

Preparation, NMR, and *ab Initio*/IGLO Study of Trifluoromethyl-Substituted Carboxonium Ions¹

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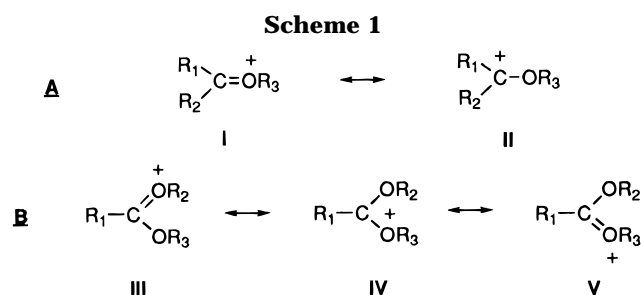
The preparation and study of trifluoromethyl-substituted carboxonium ions $\text{CF}_3\text{C}(\text{OH})\text{CH}_3^+$ (**2**), $\text{CF}_3\text{C}(\text{OCH}_3)\text{CH}_3^+$ (**3**), $\text{CF}_3\text{C}(\text{OH})\text{OCH}_3^+$ (**8**), and $\text{CF}_3\text{C}(\text{OCH}_3)_2^+$ (**9**) by ¹H and ¹³C NMR spectroscopy under superacidic conditions at low temperature and by *ab initio* molecular orbital theory at the MP2(fu)/6-31G* level are reported. Attempted preparation of bis(trifluoromethyl)-substituted ions $\text{CF}_3\text{C}(\text{OH})\text{CF}_3^+$ (**5**) and $\text{CF}_3\text{C}(\text{OCH}_3)\text{CF}_3^+$ (**6**) by protonation and methylation, respectively, of hexafluoroacetone (**4**) were not successful under similar conditions, due to the strongly electron-withdrawing effect of two trifluoromethyl groups on the carbonyl moiety.

Introduction

Carboxonium ions such as **A** and **B** ($R_1 = \text{alkyl}$; $R_{2,3} = \text{H or alkyl}$) are important intermediates in many acid-catalyzed organic reactions. Considerable interest has centered on the elucidation of their structure and electronic properties (Scheme 1).²

Carboxonium ions were first studied by Meerwein,^{2c} and their chemical behavior reflects both their oxonium and carbenium ion nature. Ions **A** can be obtained by protonation or methylation of ketones. They can be visualized as hybrids of resonance structures **I** and **II** ($R_{1,2} = \text{alkyl}$; $R_3 = \text{H or alkyl}$).^{2d} Carboxonium ions **B** result from the protonation or alkylation of esters. They can be depicted by three resonance forms, **III**, **IV**, and **V** ($R_{1,3} = \text{alkyl}$; $R_2 = \text{H or alkyl}$).^{2d} A number of carboxonium ions have been isolated as stable salts with various counterions (such as BF_4^- , SbF_6^- , SbCl_6^- , and AsF_6^-) and have found use as effective alkylating reagents in organic synthesis.^{2a,c}

The destabilizing effect of a trifluoromethyl group (CF_3) adjacent to a carbenium ion center is well documented both by theory and experiment.³ As reflected by its Hammett⁴ substituent constant ($\sigma_p^+(p\text{-CF}_3) = 0.61$), the CF_3 group is one of the strongest electron-withdrawing groups and thus inductively destabilizes carbocationic centers. In addition, the trifluoromethyl group lacks the ability to stabilize positive charge through $n\text{-}\pi$ back-donation. Thus, trifluoromethyl-substituted carbocations are generally less stable than their fluoro-substituted analogs. A number of trifluoromethyl-substituted carbocations have been observed as stable, long-lived species in superacidic solution,^{3a,b} but no study of the related



trifluoromethyl-substituted *carboxonium ions* has been reported. An investigation of trifluoromethyl-substituted carboxonium ions is of interest in view of their highly electron-deficient nature and because of the increasing role of trifluoromethylated organic compounds in the development of pharmaceutical⁵ and agricultural chemicals.⁶ Further, as high level *ab initio* calculated geometries together with IGLO⁷ (individual gauge for localized orbitals) calculated ¹³C NMR chemical shifts have become increasingly useful in predicting accurate molecular structures of such electron-deficient carbocations,⁸ such studies were also carried out.

As part of our continuing investigations into onium ions,¹ we have now prepared and characterized the trifluoromethyl-substituted carboxonium ions $\text{CF}_3\text{C}(\text{OH})\text{CH}_3^+$ (**2**), $\text{CF}_3\text{C}(\text{OCH}_3)\text{CH}_3^+$ (**3**), $\text{CF}_3\text{C}(\text{OH})\text{OCH}_3^+$ (**8**), and $\text{CF}_3\text{C}(\text{OCH}_3)_2^+$ (**9**) by ¹H and ¹³C NMR spectroscopy under stable ion conditions. We have also attempted to prepare carboxonium ions bearing three perfluoroalkyl substituents by ionizing the corresponding fluoroorthoformates.

Results and Discussion

In order to assess the effect of trifluoromethyl and related substituents on the stabilities of carboxonium

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Table 1. Total Energies (–au), ZPE (kcal/mol), and Relative Energies (kcal/mol) of Protonated and Methylated Trifluoroacetone, Hexafluoroacetone, and Methyl Trifluoroacetate

structure	HF/6-31G*//HF/6-31G*	ZPE ^a	MP2(fu)/6-31G*//MP2(fu)/6-31G*	rel energy ^b
trifluoroacetone				
1 (C ₃)	488.534 63	37.33	489.623 18	
protonated trifluoroacetone				
2 (C ₃)	488.824 19	44.68	489.904 44	
methylated trifluoroacetone				
3 (C ₁)	527.862 21	61.42	529.076 48	
hexafluoroacetone				
4 (C ₂)	785.094 84	24.23	786.694 68	
protonated hexafluoroacetone				
5 (C ₁)	785.345 95	31.62	786.938 38	
methylated hexafluoroacetone				
6 (C ₁)	824.391 94	48.17	826.118 20	
methyl trifluoroacetate				
7a (C ₃)	563.402 83	41.09	564.669 42	0.00
7b (C ₁)	563.387 57	40.98	564.656 31	8.34
protonated methyl trifluoroacetate				
8a (C ₃)	563.699 95	48.30	564.958 26	0.00
8b (C ₁)	563.695 49	48.32	564.954 04	2.62
8c (C ₁)	563.691 76	48.33	564.951 74	4.07
8d (C ₃)	563.690 29	48.10	564.947 66	6.82
methylated methyl trifluoroacetate				
9a (C ₁)	602.361 38	65.13	604.128 01	0.00
9b (C ₁)	602.723 60	65.13	604.116 31	7.32
9c (C ₃)	602.724 37	64.90	604.113 79	9.16

^a Zero-point vibrational energies at the HF/6-31G*//HF/6-31G* level scaled by a factor of 0.89. ^b Relative energy in kcal/mol at MP2(fu)/6-31G*//MP2(fu)/6-31G* + ZPE level.

Table 2. Experimental and Calculated ¹³C NMR Shifts at IGLO II//MP2(fu)/6-31G* Level

structure		C=O	CF ₃	CH ₃	OCH ₃
1 (C ₃)	trifluoroacetone				
	exptl	187.40	115.60	23.10	
	calcd	197.34	106.83	18.87	
2 (C ₃)	protonated trifluoroacetone				
	exptl	225.45	114.12	26.64	
	calcd	243.24	104.59	21.04	
3 (C ₁)	methylated trifluoroacetone				
	exptl	222.32	116.78	24.03	75.97
	calcd	239.91	104.36	25.00	75.61
4 (C ₂)	hexafluoroacetone				
	exptl	172.22	114.36		
	calcd	183.03	104.89		
5 (C ₁)	protonated hexafluoroacetone				
	calcd	224.18	104.00		
6 (C ₁)	methylated hexafluoroacetone				
	calcd	217.79	103.71		83.37
			104.57		
7a (C ₃)	methyl trifluoroacetate				
	exptl	157.98	114.48		54.36
	calcd	166.68	104.89		50.51
8a (C ₃)	protonated methyl trifluoroacetate				
	exptl	172.49	112.24		68.01
	calcd	186.21	103.00		69.38
9a (C ₁)	methylated methyl trifluoroacetate				
	exptl	171.66	114.48		68.21
	calcd	184.91	103.60		72.44
					65.23
					69.41

ions, we attempted to prepare and observe ions containing *one* CF₃ (**2**, **3**, **8**, **9**), *two* CF₃ (**5**, **6**), and *three* perfluoroalkyl groups (**10**) under superacidic stable ion conditions. The experimental ¹H and ¹³C NMR chemical shifts of the observed cations and their parent compounds are summarized in Tables 2 and 3.

To gain better insight into the structural parameters of trifluoromethyl-substituted carboxonium ions, high level *ab initio* molecular orbital calculations were carried out on trifluoroacetone **1**, hexafluoroacetone **4**, methyl trifluoroacetate **7a,b**, and their protonated and methylated forms. Geometry optimizations of all isomers were performed up to the MP2(fu)/6-31G* level and are summarized in Figure 1. Total energies (–au), ZPE (kcal/

mol), and relative energies (kcal/mol) of the ions are given in Table 1. IGLO ¹³C NMR chemical shift calculations were carried out for the most stable isomers using the MP2(fu)/6-31G* geometries and are summarized in Table 2.

Protonated Trifluoroacetone (2). Trifluoroacetone (**1**) is readily protonated in FSO₃H:SbF₅ solution at –20 °C with SO₂ClF as solvent, and the resulting carboxonium ion **2** could be observed by ¹H and ¹³C NMR spectroscopy (Scheme 2).

In theory, protonation of **1** can yield two different isomers of **2**, *syn* and *anti*. NMR spectroscopy, however, indicated the presence of only one isomer, which was characterized by a deshielding of 38 ppm at carbonyl

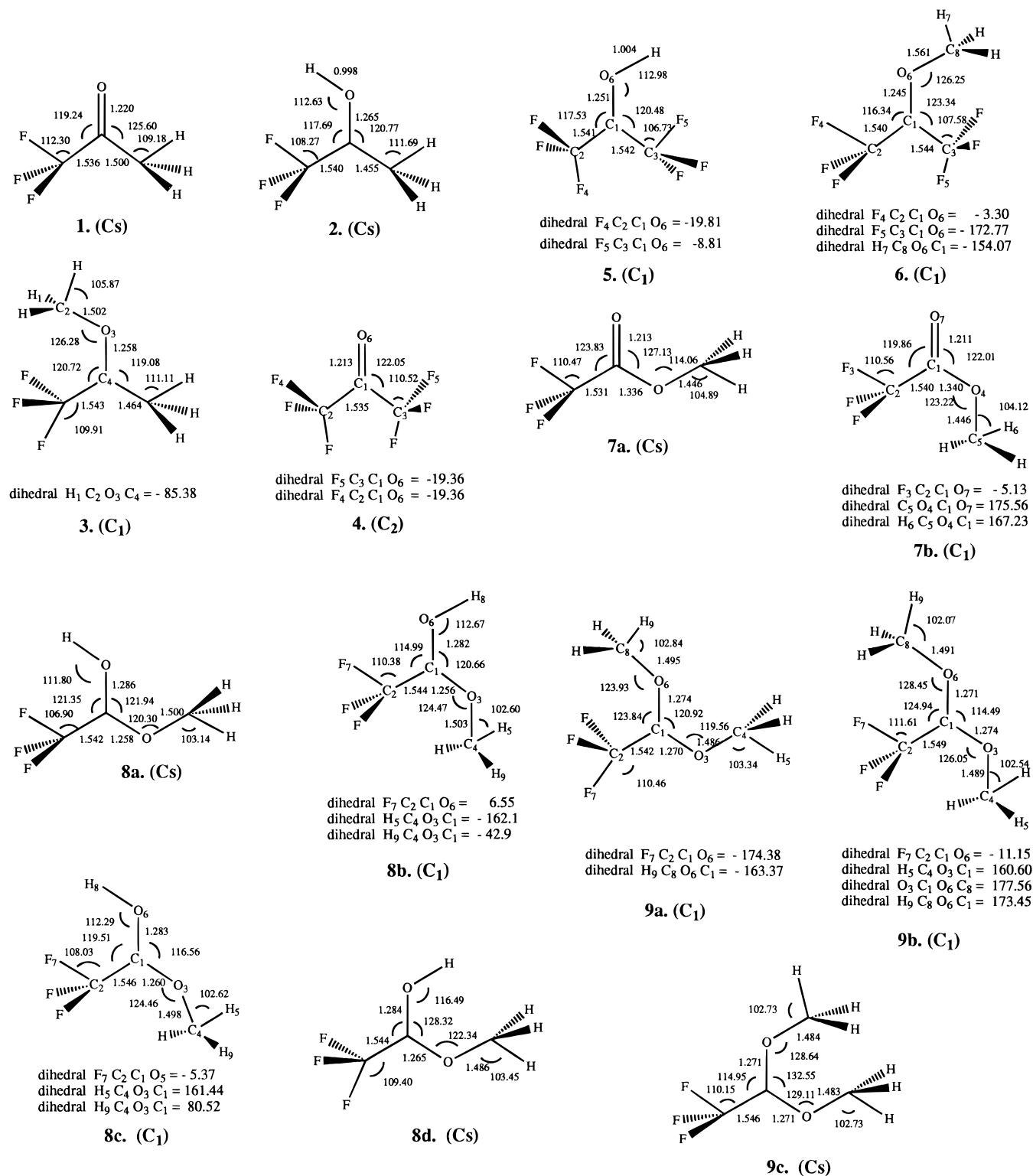
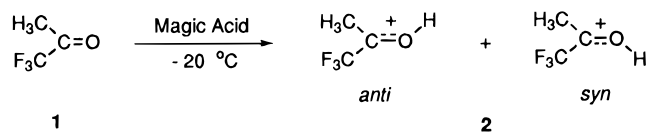


Figure 1. MP2(fu)/6-31G*-optimized geometries.

Scheme 2



carbon in **2** ($\delta^{13}\text{C}_{\text{exp}}$ C=O 225.5) with respect to **1** ($\delta^{13}\text{C}_{\text{exp}}$ C=O 187.4). In order to rationalize the experimental results, *ab initio* calculations were carried out on the two possible isomers of **2**. At the MP2(fu)/6-31G* level, only the *syn* isomer was found to be a stable minimum

structure. The experimentally observed chemical shifts of protonated trifluoroacetone (see Tables 2 and 3) were therefore assigned to the *syn* isomer of **2**. The IGLO II-calculated ^{13}C NMR chemical shifts are in reasonable agreement with the experimental data. IGLO II predicts a deshielding of 45.9 ppm for the carbonyl carbon in **2** ($\delta^{13}\text{C}_{\text{calc}}$ C=O 243.2) as compared to parent trifluoroacetone (**1**) ($\delta^{13}\text{C}_{\text{calc}}$ C=O 197.3). The deshielding (38 ppm) at the carbonyl carbon in protonated trifluoroacetone (**2**) is smaller than that observed in protonated acetone. Pro-

Table 3. Experimental $^1\text{H-NMR}$ Chemical Shifts of Carboxonium Ions

no.	molecule	-OH	-OCH ₃	-CH ₃	ref
acetone					
	(CH ₃) ₂ CO			2.09	<i>a</i>
	(CH ₃) ₂ COH ⁺	14.93		3.45	<i>b</i>
	(CH ₃) ₂ COCH ₃ ⁺		5.23	3.40	<i>c</i>
trifluoroacetone					
	CH ₃ (CF ₃)CO (1)			2.42	<i>a</i>
	CH ₃ (CF ₃)COH ⁺ (2)	12.84		2.94	<i>this study</i>
	CH ₃ (CF ₃)COCH ₃ ⁺ (3)		5.10	3.24	<i>this study</i>
methyl acetate					
	CH ₃ CO ₂ CH ₃		3.67	2.01	<i>a</i>
	CH ₃ C(OCH ₃)(OH) ⁺	12.72	4.53	2.83	<i>d</i>
	CH ₃ C(OCH ₃) ₂ ⁺		4.62	2.76	<i>e</i>
			4.36		
methyl trifluoroacetate					
	CF ₃ CO ₂ CH ₃ (7a)		3.98		<i>a</i>
	CF ₃ C(OCH ₃)(OH) ⁺ (8a)	12.10	6.86		<i>this study</i>
	CF ₃ C(OCH ₃) ₂ ⁺ (9a)		5.15		<i>this study</i>
			4.61		

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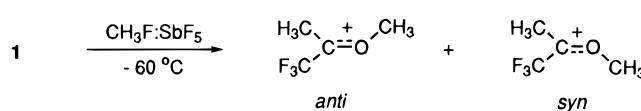
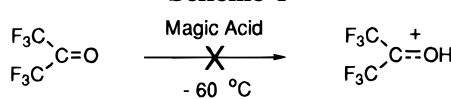
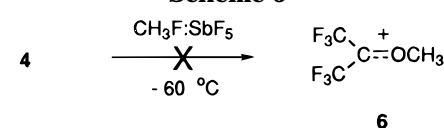
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tonated acetone⁹ ($\delta^{13}\text{C}_{\text{exp}} \text{C}=\text{O}$ 248.7) shows a deshielding of 44 ppm as compared to acetone ($\delta^{13}\text{C}_{\text{exp}} \text{C}=\text{O}$ 205.1). This difference can be rationalized by the strong inductive electron-withdrawing effect of the trifluoromethyl group in **2** which leads to a more distinct oxonium (**1**) ion nature in protonated trifluoroacetone (**2**) as compared to protonated acetone. Protonated trifluoroacetone (**2**) has also been observed as a stable species in the gas phase by ion cyclotron resonance spectrometry.¹⁰

MO calculations at the MP2(fu)/6-31G* level show that the *eclipsed-eclipsed*, *e-e*, conformation with *C_s* symmetry is preferred in protonated trifluoroacetone (**2**). Similar results have previously¹¹ been reported for protonated acetone. **2** is characterized by a C=O bond elongation of ~3.6% (0.045 Å) and a shortening of the neighboring C-C(CH₃) bond by ~3% with respect to **1**. The increase of the C=O bond length is substantially smaller than that found for protonated acetone (4.1%) by Krivdin *et al.*^{11a} at a similar level of theory and can readily be explained by a stronger contribution of the oxonium ion (**1**) resonance structure in protonated trifluoroacetone (**2**) as compared to protonated acetone.

Methylated Trifluoroacetone (3). Trifluoroacetone (**1**) is readily methylated in CH₃F:SbF₅:SO₂ solution at -60 °C, and a deshielding at the carbonyl carbon by 35 ppm is observed in the methylated species **3** ($\delta^{13}\text{C}_{\text{exp}}$ 222.3) as compared to the parent **1** ($\delta^{13}\text{C}_{\text{exp}}$ 187.4) (Scheme 3).

Again, two different isomers, *syn* and *anti*, of **3** are possible. Under the experimental conditions only one isomer was observed by NMR. In agreement with the experimental results, *ab initio* calculations at the MP2(fu)/6-31G* level resulted in the *syn* isomer as the only stable minimum structure for **3**. The experimentally observed chemical shifts of methylated trifluoroacetone

Scheme 3**Scheme 4****Scheme 5**

(see Tables 2 and 3) were therefore assigned to the *syn* isomer of **3**. IGLO II slightly overestimates the deshielding at carbonyl carbon in **3** and predicts a deshielding of 42.6 ppm in **3** ($\delta^{13}\text{C}_{\text{calc}} \text{C}=\text{O}$ 239.9) as compared to parent trifluoroacetone (**1**) ($\delta^{13}\text{C}_{\text{calc}} \text{C}=\text{O}$ 197.3). Again, the magnitude of the deshielding at carbonyl carbon is greater for acetone (40 ppm) than for trifluoroacetone (35 ppm). Methylated acetone¹² ($\delta^{13}\text{C}_{\text{exp}} \text{C}=\text{O}$ 245.5) also shows a deshielding of 40 ppm with respect to acetone ($\delta^{13}\text{C}_{\text{exp}} \text{C}=\text{O}$ 205.1). These results can be explained by a stronger contribution of the oxonium ion resonance structure (**1**) in **3**.

Similar to protonated trifluoroacetone **2**, the calculated C=O bond in methylated trifluoroacetone **3** is longer by 0.038 Å (3%) compared to **1**, whereas the C-C(CH₃) bond is shorter by 0.036 Å (2.4%), indicating charge delocalization among the three atoms.

Protonated Hexafluoroacetone (5). Protonated hexafluoroacetone (**5**) has been observed as an abundant species in the gas phase by ion cyclotron resonance spectroscopy.¹⁰ Attempts to observe long-lived protonated hexafluoroacetone in the condensed phase in FSO₃H:SbF₅:SO₂ solution at -60 °C, however, were unsuccessful (Scheme 4).

MO calculations at the MP2(fu)/6-31G* level indicate a C=O bond elongation by 0.038 Å (3%) in **5** with respect to hexafluoroacetone (**4**). The increase in C=O bond length upon protonation is smaller than those calculated for protonated trifluoroacetone (**2**) (3.6%) and protonated acetone (4.1%). This can be rationalized by a strong contribution of the oxonium ion (**1**) resonance structure in protonated hexafluoroacetone (**5**). There is almost no change in the C-C(CF₃) bond length between **4** and **5**, indicating very little charge delocalization in the protonated species. IGLO II calculations predict the carbonyl carbon in **5** ($\delta^{13}\text{C}_{\text{calc}} \text{C}=\text{O}$ 224.2) to be deshielded by 41.2 ppm with respect to **4** ($\delta^{13}\text{C}_{\text{calc}} \text{C}=\text{O}$ 183.0). It is, of course, possible that an extremely limited protonation equilibrium exists in the superacid solution, but it cannot be detected by NMR spectroscopy.

Methylated Hexafluoroacetone (6). Attempts to methylate hexafluoroacetone **4** with CH₃F:SbF₅ in SO₂ solution at -60 °C to a persistent carboxonium ion were also unsuccessful (Scheme 5).

MO calculations at the MP2(fu)/6-31G* level predict a C=O bond elongation of 0.032 Å (2.6%) for **6** with respect

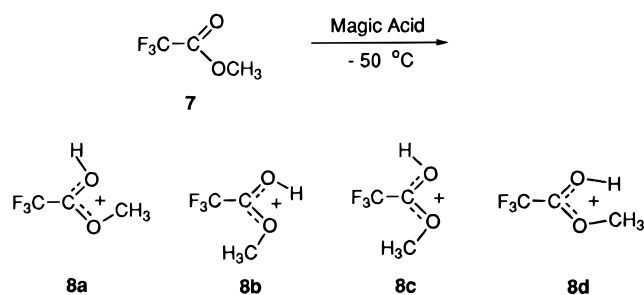
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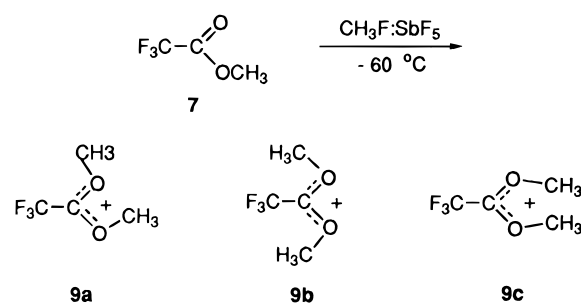
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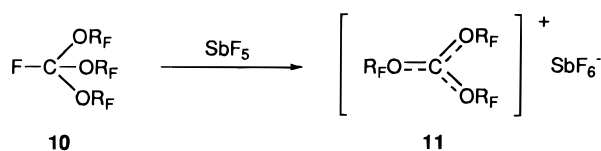
Scheme 6



Scheme 7



Scheme 8



to the neutral parent **4**. This value is similar to that calculated for protonated hexafluoroacetone **5** (3%). IGLO II calculations predict the carbonyl carbon in **6** ($\delta^{13}\text{C}_{\text{calc}} \text{C}=\text{O}$ 217.8) to be deshielded by 34.8 ppm with respect to parent **4** ($\delta^{13}\text{C}_{\text{calc}} \text{C}=\text{O}$ 183.0). Again, the NMR spectroscopic studies cannot answer the question whether an extremely limited methylation equilibrium could be present.

Protonated Methyl Trifluoroacetate (8a–d). NMR spectroscopy reveals that methyl trifluoroacetate (**7**) is readily protonated at the acyl oxygen in $\text{FSO}_3\text{H}:\text{SbF}_5:\text{SO}_2\text{-ClF}$ solution at -50°C (Scheme 6).

Four different isomers, **8a–d**, are possible for protonated methyl trifluoroacetate. Under the experimental conditions only one isomer was observed, which was characterized by a slight deshielding of 14.5 ppm at the carboxylic carbon in protonated methyl trifluoroacetate ($\delta^{13}\text{C}_{\text{exp}} \text{C}=\text{O}$ 172.5) as compared to **7** ($\delta^{13}\text{C}_{\text{exp}} \text{C}=\text{O}$ 158.0). As expected, protonation at the alkyl oxygen was not observed under the above conditions. Similar to previously¹³ reported studies on protonated methyl acetate, four stable minimum structures **8a–d** were found for protonated methyl trifluoroacetate at the MP2(fu)/6-31G* level. Structure **8a** was found to be the global minimum, differing only by a few kcal/mol from the other isomers **8b–d** (see Table 1). Accordingly, the experimentally observed chemical shifts (see Tables 2 and 3) were assigned to the most stable isomer **8a**, accordingly. The IGLO II-calculated ^{13}C NMR chemical shifts of protonated methyl trifluoroacetate (**8a**) are in good agreement with the experimental results (Table 2).

Due to the strong electron-withdrawing effect of the trifluoromethyl group, the contribution of the carbenium ion structure **IV** ($\text{R}_1 = \text{CF}_3$; $\text{R}_2 = \text{CH}_3$; $\text{R}_3 = \text{H}$) is greatly reduced in protonated methyl trifluoroacetate (**8a–d**). This explains why protonated methyl acetate⁹ ($\delta^{13}\text{C}_{\text{exp}} \text{C}=\text{O}$ 192.8) shows a considerably higher deshielding effect (22 ppm) at the carboxylic carbon with respect to the parent methyl acetate ($\delta^{13}\text{C}_{\text{exp}} \text{C}=\text{O}$ 170.7).

8a is characterized by a $\text{C}=\text{O}$ bond elongation of 0.073 Å (6%) and a shortening of the $\text{C}-\text{O}(\text{CH}_3)$ bond by 0.078 Å (5.8%) as compared to **7**.

Methylated Methyl Trifluoroacetate (9a–c). Methyl trifluoroacetate is readily methylated at the acyl oxygen in $\text{CH}_3\text{F}:\text{SbF}_5:\text{SO}_2$ solution at -60°C , and the methylated species could be observed as a long-lived stable ion by ^1H and ^{13}C NMR spectroscopy.

Three isomers, **9a**, **9b**, and **9c** (Scheme 7) are possible for methylated methyl trifluoroacetate. Under the stable ion conditions, however, only one isomer was observed by NMR spectroscopy, which exhibited a deshielding of 13.7 ppm at the carboxylic carbon ($\delta^{13}\text{C}_{\text{exp}} \text{C}=\text{O}$ 171.7) compared to its precursor **7** ($\delta^{13}\text{C}_{\text{exp}} \text{C}=\text{O}$ 158.0). Similar

to previously^{13a,b} reported studies on methylated methyl acetate, there are three minimum structures for methylated methyl trifluoroacetate **9a–c**. Structure **9a** was found to be the global minimum and is calculated to be 9.16 kcal/mol more stable than structure **9c** at the MP2/6-31G* + ZPE level. The experimental chemical shifts of methylated methyl trifluoroacetate were assigned to structure **9a**. The calculated deshielding of 18.2 ppm (IGLO II) at the carbonyl carbon in **9a** compares well with the observed deshielding of 13.7 ppm. The magnitude of the deshielding is similar to that of in protonated methyl trifluoroacetate (**8a–d**) and reflects a strong contribution of oxonium resonance forms **III** and **V** ($\text{R}_1 = \text{CF}_3$; $\text{R}_{2,3} = \text{CH}_3$). When compared to **9a–c**, methylated methyl acetate^{13a} ($\delta^{13}\text{C}_{\text{exp}} \text{C}=\text{O}$ 192.8) shows a considerably higher deshielding (22 ppm) at the carboxylic carbon with respect to methyl acetate ($\delta^{13}\text{C}_{\text{exp}} \text{C}=\text{O}$ 170.7).

Perfluoroalkoxymethyl Cations (10). Attempts to generate carboxonium ions with three perfluoroalkoxy groups were unsuccessful. Perfluoroethyl orthoformate (**10**, $\text{R}_F = \text{C}_2\text{F}_5$) and perfluorobutyl orthoformate (**10**, $\text{R}_F = \text{C}_4\text{F}_9$) did not ionize with SbF_5 in Freon 113 solution at -40°C to give the corresponding perfluoroethoxy-methyl (**11**, $\text{R}_F = \text{C}_2\text{F}_5$) and perfluorobutoxymethyl (**11**, $\text{R}_F = \text{C}_4\text{F}_9$) cations, respectively (Scheme 8).

Conclusions

We have prepared and studied by NMR spectroscopy the highly electron-deficient trifluoromethyl-substituted carboxonium ions $\text{CF}_3\text{C}(\text{OH})\text{CH}_3^+$ (**2**), $\text{CF}_3\text{C}(\text{OCH}_3)\text{CH}_3^+$ (**3**), $\text{CF}_3\text{C}(\text{OH})\text{OCH}_3^+$ (**8**), and $\text{CF}_3\text{C}(\text{OCH}_3)_2^+$ (**9**). ^1H and ^{13}C NMR studies were carried out at low temperature. The IGLO II-calculated ^{13}C chemical shifts of these ions are in good agreement with the experimental data, as shown in Figure 2. Preparation of carboxonium ions containing two or three perfluoroalkoxy groups such as $\text{CF}_3\text{C}(\text{OH})\text{CF}_3^+$ (**5**), $\text{CF}_3\text{C}(\text{OCH}_3)\text{CF}_3^+$ (**6**), and $\text{C}(\text{OR}_F)_3^+$ (**10**) were unsuccessful under similar conditions.

Experimental Section

Trifluoroacetone and methyl trifluoroacetate are commercially available (Aldrich) and were distilled prior to use. Hexafluoroacetone (Aldrich) was used without further purifi-

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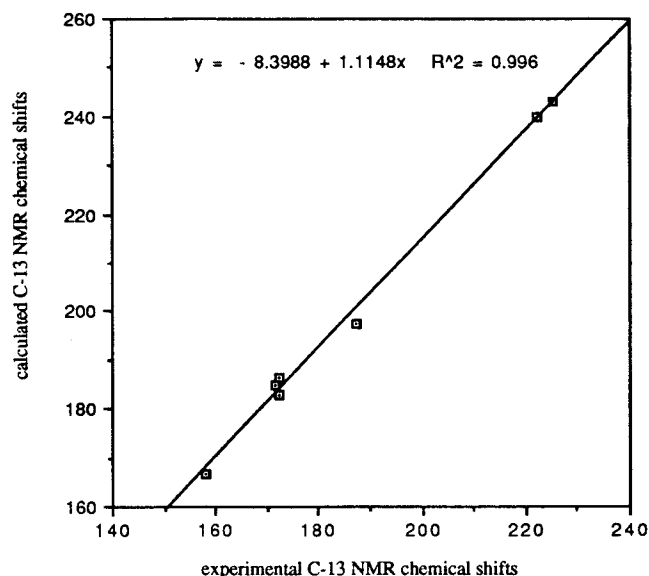


Figure 2. Experimental vs. calculated C-13 NMR chemical shifts of carbonyl carbons of **1–4**, **7a**, **8a**, and **9a**.

cation. Doubly distilled FSO_3H , SbF_5 , and SO_2ClF were used for the preparation of the ions. CH_3F and SO_2 were purchased from Matheson Gas Co. and used as received. Perfluoroethyl orthoformate and perfluorotributyl orthoformate were prepared in Prof. R. J. Lagow's laboratory by direct fluorination of the corresponding orthoformates in Freon 113 as solvent.¹⁴ ^1H and ^{13}C NMR spectra were obtained on a spectrometer equipped with a variable-temperature probe at 300 and 75.4 MHz, respectively. ^1H and ^{13}C NMR spectra were obtained with respect to TMS by using an acetone- d_6 capillary as external standard.

Ab initio molecular orbital calculations were carried out by using the GAUSSIAN 94¹⁵ package of programs. Restricted

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Hartree–Fock calculations were performed throughout. All geometries were fully optimized at the MP2(fu)/6-31G* level. Chemical shifts have been evaluated using the direct IGLO⁷ method employing the II basis set. MP2(fu)/6-31G*-optimized geometries were used for the chemical shift calculations. The calculated ^{13}C chemical shifts (δ values) are referenced to TMS.

Protonation Experiments. The appropriate precursor (~30 mg) was dissolved in approximately 0.5 mL of SO_2 or SO_2ClF (see text) in a 5 mm NMR tube and cooled to -78°C in a dry ice/acetone bath. Approximately 1.5 mL of 50% v/v solution of $\text{FSO}_3\text{H}:\text{SbF}_5$ (1:1 molar solution) in SO_2 or SO_2ClF (see text) was added to the solution at -78°C . The ensuing mixture was vigorously stirred (Vortex stirrer) under periodic cooling prior to transfer to a precooled NMR instrument.

Methylation Experiments. The appropriate precursor (~30 mg) was dissolved in approximately 0.5 mL of SO_2 in a 5 mm NMR tube and cooled to -78°C in a dry ice/acetone bath. A solution of $\text{CH}_3\text{F}:\text{SbF}_5:\text{SO}_2$ was prepared by bubbling CH_3F through a complex of SbF_5 in SO_2 (ratio of 1:5 by volume) for approximately 1–2 min at -78°C and subsequently added in excess to the reaction mixture. The mixture was vigorously stirred under periodic cooling until clear (Vortex stirrer) and then transferred to a precooled NMR instrument.

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