ORGANIC LETTERS

2013
Vol. 15, No. 17
4512–4515

Synthesis of Polyfluoroalkyl Cyclobutenes from 3-Aza-1,5-enynes via an Aza-Claisen Rearrangement/ Cyclization Cascade

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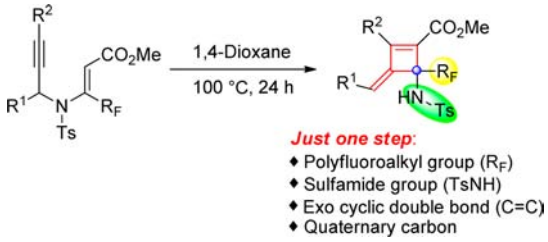
Received July 23, 2013

ABSTRACT



A facile synthetic route to access polyfluoroalkyl functionalized cyclobutenes bearing an exo cyclic double bond from 3-aza-1,5-enynes is reported. The reaction proceeds via a thermal aza-Claisen rearrangement to give an allene-imine intermediate; subsequent cyclization affords the cyclobutene core. The kinetics of the transformation of starting material and the intermediate was studied by ^{1}H NMR spectroscopy, where a consecutive reaction was revealed.

Cyclobutenes are fascinating small-ring compounds found in many natural products and biologically active compounds,[1] and they are also versatile building blocks for the synthesis of a wide range of organic compounds due to the inherent ring strain.[2]Accessing cyclobutenes that are not easily synthesized by conventional methods remains a topic of considerable interest. The synthetic procedures for the construction of a cyclobutene ring are divided into four major categories: (1) [2 + 2] cycloaddition of alkynes with alkenes or allenes (Scheme 1a),[3] which represents the most straightforward method to access cyclobutene structures; (2) ring expansions of cyclopropane derivatives (Scheme 1b);[4] (3) cycloisomerization reactions of enynes (Scheme 1c);[5] and (4) electrocyclization of vinylallenes (Scheme 1d).[6] Besides these major methodologies, other sporadic diverse strategies have also been developed.[7] Here we report an approach for the synthesis of polyfluoroalkyl substituted cyclobutenes from 3-aza-1,5-enynes via an aza-Claisen rearrangement/ cyclization process (Scheme 1e, left). This transformation

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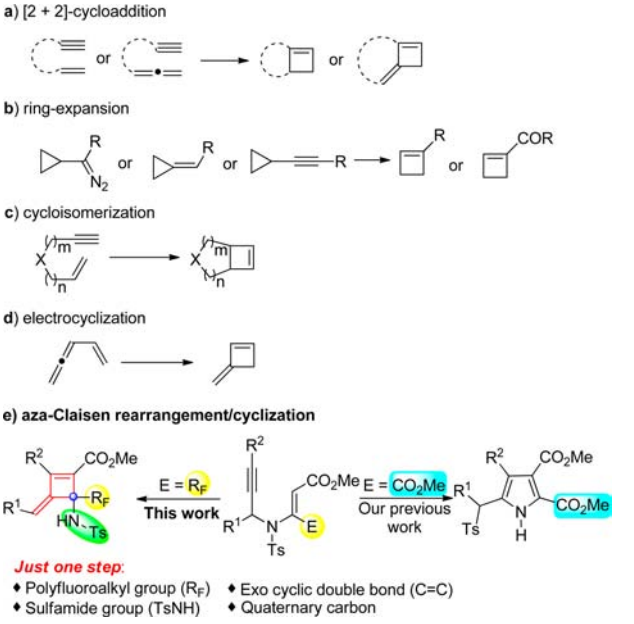
10.1021/ol4020738
Published on Web 08/22/2013

allows the preparation of fully substituted cyclobutene derivatives bearing a new pattern of substituents.

The 3-aza-1,5-enyne framwork is versatile for their selectivities and could be switched by simple changes in the reaction conditions or structure of starting materials.[8] It is known that introduction of the trifluoromethyl (CF_3) group (or other perfluoroalkyl/polyfluoroalkyl groups) into organic molecules can significantly change their physical, chemical, and biological properties.[9] In our previous work, diester-substituted 3-aza-1,5-enynes were successfully transformed into functionalized pyrroles via sulfonyl group migration (Scheme 1e, right).[8b] We envisioned that replacing one of the two ester groups of this framework with polyfluoroalkyl groups may switch the reaction selectivity (see infra). As a result, an enlightening reaction pathway was revealed and amazing carbocycles were obtained. Experimentally, 3-aza-1,5-enyne **1a** ($R^1 = R^2 = Ph$, $R_F = CF_3$) was used as a starting substrate (Table 1). When **1a** was heated in toluene in the absence of any transition metal or additive, cyclobutene **2a** was obtained in 36% isolated yield. The structures of **2a** and its *p*-Cl-substituted derivative **2r** were unambiguously confirmed by X-ray crystallography (see the Supporting Information). This highly substituted cyclobutene product with a quaternary carbon center[10] is functionalized with a polyfluoroalkyl group, a sulfamide group,[11] and an exo cyclic double bond.

Scheme 1. Summary for Approaches



The solvent effect was next investigated. The reaction carried out in toluene at 100 °C provided a 53% NMR yield of **2a** (Table 1, entry 1). The use of DMF, CH_2Cl_2, MeCN, or acetone as a solvent did not improve the product yield (Table 1, entries 2−5). Utilization of benzene or MeOH slightly improved the yield (Table 1, entries 6 and 7). When 1,2-dichloroethane or THF was employed, the yield of **2a** was further improved (Table 1, entries 8 and 9). The highest yield of **2a** (95% NMR yield) was achieved using 1,4-dioxane as a solvent (Table 1, entry 10). Reactions performed at a lower temperature gave a diminished yield (Table 1, entry 11). Therefore, 1,4-dioxane and 100 °C were chosen as the optimal reaction conditions.

Following the optimization of the reaction conditions, the scope and limitations of this reaction were explored. Aryl R^1 groups bearing different substituents, including an electron-neutral (Table 2, entry 1), -donating (Table 2,

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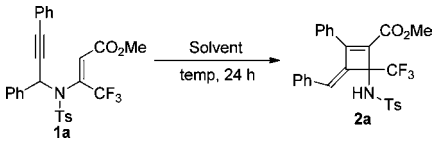
Table 1. Optimization of Reaction Conditions[a]



entry	solvent	temp (°C)	yield (%)[b]
1	toluene	100	53 (36)[c]
2	DMF	100	57
3	CH_2Cl_2	100	47
4	MeCN	100	50
5	acetone	100	51
6	benzene	100	68
7	MeOH	100	77
8	1,2-dichloroethane	100	85
9	THF	100	88
10	1,4-dioxane	100	95
11	1,4-dioxane	80	91

[a] Conditions: **1a** (0.1 mmol) in the corresponding solvent (0.5 mL) was stirred under argon protection for 24 h. [b] NMR yield using CH_2Br_2 as an internal standard. [c] The number in the parentheses refers to the isolated yield of **2a**. Conditions: **1a** (0.5 mmol) in toluene (2.5 mL) was stirred at 80 °C for 10 h under an argon atmosphere.

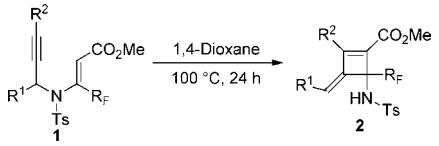
entries 2−5), -withdrawing (Table 2, entry 6), and halogen group (Table 2, entries 7−10) were well tolerated, and the desired products were isolated in moderate to high yields (54−91%). Interestingly, a mixture of *Z*/*E* isomers was obtained in 54% yield when 2-MeO-substituted 3-aza-1,5-enyne **1e** was studied (Table 2, entry 5). A fused aryl R^1 was also suitable for this process, although a lower yield was obtained (44%, Table 2, entry 11). However, an alkyl R^1 substituent was not tolerated (Table 2, entry 12). Thus when isopropyl-substituted **1l** was allowed to react under the standard conditions, the desired reaction did not take place. Both aryl- and alkyl-substituted alkyne (R^2) units in the substrate were well tolerated (Table 2, entries 13−21). The polyfluoroalkyl group (R_F) was also investigated. CF_2Cl- and C_2F_5-substituted **1v** and **1w** were also good substrates (Table 2, entries 22 and 23). In contrast, under the same conditions, a diester-substituted substrate (the CF_3 group of **1a** was changed to CO_2Me) afforded 1,2-dihydropyridine[8c] as the only product (95% NMR yield).

A deuterium-labeling experiment was performed to explore the reaction mechanism (Scheme 2). A substrate deuterated at the C(4)-position (**1a-D**, 100 atom % of D) was subjected to the standard reaction conditions, and the deuterium was incorporated in the olefinic position of the product **2a-D** without any scrambling, indicating that C−H cleavage is not likely involved at this position.

To gain further insight into the reaction mechanism, a reaction intermediate was studied. When the reaction was carried out at 80 °C, the allene-imine intermediate **3a** was observed in 63% NMR yield as a major product, together

(12) Reviews on aza-Claisen rearrangement: (a) Majumdar, K. C.; Bhattacharyya, T.; Chattopadhyay, B.; Sinha, B. *Synthesis* **2009**, 2117. (b) Nubbemeyer, U. *Synthesis* **2003**, 961. (c) Nubbemeyer, U. *Top. Curr. Chem.* **2005**, *244*, 149.

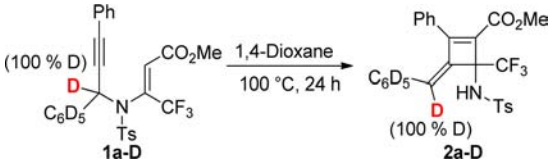
Table 2. Scope of the Synthesis of Cyclobutenes[a]



entry	**1**	R^1	R^2	R_F	**2**, yield[b]
1	**1a**	Ph	Ph	CF_3	**2a**, 91%
2	**1b**	2-MeC_6H_4	Ph	CF_3	**2b**, 76%
3	**1c**	3-MeC_6H_4	Ph	CF_3	**2c**, 91%
4	**1d**	4-MeC_6H_4	Ph	CF_3	**2d**, 62%
5	**1e**	2-$MeOC_6H_4$	Ph	CF_3	**2e**,[c] 54%
6	**1f**	2-$CF_3C_6H_4$	Ph	CF_3	**2f**, 81%
7	**1g**	2-FC_6H_4	Ph	CF_3	**2g**, 85%
8	**1h**	4-FC_6H_4	Ph	CF_3	**2h**, 87%
9	**1i**	2-ClC_6H_4	Ph	CF_3	**2i**, 62%
10	**1j**	2-BrC_6H_4	Ph	CF_3	**2j**, 83%
11	**1k**	1-naphthyl	Ph	CF_3	**2k**, 44%
12	**1l**	^{i}Pr	Ph	CF_3	–[d]
13	**1m**	Ph	2-MeC_6H_4	CF_3	**2m**, 59%
14	**1n**	Ph	3-MeC_6H_4	CF_3	**2n**, 60%
15	**1o**	Ph	4-MeC_6H_4	CF_3	**2o**, 76%
16	**1p**	Ph	4-$MeOC_6H_4$	CF_3	**2p**, 48%
17	**1q**	Ph	4-FC_6H_4	CF_3	**2q**, 93%
18	**1r**	Ph	4-ClC_6H_4	CF_3	**2r**, 82%
19	**1s**	Ph	^{n}Pr	CF_3	**2s**, 92%
20	**1t**	Ph	^{n}Bu	CF_3	**2t**, 88%
21	**1u**	Ph	Cy	CF_3	**2u**, 78%
22	**1v**	Ph	Ph	CF_2Cl	**2v**, 73%
23	**1w**	Ph	Ph	C_2F_5	**2w**, 82%

[a] Reaction conditions: **1** (0.2 mmol) in 1,4-dioxane (1 mL) was stirred at 100 °C for 24 h under argon protection. [b] Isolated yields. [c] *Z*/*E* = 1:1 mixture, in 0.4 mmol scale. [d] No reaction.

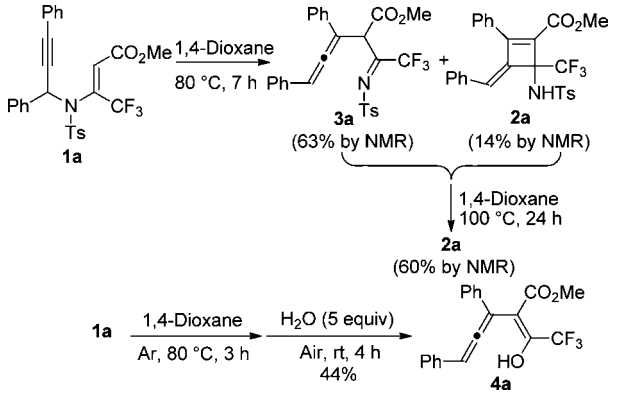
Scheme 2. Deuterium-Labeling Experiment



with product **2a** (14% NMR yield, Scheme 3). The allene-imine intermediate **3a** resulted from aza-Claisen rearrangement,[12] and the hydrolysis of the imine moiety during the course of chromatographic purification hampered its isolation. The crude mixture of **3a** and **2a** was allowed to react in 1,4-dioxane at 100 °C for an additional 24 h, and cyclobutene **2a** was generated in 60% NMR yield, indicating that allene-imine **3a** is a reaction intermediate. To further confirm the intermediacy of **3a**, water was added to the system after **1a** was stirred in 1,4-dioxane at 80 °C for 3 h, and the resulting

(13) Reviews on Claisen rearrangement: (a) Tejedor, D.; Méndez-Abt, G.; Cotos, L.; García-Tellado, F. *Chem. Soc. Rev.* **2013**, *42*, 458. (b) Majumdar, K. C.; Alam, S.; Chattopadhyay, B. *Tetrahedron* **2008**, *64*, 597. (c) Hiersemann, M.; Abraham, L. *Eur. J. Org. Chem.* **2002**, 1461. (d) Ito, H.; Taguchi, T. *Chem. Soc. Rev.* **1999**, *28*, 43.

Scheme 3. Mechanistic Studies



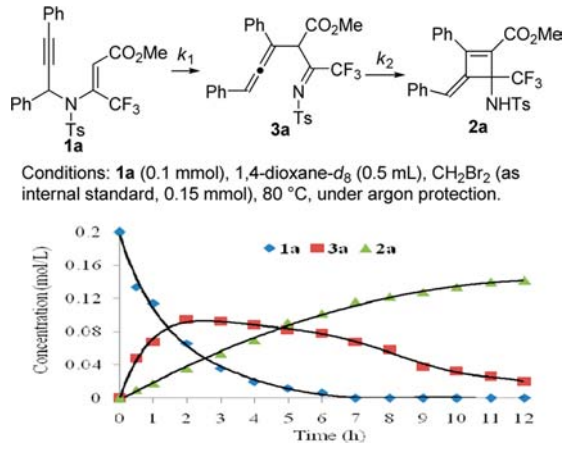


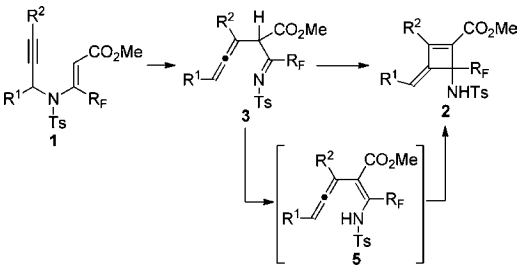
Figure 1. Kinetic profile of starting material **1a**, intermediate **3a**, and product **2a**.

mixture was allowed to react at rt for 4 h. As expected, allene-enol **4a**, which is the hydrolyzed product of **3a**, was obtained in 44% yield (Scheme 3). Moreover, **4a** is a corresponding product of the Claisen rearrangement of propargyl vinyl ethers.[13] Therefore, this transformation provided an alternative approach to allene-enols.

To gain more reaction information, we monitored the reaction of **1a** using ^{1}H NMR spectroscopy in 1,4-dioxane-d_8 at 80 °C (Figure 1). In the first 0.5 h, the amount of reactant **1a** decreased sharply, and ~90% of **1a** was consumed in ~4 h. The formation and consumption of **3a** took place simultaneously, and after ~2 h, the concentration of **3a** reached its maximum amount. In the whole process, the amount of **2a** increased steadily, and the product formed in ~60% yield after 8 h.

The kinetic profile follows a two-step irreversible consecutive process (Figure 1). The calculated first-order rate constants using the data in the first 6 h were as follows:

Scheme 4. Proposed Mechanism



$k_1 = 0.57 \pm 0.01\ h^{-1}$, $k_2 = 0.26 \pm 0.02\ h^{-1}$ (based on **3a**) or $0.18 \pm 0.01\ h^{-1}$ (based on **2a**). Thus the transformation of **3a** to **2a** was the rate-determining step.

A reaction mechanism was proposed based on the above results (Scheme 4). Aza-Claisen rearrangement of 3-aza-1,5-enyne **1** leads to allene-imine **3**. A polyfluoroalkyl group is more electronegative than an ester group; therefore, the polyfluoroalkyl substituted allene-imine intermediate probably tends to isomerize to allene-enamine instead of direct cyclization.[8b] Isomerization of the imine moiety of **3** to allene-enamine **5** and subsequent 4π-electrocyclization[6] give cyclobutene **2**.

In summary, we have realized an efficient route to access polyfluoroalkyl functionalized cyclobutenes from 3-aza-1,5-enynes. The reaction proceeded through an aza-Claisen rearrangement/cyclization process. The observed aza-Claisen rearrangement intermediate allene-imine and the kinetics of the transformation of the consecutive reaction support the proposed reaction mechanism. The use of easily available 3-aza-1,5-enynes as starting materials for generation of reactive intermediates emphasizes the versatile reactivity and synthetic value of this framework. The multifunctionalized cyclobutenes bearing an exo cyclic double bond are advantageous for further derivatization. Further studies on the scope, mechanism, and synthetic applications of this reaction are underway.

Acknowledgment. We thank the National Natural Science Foundation of China (21172218) for financial support. We thank Prof. Xingwei Li (Dalian Institute of Chemical Physics, Chinese Academy of Sciences) for helpful discussions on experiment details and proofreading this manuscript. We also thank Prof. Hongjun Fan (Dalian Institute of Chemical Physics, Chinese Academy of Sciences) for the help in calculating rate constants.

Supporting Information Available. Experimental procedures; characterization data for new compounds; copies of spectra; and X-ray crystallographic data (CIF) for **1a**, **2a**, and **2r**. This material is available free of charge via the Internet at http://pubs.acs.org.

The authors declare no competing financial interest.