



The addition of polyfluoroalkanesulfenic acids to alkenes



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ABSTRACT

The addition of polyfluoroalkanesulfenic acids, *in-situ* formed from various imines, to C=C double bond was investigated. Both Markovnikov adduct and Michael-type adduct could be obtained with different alkenes. A series of sulfoxides were synthesized with excellent regioselectivities under mild conditions.

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1. Introduction

Sulfenic acids (RSOH) have been recognized as key intermediates in the metabolic activation of antithrombotic agents, such as ticlopidine and prasugrel [1], and in the biosynthesis of the odorous thiosulfonates in allium species, such as garlic and onions [2]. They also figure prominently in biological and natural product chemistry. For example, cysteine-derived sulfenic acids are important in signal transduction, responding to the redox state of the cell and modulating gene transcription accordingly [3], and have also been shown to play significant roles in nonenzymatic protein folding [4] and enzymes [5]. However, most sulfenic acids are unstable due to their self-condensation reactions which can be promoted by dimerization through intermolecular hydrogen-bond [6], and those sulfenic acids stable enough for isolation or characterization usually have a huge steric hindrance [7] or intramolecular hydrogen-bonding construction [8], or both of them [9]. This made it difficult to study their properties.

Recently, we reported the synthesis and characterization of polyfluoroalkanesulfenic acids for the first time [10]. As a new type of stable sulfenic acids, these fluorinated sulfenic acids bear only electron-withdrawing polyfluoroalkyl group without any bulky residue or intramolecular hydrogen bond, and have good stability in solutions. More recently, Goto and coworkers reported a primary-alkyl-substituted sulfenic acid and its reactions [11]. These stable sulfenic acids with simple construction provide a

convenient way for researchers to further study the chemistry of sulfenic acids in a normal fashion.

In our previous research, it was found that the reaction of polyfluoroalkanesulfinimine **1a** with 1,3-cyclopentadiene in a sealed tube gave sulfoxides **3a** and **3b** rather than the expected Diels-Alder products, and the corresponding polyfluoroalkanesulfenic acid *in-situ* formed from the decomposition of **1a** was the key intermediate for the formation of **3a** and **3b** [10] (Scheme 1). As an extension of our study on the reactivity of polyfluoroalkanesulfenic acids, we further investigated the addition reaction of polyfluoroalkanesulfenic acids to various alkenes. The results are reported in this paper.

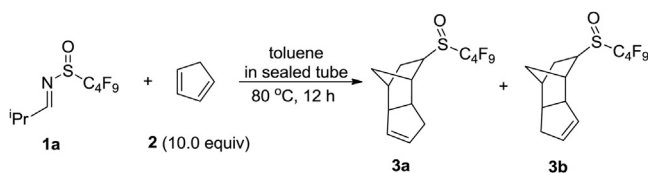
2. Results and discussion

On the basis of previous results, we first studied the reaction of polyfluoroalkanesulfenic acids with dienes. Diene **2b** was synthesized from 1,3-cyclopentadiene and allowed to react with **1a** at 80 °C in a similar way. As expected, isomers **3a** and **3b** were obtained in 82% yield after 12 h (Table 1, entry 2). Then other unconjugated dienes were tested. When diallyl ether (**2c**) was used, the reaction took place smoothly and the corresponding Markovnikov adduct **3c** was isolated in 70% yield (entry 3). 1,7-Octadiene (**2d**) and 1,5-hexadiene (**2e**) also reacted well to give the desired sulfoxides **3d** and **3e** in good yields (entries 4–5).

The reactions of 1,5-hexadiene with different polyfluoroalkanesulfinimines were next investigated. As shown in Table 1, similar result was obtained when the propyl group in imine was replaced by a *tert*-butyl group (entry 6). However, the addition reaction of sulfinimine **1c** containing a phenyl substituent afforded product **3e**

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Scheme 1. The reaction of **1a** with 1,3-cyclopentadiene.

Table 1
Reactions of polyfluoroalkanesulfinimines **1** with dienes **2**.

entry	1 , R ¹ /R ²	2	3	yield (%)
1	1a , ⁿ Pr/ ⁿ C ₄ F ₉	2a	3a, 3b	81 (3a+3b)
2	1a , ⁿ Pr/ ⁿ C ₄ F ₉	2b	3a, 3b	82 (3a+3b)
3	1a , ⁿ Pr/ ⁿ C ₄ F ₉	2c	3c	70
4	1a , ⁿ Pr/ ⁿ C ₄ F ₉	2d	3d	73
5	1a , ⁿ Pr/ ⁿ C ₄ F ₉	2e	3e	77
6	1b , ^t Bu/ ⁿ C ₄ F ₉	2e	3e	73
7	1c , Ph/ ⁿ C ₄ F ₉	2e	3e	36
8	1d , ^t Bu/CF ₂ CF ₂ Cl	2e	3f	56
9	1e , ^t Bu/ ⁿ C ₆ F ₁₃	2e	3g	45

^a Reaction conditions: **1** (0.44 mmol), **2** (4.4 mmol), toluene, 80 °C, 12 h; ^b Isolated yields.

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