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Furfuryl Cation Induced Cascade Formal [3 + 2] Cycloaddition/Double Ring-Opening/Chlorination: An Approach to Chlorine-Containing Complex Triazoles

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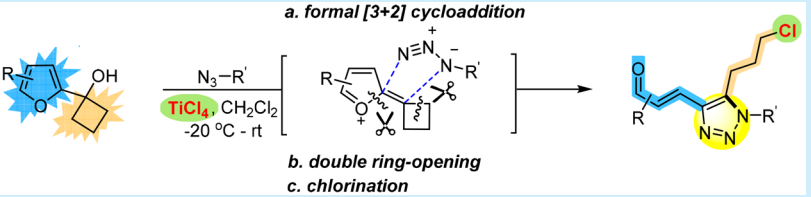
Supporting Information



ABSTRACT: A $TiCl_4$-promoted cascade formal [3 + 2] cycloaddition/double ring-opening/chlorination of 2-furylcyclobutanols with alkyl or aryl azides is described. This highly efficient transformation involves the formation/cleavage of several C−N, C−Cl, C−C, and C−O bonds in a single operation. It enables the quick construction of trisubstituted 1,2,3-triazoles with an (*E*)-enone moiety and a 3-chloropropyl unit. The chlorinated products are readily transformed into other structurally diverse analogues.

A large number of natural products contain chlorine and many of them show significant bioactivity.[1] Additionally, more than 70% of all pharmaceutical products possess chlorine or are produced using chlorine.[2] Chlorine-containing molecules have gained considerable attention owing to their widespread applications in organic synthesis as versatile building blocks and intermediates. The importance of the development of synthetic methods for C(sp^3)−Cl bond construction has been continually pursued using atom-economy and step-economy principles. Many existing approaches to synthesis of alkyl chlorides start from alcohols,[3] carboxylic acids,[4] and diazo compounds.[5] Also, olefin[6] and alkyne[7] precursors can be converted into corresponding alkyl chlorides easily via chlorination.

As an alternative strategy, direct chlorination of unreactive alkanes can be a more attractive strategy to generate alkyl chlorides. Recently, radical ring-opening of cycloalkanols via C−C bond cleavage to form a C(sp^3)−halide bond has been widely reported.[8] By contrast, carbon cation initiated ring-opening of strained ring systems could barely achieve the formation of carbon−halogen bonds during the C−C single-bond cleavage, and the ring expansion and subsequent rearrangements commonly were observed.[9] Herein, we report an unprecedented cascade formal [3 + 2] cycloaddition/double ring-opening/chlorination of 2-furylcyclobutanols with azides in which Lewis acid $TiCl_4$ is employed not only as a cationic promoter but also as a chlorine source for chlorination.

Biomass-derived furan is a well-known chemical scaffold present in many bioactive molecules.[10] It also represents a versatile synthetic tool, and quite a few transformations have been documented for it.[11] Owing to its low aromaticity, a furan ring can serve as masked alkenes, enol ethers,[12] 1,4-diketones,[13] and carboxylic acids.[14] Meanwhile, it usually can allow for facile ring transformation reactions into different carbo-[15,16,18] and heterocycles.[17] Toward this topic, we have explored the intermolecular cascade formal [3 + 2] cycloaddition/furan ring-opening of 2-furylcarbinols with organoazides by using the Lewis acid promoters as well as the corresponding three-component reactions (3-CR) to synthesize the complex triazoles (Scheme 1a).[19] The primary and secondary 2-furylcarbinols were applied as starting materials in these furan recyclizations. Encouraged by these results, our efforts turned to developing more efficient furfuryl cation-based cascade reactions to construct structurally more complex and easily derived triazole architectures. We assumed that the reactive tertiary 2-furylcarbinols could form more stable furfuryl cations, which could be more favorable for the formal [3 + 2] cycloaddition with azides. Moreover, the strained cyclobutyl linked with 2-furan could be opened via C−C cleavage after furan-dearomatized ring opening. Hence, this reaction could realize a conversion from a bicyclic system to a trisubstituted triazole (Scheme 1b).

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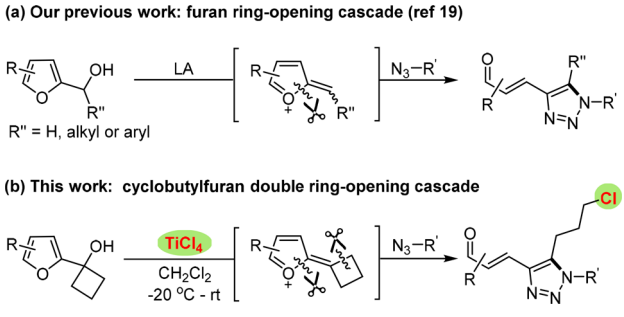
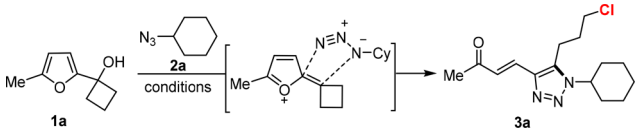
Scheme 1. Furfuryl Cation Induced Cascade for Construction of Chlorine-Containing Triazoles



With this guideline, we initially attempted the double ring-opening cascade reaction toward constructing the trisubstituted triazoles (Table 1). Thus, 5-methyl-2-furylcyclobutanol

Table 1. Optimization of the Cascade Reaction Conditions[a]



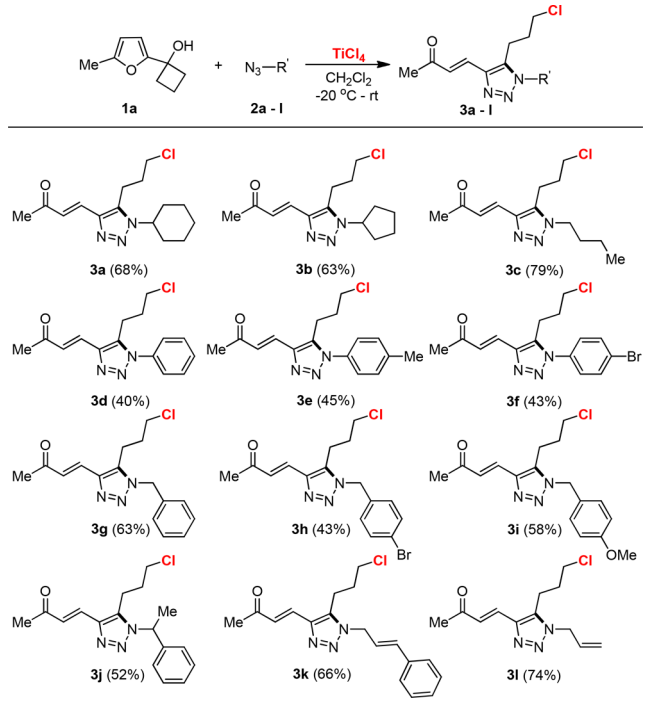
entry[a]	conditions (equiv)	t(°C)/time (min)	yield[b] (%)
1	$AlCl_3$ (1.1)/CH_2Cl_2	−20 to rt/20	trace
2	$FeCl_3$ (1.1)/CH_2Cl_2	−20 to rt/20	trace
3	$InCl_3$ (1.1)/CH_2Cl_2	rt to 80/120	0
4	$ZnCl_2$ (1.1)/CH_2Cl_2	rt to 80/120	0
5	**$TiCl_4$ (1.1)/CH_2Cl_2**	**−20 to rt/20**	**68**[c]
6	$TiCl_4$ (1.1)/Et_3N (1.5)/CH_2Cl_2	−20 to rt/20	0
7	$SnCl_4$ (1.1)/CH_2Cl_2	−20 to rt/20	30[c]

[a]Conditions: 5-methyl-2-furylcyclobutanol **1a** (1.0 mmol), cyclohexyl azide **2a** (1.1 mmol), CH_2Cl_2 (10 mL). [b]Isolated yield. [c]Only the *E* isomer was observed as determined by ^{1}H NMR spectroscopy.

1a and cyclohexyl azide **2a** were selected as model substrates and subjected to our previously reported reaction conditions using stoichiometric $TiCl_4$ as cationic promoter in CH_2Cl_2. Fortunately, the 1,2,3-triazole **3a** with an (*E*)-enone moiety was observed in 68% yield at ambient temperature (entry 5). Importantly, **3a** possesses a primary 3-chloropropyl side chain, which proved the concept that tertiary furylcyclobutanols could react with azides to achieve a formal [3 + 2] cycloaddition/double ring-opening/chlorination. Apparently, the Lewis acid $TiCl_4$ serves as a Cl source in this transformation as well. The desired product **3a** was not observed when base Et_3N was added, although it is a crucial additive in our previous 3-CR reaction conditions[19b,c] (entry 6). $AlCl_3$ and $FeCl_3$ could afford **3a** in very low yields (entries 1 and 2). Similarly, weaker Lewis acids such as $InCl_3$ and $ZnCl_2$ could not promote the cascade reaction (entry 3 and 4). Additionally, $SnCl_4$ was found to give a relatively worse result with 30% yield of **3a** (entry 7).

With the optimized conditions in hand, we studied the scope of the reaction with different azides **2**. As shown in Scheme 2, 5-methyl-2-furylcyclobutanol **1a** could react well with both secondary cyclopentyl and primary *n*-butyl azides, affording the corresponding trisubstituted products **3b** and **3c** in 63% and 79% yields, respectively. As indicated by examples with phenyl azides **2d**−**f**, substituents including bromo and methyl groups gave the corresponding triazoles in 40−45% yields. The

Scheme 2. Azide 2 Variations[a]



[a]Conditions: 5-methyl-2-furylcyclobutanol **1a** (1.0 mmol), azide **2** (1.1 mmol), $TiCl_4$ (1.1 mmol), CH_2Cl_2 (10 mL), −20 °C to rt; only the *E*-isomer was observed by ^{1}H NMR in each example; isolated purified yield (average of two runs).

relatively low yields might be caused by the conjugation effects of phenyl, which could weaken the nucleophilicity of azide in the formal [3 + 2] stage. Although both primary and secondary benzylic azides commonly are considered as unstable when treated with Lewis acids, they were effective in affording trisubstituted triazole products **3g**−**j** in 43−63% yields under the standard conditions. When the allylic azides **2k** and **2l** was employed, the allyl-substituted products **3k** and **3l** was obtained in 66% and 74% yields, respectively. The structures of **3a** and **3k** were determined by single-crystal X-ray diffraction analysis (Figure 1). The *trans*-stereospecificity of olefins for the other products was assigned by analogy to **3a** and **3k** and also with ^{1}H NMR.

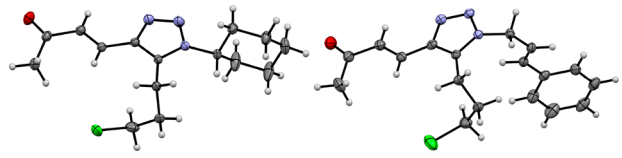


Figure 1. ORTEP drawing of **3a** (left, CCDC no. 1870537) and **3k** (right, CCDC no. 1870538).

We then applied this one-pot protocol to exam a range of different 2-furylcyclobutanols under the optimal conditions with cyclohexyl azide **2a** (Scheme 3). Pleasingly, this series of substrates also produced the desired 3-chloropropyl products in moderate yields. When the substrate **1m** without methyl at the 5-position of furan was subjected to the standard conditions, the reaction afforded the desired aldehyde **3m** with a *trans* double bond in a yield of 56%. 4,5-Dimethylfuran substrate **1n** was investigated and gave **3n**, which has a

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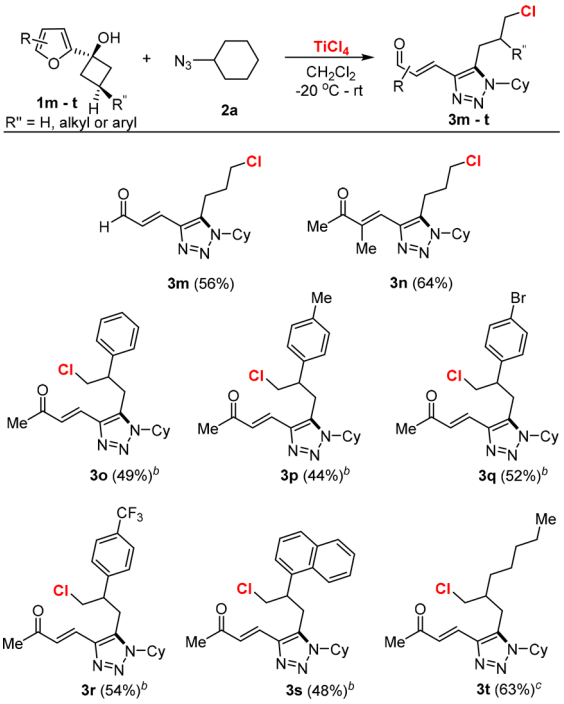
Scheme 3. 2-Furylcyclobutanol 1 Variations[a]

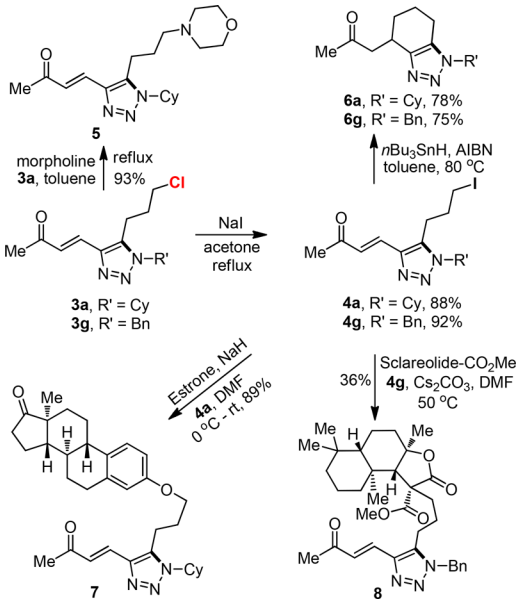


[a]Conditions: 2-furylcyclobutanols **1** (1.0 mmol), cyclohexyl azide **2a** (1.1 mmol), $TiCl_4$ (1.1 mmol), CH_2Cl_2 (10 mL), −20 °C to rt; only the *E*-isomer was observed by ^1H NMR in each example; isolated purified yield (average of 2 runs); Cy = cyclohexyl. [b]The reaction was prolonged to 60 min. [c]The reaction was prolonged to 120 min.

trisubstituted double bond with *E*-configuration. 3-Aryl-substituted cyclobutanols containing electron-withdrawing or -donating substituents at the *para* position of the benzene ring were good substrates to afford the desired products **3o**−**r** in moderate yields (44−54%). Naphthyl-substituted cyclobutanol **1s** was found to be compatible under optimized conditions, leading to the desired product **3s** in 48% yield. Generally, the reaction rate of the cyclobutanol bearing a substituent was slower than the reaction rate of the substrates without a substituent, which could be ascribed to the more steric effects of the former to hinder the approaching of azide. The introduction of a more flexible *n*-hexyl at the 3-position of cylobutanol of the substrate dramatically reduced the reaction rate but did not interrupt the reactivity (63% yield).

Chlorine-contained compounds are usually useful precursors for further functionalization and easily provide other valuable synthetic intermediates. To demonstrate their utility, a variety of transformations were developed by using 3-chloropropyl triazole **3a** or **3g** as starting materials (Scheme 4). The chlorine of **3a** could be attacked selectively by morpholine to form C−N bond and give **5** in excellent yield, while the existence of an enone moiety does not affect the reaction. The iodinations of **3a** and **3g** occurred smoothly to convert Cl into I of the propyl group and provided **4a** and **4g** in 88% and 92% yields individually, which serve as the common intermediates for derivatizations. The subsequent radical ring-closure reactions with nBu_3SnH/AIBN rapidly prepared the cyclohexyl-fused triazoles **6a** and **6g** by forming C−C bonds. In particular, biologically interesting molecules, such as estrone and sclareolide derivative, can be coupled with **4a** and **4g** directly to give the corresponding conjugated compounds **7** and **8**,

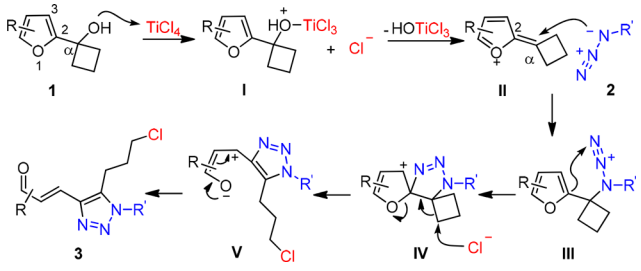
Scheme 4. Transformations of 3-Chloropropyl Triazole



respectively. It indicated that our well-established chlorine-contained triazole synthesis via a biomass furan-based cascade reaction could provide many opportunities for the late-stage diversification to drug and bioactive molecule synthesis.

On the basis of the experimental results above, a plausible reaction mechanism has been proposed (Scheme 5). The

Scheme 5. Proposed Reaction Mechanism



reaction is initiated by coordination of the tertiary α-hydroxyl with strong Lewis acid $TiCl_4$, followed by dehydroxylation to produce bicyclo-conjugated oxocarbenium **II** and a Cl anion. Then the more electron-poor α-C, rather than C2 of furan, undergoes nucleophilic attack of the azides to form the aminodiazonium **III**. The subsequent intramolecular Friedel−Crafts like reaction gives a formal [3 + 2] cycloaddition spiro-intermediate with exclusive regioselectivity. Furthermore, a synergic driving force from the aromatization of triazoles and the nucleophilic chlorination of Cl^- to strained cyclobutyl leads to a double ring-opening of furan and cyclobutyl to deliver zwitterions **V**. Finally, tautomerization of enolates leads to the formation of the corresponding enones in an exclusive *trans*-configuration, which is thermodynamically favored in this single-step transformation. Further studies are underway to help elucidate the mechanism of this cascade transformation.

In summary, we have developed a novel intermolecular formal [3 + 2] cycloaddition/double ring-opening/chlorination cascade reaction with high step-economy of 2-furylcyclobutanols and organoazides. A variety of trisubstituted complex triazoles with a 3-chloropropyl unit and an (*E*)-enone

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moiety may be synthesized in a single step. The resulting products could be transformed into biologically valuable derivatives through C−C, C−O, and C−N bond formation. Further studies on the mechanism of this reaction and its synthetic application are currently underway.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.orglett.8b03121.

Experimental procedures, product characterization, copies of NMR spectra, and crystallographic data for **3a** and **3k** (PDF)

Accession Codes

CCDC 1870537−1870538 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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Notes

The authors declare no competing financial interest.

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