetic organic chemistry.



Scheme 2. General mechanistic aspects of Hofmann rearrangement.

Reagents used in Hofmann Rearrangement: The halogen reagents such as sodium or potassium hypobromite, sodium hypochlorite, calcium hypochlorite or barium hypobromite *etc* are generally used as oxidant in the traditional Hofmann rearrangement. It has been observed that the halogen based procedure requires harsh conditions for the conversion of primary amides to amines and provides lower yield of the product. Many efforts have been made by the scientists over the globe to develop novel oxidative reagents to affect the Hofmann rearrangement in higher yield. The reagents are classified into two categories: halogen reagents and hypervalent iodine species. The most commonly used oxidizing reagents employed in the Hofmann reaction include *N*-bromosuccinimide (NBS) (Huang et al. 1997, Senanayake et al. 1994), trichloroisocyanuric acid (TCCA) (Crane et al. 2011), 1,3-dibromo-5,5-dimethylhydantoin (DBDMH) (Engstrom et al. 2006), 1,3-dichloro-5,5-dimethylhydantoin (DCDMH) (Katuri et al. 2019), *N*-bromoacetamide (NBA) (Jevtic et al. 2016), bis (1,3-dimethyl-2-imidazolidinone) hydrotribromide (Nishio et al . 2019), *N,N*-dibromo-*p*-toluenesulfonamide ($TsNBr_2$) (Borah and Phukan, 2012), tribromoisocyanuric acid (TBCA) (Miranda et al. 2011), bromine, tetraalkylammonium tribromide, and similar reagents (Figure 1).

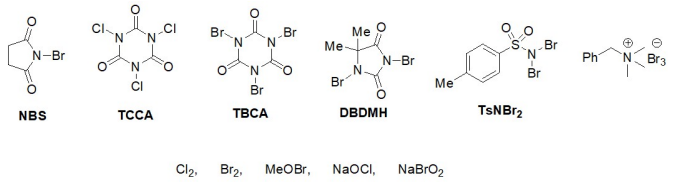
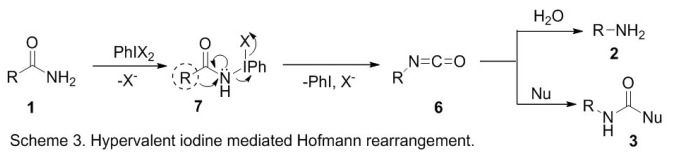


Figure 1. Common halogen reagents used in the Hofmann rearrangement.

On the other hand, hypervalent iodine reagents are widely employed in the organic rearrangements. The hypervalent iodine reagents have ability to react as an electrophile and later it act as leaving group with the migration of various substituents, leading to rearrangement within the molecule. This characteristic of the hypervalent iodine enabled the development of a new variant of Hofmann rearrangement by using hypervalent iodine (III) species as green oxidant. In this reaction, amide reacts with the hypervalent iodine to form an N-iodine (III) species (**7**) which on rearrangement lead an isocyanate (Scheme 3). It has been observed that hypervalent iodine reagents are more effective oxidant than the halogen based oxidants to effect the Hofmann rearrangement of electron deficient amides.



Scheme 3. Hypervalent iodine mediated Hofmann rearrangement.

The commercially available hypervalent iodine(III) reagents such as phenyliodine(III) diacetate (PIDA) (Togo et al. 2000), phenyliodine(III) bis(trifluoroacetate (PIFA)] (Radhakrishna et al. 1979), [hydroxyl(tosyloxy)]iodobenzene (Lazbin and Koser, 1987), (tosylimino)phenyl-λ^3–iodane (Toshimura et al. 2012), and iodosylbenzene are commonly used in Hofmann rearrangements (Figure 2). These reagents are very mild, stable, environmentally friendly, and compatible with a variety of functional groups. They are a good choice as green reagents for oxidation reaction, rearrangement reaction, and C-C/C-N bond forming reactions, offered useful alternatives to older electrophilic halogenating agents. Hofmann rearrangements using hypervalent iodine reagents avoid the use of elemental bromine or heavy metal reagents such as $Pb(OAc)_2$, AgOAc and $Hg(OAc)_2$ etc.

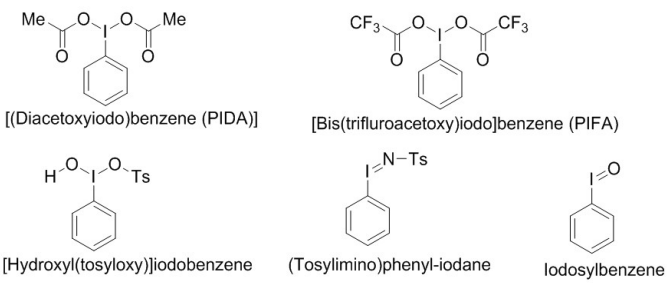
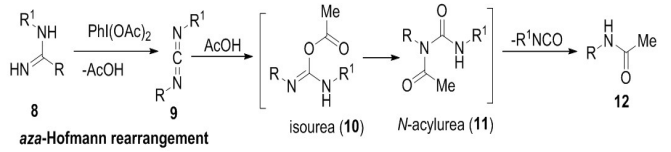


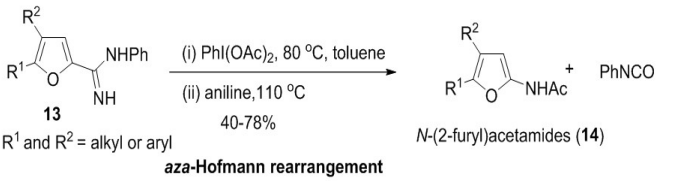
Figure 2. Common hypervalent iodine reagents used in Hofmann rearrangement.

Aza-Hofmann Rearrangement of Amidine: Amidines are a class nitrogenous compound bearing strong basic characteristics having the general functional group R-C(=NR)-NR_2, acting as imine derivatives of amides. They are characterized by a nitrogen-carbon-nitrogen backbone that provides high basicity, hydrogen bonding, and metal-complexing capabilities. In drug and pharmaceutical industries, amidines are used as synthetic precursors for the preparation of complex nitrogenous compounds. In 1995, Ramsden and co-workers have reported an *aza*-Hofmann rearrangement of amidine (Ramsden and Rose, 1995; 1997). Ramsden group observed that *N*-substituted amidines on treatment with $PhI(OAc)_2$ underwent an *aza*-Hofmann type rearrangement to give carbodiimide intermediates. The author observed that final products of the reaction of *N*-substituted amidines depend on the nature of the amidine substituents. It was reported that *C*-alkyl-*N*-arylamidines on treatment with $PhI(OAc)_2$ cyclize with formation of 1*H*-benzimidazoles. On the other hand, other substituted amidines such as *C,N*-dialkylamidines, *C,N*-diarylamidinesand *C*-aryl-*N*-alkylamidines under similar reaction conditions undergo an *aza*-Hofmann rearrangementto give *N*-acylureas **11** *via* the formation of carbodiimides **9**. The *N*-acetylureas undergo thermal cleavage at 110 °C to secondary acetamides **12** by the elimination of isocyanate (Scheme 4).



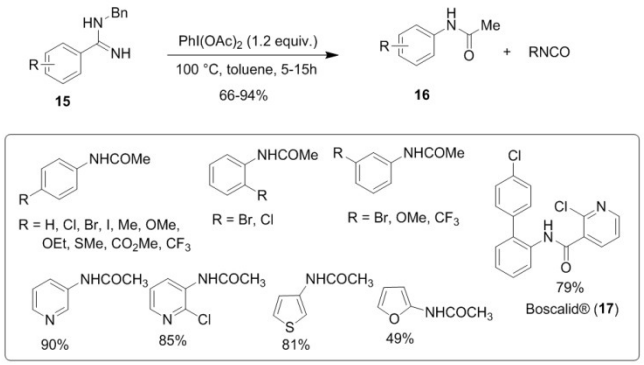
Scheme 4. $PhI(OAc)_2$-mediated *aza*-Hofmann rearrangement of *N*-substituted amidines.

The authors demonstrated the potential utility of this oxidative rearrangement by the conversion of *N*-phenylfuran-2-carboximidamides (13) to stable derivatives of 2-aminofuran (14) (Scheme 5) (Bobosikova et al. 2001). Generally, 2-aminofurans are unstable at ambient temperature for long time. This protocol provided the *N*-protected 2-aminofuran which is stable for long duration of time without decomposition.



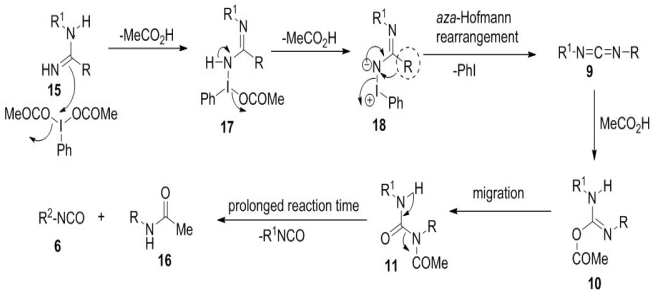
Scheme 5. Synthesis of 2-aminofuran via aza-Hofmann rearrangement.

Recently, we reported a detailed study on aza-Hofmann rearrangement of amidines using $PhI(OAc)_2$ as oxidant. A variety of *N*-substituted amidines (15) were converted into the corresponding secondary amides (16) *via* $PhI(OAc)_2$ mediated aza-Hofmann rearrangement (Debnath et al. 2015). The reaction proceeds smoothly with 1.2 equiv. of $PhI(OAc)_2$ in toluene at 100 °C. Under the optimized conditions, a full conversion of starting materials was observed with the formation of acetanilides (16**)** in excellent yields (Scheme 6). The reaction tolerated both the electron-withdrawing and electron-donating substituents in the phenyl ring of the benzamidines under the reaction conditions. As an application of this protocol, we successfully synthesized Boscalid®, an important fungicide in high yield (17).



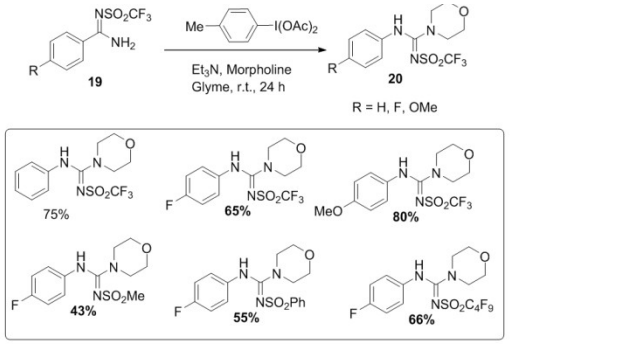
Scheme 6. Hofmann rearrangement of *N*-substituted amidines leading to secondary amides.

Mechanistically, the reaction proceeds through the formation of *N*-activated compound 17 by the reaction of amidine with $PhI(OAc)_2$. Subsequently, an ylide 18 is formed by the elimination of carboxylic acid from the *N*-activated compound 17. The resulted ylide18 underwent a rearrangement to form a carbodiimide intermediate 9. The nucleophilic attack of the carboxylate on the protonated carbodiimide (carbodiimidium) leads to the formation of *N*-acylurea 11 via isourea 10. The secondary amides 16 are formed by the elimination of isocyanate from *N*-acylurea 11 (Scheme 7). It is important to mention that the selectivity of the reaction and nature of product depend on the basicity of the nitrogen atoms of the carbodiimide 9.

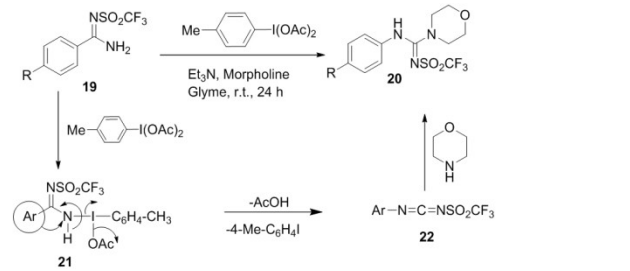


Scheme 7. Propable mechanism of Hofmann rearrangement of amidines.

Another *aza*-Hofmann type rearrangement of amidines has been reported by Yagupolskii and co-workers (Yagupolskii et al. 2008). The reaction of *N*-perfluoroalkylsulfonyl arenecarboxamidines 19 with 4-(diacetoxyiodo) toluene allows the formation of substituted guanidines (Scheme 8). The reaction proceeds through the formation of the intermediate carbodiimides 22 which then reacts with an amine to produce the guanidine products 20 (Scheme 8). The author observed that the reactivity of amidines increases with the increasing electron-withdrawing ability of substituent R (R = CF_3, C_4F_9) in $ArC(=NSO_2R)NH_2$. It has been observed that the rearrangement of related substrates bearing fluorine free substituents at the sulfonyl group such as $ArC(=NSO_2R)NH_2$ (R = Me, Ph) also occurred under similar conditions. The author proposed a mechanism for the conversion of *N*-perfluoroalkylsulfonyl arenecarboxamidines to guanidine (Scheme 9). Initially, an *N*-activated intermediate 21 is formed which undergoes 1,2-migration of aryl group from carbon to nitrogen atom with the elimination of 4-iodotoluene to afford carbodiimide intermediate 22. The nucleophilic attack of amine (morpholine) on carbodiimide carbon leads to the formation of the guanidine product 20.

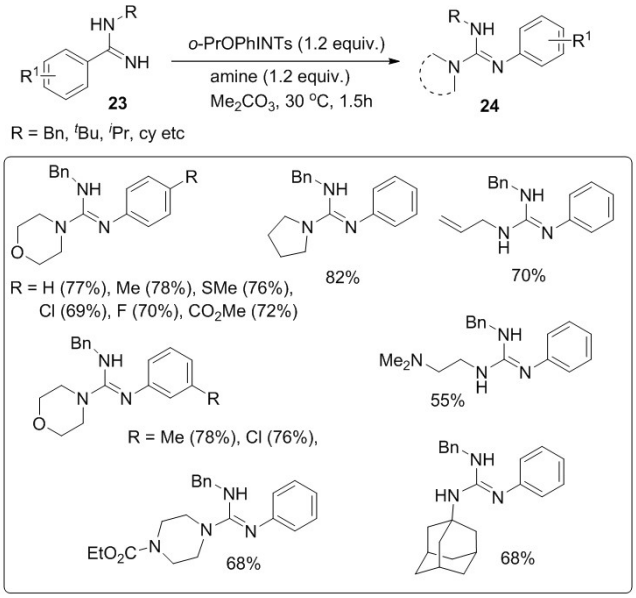


Scheme 8. Hypervalent iodine mediated *aza*-Hofmann rearrangement of of *N*-perfluoroalkylsulfonyl amidines.



Scheme 9. Hypervalent iodine mediated *aza*-Hofmann rearrangement of of *N*-perfluoroalkylsulfonyl amidines.

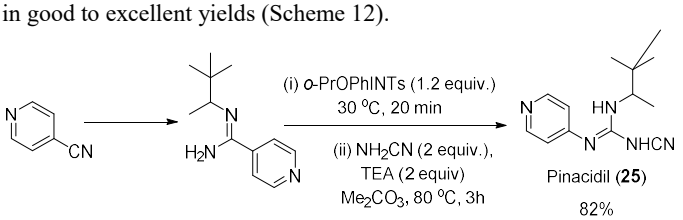
Very recently, Bert and co-workers reported hypervalent iodine mediated *aza*-Hofmann rearrangement of *N*-substituted amidines (23) which lead to the formation of guanidines in high yields (Baeten et al. 2016).The reaction proceeded with hypervalent iodine *o*-PrOPhINTs (1.2 equiv.) in presence of amines (1.2 equiv.) in dimethylcarbonate (Me_2CO_3) at 30 °C (Scheme 10). Variety of amidines substrates (23) bearing electron-donating and electron-withdrawing groups have been applied for the preparation of guanidines (24) under oxidative reaction conditions. A large numbers of amines including sterically hindered, oxidation-sensitive and chiral amines were tolerated under the reaction conditions. As an application of the protocol, Bert et al synthesized Pinacidil (25), an antihypertensive drug starting from 4-cyanopyridine (Scheme 11).



Scheme 10. Synthesis of guanidines via hypervalent iodine mediated *aza*-Hofmann rearrangemnt of *N*-substituted amidines.

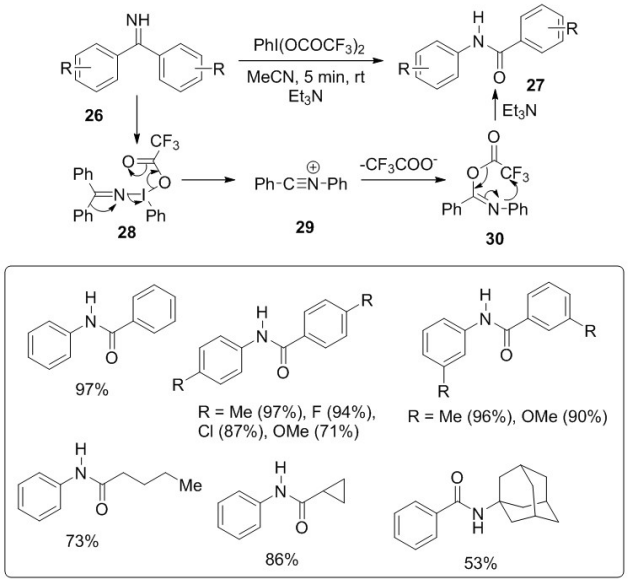
Recently, Zhao and co-workers have described an umpolung approach for the synthesis amide via $PhI(OCOCF_3)_2$-mediated

oxidative rearrangement of N−H ketimines (Zhao et al. 2017). Treatment of ketimines (26) with $PhI(OCOCF_3)_2$ in MeCN at room temperature provides the target amides (27) with excellent selectivity in good to excellent yields (Scheme 12).



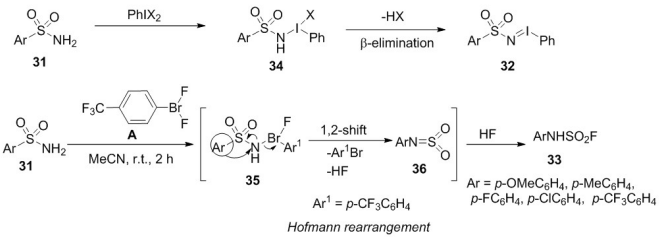
Scheme 11. Synthesis of pinacidil via Hofmann rearrangement.

The optimized reaction conditions tolerated a variety of ketimines bearing electron-donating and electron-withdrawing substituents at the benzene ring of ketimines. Mechanistically, ketimine reacts with $PhI(OCOCF_3)_2$ to form an *N*-activatedintermediate 28 which undergoes rearrangement to form nitronium species 29. The nucleophile attack of trifluoroacetate on nitronium species (29) followed by the rearrangement to afford amides (27) (Scheme 12). The preliminary mechanistic studies indicated that the migration preference depends on both steric and electronic effects of the migrating groups.



Scheme 12. $PhI(OCOCF_3)_2$-mediated oxidative rearrangement of ketimines.

Ochiai and co-workers reported difluoro-λ^3-bromane-induced Hofmann rearrangement of primary arenesulfonamides (Ochiai et al. 2009). The reaction of arenesulfonamides (31) with *p*-trifluoromethylphenyl (difluoro)-λ^3-bromane (A) afforded *N*-arylsulfamoyl fluorides (33) selectively at room temperature via Hofmann rearrangement (Scheme 13). This variant of *aza*-Hofmann rearrangement is more difficult to develop because of the greater acidity of sulfonamides relative to amides. A competing β-elimination has been occurred from the reaction of *p*-toluenesulfonamide (31, Ar = *p*-MeC_6H_4) with aryl-λ^3-iodanes, leading to sulfonylimono-λ^3-iodanes (32) *via* the formation of intermediate 34. In contrast, reaction of the difluoro-λ^3-bromane (A) with *p*-toluenesulfonamides (31) in MeCN produced unique *N*-*p*-tolylsulfamoyl fluorides (33) in a high yield, through Hofmann rearrangement (1,2-migration). Arenesulfonamides with electron-donating groups (*p*-MeO and *o*-Me) and -withdrawing substituents (*p*-F, *p*-Cl, and *p*-CF_3) efficiently underwent the λ^3-bromane-induced Hofmann rearrangement. The author observed that with increasing the nucleofugality of the hypervalent iodine-leaving group would enhance the tendency toward 1,2-migration of R groups i.e. Hofmann rearrangement rather than β-elimination. Thus, when traditional hypervalent iodine reagents were used, β-elimination occurred to yield imino-λ^3-iodane **32**, whereas, an aryl-λ^3-bromane such as difluoro-λ^3-bromane **(A)** promoted Hofmann rearrangement leading to the formation of *N*-arylsulfamoyl fluorides in good yields without formation of β−elimination product.



Scheme 13. The *aza*-Hofmann rearrangement of arenesulfonamides.

CONCLUSION

In summary, the hypervalent iodine mediated aza-Hofmann rearrangement of amidines has been discussed. It has been observed that amidines are smoothly converted to *N*-protected amines via the formation of carbodiimide. This protocol has also been applied for the preparation of a variety of guanidines from amidines using amine as nucleophile.Use of hypervalent iodine reagents makes these protocols green, environmentally friendly and attractive from the sustainable point of view for the preparation of secondary amides and guanidine staring from amidines substrates.

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