ARTICLE

N-Acyl-1,2,3-triazoles – key intermediates in denitrogenative transformations

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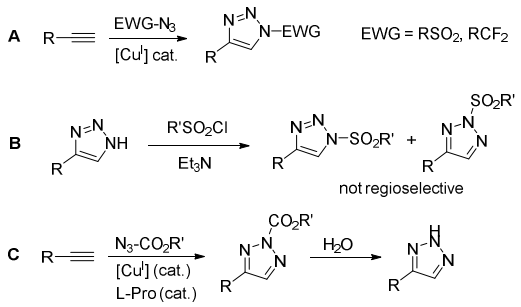
Direct N-acylation of 1,2,3-NH-triazoles aimed at obtaining elusive N-acyl-1,2,3-triazoles was investigated. A preference for the formation of thermodynamically favoured N2 isomers was established and an influence of the hard/soft character of the electrophile on the regioselectivity of acylation was found. Although N-acylated 1,2,3-triazoles are hydrolytically unstable compounds, they were isolated and fully characterized, including crystal structure determination of examples of N1 and N2 acylated products by X-ray difraction. N1- and N2-acyltriazoles interconvert in the presence of Brønsted or Lewis acids, which explained the efficiency of triazole cleavage transformations proceeding *via* N1-acylated triazoles. Efficient synthesis of enamido triflates from NH-triazoles proceeding *via* the intermediacy of N2-acyl-1,2,3-triazoles was developed.

1,2,3-Triazoles are important heterocyclic compounds with various biological activities and high synthetic value.[1] There are two general synthetic routes to N-substituted 1,2,3-triazoles – cycloaddition reactions of azides with alkynes,[2] activated ketones[3], or nitroalkenes,[4] and nitrogen functionalization of NH-1,2,3-triazoles with electrophiles.[5] Whereas the cycloaddition reaction is widely investigated and established as an efficient and robust method, functionalization of NH-1,2,3-triazoles containing three nucleophilic nitrogen atoms is considered problematic because of unpredictable regioselectivity.[1a,5] However, NH-1,2,3-triazoles are available starting materials that can be efficiently prepared from inexpensive azide sources, such as NaN_3[6] or $TMSN_3$[7] and alkynes, or NaN_3 and commercially available aldehydes and nitroalkanes *via* tandem Henry reaction/[3+2] cycloaddition.[8] Recently, a number of regioselective protocols for the synthesis of either N2[9] or N1-substituted[10] isomers of 1,2,3-triazoles have been developed. Thus, alkylation, arylation, vinylation and Michael addition with NH-1,2,3-triazoles as nucleophiles have been described and extensively studied.[5, 9-10] It is important to note that sulfonylation of NH-1,2,3-triazoles, which would be a tempting route to synthetically useful N1-sulfonyl-1,2,3-triazoles, is not regioselective (Scheme 1B),[11] and only regioselective N2-sulfonylation via radical reaction is known.[12]

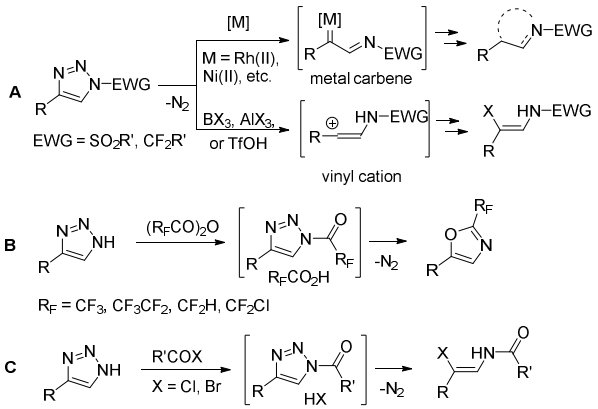
In contrast to a broad variety of known N-alkyl-, N-fluoroalkyl, N-aryl- and N-sulfonyl-1,2,3-triazoles (Scheme 1A), N-acyl-1,2,3-triazoles are almost unexplored, and only rare and scattered examples have been reported.[13] Indeed, a click reaction with acyl azide is not a viable route because of the low stability of acyl azides in the presence of a Cu(I) catalyst, resulting in nitrene formation.[14] N-Carbamoylation of NH-1,2,3-triazoles was studied and the formation of a mixture of N1- and N2-isomers was observed.[15] These compounds possess significant application potential in biological studies. For example, 2-carbamoyl-4-aryl-1,2,3-triazole derivatives were used for site-selective incorporation into proteins,[15c] as selective chemical probes of endocannabinoid biosynthesis enzymes such as diacylglycerol lipase and ABHD6.[15d,e] Very recently, the first example of selective formation of N2-alkoxycarbonyl-1,2,3-triazoles was observed in proline-catalyzed click reaction of carbamoyl azides with alkynes followed by spontaneous carbamoyl group migration to N2-position.[16] The resulting N2-carbamoyl triazoles were highly sensitive to hydrolysis to NH-triazoles (Scheme 1C).



Scheme 1 Synthetic approaches to N-EWG-substituted 1,2,3-triazoles.

1,2,3-Triazoles bearing an electron-withdrawing group at position N1 are useful starting materials in denitrogenative ring opening transformations.[1, 17] Among them, N-sulfonyl-1,2,3-triazoles are the most widely explored in denitrogenative transformations, which are possible under metal catalysis[17] or by the action of Lewis or Brønsted acids (Scheme 2A).[18] The transannulation process was recently extended by us to N-fluoroalkylated triazoles to give access to a number of N-fluoroalkylated nitrogen heterocycles.[19] Moreover, there has been one report about denitrogenative cleavage of N-(1,2,4-triazolyl)-1,2,3-triazoles.[20] However, it is remarkable that N-acyltriazoles have never been used as substrates in denitrogenative transformations. This can be attributed to the low stability of these compounds and their sensitivity to

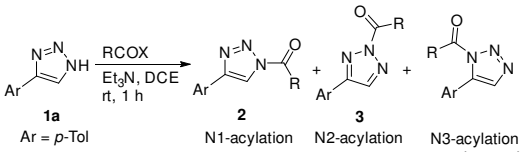
moisture, as their hydrolysis results in deacylation to NH-triazoles.[16] Also, it has been reported that reactions of N-acylbenzotriazoles with nucleophiles (amines, alcohols) result in deacylation as well.[21] Thus, N-acylbenzotriazoles have been used as mild acylation reagents with limited applicability in ring transformations. Only recently, the first reports of efficient monocyclic 1,2,3-triazole ring cleavage starting from NH-triazoles *via in situ* acylation were published by us (Scheme 2B)[22] and Li's group (Scheme 2C).[23] The formation of unstable N-acyltriazoles as intermediates in these processes has been proposed. Indeed, the utilization of readily available NH-triazoles is more atom-economical compared to N-sulfonyl- and N-fluoroalkyl-triazoles. However, the formation, stability and reactivity of N-acyl-1,2,3-triazoles remains unexplored. A high efficiency of NH-triazole ring cleavage transformations could support the hypothesis of regioselective N1-acylation,[23] while it is well-established that in reactions of NH-triazoles with electrophiles the formation of N2-substituted isomers is preferred.[9h-l] We hypothesized that a rapid interconversion between N1 and N2-acyltriazoles in the presence of an excess of acylation agent might enable the conversion of N-acyltriazole into ring cleavage products. Herein we report on our systematic study on N-acylation of 1,2,3-NH-triazoles and their regioselectivity, as well as on our study of ring cleavage reactions of N-acyltriazoles with Brønsted and Lewis acids.



Scheme 2 Transformations of N-EWG-substituted 1,2,3-triazoles and denitrogenative reactions of NH-1,2,3-triazoles with acylating reagents.

We initiated our study of the acylation of the model 1,2,3-triazole **1a** with different acylating agents in the presence of stoichiometric amount of base (Et_3N). Acylation of **1a** proceeded quickly at ambient temperature, with nearly quantitative yields (Table 1). In the case of benzoyl chloride or benzoic anhydride, mostly N2-acylated triazole **3a** formed (entries 1 and 2). The more electron-deficient 4-nitrobenzoyl chloride led to the exclusive formation of N2-substituted acyl triazole **3b** (entry 3), while 4-methoxybenzoylchloride, by contrast, showed a preference for N1-isomer **2c** (entry 4). The presence of halogen atoms in *ortho*-positions, exerting steric hindrance, also favoured the formation of N1-isomers (entries 5-6). Acetic anhydride and fluorinated acid anhydrides afforded almost exclusively N2-isomers (entries 7-9). However, electron-rich electrophile ethyl chloroformate gave a nearly 1:1 mixture of isomers (entry 10). Thus, the general observation is that N2-acylation is favoured and that only soft, weak and bulky acylating reagents favour N1-acylation. Solvent effects and effects of substituents at position 4 affect only slightly the reaction outcome, compared to the remarkable effect of acylating agents (see the SI for full details).

Table 1. Acylation of NH-triazole **1a**.[a]



Entry	RCOX	Products	Yield[b] (%) **2** + **3**	Acylation ratio[c] N1/N2 (**2**/**3**)
1	PhCOCl	**2a** + **3a**	>98	14:86
2	$(PhCO)_2O$	**2a** + **3a**	>98	8:92
3	4-O_2N-C_6H_4COCl	**3b**	quant.[d]	<1:99
4	4-MeO-C_6H_4COCl	**2c** + **3c**	>98	73:27
5	2-Cl-C_6H_4COCl	**2d** + **3d**	94	80:20
6	2-Br-C_6H_4COCl	**2e** + **3e**	96	79:21
7	Ac_2O	**2f** + **3f**	98	5:95
8	$(HCF_2CO)_2O$	**3g**	quant.[d]	<1:99
9	$(CF_3CO)_2O$	**3h**	quant.[d]	<1:99
10	$ClCO_2Et$	**2i** + **3i**	97	45:55

[a] Reaction conditions: **1a** (0.10 mmol) and acyl chloride or anhydride (0.10-0.11 mmol) mmol), Et_3N (0.10-0.11 mmol), DCE (0.5 ml), rt, 1 h. [b] Isolated yield. [c] Ratio determined by ^1H NMR. [d] Yield of crude products, not purified from triethylammonium salt because of hydrolytic instability of N-acyltriazoles.

X-ray diffraction analysis of N1-isomer **2c** and N2-isomer **3f** confirmed their structure (Figure 1). Surprisingly, acylated triazoles **2** and **3** are stable enough to be isolated by solvent extraction using aqueous workup and to be fully characterized spectroscopically. Products **3b**, **3g** and **3h** were found to be hydrolytically very unstable and aqueous workup could not be used. All acylated triazoles underwent partial or full decomposition during silica gel column chromatography.

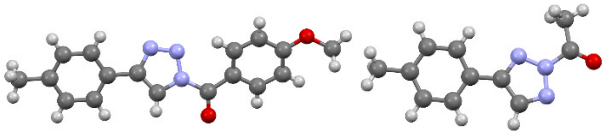
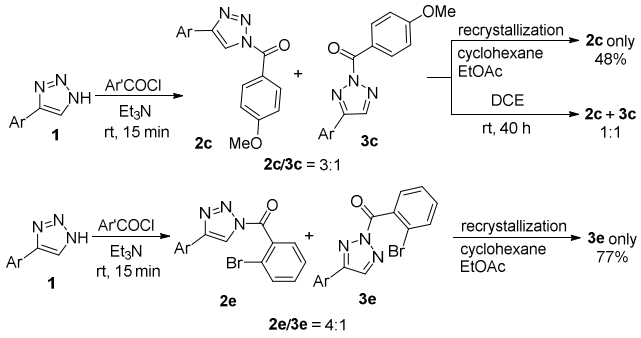


Figure 1. X-ray crystal structures of **2c** (left, CCDC 2244997) and **3f** (right, CCDC 2244996). Ellipsoids are set at a 50% probability level.

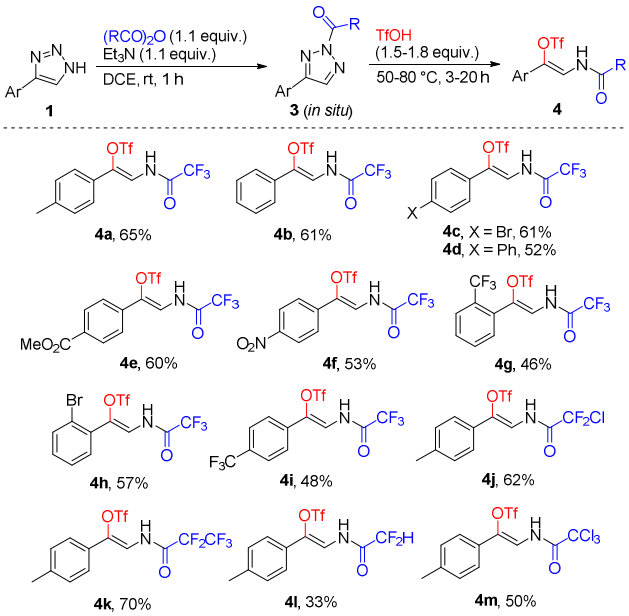
The structures of the obtained N1- and N2-acyltriazoles were additionally confirmed by ^{1}H-^{15}N HMBC NMR data. ^{1}H-^{15}N HMBC data values, namely ^{15}N chemical shifts and $J(^{1}H,^{15}N)$ for fluoroacylated triazoles, were compared with calculated values for 4-phenyl-1-difluoroacetyl-1,2,3-triazole and 4-phenyl-2-difluoroacetyl-1,2,3-triazole, which confirmed the presence of a difluoroacetyl group at the N2 position (see SI for full details). Importantly, ^{1}H-^{15}N HMBC NMR of pure acyltriazole **2c** confirmed the presence of an acyl group at position N1; this result is corroborated by single crystal X-ray analysis data (Figure 1). Regarding ^{1}H NMR of N-acyltriazole mixtures, the isomers could be identified by their chemical shifts of H5, which was shifted by 0.2-0.4 ppm downfield for N1-acyltriazoles (δ_{H5} = 8.4-8.7 ppm) compared to N2-acyltriazoles (δ_{H5} = 8.1-8.3 ppm). This tendency corresponds to literature δ_{H5} shifts observed for N-tosyl-4-phenyl-1,2,3-triazoles,[12,24] where δ_{H5} is 0.27 ppm downfield for the N1- substituted isomer.



Scheme 3 Evidence of N1- to N2-acyltriazole interconversion process (Ar = *p*-tolyl).

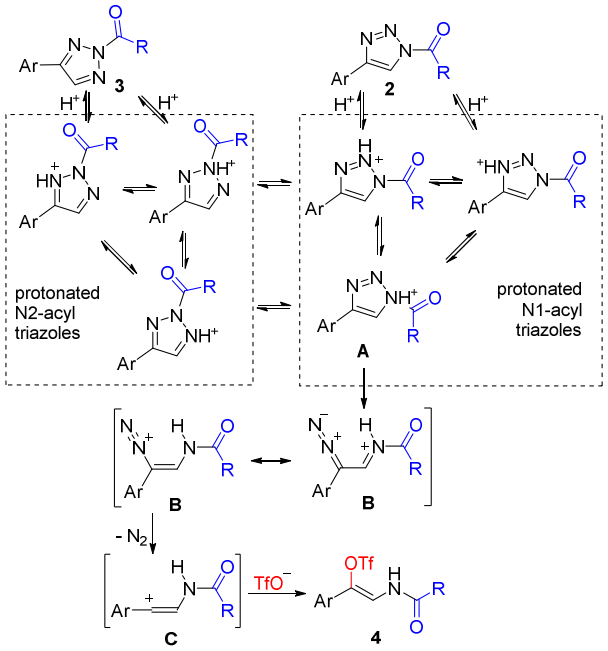
N1- and N2-isomers of acylated triazoles convert to one another. N1- to N2-acyltriazole interconversion (Scheme 3) can be driven by thermodynamics, as in the case of the slow conversion of **2c** to **3c** at ambient temperature, or by the formation of a crystal lattice during crystallization, which is likely the case for sterically hindered N2-isomer **3e** (Scheme 3). By contrast, we succeeded in isolating pure N1-isomer **2c** by recrystallization of a **2c**/**3c** mixture. The process of N1- to N2-interconversion can depend on solvent system, the concentration and even the reaction scale, which complicated its detailed study.

Nevertheless, denitrogenative triazole ring cleavage can only take place from N1 isomers. We have demonstrated that the reverse process of N2- to N1-acyltriazole interconversion is crucial for the success of N-acyltriazole cleavage with the involvement of N2-isomers in denitrogenative transformations. *In situ* formed N2-acylated triazoles **3** react efficiently with triflic acid to produce enamido triflates **4** (Scheme 4). Previously, trifluoroacetylated enamido triflates were prepared by the reaction of N-perfluoroalkyl-1,2,3-triazoles with triflic acid,[19e] but the present methodology benefits from the use of readily available NH-triazoles and trifluoroacetic anhydride. The reaction was found to be applicable for the synthesis of products **4**, bearing neutral aryl substituents (**4a**, **4b**, **4d**) or a bromine atom (**4c**), in good yields. Electron-withdrawing substituents on the aryl ring (CO_2Me, NO_2, CF_3) were also tolerated (compounds **4e**-**4g**), while a longer reaction time was required for complete conversion. A sterically hindered *ortho*-bromo-substituted compound (**4h**) was synthesized in good yield as well. Importantly, the method broadens the scope of enamido triflates to compounds with other fluoroalkyl groups than trifluoromethyl (CF_2Cl, CF_2CF_3, CF_2H; compounds **4j-4l**). Whereas in the first two cases, acyltriazoles afforded triflates **4** as the sole products after treatment with TfOH, in the case of N-difluoroacetyl-1,2,3-triazole, a 33% yield was obtained, due to competitive cyclization to 2-difluoroacetyloxazole, which was observed as a side-product. Similarly, enamido triflate **4m** bearing a trichloroacetyl group was obtained from trichloroacetic anhydride.



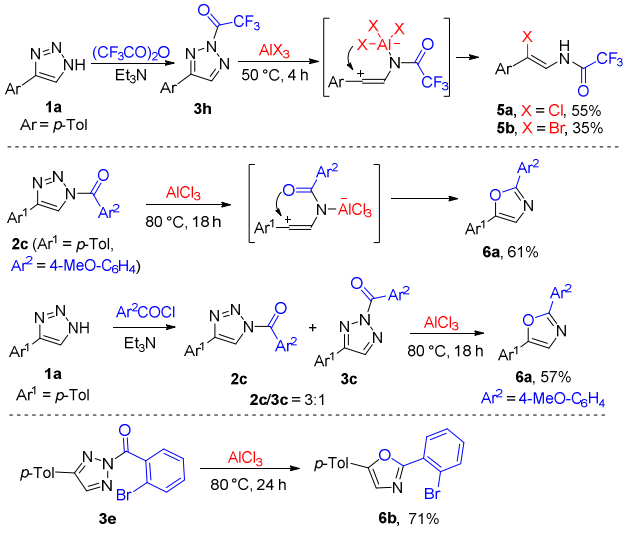
Scheme 4 Formation of enamido triflates **4** from NH-triazoles **1** acid anhydrides and triflic acid via N2-acylated triazoles **3**. Reaction conditions: **1** (0.3 mmol), $(RCO)_2O$ (0.33 mmol), Et_3N (0.33 mmol) in DCE (1 ml) stirred for 1 h, then TfOH (0.45-0.54 mmol), 50-80 °C, 3-20 h.

For the above-mentioned transformations, the following mechanism of acyltriazole cleavage to form enamido triflates is proposed: Protonation of acyltriazoles **2** or **3** can theoretically lead to six protonated species, which are in equilibrium due to acyl group and proton shifts. Certainly however, not all protonated acyltriazoles are equally populated. By analogy to our earlier mechanistic experiments and DFT calculations[19f] only species **A** undergoes N1-N2 cleavage to give the diazo/diazonium intermediate **B**. Diazonium **B** undergoes denitrogenation to vinyl cation **C**, and recombination with the triflate anion gives enamido triflate **4**.



Scheme 5 Mechanism of β-enamido triflate formation from acyl-1,2,3-triazoles.

Acylated triazoles can be cleaved not only with Brønsted acids, but also with Lewis acids. *In-situ*-formed **3h** reacted with an equimolar amount of AlX_3 to produce β-haloenamides **5**, presumably via cleavage of forming N1-acyltriazole to a vinyl cation (Scheme 6). The less electron-deficient N1- or N2-acylated triazoles **2c**, **3c**, or **3e** cyclized with oxygen to give oxazoles **6**, showing that both isomers can be converted to the same ring-cleavage and cyclization products.



Scheme 6 Triazole ring cleavage of acylated triazoles using Lewis acids.

In conclusion, N-acylation of 1,2,3-NH-triazoles was investigated and N2-acyltriazoles were found to be the main products; however, electron-rich and bulky acylating reagents induced the formation of a mixture of N1- and N2-acylatated triazoles. Interconversion between regioisomers of N-acyltriazoles under thermodynamic conditions, during crystal formation, or in the presence of Brønsted or Lewis acids was observed. Triazole denitrogenative ring cleavage starting from N2-acyltriazoles is reported for the first time. Efficient synthetic access to valuable β-trifluoroacetylamido triflates from NH-triazoles was developed.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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