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Sulfated Tin Oxide (STO)-Catalyzed Efficient Synthesis of 4-Aryl-*NH*-1,2,3-triazoles

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The synthesis of 4-aryl-*NH*-1,2,3-triazoles in good to excellent isolated yields (75-95%) has been achieved *via* a [3+2] cycloaddition of aromatic nitroolefins and sodium azide catalyzed by recyclable heterogeneous sulfated tin oxide (STO, 10 mol%) in toluene at 60 ^{0}C. Aliphatic nitrooefines proved to be unsuccessful partners in the present methodology.

1. Introduction

Azoles are nitrogen-containing heterocyclic moieties with five members that are crucial structural components of a variety of naturally occurring biologically active compounds.[1] One of the many biological impacts of azoles and their derivatives is their potent antibacterial action.[2-4] The scientific community has been fascinated by the unusual five-membered heterocyclic nucleus known as 1,2,3-triazole up to this point because of its remarkable biological characteristics and wide range of applications in the organic and material sciences.[5-7] Not only can these aromatic monocyclic compounds be used to a plethora of pharmaceutical products, such as anti-allergic, anti-cancer, anti-bacterial, herbicidal, and fungicidal drugs,[8-12] but they are also specifically identified by their presence in dyes, photostabilizers, and chelating agents in numerous metal complexes.[13-15]

Alternatively, *N*-unsubstituted triazoles have entered the scientific community as hopeful contenders for the synthesis of numerous biological motifs to compete with *N*-substituted triazoles in the fight against diseases like HIV, Alzheimer's, and tuberculosis, which are fatal to humans if left untreated.[16] The literature is largely silent on the roles played by 4-aryl-*NH*-1,2,3-triaozles in cancer immunotherapy, methionine aminopeptidase enzyme inhibition, and the development of antibacterial and anticancer drugs.

A few of the significant drugs with the *NH*-triazole moiety are shown in **Fig. 1**. Several methodologies have been developed to synthesize these molecular structures because of their broad applicability. The fundamental processes utilized in the synthesis of the aforementioned compounds are primarily the azide and alkyne condensation reaction, the one-pot multicomponent fusion between sodium azide and nitrostyrene produced *in situ* from nitromethane and aldehyde, and the direct synthesis from nitroalkene and sodium azide.[17-21] Most universal strategy for the preparation of the 1,2,3-triazole molecular system are the non-catalyzed [3+2] cycloaddition reacitons with the participation of azides.[22-23] Many examples of these-type transformations were described in the literature. Next, some examples of transition-metals catalyzed process were also described.[24] The cycloaddition based on the azidium anion is a analog of these protocols. Catalysts that were

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effectively used were amberlyst-15, *p*-toluenesulfonic acid, Al-MCM-41, $AlCl_3$, sulfamic acid, sulfated zirconia, $NH_4OAc/AcOH$, $NaHSO_3$ or Na_2SO_3, etc.[25-30]

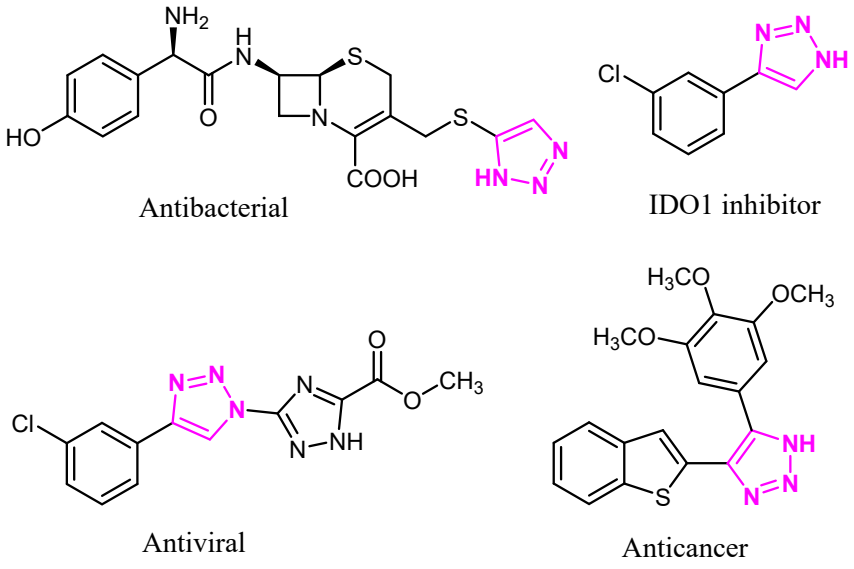


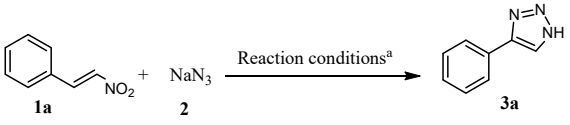
Fig. 1. Representative biologically relevant *NH*-1,2,3-triazoles

Solid heterogeneous catalysts are known to offer anticipated advantages in synthetic chemistry, including straightforward regeneration, decreased corrosiveness, cost, convenience of handling, and effective reusing.[31-34] Sulfated tin oxide, also known as SO_4^{-2}/SnO_2, has become a popular and efficient catalyst due to its large surface area, high efficiency, non-corrosive nature, low cost, and wide surface area. Utilized widely in chemical and industrial conditions, it comprises sulfated and sulfonic acid moieties on a variety of heterogeneous solid bases.[35-44] Very recently, we have successfully exploited the applications of STO in the synthesis of β-amino alcohols.[45] In keeping with our efforts to create innovative methodologies,[46-47] we report here the efficient synthesis of 4-aryl-1,2,3-triazoles *via* STO catalysis, which is derived from the reaction of nitro styrenes with sodium azide.

2. Results and Discussion

Substituted nitrostyrenes were produced using a process developed by Pellacani et al.[48] First, we used sulfated tin oxide in various solvents and reaction conditions to carry out several of the model reactions with nitrostyrene (**1a**) and NaN_3 (**2**), resulting in the product 4-phenyl-*NH*-1,2,3-triazole (**3a**, **Table 1**). When STO was not present, the reaction produced significant amounts of triarylbenzene, which was consistent with previous reports. The yields of 3a were observed to be slow even at 80 °C when DMSO or DMF were used as the solvent (28 and 40% yields, respectively, entries 1-2, Table 1).

Table 1. Optimization studies



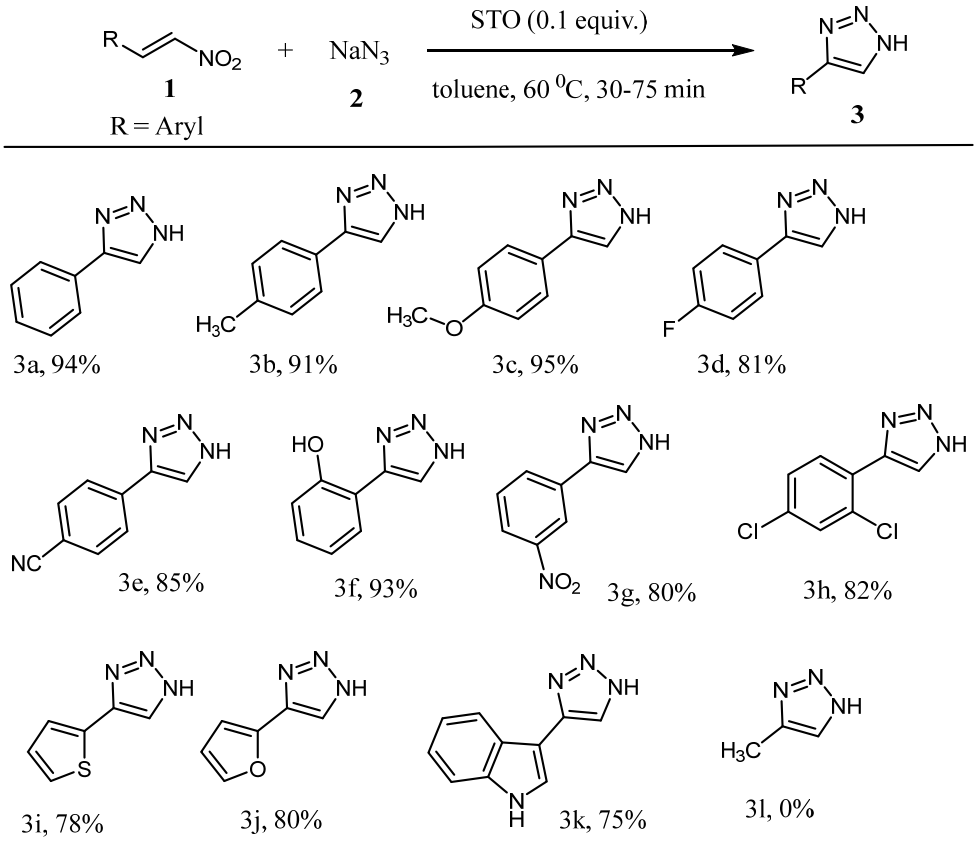
1a **2** **3a**

Entry	STO (equiv.)	Solvent	Time (h/min)	Temp./ ^{0}C	Yield (%)[b]
1	--	DMSO	1 h	80	28
2	--	DMF	2 h	80	40
3	0.2	DMF	1 h	rt	69
4	0.2	DMSO	30 min	60	79
5	0.2	DMF	30 min	60	80
6	0.2	Toluene	30 min	60	92
7	0.2	CH_3CN	30 min	60	85
8	0.2	Neat	45 min	60	55
9	**0.1**	**Toluene**	**30 min**	**60**	**94**
10	0.5	Toluene	30 min	60	92
11	0.05	Toluene	30 min	60	81

[a]Reaction was carried out with **1a** (1 mmol), NaN_3 (1.5 mmol) and STO (indicated as above)
[b]isolated yield

To our delight, adding STO (0.2 equiv.) to DMSO and DMF at room temperature for 30 minutes resulted in a considerable increase in yield (79% and 80%, respectively, entries 4-5, Table 1). When the model reaction was carried out in toluene, the yield increased to its maximum (entry 6, Table 1). Later, we considered testing the STO stoichiometric ratio (from 0.2 to 0.05 equiv.) and optimizing the reaction temperature. It's intriguing to see that even with a shorter reaction time, the reaction conversion and yields (94, 92, and 81%, respectively, entries 9-11, Table 1) increased. We then reduced the STO ratio even further (up to 0.05 equiv.), but the yields did not show any improvement. Ultimately, it was found that the ideal reaction conditions in toluene were 0.1 equivalent of STO at 60 ^{0}C (entry 9, Table 1).

After obtaining the ideal reaction conditions, we investigated the protocol's substrate scope using a range of decorated nitroolefins to produce distinct *NH*-1,2,3-triazoles (**Scheme 1**). This approach underwent [3+2] cycloaddition smoothly, regardless of the substitution pattern, and produced the relevant products in moderate to good yields (75-95% yields, **3a-k**, Scheme 1). The cycloaddition course of the reaction with the participation of conjugated nitroalkenes are determined by the local strong electrophilic nature of the β-position of the nitrovinyl moiety.[49-52] Furthermore, as seen in **Scheme 1**, this approach is very compatible with a wide range of functional groups, including fluoro, chloro, methyl, methoxy, hydroxy, cyano, and nitro. We noticed with great interest that every cycloaddition reaction was finished in less than 1.25 h.



Scheme 1. STO-Catalyzed 4-aryl-*NH*-1,2,3-triazoles

Notably, nitroolefins containing methyl and methoxy groups on the aryl ring, which are electron-donating groups, produced products in excellent yield (91-95%, **3b-c**, Scheme 1). When nitroolefin was substituted with an aryl group at the *ortho*-position, the product was produced faster than with other substrates (93%, **3f**, Scheme 1). Motivated by these outcomes, we shifted our focus to heterocyclic substrates, which are prevalent scaffolds in medicinal chemistry, such as furan, thiophene, and indole. We were delighted to find that the cycloaddition process of the heterocyclic substituted nitroolefins went well, yielding good yields of **3i**, **3j**, and **3k** (78, 80, and 75%, respectively, Scheme 1). It's interesting to note that this reaction is unaffected by strongly coordinating heteroatoms like sulphur, oxygen, and nitrogen. Using di-substituted nitroolefine, the [3+2] cycloaddition reaction proceeded efficiently with a high yield (82%, **3h**, Scheme 1), which was rather fascinating to note. These findings unambiguously demonstrated the applicability and universality of sulfated tin oxide as a catalyst or additive for the production of various 4-aryl-*NH*-1,2,3-triazoles employing a broad variety of nitroolefins. Nevertheless, it was discovered that the aliphatic amine was an unsuccessful partner in the intended reaction (entry **3l**, Scheme 1).

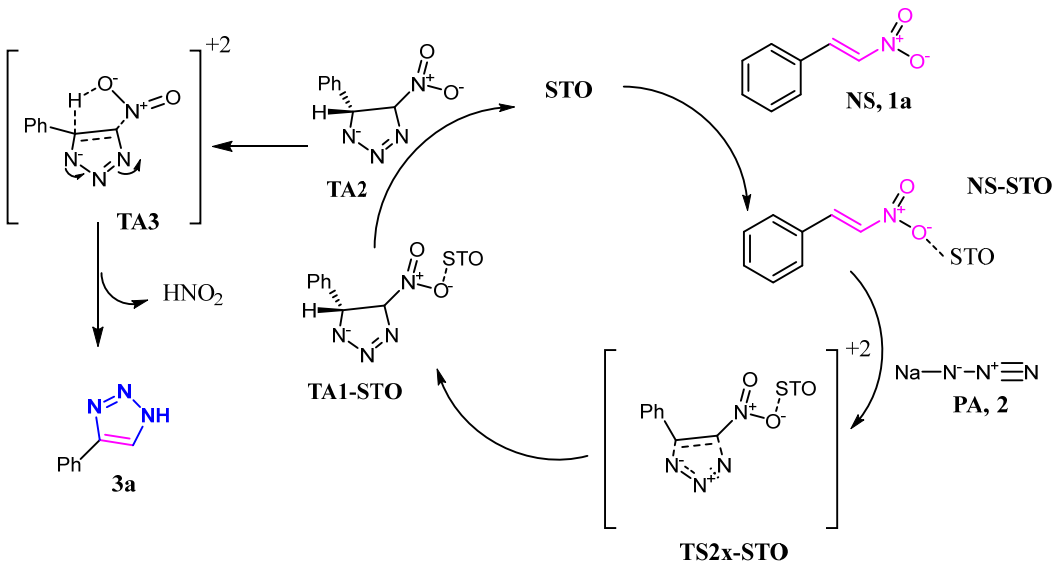


Fig. 2. Plausible reaction mechanism

In **Fig. 2**, a plausible reaction pathway is proposed. The nitro styrene (**NS**, **1a**) and STO interact in the first stage to create an active intermediate **NS-STO** that can be immobilized in the solid/liquid interface. The triazoline intermediate **TS2x-STO** is created when this intermediate (**NS-STO**) combines with the **PA** (NaN_3, **2**). In order to obtain the desired triazole (**3a**), the last step involves regenerating STO to its initial quantity and removing HNO_2 through a transition state called **TA3**.

In the practice however, the wide range of mechanisms are possible: polar one step mechanism; polar stepwise mechanism with the zwitterionic intermediate, non-polar one step mechanism, non-polar mechanism with the biradical intermediate. Stepwise mechanism is especially probable in the case of the reaction with the participation of conjugated nitroalkenes,[53-58] based on the observations from previous literature reports. **Fig. 2** suggested the one step" concerted" mechanism of the nitrous acid extrusion. In the practice however, the wide range of mechanisms are possible: one-step synchronical, one-step asynchronous and stepwise E1-like or E1cB-like.[59-62]

The synthesis of 4-aryl-*NH*-1,2,3-triazoles (**3**) in the presence of sulfated tin oxide was compared with some of the earlier approaches, as indicated in **Table 2**, to demonstrate the value of this methodology. The data clearly showed that the phenylacetylene reaction took longer to complete (entry 3, Table 2). Moreover, nitrostyrene **1a** and sodium azide **2** reacted with STO in a shorter amount of time and produced in excellent isolated yield (entry 4, **Table 2**).

Table 2. Comparison of the reaction scope with the literature reports

Entry	Reaction	Catalyst	Solvent	Time (min/h)	Temp (^{0}C)	Yield (%)[a]
1	1a+NaN_3	*p*-TsOH (0.5 equiv.)	DMF	60 min	60	93[22]
2	1a+NaN_3	NH_2SO_3H (0.4 equiv.)	DMF	20 min	60	94[19]
3	Ph-C≡C-H, $TMSN_3$	Cu^I (20 mol%)	MeOH/ DMF	11 h	100	87[18]
4	**1a+NaN_3**	**Sulfated tin oxide (10 mol%)**	**toluene**	**30 min**	**60**	**94 (present work)**
5	1a+NaN_3	Amberlyst-15 (30 mg)	DMF	1-3 h	50	95[23]
6	1a+NaN_3	$AlCl_3$ (10 mol %)	DMSO	5-8 h	70	95[27]
7	PhCHO+CH_3NO_2+NaN_3	Fe_3O_4@SiO_2@Propyl-HMTA (MNPs) (0.05 g)	DMF	40 min	110	95[20]
8	PhCHO+CH_3NO_2+NaN_3	NH_4OAc (1 equiv.) AcOH (0.5 equiv.)	DMF	-	100	93[25]
9	PhCHO+CH_3NO_2+NaN_3	Nanostructured $Ni(OH)_2$-ZnO mixed crystals	PEG-400	3.5 h	100	88[21]
10	PhCHO+CH_3NO_2+NaN_3	$NaHSO_3$ (1 equiv.) Na_2SO_3 (1 equiv.)	DMSO	5 h	110	73[26]
11	1a+NaN_3	Piperidine (0.1 equiv.) Al-MCM-41 (50 mg) Sulfated zirconia (50 mg)	DMF/μw	30 min	80	70[24] 85[24]

Subsequently, an analysis was conducted on the STO catalyst's recycling in the reaction between sodium azide **2** and nitrostyrene **1a**. Following the completion of the reaction, diethyl ether was used to wash the STO and the solution was vacuum-filtered *via* a sintered glass funnel. After being dried, the recovered catalyst was employed again right away without needing to be further purified. With no significant reduction in its catalytic activity, the catalyst could be extracted and employed up to five more times (88% isolated yield for **3a** after the fifth run).

3. Conclusions

In conclusion, by using STO as an additive to synthesize a useful substituted 4-aryl-*NH*-1,2,3-triazoles, we have created a simple and reproducable [3+2] cycloaddition procedure using nitroolefins. It proved to serve as a substitute for the conventional [3+2] cycloaddition of azides with alkynes. The key components of this protocol are its open-air reaction conditions, recyclable heterogeneous catalyst, and straightforward method. This approach demonstrated excellent functional group compatibility and is practically applicable to all types of aromatic nitroolefins. Above all, this approach facilitates the quick confirmation of 1*H*-1,2,3-triazole library creation as novel chemical entities in drug development.

4. Experimental

Typical procedure for the synthesis of 4-aryl-NH- 1,2,3-triazoles

Nitroolefine **1** (1 mmol) and sodium azide **2** (1.5 mmol) were stirred in toluene (3 mL), then, STO (10 mol%) was carefully added to the reaction mixture. Then, the reaction mixture was stirred at 60 ^{0}C in air. When the reaction was completed (detected by TLC), the mixture was cooled to room temperature and the reaction mixture was diluted with 10 ml of diethyl ether, filtered, and the catalyst was cleaned with 4×5 ml of diethyl ether. The crude product was washed with aqueous $NaHCO_3$ solution, and brine, respectively. Drying the organic layer on sodium sulphate and vacuum concentrating, the corresponding crude triazole was obtained. After purification by flash chromatography on silica gel with hexane/ethyl acetate (*v*/*v*= 5:1) as the eluent, pure 1*H*-1,2,3-triazole (**3**) was synthesized.

Representative spectral data

4-Phenyl-1*H*-1,2,3-triazole (**3a**): White solid; mp 140-142 ^{o}C; ^{1}H NMR (DMSO-d_6, 400 MHz): δ 15.2 (s, 1H), 8.3 (s, 1H), 7.8 (d, J = 6.80 Hz, 2H), 7.4 (d, J = 7.20 Hz, 2H), 7.3 (d, J = 6.81 Hz, 1H); ^{13}C NMR (DMSO-d_6, 100 MHz): δ 145.3, 130.4, 129.0, 128.2, 127.4, 125.7. HRMS Calcd (ESI) *m/z* for $C_8H_8N_3$: $[M+H]^+$ 146.0713, found: 146.0709.

Caution! Sodium azide is a hazardous and possibly explosive substance. In the meantime, hydrazoic acid-which is also exceedingly toxic-is produced when powerful acids are used to cure sodium azide. It is possible for hydrazoic acid to develop during the reaction; in that case, it should be removed with water before evaporating over rotovap. A chemical fume hood should be used for all operations, including extraction and evaporation, and strong acids should not come into touch with the work being done. To capture off any volatile HN_3, the top of the condenser was connected *via* a gas bubbler to an aqueous NaOH (1 M) solution.

Supporting Information is available

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