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tert-Butyl nitrite mediated nitrogen transfer reactions: Synthesis of benzotriazoles and azides at room temperature

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A conversion of *o*-phenylenediamines into benzotriazoles was achieved at room temperature using *tert*-butyl nitrite. The optimized condition is also well suited for the transformation of sulfonyl and acyl hydrazines into corresponding azides. This protocol does not require any catalyst or acidic medium. The desired products were obtained in excellent yields in a short span of time.

Benzotriazoles belong to a family of nitrogen-containing heterocyclic compounds which play pivotal roles in synthetic organic chemistry as well as in medicinal chemistry.[1] In organic synthesis, benzotriazoles have been explored as synthetic auxiliaries, intermediates, protecting groups, activating groups and ligands.[1a,1b,2] In addition, benzotriazoles have been employed in the preparation of various functional materials, polymers, dyes, corrosion inhibitors, pharmaceuticals and agrochemicals, etc.[3] On the other hand, benzotriazole derivatives were clinically used as dopamine antagonist (Alizapride), sunscreen agent (Bisoctrizole), antineoplastic agent (Vorozole), etc. (Figure 1). Nevertheless, several other benzotriazole derivatives exhibit anticancer, anti-malarial, anti-bacterial, antiviral, antifungal and anti-HIV activities.[1c, 1d, 4]

Synthesis of benzotriazoles has been achieved through few methods including diazotization of *o*-phenylenediamine,[4] [3+2] cycloaddition of azides to benzynes,[5] palladium catalyzed cyclization of triazenes,[6] and reaction of *ortho*-chloronitrobenzene with hydrazine followed by reduction.[7] Among them, a simplest approach is diazotization of *o*-phenylenediamines which is typically achieved using aqueous sodium nitrite in AcOH at 70-80 °C (Scheme 1, eq-1).[2,4] Recently, Török *et al.* reported a microwave-assisted diazotization of *o*-phenylenediamines into benzotriazoles with sodium nitrite and K-10 montmorillonite at 110 °C (Scheme 1, eq-2).[8] However, use of acid medium and requirement of higher reaction temperature make these methods less attractive in synthetic perspective. In this context, our interest was to develop/identify a suitable acid free reagent which can be used for the efficient conversion of *o*-phenylenediamines into benzotriazoles at room temperature.

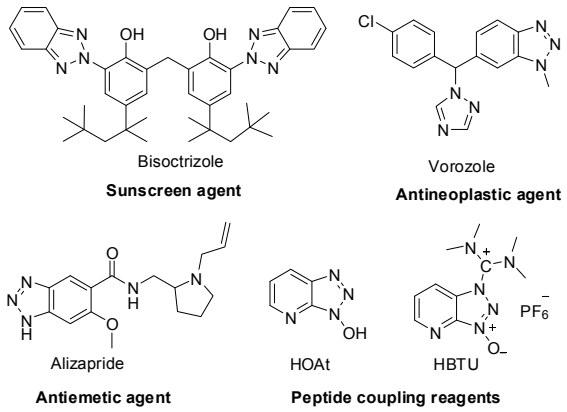

Figure 1. Benzotriazole based drugs and coupling agents.

tert-Butyl nitrite (TBN) is a highly useful synthetic reagent that has been explored in many organic transformations.[9] In this context, an efficient conversion of anilines to aryl azides in the presence of TBN and TMS-N_3 was demonstrated by Moses *et al.*[9b] Subsequently, TBN has been explored for the nitration of phenols,[9c] alkenes,[9d] alkynes,[9e] sulfonanilides[9f] and acetanilides.[9g] Recently, Bhanage *et al.* have demonstrated *N*-nitrosation of amides using *tert*-butyl nitrite under mild conditions.[9h] TBN is also employed as a source of nitrogen in many organic reactions.[9i-k] *tert*-Butanol is the only by-product results from *tert*-butyl nitrite, hence TBN can be regarded as a green reagent. It is an acid-free reagent which is cheap and commercially available. Our research group is focused on the chemistry of *N*-nitrosamines[10] and we have recently demonstrated the applications of *tert*-butyl nitrite in *N*-nitrosation of secondary amines[10a] and oxidative dimerization of thioamides to 1,2,4-thiadiazoles under mild conditions.[10d] In continuation of these works, here we report *tert*-butyl nitrite mediated conversion of *o*-

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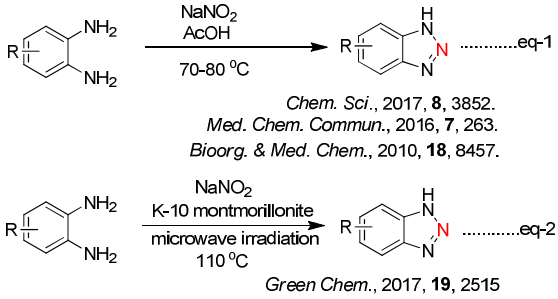
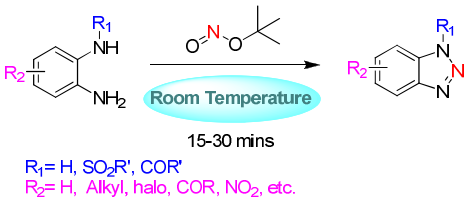
phenylenediamines into benzotriazoles at room temperature (Scheme 2).

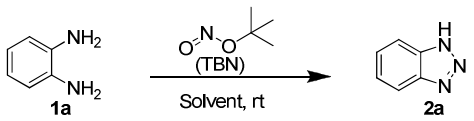


Scheme 1. Sodium nitrite mediated diazotization of *o*-phenylenediamines.



Scheme 2. *tert*-Butyl nitrite (TBN) mediated diazotization of *o*-phenylenediamines.

Table 1. Optimization for synthesis of benzotriazoles under various solvents.[a, b]



1a **2a**

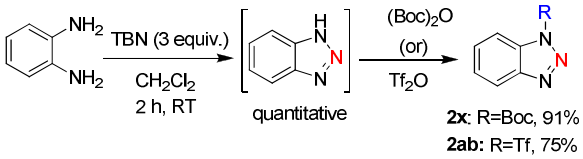
S.No.	Solvent	TBN (equiv.)	Time (min)	Yield (%)[b]
1	THF	1	60	25
2	Toluene	1	60	30
3	Benzene	1	60	21
4	DCM	1	60	32
5	DCE	1	60	41
6	CH_3CN	1	60	65
7	CH_3OH	1	60	45
8	C_2H_5OH	1	60	38
9	H_2O	1	60	20
10	Solvent- free	1	60	37
11	**CH_3CN**	**2**	**15**	**95**
12	CH_3CN	3	15	96

[a]Reaction conditions: Substrate (1 mmol) and TBN was stirred in the appropriate solvents (5 mL) at room temperature. [b]Isolated yields.

To establish the optimized condition, *o*-phenylenediamine (**1a)** was chosen as a model substrate and subjected for diazotization with one equiv. of *tert*-butyl nitrite in various solvents at room temperature. Aprotic solvents such as THF, toluene, benzene, dichloromethane, dichloroethane and acetonitrile gave the benzotriazole (**2a**) in 21-65% yield after 1 h (Table 1, entries 1-5). Among them, acetonitrile gave the desired product **2a** in high yield (i.e. 65% yield) when compared with other solvents (Table 1, entries 1-5). On the other hand, protic solvents such as methanol, ethanol and water gave the desired product in 20-45% yields (Table 1, entries 7-9). The reaction was also attempted under solvent free condition, which gives the desired product only in 37% yield (Table 1, entry 10). Furthermore, the reaction was investigated with 2.0 and 3.0 equiv. of *tert*-butyl nitrite in acetonitrile (Table 1, entries 11 and 12). To our delight, a quantitative conversion of *o*-phenylenediamine into benzotriazole was achieved with 2.0 equiv. of TBN in acetonitrile within 15 min at room temperature (Table 1, entry 11).

With optimized condition in hand, transformation of various substituted *o*-phenylenediamines into corresponding benzotriazoles was investigated (Table 2). To our delight, *o*-phenylenediamines bearing electron donating groups (e.g. methyl, *tert*-butyl) and withdrawing groups (e.g. halogens, nitro, trifluoromethane, etc.) underwent diazotization smoothly. These reactions provided the corresponding benzotriazoles in quantitative yields within 15 minutes at room temperature (Table 1, **2b-2m**). It is noteworthy that the substitutions present on the aryl ring (i.e. EDG or EWG) did not influence the reaction yield and time. Encouraged, we further investigated the conversion of various mono-*N*-sulfonyl and *N*-acyl *o*-phenylenediamines into corresponding benzotriazoles using *tert*-butyl nitrite under optimized condition. To our delight, all these substrates underwent triazolation smoothly and gave the corresponding *N*-sulfonyl and *N*-acyl benzotriazoles in 84-96% within 15 min at room temperature (Table 2, **2n-2w**).

To evaluate the merits of the current methodology, triazolation of acid labile (*i.e. tert*-butoxycarbonyl (Boc), trimethylsilyl (TMS) and *tert*-butyldimethylsilyl (TBS)) groups protected *o*-phenylenediamines was attempted. To our delight, all these substrates gave the desired products **2x**, **2y** and **2z** in quantitative yields with *tert*-butyl nitrite. In fact, no deprotection was observed even after prolonged stirring at room temperature with TBN. In this context, the traditional method *i.e.* $NaNO_2$/AcOH was found to be inferior. For instance, Boc and TMS groups were completely deprotected during the process of triazole formation. These reactions provided **2a** and **2aa**, respectively, as the sole product. In the case of TBS protected substrate, only 21% of the desired product was obtained along with **2aa** in 69% yield.



Scheme 3. One-pot synthesis of *N*-protected benzotriazoles.

In order to explore further advantages of the developed protocol, one-pot synthesis of *N*-protected benzotriazoles was investigated. *o*-Phenylenediamine **1a** was quantitatively converted into benzotriazole using three equiv. of TBN in dichloromethane which was subsequently treated with acid anhydrides. This one-pot procedure gave the desired products *i.e. N*-Boc and *N*-Tf protected benzotriazoles (**2x** and **2ab**, respectively) in 75-91% yields (Scheme

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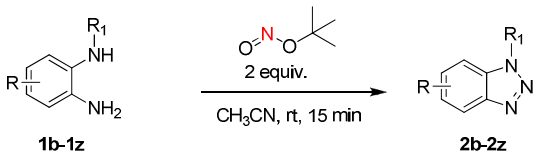
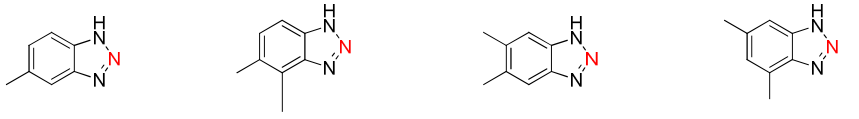
3). In contrast, one-pot procedure has failed while attempting the preparation of *N*-Boc and *N*-Tf protected benzotriazoles (**2x** and **2ab**) with sodium nitrite-acetic acid system. This observation clearly indicates the merits of TBN over the traditional method.

Table 2. Synthesis of benzotriazoles using *tert*-butyl nitrite in acetonitrile.[a,b]



1b-1z **2b-2z**

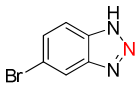


2b: 93%

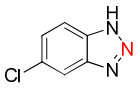
2c: 97%

2d: 95%

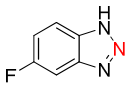
2e: 95%



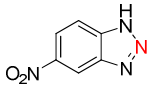
2f: 95%



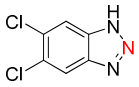
2g: 97%



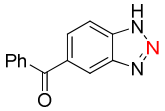
2h: 95%



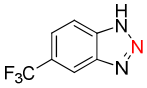
2i: 97%



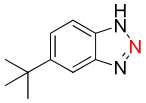
2j: 96%



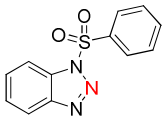
2k: 94%



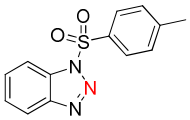
2l: 93%



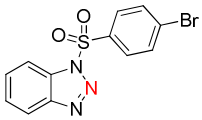
2m: 94%



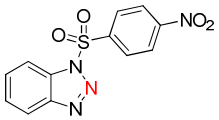
2n: 96%



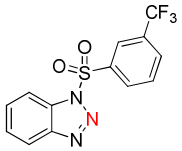
2o: 93%



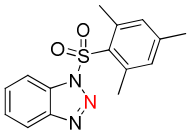
2p: 90%



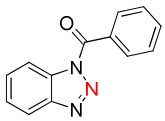
2q: 89%



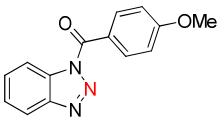
2r: 84%



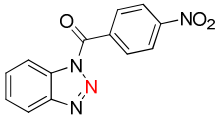
2s: 85%



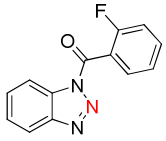
2t: 95%



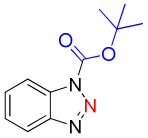
2u: 92%



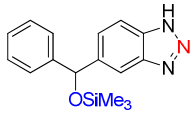
2v: 90%



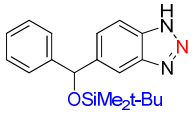
2w: 88%



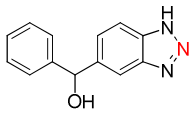
2x: 95% (0%)[c,d]



2y: 90% (0%)[c,e]



2z: 93% (21%)[c,f]



2aa (Obtained as the byprodcut druring the preparation of **2y** and **2z** with sodium nitrite and acetic acid)

[a]Reaction conditions: Substrate (1 mmol), TBN (2 equiv.) in acetonitrile (5 mL) at room temperature. [b]Isolated yields, [c] Reaction was performed using $NaNO_2$/AcOH as described in the literature procedure (Ref 2). [d]Benzotriazole (**2a**) was obtained in 91% yield. [e]**2aa** was obtained in 94%. [f]**2aa** was obtained in 69% yield.

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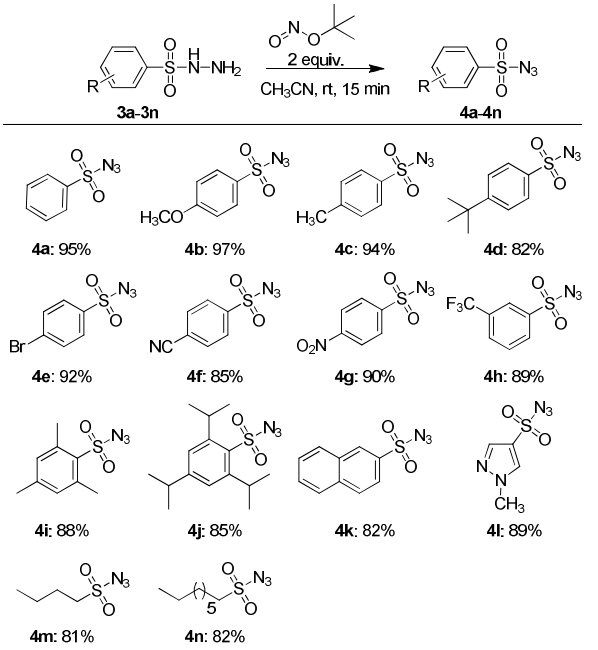
Similar to benzotriazoles, sulfonyl and acyl azides have found wide applications in organic synthesis.[11] For instance, sulfonyl azides were employed in diazo and azido transfer reactions,[12] click chemistry,[13] coupling reactions,[14] aziridation[15] and radical amination reactions[16,] etc. Likewise, acyl azides were utilized in peptide synthesis,[17] cycloaddition reactions[18] and also in the preparation of isocyanates (i.e. Curtius rearrangement), amides, urethanes, ureas, etc.[11, 18] Sulfonyl and acyl azides were typically prepared from corresponding acid chlorides in the presence of sodium azide.[11, 18] Alternatively, they have been achieved from corresponding hydrazines (or hydrazides) in the presence of nitrosating reagents. The advantages of using later method is that sulfonyl and acyl hydrazines are usually exist in solid form that are noncorrosive, odorless and compatible with water and moisture.[19] It is also worth mentioning that the conversion of acyl hydrazines into corresponding azides is most frequently used transformation in peptide synthesis.[17, 20]

Conversion of sulfonyl and acyl hydrazines into corresponding azides was previously reported with $NaNO_2$/HCl,[20,21] dinitrogen tetroxide,[22] nitrosyl tetrafluoroborate[23] and Ph_3P/Br_2/n-Bu_4NNO_2.[24] The major limitations of the existing methods are use of an acidic medium and harmful (or unstable) reagents. To best of our knowledge, *tert*-butyl nitrite has not been explored for these transformations. Therefore, the conversion of various sulfonyl and acyl hydrazides into corresponding azides was attempted using *tert*-butyl nitrite and results are summarised in Table 3 and Table 4.

Table 3. Conversion of sulfonyl hydrazines into sulfonyl azides using *tert*-butyl nitrite.[a,b]



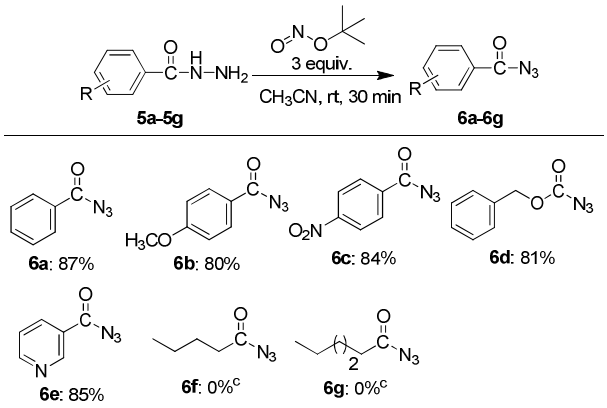
[a]Reaction conditions: Substrate (1 mmol), TBN (2 equiv.) in acetonitrile (5 mL) at room temperature. [b]Isolated yields.

Initially, the reaction was investigated with benzenesulfonyl hydrazide in the presence of 2.0 equiv. *tert*-butyl nitrite in acetonitrile at room temperature. To our delight, the desired product, *i.e.* benzenesulfonyl azide was achieved in quantitative yield within 15 minutes (Table 3, **4a**). Encouraged, we further investigated the reaction with different arylsulfonyl hydrazides bearing electron-donating groups (e.g. methoxy, methyl and *tert*-butyl) as well as withdrawing groups (e.g. bromo, cyano, nitro and trifluoromethane). Irrespective of their electronic nature, all these substrates were smoothly converted into the desired products with excellent yields (Table 3, **4b**-**4h**).

It is worth mentioning that the sterically hindered substrates (*i.e.* 2,4,6-trimethylbenzene sulfonyl hydrazide and 2,4,6-triisopropylbenzene sulfonyl hydrazide) also gave the desired azides (**4i** and **4j)** in >85% yields. Likewise, 2-naphthalenesulfonyl azide **4k** was obtained in 82% yield from corresponding hydrazide. To our surprise, this protocol works very well with heteroaromatic substrate, for instance, 1-methyl-1H-pyrazole-4-sulfonyl hydrazide was successfully converted into corresponding azide (**4l**) in 89% yield within 15 min. Similar to aryl substrates, alkyl sulfonyl hydrazides were also smoothly transformed into corresponding azides in good yields (Table 3, **4m** and **4n**).

Having studied the reaction of sulfonyl hydrazides with *tert*-butyl nitrite, we extended our investigation with acyl hydrazines (Table 4). To our delight, unsubstituted as well as electron donating or withdrawing groups (e.g. methoxy and nitro) substituted benzoyl hydrazines were successfully converted into corresponding azides in 80-87% yield with 3.0 equiv. of *tert*-butyl nitrite (Table 4, **6a**-**6c**). Moreover, conversion of carbonate hydrazides, heterocylic hydrazides and alkyl carboxylic hydrazides into respective azides was achieved in 80-94% yield (Table 4, **6d**-**6g**),[25] which illustrate the broad scope of the methodology.

Table 4. Conversion of acyl hydrazines using *tert*-butyl nitrite in acetonitrile.[a,b]



Reaction conditions: Substrate (1 mmol), TBN (3 equiv.) in acetonitrile (5 mL) at room temperature. [b]Isolated yields. [c]Alkyl carboxylic azides were found extremely unstable and could not be isolated, hence, yields were given as 0%. See the reference 25.

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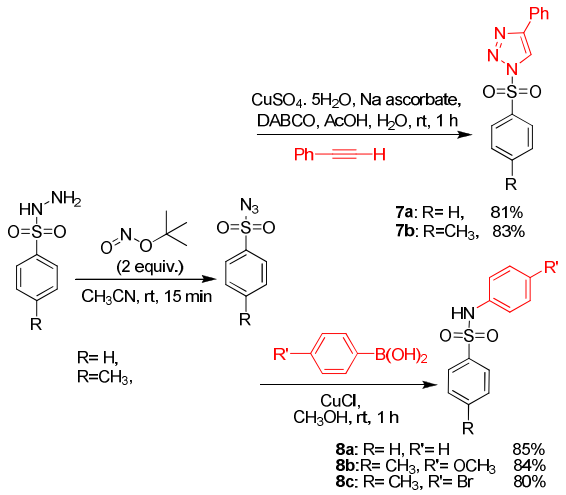
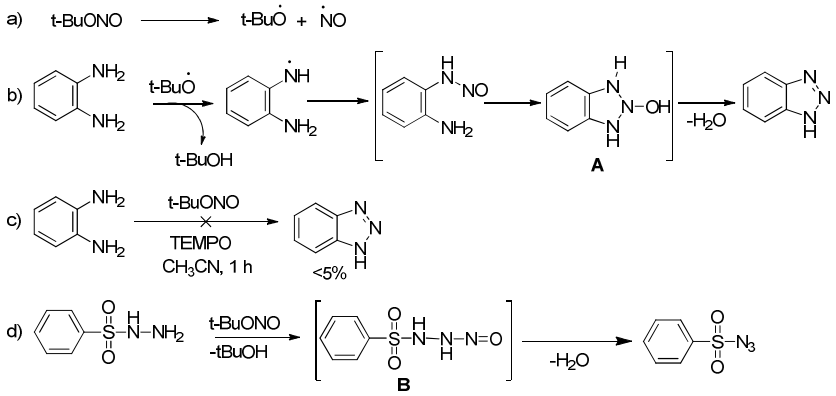
Having established a simple and efficient method for the conversion of hydrazides into azides, we have attempted one-pot click reaction with alkynes. For this study, sulfonyl hydrazides **4a** and **4c** were converted into corresponding azides *in situ* and subsequently reacted with phenylacetylene in the presence of copper sulphate.[13a] To our delight, the desired triazole product was obtained in 81-83% yields (Scheme 3, **7a** and **7b**). Further, we performed the coupling reaction between *in situ* generated sulfonyl azides and boronic acids in the presence of copper chloride,[14a] which gave the corresponding sulfonamides in excellent yields as illustrated in Scheme 3 (**8a**-**8c**).



Scheme 3. Applications of sulfonyl azides in one-pot synthesis.

A proposed mechanism for the TBN prompted nitrogen transfer reactions is shown in Scheme 4. Initially, *tert*-butyl nitrite undergoes homolytic cleavage and forms *tert*-butoxy and nitroso radicals (Scheme 4, a).[9] For benzotriazole formation: *o*-phenylenediamine undergoes radical mono-*N*-nitrosation to form the intermediate **A**, which gives the desired product upon releasing a water molecule (Scheme 4, b). To confirm the radical path, diazotization of *o*-phenylenediamine was performed with radical scavenger TEMPO (Scheme 4, c). The desired product, *i.e.* benzotriazole was not observed even after 1 h at room temperature. This observation lends support to our assumption. Similarly, *tert*-butyl nitrite (TBN) reacts with sulfonyl hydrazide to form corresponding *N*-nitroso intermediate **B**, which leads to the azide formation upon releasing a water molecule (Scheme 4, d).

In conclusion, a mild and practical methods for the i) transformation of *o*-phenylenediamines into benzotriazoles and ii) conversion of sulfonyl and acyl hydrazines into corresponding sulfonyl and acyl azides, were demonstrated with green reagent *tert*-butyl nitrite. All the reactions were carried out at room temperature to obtain the desired products in excellent yields. Moreover, this protocol does not require any catalyst, acid medium or high temperature which clearly demonstrates the merits of the current methodology. Acid labile groups were found to be very stable during the triazole formation with TBN. The developed methodology has been used as a key in one-pot synthesis of *N*-protected benzotriazoles, benzene sulfonyl triazoles and benzene sulphonamides.



Scheme 4. Proposed mechanism for the TBN prompted nitrogen transfer reactions.

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