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Synthesis of *β*-triazolylenones via metal-free desulfonylative alkylation of *N*-tosyl-1,2,3-triazoles

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Abstract

Desulfonylative alkylation of N-tosyl-1,2,3-triazoles under metal-free conditions leading to *β*-triazolylenones is reported here. The present study encompasses the synthesis of triazoles with a new substitution pattern in a single step from cyclic 1,3-dicarbonyl compounds and N-tosyl triazole in moderate to high yields. Our synthesis takes place with complete regioselectivity as confirmed by crystallographic analysis which is rationalized by suitable mechanistic proposal. This method provides an efficient, versatile and straightforward strategy towards the synthesis of new 1,2,3-triazoles.

Introduction

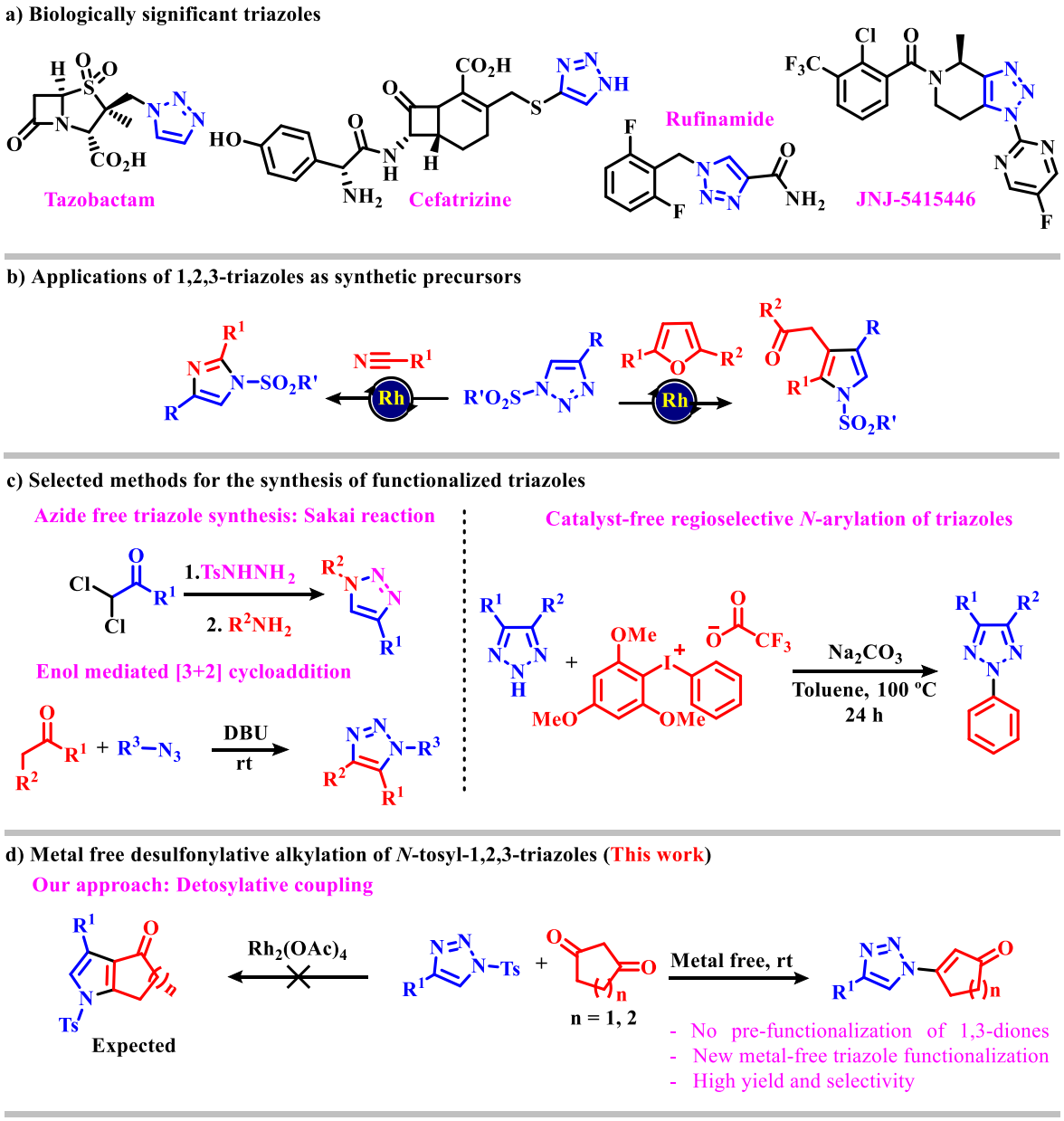
1,2,3-Triazoles are significant non-natural heterocyclic scaffolds with extensive applications in biochemistry, agrochemistry and materials chemistry [1–5]. This class of heterocycles presents important biological properties, such as antiviral, anti-inflammatory, antimicrobial etc and are considered as key building blocks in pharmaceutical industry [6–9]. Thus, they marked their presence as prominent scaffolds in many drug molecules such as tazobactam, cefatrizine, rufinamide and JNJ-5415446 (Scheme 1a) [10].

In addition to their biological activities, triazolic compounds are widely employed in organic synthesis and have outstanding synthetic versatility. In this sense, extensive scientific research has been conducted, using triazoles as synthetic precursors in denitrogenative transannulation reactions under metal-catalysed conditions to form other heterocycles such as functionalized pyrroles, imidazoles and pyridines (Scheme 1b) [11–13].

The traditional method for the synthesis of triazole unit is the Huisgen 1,3-dipolar cycloaddition between azides and alkynes [14,15]. However, the formation of the nitrogenated azoles by the classical Huisgen methodology is slow due to its high activation energies and also lack of regiochemical control, in general, leading to a mixture of 1,4- and 1,5-regioisomers of 1,2,3-triazoles. Later, Sharpless and Meldal have independently developed a copper-catalysed azide–alkyne cycloaddition that accelerated the rate of the reaction and allows the selective preparation of 1,5-disubstituted 1,2,3-triazoles [16–19].

As noted above, a wide range of methods are available in the literature for the efficient synthesis of triazoles with different substitution pattern. One important methodology developed by Sakai group involved the reaction of α,α-dichloroketone, tosyl hydrazide and primary amine [20]. However, in this case, the unstable α,α-dichlorohydrazone intermediate had to be isolated which paved the way for further modification of the protocol (Scheme 1c). In another approach, these *N*-alkylated triazoles can be prepared by using either direct alkylation of triazole under metal-free as well as transition metal catalyzed conditions [21,22]. Later, metal-free conditions were also developed to synthesize triazole derivatives, which included 1,3-dipolar cycloaddition of alkyl azide to enols generated from carbonyl compounds, N^2-arylation using hypervalent iodine (Scheme 1c), N^2-alkylation involving radical intermediate, pyridine-*N*-oxide mediated N^1-

arylation [23–25]. It is important to note here that the regioselective desulfonylative alkylation of *N*-tosyl-1,2-3-triazoles under metal-free and base-free conditions still remains unexplored.



Scheme 1. Synthesis, functionalization and applications of triazoles

From another perspective, compounds containing 1,3-dicarbonyl moiety are essential building blocks in organic synthesis whose reactivity is well-established in the literature [26,27]. Besides, these are the precursors of *β*-enamines which are employed for the synthesis of many bioactive heterocycles [28]. These are also important precursors of diazo adducts which are used

in insertion, cyclopropanation, and various rearrangements to construct various cyclic as well as acyclic moieties under metal catalyzed conditions [29,30]. On the contrary, under basic conditions, these diazo compounds undergo [3+2] cycloadditions with suitable substrates to render various nitrogen-rich heterocycles [31]. In addition to their synthetic importance, these are frequently encountered as ligands in many metal complexes [32–35]. Our group has also employed 1,3-dicarbonyl compounds as binucleophiles for the construction of various carbocycles, heterocycles as well as in asymmetric catalysis [36–42]. Our initial objective to trap the aza vinyl rhodium carbenoid using the 1,3-dicarbonyl compounds to form pyrazolone was unsuccessful which instead led to the formation of an unexpected product, i.e. *β*-triazolylenone. Being inspired by the results, we intended to use 1,3-dicarbonyl compounds as detosylative alkylating agents that would lead to the formation of *β*-triazolylenones in a highly regioselective manner under mild conditions (Scheme 1d).

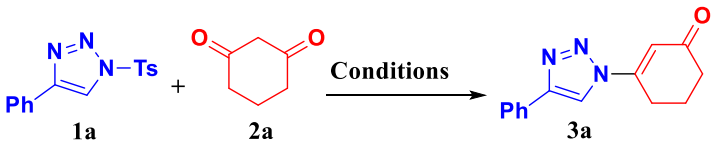
Result and Discussion

In order to execute our idea, triazole **1a** and 1,3-cyclohexanedione **2a** were selected as our model substrates and the reaction was performed using 4 mol% of $Rh_2(OAc)_4$ in chloroform under reflux conditions which afforded the *β*-1,2,3-triazolylcyclohexenone **3a** in 66% yield (Table 1, entry 1). The alternative approach for the synthesis of such triazole moiety **3a** is the [3+2] cycloaddition between the alkynes and the corresponding azides. However, the major disadvantage of such a strategy is the use of 3-azidoenone which is difficult to handle owing to its explosive nature. Therefore, our method provides an easy pathway to synthesize such triazolylenones.

Inspired by this result, we proceeded to optimize the reaction conditions to further improve the yield. Replacement of rhodium by copper (II) acetate slowed down the reaction with a marginal change in the yield of the product **3a** (entry 2). Surprisingly, when the reaction was conducted in the absence of any metal catalyst, the reaction proceeded sluggishly and the coupling product **3a** was isolated in 49% yield (entry 3). This suggested that the reaction could also proceed even in the absence of metal catalyst. However, the lower yield of the product **3a** might be attributed to certain side products obtained at high temperature as evident from TLC analysis. To avoid such side reactions, the reaction was performed at room temperature and to

our delight, the product **3a** was obtained in 78% yield (entry 4). For further improvement in the yield, the reaction was carried out in different solvents such as THF, EtOAc, toluene, DCM and 1,2-DCE which led to inferior results (entries 5-9). Since, there was no further improvement in the yield, the conditions described in entry 4 were considered as the best to generalize the scope of the reaction.

Table 1. Optimization studies[a]



1a 2a 3a

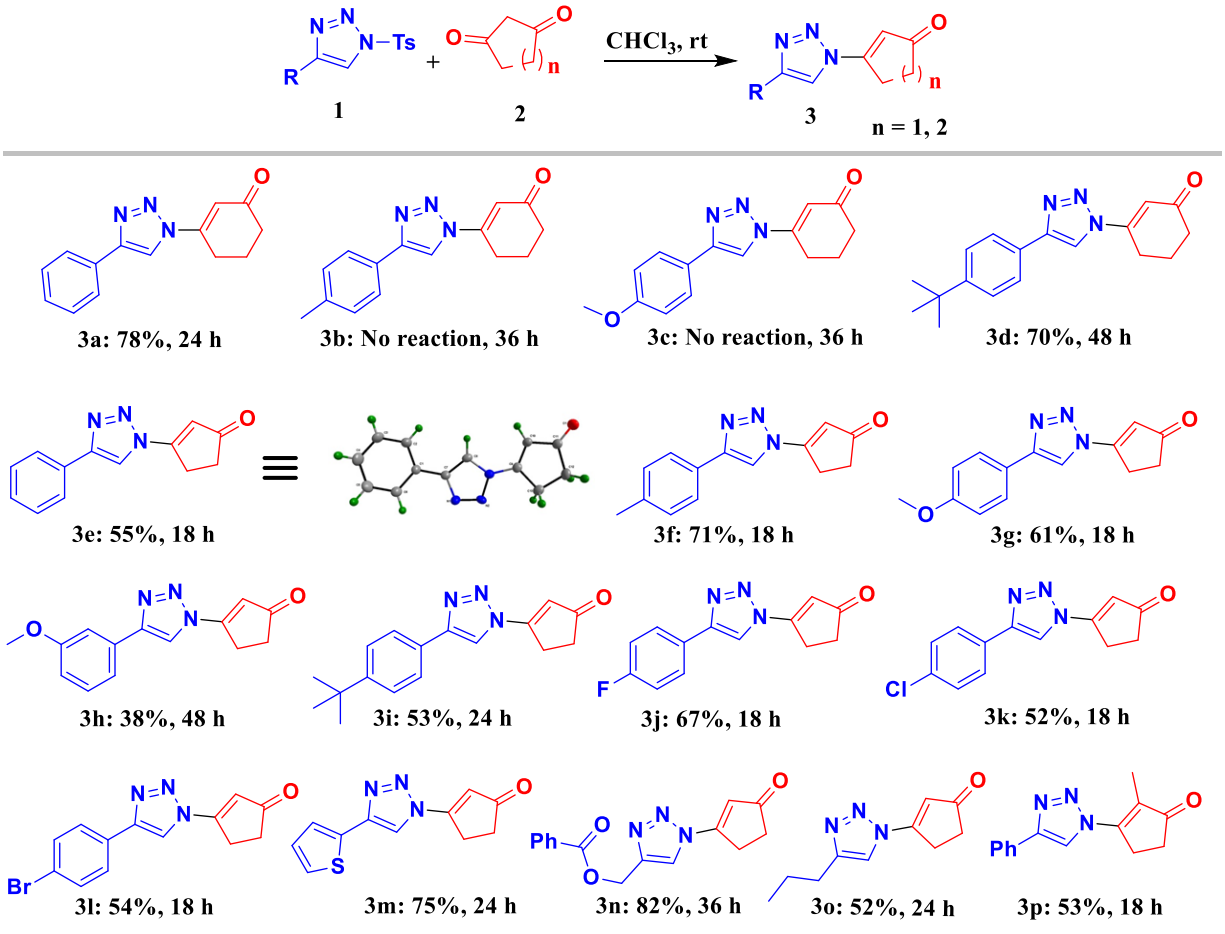
Entry	Catalyst (mol%)	Solvent	Temp. (^{o}C)	Time (h)	Yield (%)[b]
1	$Rh_2(OAc)_4$ (4)	$CHCl_3$	60	2.5	66
2	$Cu(OAc)_2$ (4)	$CHCl_3$	60	6	65
3	-	$CHCl_3$	60	5	49
4	**-**	**$CHCl_3$**	**rt**	**24**	**78**
5	-	THF	rt	48	NR
6	-	EtOAc	rt	48	Trace
7	-	Toluene	rt	72	Trace
8	-	CH_2Cl_2	rt	96	56
9	-	1,2-DCE	rt	72	Trace

[a]Performed by using 0.1 mmol 4-phenyl-*N*-tosyl-1*H*-1,2,3- triazole **1a** and 0.1 mmol of cyclohexyl-1,3-dione **2a**. [b]After silica gel column chromatography.

At the outset, various triazoles **1** were screened under the optimized conditions (Table 2). As mentioned earlier, the model triazole **1a** afforded the product **3a** in 78% yield within 24 h. But to our surprise, triazoles **1b** and **1c** containing electron donating groups such as 4-tolyl and 4-methoxyphenyl groups could not deliver the products **3b** and **3c**, respectively, even after prolonged reaction time whereas 4-*tert*-butyl analog **1d** underwent the reaction smoothly to form the corresponding product **3d** in 70% yield. However, due to the inconsistent results with cyclohexanedione **2a**, further scope was investigated by employing cyclopentane-1,3-dione **2b**. The model triazole **1a** furnished the product **3e** in 55% yield within 18 h. To our delight, triazoles **1b** and **1c**, bearing 4-tolyl and 4-methoxyphenyl groups, which did not react with 1,3-cyclohexanedione **2a** reacted smoothly with cyclopentane-1,3-dione **2b** to deliver the products **3f** and **3g** in 71% and 61% yields, respectively. The reaction of mild electron withdrawing 3-

methoxyphenyl-1,2,3-triazole **1e** led to product **3h** in low yield (38%) whereas the corresponding 4-*tert*-butylphenyl-1,2,3-triazole **1f** afforded the product **3i** in 53% yield. Later, the reaction was performed using various haloaryltriazoles such as 4-fluorophenyl **1f**, 4-chlorophenyl **1g** and 4-bromophenyl **1h** which also gave the corresponding products **3j**, **3k** and **3l** in 67%, 52% and 54%, respectively. The heteroaryl derivative thienyltriazole **1i** also reached well to afford the product **3m** in 75% yield. While the benzoyloxymethyltriazole **1j** furnished the product **3n** in excellent (82%) yield, the performance of another alkyltriazole **1k** was less impressive giving the corresponding product **3o** only in moderate (52%) yield. The reaction of model triazole **1a** with 2-methyl-1,3-cyclopentanedione **2c** also led to the product **3p** in moderate (53%) yield. Unfortunately, the reaction was not successful with acyclic 1,3-dicarbonyl compounds.

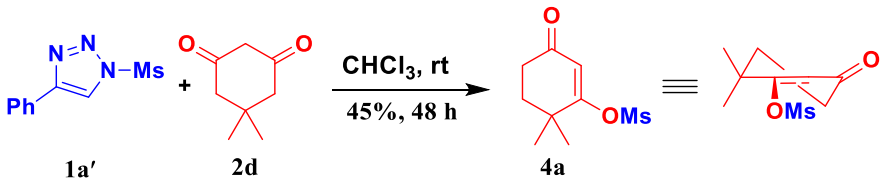
Table 2. Substrate scope[a,b]



[a]The reaction was performed using 0.2 mmol *N*-tosyl-1,2,3-triazole **1** and 0.2 mmol of cyclohexyl-1,3-dione **15**.[b] After silica gel column chromatography.

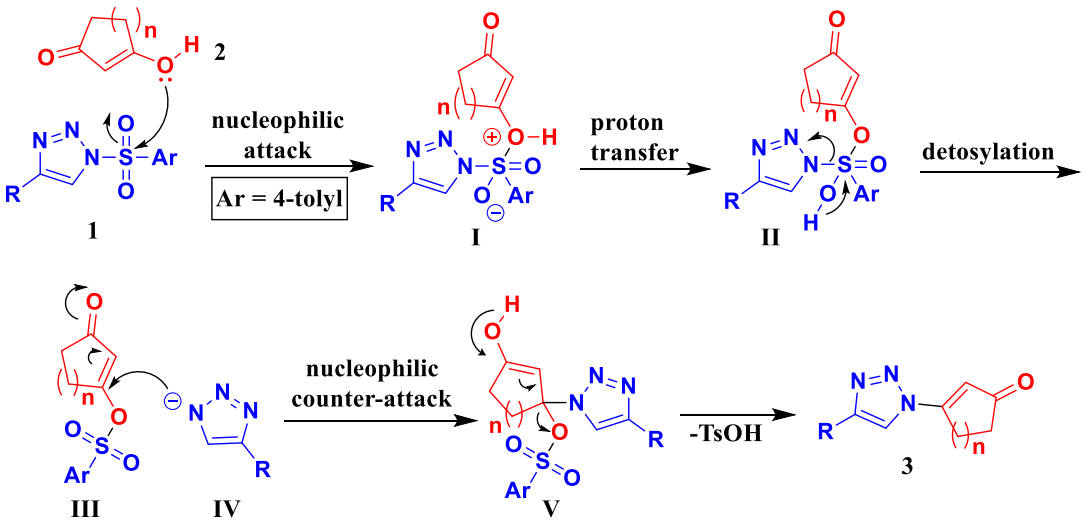
The structure and regiochemistry of all the products were confirmed by detailed analysis of their spectral data (IR, ^{1}H, ^{13}C and Mass) which were further unambiguously established by single crystal X-ray analysis of a representative compound **3e** (Table 2 and SI).

Although triazole **1a** reacted with cyclohexanedione **2a** (vide supra), its reaction with dimedone **2d** provided a complex mixture. Therefore, we employed triazole **1a'** bearing a mesyl group for the reaction with **2d** (Scheme 3). Surprisingly, this reaction delivered the *β-O*-mesyl-4,4-dimethylcyclohexenone **4a** instead of the expected *β*-triazolylenone in 45% yield. This result provided crucial evidence for the mechanism of the reaction which suggested that *β*-sulfonyloxyenone could be the key intermediate in the formation of *β*-triazolylenone **3**.



Scheme 3. Formation of enone **4a** triazole **1a** dimedone **2d**.

Based on the above observation, the following mechanism is proposed. Initially, the enol form of 1,3-dicarbonyl **2** attacks the sulfonyl group in **1** to form intermediate **I** which later undergoes proton transfer to form intermediate **II**. Cleavage of N-S bond in intermediate **II** generates the *β-O*-tosylcyclopentenone **III** and triazolyl anion **IV**. Subsequent counter-attack of the triazolyl anion **IV** on the enone intermediate **III**, followed by elimination of OTs affords the corresponding *β*-triazolylenone **3** (Scheme 4).



Scheme 4. Mechanistic proposal for the formation of *β*-triazolylenones.

It may be noted that the outcome of the reaction is highly dependent on the nature of the 1,3-dicarbonyl compound. In the case of cyclic-1,3-dicarbonyls, cyclopentane-1,3-dione **2b** reacts smoothly in almost all cases whereas the scope of cyclohexane-1,3-dione **2a** is limited. On the contrary, dimedone **2d** did not react with *N*-tosyl-1,2,3-triazole, but reacted with *N*-mesyl-1,2,3-triazole to form *β*-*O*-mesyl-5,5-dimethylhexenone intermediate. The highly substrate dependent nature of the reaction can be explained by taking both hydrogen bonding and steric factor into consideration. In the solid as well as solution state, all the three above mentioned 1,3-dicarbonyls exist in the enol form which are considerably stable and therefore undergo tosylation easily to form the corresponding *O*-tosylenone intermediates. The five membered tosyloxyenone intermediate is a planar molecule and therefore free of any steric crowding (Figure 2). Hence, the incoming nucleophile can easily attack the *β*-position without any difficulty. On the other hand, the six membered *o*-tosyl intermediate exists in twist-boat conformation. In this case, the approach of the nucleophile towards the *β*-position suffers from steric crowding exerted by the adjacent allylic hydrogen atoms. Therefore, cyclohexane-1,3-dione **2a** has limited substrate scope. In the case of dimedone **2d**, the two hydrogen atoms are replaced by two bulky methyl groups which impart greater steric hinderance to the incoming nucleophile as compared to cyclohexanedione **2a**. Therefore, the reaction stops at the tosyl/mesyl migration step and does not proceed further. Unlike cyclic 1,3-dicarbonyls, the acyclic 1,3-dicarbonyls possess intramolecular hydrogen bonding and are in rapid equilibrium with their keto-form. In polar

solvents, the stability of the enol form is further decreased and, therefore, the keto-enol equilibrium lies more towards the keto-form [42–45]. Presumably for this reason, the acyclic 1,3-dicarbonyls did not react in the desired way under our experimental conditions.

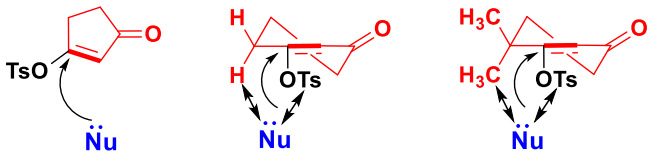


Figure 2. Nucleophilic addition to 5- and 6-membered cyclic tosyloxyenones

Conclusions

In conclusion, we have developed a metal-free catalyst-free approach for the desulfonylative coupling of *N*-tosyl-1,2,3-triazoles with cyclic 1,3-diketones to form various *β*-triazolylenones. Although the scope of the 1,3-dicarbonyl compound is limited, the protocol is very convenient and useful as it employs very mild reaction conditions. It is also highly regioselective and `affords only N^1-alkylated products in moderate to excellent yields.

Supporting Information

Supporting Information File 1
Experimental details and characterization data of new compounds.

Supporting Information File 2
Crystallographic data for compound **3e**.

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