Journal of Fluorine Chemistry 132 (2011) 63–67

Contents lists available at ScienceDirect

Journal of Fluorine Chemistry

journal homepage: www.elsevier.com/locate/fluor

Thermal rearrangement of substituted difluoro(methylene)cyclopropane

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ARTICLE INFO

Article history:
Received 23 July 2010
Received in revised form 15 November 2010
Accepted 16 November 2010
Available online 24 November 2010

Keywords:
Difluoro(methylene)cyclopropane
Thermal rearrangement
DFT calculations
Transition state

ABSTRACT

Both experimental and computational approaches have been employed in the present work to investigate the thermal conversion of substituted difluoro(methylene)cyclopropanes (F_2MCP) E-1,1-difluoro-2,2-dimethyl-3-tosylmethylene cyclopropane **1**, to the thermodynamically more stable F_2MCP products, 1,1-difluoro-2-tosyl-3-(propan-2-ylidene)cyclopropane **2**, and 1-(3-(difluoromethylene)-2,2-dimethylcyclopropylsulfonyl)-4-methylbenzene **3**. The X-ray crystal structure has been obtained for both **1** and **2**, respectively, based on which theoretical analyses on their structure and stability have been carried out. Possible reaction mechanisms are proposed.

1. Introduction

Thermal rearrangement of methylenecyclopropane (MCP) derivatives has been of continuous recent interest in the literature and trimethylenemethane (TMM) intermediates are often considered to be produced in the rearrangement process [1]. There are two different kinds of TMM conformations in the form of conjugated diradicals, and dipolar processes can be undertaken under the thermal conditions, which have been well studied in the past decades [2]. It is well known that introduction of fluorine atoms into organic molecules causes special electrostatic and steric consequences [3]. For this reason, the investigation of fluorinated MCPs rearrangements has generated considerable interests in the literature [4]. Recently, we discovered that the difluoro(methylene)cyclopropanes (F_2MCPs) can be readily prepared from the direct difluorocyclopropanation of sulfonylated allenes [5]. This class of F_2MCPs has a particularly interesting skeleton substituted by both electron-donating methyl and electron-withdrawing tosyl groups. During the difluorocarbene addition process, carbene has been revealed to exclusively add to the electron-rich double bond via the kinetically controlled process as recently vindicated by computational studies in the literature [4], giving the F_2MCP (E)-1,1-difluoro-2,2-dimethyl-3-tosylmethylenecyclopropane **1** as the product [6]. In this work, we examine the thermal stability of this F_2MCP by both experimental and computational approaches.

2. Results and discussion

Thermolysis of **1** at 120 °C in chloroform for three days resulted in the diminution of the singlet fluorine signal intensity in ^{19}F NMR spectra at −138.4 ppm and the appearance of several new peaks. Product isolation, purification and characterization demonstrated that **1** was rearranged to **2** and **3** with the yield of 45% and 30%, respectively (Scheme 1). The same rearrangement reaction can also take place in other solvents such as methanol and toluene, giving almost the same ratio of **2**–**3**. It should be noted that F_2MCP **1** was synthesized by the addition of difluorocarbene to 1-tosyl-3,3-dimethyl allene at 120 °C and the reaction was completed within 2 h, where the formation of **2** was not observed (Scheme 2). With putting the above together, this rearrangement reaction provides a good manifestation of the chemical characteristics of difluorocarbene whose addition reaction has been shown earlier to favor the electron rich alkenes [7]. That is, the addition of difluorocarbene to 1-tosyl-3,3-dimethyl allene leading to **1** should be is a kinetically controlled process.

X-ray crystallographic analysis of **1** and **2** was carried out (Figs. 1 and 2) [8]. Thermal rearrangement of **1** into **2** involves the cleavage of C3–C4 bond, which has a normal bond length (1.4863 Å), while several carbon–carbon bonds in the three-membered ring structure such as C2–C4 of F_2MCP **1** and C1–C2 of F_2MCP **2** are found to be longer than the distal bond of F_2MCPs **1** (numbering of carbon atoms: see Figs. 1 and 2). The fact that the C3–C4 bond in **1** breaks in the thermal conversion process of **1** into

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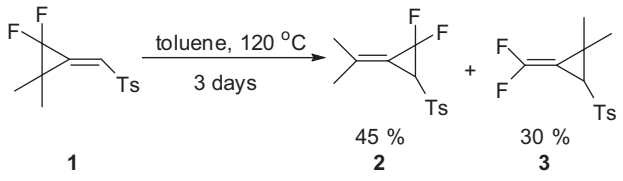
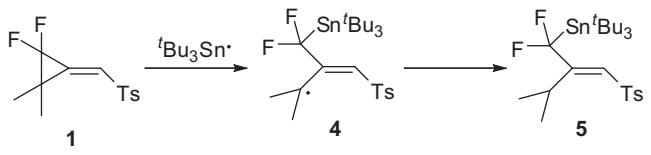
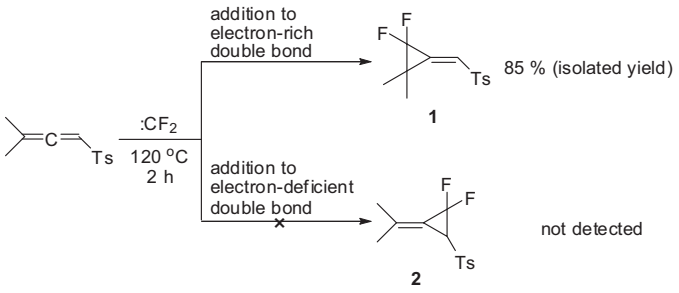
doi:10.1016/j.jfluchem.2010.11.007



Scheme 1. Thermal rearrangement of F_2MCP **1**.



Scheme 3. The reaction of **1** with radical.



Scheme 2. Addition of difluorocarbene to 1-tosyl-3,3-dimethyl allene.

2 suggests the possibility of energetically favorable C3–C4 bond cleavage process.

Two mechanisms for the above conversion would be possible, one via radical intermediate and the other through polar intermediate, although there is no direct experimental evidence to determine this process. Our earlier results suggested that the distal bond can be opened under the stannyl radical condition, giving rise to the ring-opened addition product **5** via the radical pathway (Scheme 3) [9].

To better understand the relative stability of **1** and **2** and their conversion, theoretical approach was carried out. Density functional theory (DFT) calculations at the B3LYP/6-311+G(d) level of theory were performed using Gaussian 03E01 package [10] to study the structure of **1**, **2**, and **3**, and the transition state TS1 (from **1** to **2**) and TS2 (from **1** to **3**). The optimized structures of TS1 and TS2 are shown in Fig. 3.

Shown in Table 1 are a few selected structural parameters from the optimized structures together with X-ray data. The main difference between **1** and **2** is that the 3-membered cyclopropane ring and the two methyl groups (i.e., 5 carbon atoms in total) are in the same plane in **2**, whereas in **1**, they are in the almost perpendicular position. This difference can be seen from the CF2–C2–C4–CH3 (see Fig. 1 for the numbering sequence of the carbon atoms) dihedral angle in Table 1, where in **2** the value is close to 0° (8.7 from theory and 14.0 from the X-ray structure) and in **1** it is about 107°. The value of the dihedral angle in the transition state (TS1) falls just in-between, giving 65.3° (Fig. 3). The structural difference between **1** and **3** is small where the dihedral angle between the ring and two methyl groups in **3** is also far from 0° (64.4°). Computational results agree well with experimental data.

These structural differences dedicate the stability difference of these compounds. The nature of the stability difference can be discussed by hyperconjugation effects [11]. It was quantitatively examined by the second-order perturbation theory analysis of the Fock matrix in the NBO basis (Table 2). It is likely that the conversion reaction site from **1** to **2** consists of three relatively independent components from the viewpoint of the classical Lewis structure: a C=C double bond, a cyclopropane ring and methyl groups. The

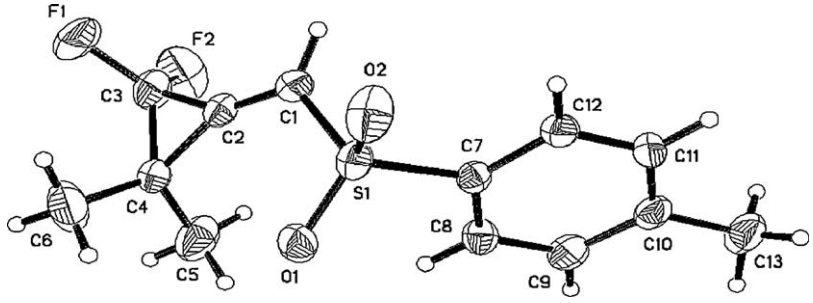


Fig. 1. The single crystal structure of F_2MCPs **1**. Selected bond lengths [Å], bond angles [°]: C(1)–C(2) 1.307(3), C(2)–C(3) 1.447(3), C(2)–C(4) 1.488(2), C(3)–C(4) 1.486(3); C(1)–C(2)–C(3) 148.7(2), C(1)–C(2)–C(4) 150.4(2), C(3)–C(2)–C(4) 61.84(17), C(2)–C(3)–C(4) 60.93(16); C(3)–C(4)–C(2) 58.23(15).

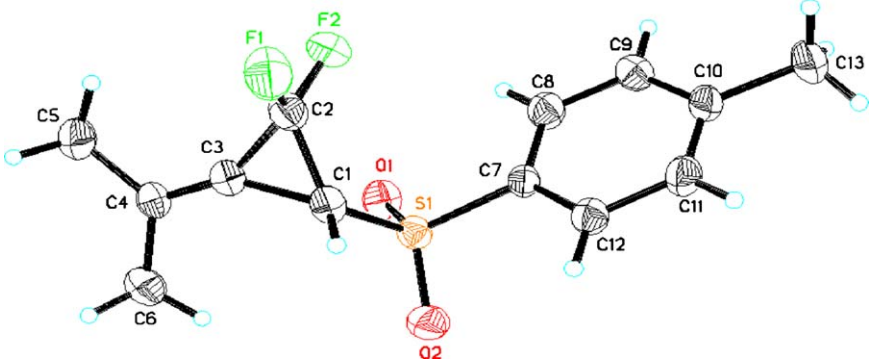


Fig. 2. Single crystal structures of F_2MCPs **2**. Selected bond lengths [Å], bond angles [°]: C(1)–C(2) 1.500(3), C(1)–C(3) 1.487(3), C(2)–C(3) 1.416(3), C(3)–C(4) 1.314(3); C(1)–C(2)–C(3) 61.22(14), C(4)–C(3)–C(2) 150.6(2), C(4)–C(3)–C(1) 145.7(2), C(2)–C(3)–C(1) 62.17(14); C(3)–C(1)–C(2) 56.60(14).