



# Synthesis of superacidic carbon acid and its derivatives



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## ABSTRACT

In this review, we provide an outline of synthetic efforts for carbon acids (C–H acids) bearing  $(R_fSO_2)_2CH$  group as an acidic functionality. Unlike conventional active methylene compounds such as acetoacetates and malonates are not enough acidic to work as acid catalysts,  $(R_fSO_2)_2CH$ -type carbon acids are superacidic in gas phase and catalyze organic reactions in organic solvents.

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## 1. Introduction

Since discovery of sulfuric acid in the 8th or 9th centuries, strong acids have captured minds of a number of chemists. As organic chemistry had been developed in the 20th century, chemists sought stronger organic acids comparable to 100% sulfuric acid. As one of early achievements, Haszeldine and Kidd synthesized trifluoromethanesulfonic acid (TfOH;  $Tf=CF_3SO_2$ ) [1,2]. The Hammett acidity function  $H_0$  of this compound was reported as approximately  $-14$  [3], which means that TfOH serves as a stronger acid than sulfuric acid ( $H_0 = -12$ ) [4]. Recent calculation proposed  $pK_a$  value of TfOH in  $H_2O$  as  $-14.2$  [5,6]. Structurally related bis(trifluoromethylsulfonyl)imide ( $Tf_2NH$ ) was synthesized by DesMarteau in 1984 [7]. Today these acids are widely utilized in various fields including catalysts, ionic liquids, material sciences and so on (Fig. 1).

In marked contrast, chemistry of strongly acidic carbon acids (C–H acids) has been extremely limited for over many years, even though such strong carbon acids were already discovered in an early time. Usually, acidic C–H structure in carbon acids is essentially homopolar bond, therefore the dissociation of the C–H bond is less facile than those of O–H and N–H bonds. In fact, acidities of typical carbon acids such as carbonyl compounds bearing  $\alpha$ -hydrogen atom(s) are too weak to undergo proton transfer reaction to non-charged basic species. However, it is easily

predictable that stabilization of the carbanions, *i.e.* the conjugate bases, facilitates the ionization of the carbon acids.

In the middle of the 1950's, Brice [8] and Haszeldine [9] independently noted synthesis of bis(triflyl)methane; the reaction of triflyl fluoride **1a** with 2 equiv. of methylmagnesium iodide in  $Et_2O$  followed by vacuum sublimation afforded disulfone **2a** in low yield (approximately 10%) along with formation of mono-sulfone **3a** (Scheme 1). Subsequently, 3M Company researchers, Koshar and Mitsch, experimentally demonstrated that **2a** is one of the strongest carbon acids of the methylene series [10]. They determined the  $H_0$  value of **2a** as 1.0 and its  $pK_a$  value in  $H_2O$  was estimated about  $-1$ . Based on a high level computation by Dixon, it was proposed that its  $pK_a$  value in  $H_2O$  is  $-1.3$  [5]. Bordwell also measured its  $pK_a$  value in a DMSO solution as 2.1 [11]. This value indicates that the acidity of **2a** is at least 20 times as strong as that of  $CF_3CO_2H$  ( $pK_a$  in DMSO = 3.45). Such notably enhanced acidity of **2a** is attributed to significant stabilization of the corresponding conjugate base by *gem*-disubstitution of the carbon atom by two triflyl groups, which are the strongest neutral electron-withdrawing group. As related carbon acids, a series of  $Tf_3CH$  **4a** [12],  $(FSO_2)_2CH_2$  [13], and  $(FSO_2)_3CH$  [14] was synthesized in the 1970's and the 1980's.

Because of notably strong acidity of  $Tf_2CH_2$  **2a**, it easily forms the corresponding salts by neutralization with the corresponding carbonates in protic solvents such as  $H_2O$ , MeOH, and EtOH (Scheme 2) [9,10]. According to this procedure, sodium, potassium, and silver salts were obtained in pure forms. Cesium salts of  $(R_fSO_2)_3CH$  **4**, which form by neutralization using  $Cs_2CO_3$  in  $H_2O$ , are generally insoluble or less soluble in  $H_2O$  contrary to high solubility of  $CsCH(SO_2R_f)_2$  in  $H_2O$ . This property was often used for

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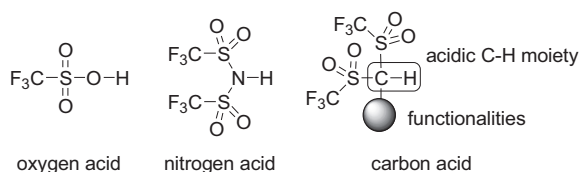
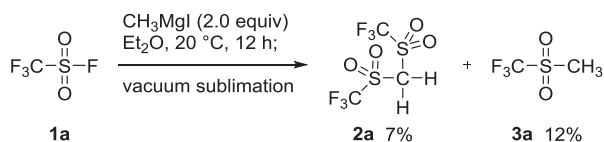
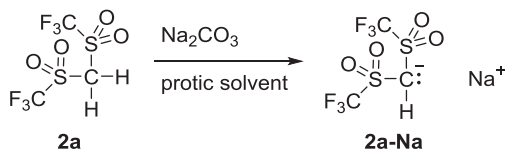


Fig. 1. Structures of triflylated organic acids.



Scheme 1. Haszeldine's synthesis of Tf<sub>2</sub>CH<sub>2</sub> **2a**.



Scheme 2. Salt formation reaction.

purification of (R<sub>f</sub>SO<sub>2</sub>)<sub>2</sub>CH type carbon acids. In addition, it was mentioned that **2a** is smoothly transformed to organic salts by treating with some aliphatic and aromatic amines including Et<sub>2</sub>NH, *N*-methylaniline [10].

To understand acidity scale of such strongly acidic compounds, the gas-phase acidity Δ*G*<sub>acid</sub> (or *GA*) is well employed (Table 1). Experimentally determined Δ*G*<sub>acid</sub> values of Tf<sub>2</sub>CH<sub>2</sub> **2a** and Tf<sub>3</sub>CH **4a** (300.6 kcal mol<sup>-1</sup> and 289.0 kcal mol<sup>-1</sup>, respectively) are smaller than that of sulfuric acid (302.2 kcal mol<sup>-1</sup>) [15]. In gas phase, the methane derivatives substituted by two or three Tf groups work as superacids. As an acidity scale in solution phase, the p*K*<sub>a</sub> data of several acids in DMSO solutions are available. As remarked above, Boldwell reported that p*K*<sub>a</sub> value of **2a** in a DMSO solution is 2.1. Considering the p*K*<sub>a</sub> value of (PhSO<sub>2</sub>)<sub>2</sub>CH<sub>2</sub> is 12.25, it is obvious that the triflyl group plays a crucial role for the strong acidity of Tf<sub>2</sub>CH<sub>2</sub> **2a** [11].

Such carbon acids and their salts have been occasionally used in specific fields of chemistry. As an early example, 3M Company investigated that the carbon acids as catalysts [16] or co-catalysts [17] for epoxide polymerization in the 1980's. Tf<sub>2</sub>CH<sub>2</sub> **2a** was also utilized for protonation of organometallic species by Siedle and co-workers [18]. In 2001, Yamamoto and Ishihara brought innovation to the carbon acid chemistry; they firstly found that Tf<sub>2</sub>CHC<sub>6</sub>F<sub>5</sub> **5a** and its polystyrene-bound derivative can be used as effective catalysts for several organic reactions including esterification reaction of menthol, which do not proceed by using strongly acidic Nafion SAC-13 resin [19,20]. Besides, the authors demonstrated

Table 1  
Acidities of sulfuric acid and strong organic acids.

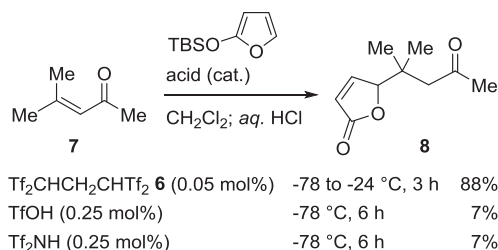
Acid	Δ <i>G</i> <sub>acid</sub> (kcal mol <sup>-1</sup> )	p <i>K</i> <sub>a</sub> (DMSO)
H <sub>2</sub> SO <sub>4</sub>	302.2	1.4
TfOH	299.5	0.3
Tf <sub>2</sub> NH	286.5	–
Tf <sub>3</sub> CH <b>4a</b>	289.0	–
Tf <sub>2</sub> CH <sub>2</sub> <b>2a</b>	300.6	2.1
CF <sub>3</sub> CO <sub>2</sub> H	–	3.45
(PhSO <sub>2</sub> ) <sub>2</sub> CH <sub>2</sub>	–	12.25
(EtO <sub>2</sub> C) <sub>2</sub> CH <sub>2</sub>	–	16.2
TfCH <sub>3</sub> <b>3a</b>	339.8	18.8

that, compared to TfOH and Tf<sub>2</sub>NH, some carbon acids were more potent acid catalysts for several C–C bond forming reactions with silicon enolates. For instance, only 0.05 mol% of Tf<sub>2</sub>CHCH<sub>2</sub>CHTf<sub>2</sub> **6** was effective enough to promote the vinylogous Mukaiyama–Michael reaction of mesityl oxide **7** with 2-silyloxyfuran giving rise to production of the compound **8** [21,22]. Moreover, nowadays, Lewis acid catalysis by some metal salts such as M(CTf<sub>3</sub>)<sub>n</sub> (M = rare earth metals [23], and Cu [24]) and Me<sub>2</sub>AlCTf<sub>2</sub>R [25] appear (Scheme 3).

In this review article, we provide an outline of the strong carbon acids and their derivatives from the viewpoint of synthetic strategies for these compounds. Although these acids have not been much referred to in community of organic chemists for a long time, in the present century some chemists including us have been attracted by very unique behaviors of them. We believe that this review touches off wider investigations on this kind of acids.

## 2. Construction of 1,1-bis((perfluoroalkyl)sulfonyl)methyl groups

Bis(triflyl)methane **2a** is the simplest compound bearing bis(perfluoroalkyl)methyl structure. As mentioned above, it was originally reported in the middle of the 1950's by Brice [8] and Haszeldine [9]. Currently, this compound is commercially available. In their reports, the reaction of commercially unavailable and inconvenient gaseous reagent CF<sub>3</sub>SO<sub>2</sub>F **1a** with MeMgI in Et<sub>2</sub>O as a solvent was adopted and the desired Tf<sub>2</sub>CH<sub>2</sub> **2a** was obtained in very poor yield. Koshar and Mitsch presented more effective conditions for practical preparation of (R<sub>f</sub>SO<sub>2</sub>)<sub>2</sub>CH<sub>2</sub> **2** in 1973 [10]. As shown in Table 2, they revealed that the reaction of CF<sub>3</sub>SO<sub>2</sub>F **1a** with the Grignard reagent in Et<sub>2</sub>O mainly gave the corresponding monosulfone **3a**, whereas similar reaction in THF yielded the disulfone **2a** as a major product. By applying these conditions, (R<sub>f</sub>SO<sub>2</sub>)<sub>2</sub>CH<sub>2</sub> **2** bearing some linear perfluoroalkyl



Scheme 3. Tf<sub>2</sub>CHCH<sub>2</sub>CHTf<sub>2</sub>-induced Mukaiyama–Michael reaction.

Table 2  
Reaction of perfluoroalkanesulfonyl fluorides with MeMgCl.

Entry	1	R <sub>f</sub>	CH <sub>3</sub> MgCl (equiv.)	Solvent	Yield <sup>a</sup> (%)	
					2	3
1	<b>1a</b>	CF <sub>3</sub>	1.5	Et <sub>2</sub> O	11	12
2	<b>1a</b>	CF <sub>3</sub>	3.0	Et <sub>2</sub> O	7	70
3	<b>1a</b>	CF <sub>3</sub>	3.0	THF	75	5
4	<b>1b</b>	<i>n</i> -C <sub>4</sub> F <sub>9</sub>	3.0	THF	60	–
5 <sup>b</sup>	<b>1c</b>	<i>n</i> -C <sub>8</sub> F <sub>17</sub>	3.0	THF	50	–

<sup>a</sup> Isolated yield.

<sup>b</sup> A solution of MeMgBr in Et<sub>2</sub>O was used.

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