The Search for Persistent Cyclobutylmethyl Cations in Superacidic Media and Observation of the Cyclobutyldicyclopropylmethyl Cation[1a]

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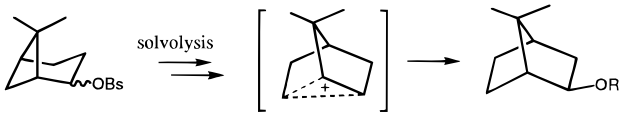
Abstract: Primary and secondary cyclobutylmethyl cations were found to be elusive in superacidic media even at low temperatures. They give thermodynamically more stable rearrangement products, i.e., the dimeric bicyclo[4.4.0]dec-1-yl cation and substituted cyclopentyl cations, respectively. In the search for a persistent cyclobutylmethyl cation, the more stabilized cyclobutyldicyclopropylmethyl cation was prepared from its corresponding alcohol in FSO_3H/SO_2ClF at −90 °C. Using variable-temperature ^{13}C NMR studies and theoretical calculations, the ion was shown to exist preferentially in its bisected conformation at −80 °C. The ion is predominantly classical, with expected significant delocalization into the neighboring cycloalkyl rings.

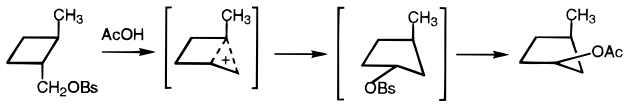
Introduction

The anchimeric assistance of the strained cyclobutyl ring in the solvolysis of cyclobutylmethyl substrates is well documented. The pioneering studies of Winstein and Holness revealed the unusually high reactivities of the cyclobutylmethyl brosylates and their ring expansion rearrangements. The ring expansion of the cyclobutylmethyl substrates was originally observed in the solvolysis of the nopinyl brosylates (**1**), the bicyclic analogues of the cyclobutylmethyl system.[1b] A nonclassical cyclobutylmethyl cation (**2**) was proposed to account for these results. Dauben's work on the selectively ^{18}O-labeled bicyclo[2.2.0]hexane-1-methyl *p*-nitrobenzoates also revealed significant rate acceleration (7×10^6 times faster than the neopentyl system), and the ring enlarged compound 1-bicyclo-[2.2.1]heptyl *p*-nitrobenzoate was the predominant product. Of particular interest was the observation of the absence of scrambling of the ^{18}O label, which supports neighboring group participation of the cyclobutyl ring during the solvolysis and the nonclassical structure for the intermediate carbocationic species.[2] Wiberg and Lorry similarly observed that bicyclo-[2.1.1]hexane-1-methyl tosylate undergoes 90% internal return to give bicyclo[2.2.1]hept-1-yl tosylate, the ring enlarged product.[3] The rate acceleration and the internal return with rearrangement due to the anchimeric assistance is a general phenomenon.[4,5]



1 **2** **3**

Gajewski and co-workers,[6] from their stereochemical studies of the solvolysis of *cis*- and *trans*-2-methylcyclobutylmethyl brosylates, confirmed the nonclassical structure for the primary cyclobutylmethyl cation. The rearranged product 3-methylcyclopentyl brosylate was shown to form with predominant retention of configuration, which undergoes rapid solvolysis with solvent assistance (k_s) to give the inverted products. *trans*-2-Methylcyclobutylmethyl brosylate (**4**), for example, on acetolysis gives *cis*-3-methylcyclopentyl acetate (**6**), through the intermediacy of *trans*-3-methylcyclopentyl brosylate (**5**). The observation of the retention of the configuration of the ring-enlarged product strongly implicates the involvement of the nonclassical species, **4′**. Coates also demonstrated ring expansion and Wagner−Meerwein rearrangements in the diterpene-derived cyclobutylmethyl tosylates.[7] Roberts[8] has systematically studied the kinetics of several cyclobutylmethyl substrates which reiterated the earlier observation of the anchimeric assistance of the cyclobutyl ring.



4 **4′** **5** **6**

Cyclobutylmethyl cations so far have not been observed as long-lived (persistent) species in superacidic media due to the propensity of the cyclobutyl ring to ring expansion rearrangements. Herein, we report our attempts of the preparation of several substituted cyclobutylmethyl cations and the successful preparation and characterization of the persistent cyclobutyldicyclopropylmethylium cation. We also describe the variable-temperature NMR studies of the cation and substantiate the results by theoretical calculations.

(1) (a) Stable Carbocations. 308. For part 307, see: Olah, G. A.; Liao, Q.; Casanova, J.; Bau, R.; Rasul, G.; Prakash, G. K. S. *J. Chem. Soc., Perkin Trans. 2*, in press. (b) Winstein, S.; Holness, N. J. *J. Am. Chem. Soc.* **1955**, *77*, 3054−3061.

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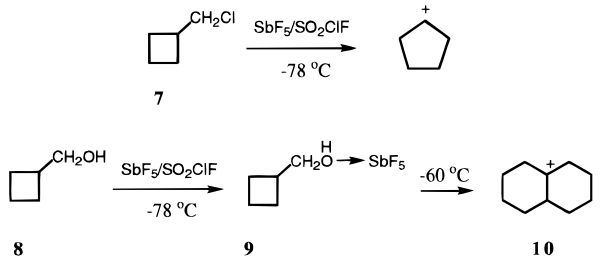
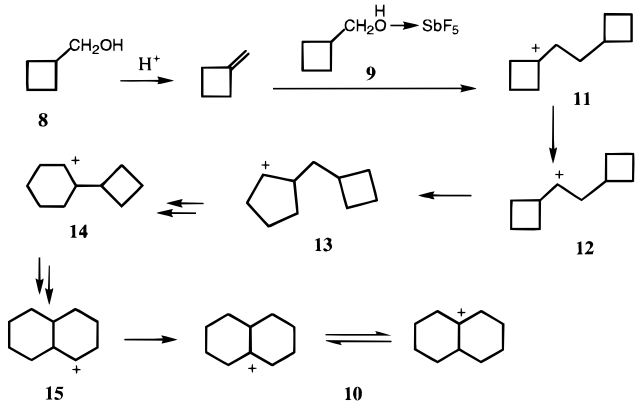
Scheme 1. Attempted Preparation of Primary Cyclobutylmethyl Cations



Scheme 2. Mechanistic Pathway for the Formation of 1-Bicyclo[3.3.0]dec-1-yl Cation from Cyclobutylmethanol



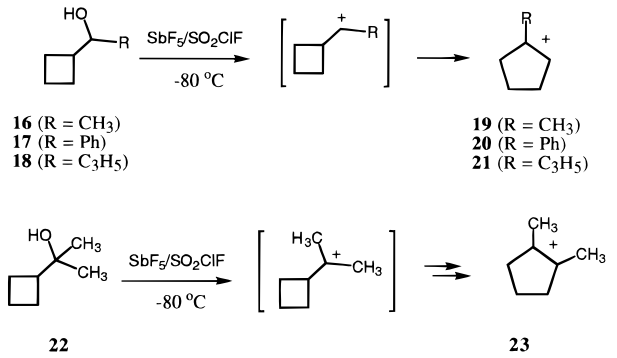
Results and Discussion

At the outset we anticipated on the basis of the earlier solvolytic studies, that cyclobutylmethyl cations should be observable species, at least at low temperatures in superacidic media. We have therefore systematically examined the ionization of various suitable precursors in attempting the preparation of the corresponding carbocations. The reaction of chloromethylcyclobutane (**7**) with SbF_5 in sulfuryl chloride fluoride at −78 °C gave, however, not the cyclobutylmethyl cation but the 5-fold degenerate cyclopentyl cation [δ ^{13}C 99.2 (sextet)].[9] The ionization of cyclobutylmethanol (**8**) using SbF_5/SO_2ClF at −78 °C, on the other hand, gave only the Lewis acid−base complex **9**, as evident from its ^{13}C NMR spectrum (δ ^{13}C 84.0, 33.4, 24.5, 18.8). Upon warming to −60 °C, a clean spectrum characteristic of the equilibriating 1-bicyclo(4.4.0)dec-1-yl cation (**10**) was formed (δ ^{13}C 200, 44.9, 26.2). The characterization of the cation was achieved by comparison of its NMR spectrum with that of the authentically synthesized carbocation, **10**, by the reaction of the bicyclo(4.4.0)dec-1,4-ene with Magic Acid (1:1 FSO_3H + SbF_5) in sulfuryl chloride fluoride at −78 °C (Scheme 1).

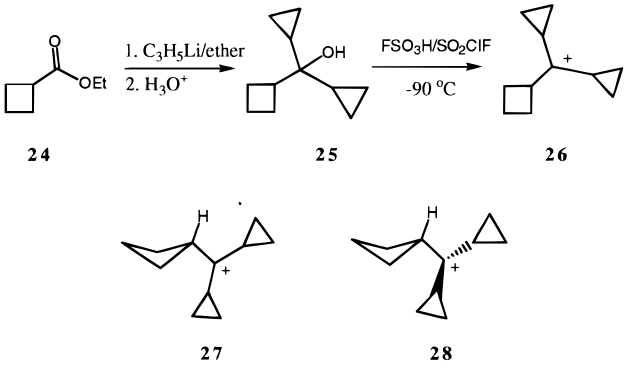
The unexpected formation of the 1-bicyclo[4.4.0]decan-1-yl cation (**10**) from cyclobutylmethanol can be explained by the mechanism shown in Scheme 2. The dehydrative dimerization of cyclobutylmethanol gives the 1-(cyclobutylethyl)cyclobutyl cation (**11**) which undergoes a series of Wagner−Meerwein rearrangements and 1,2-hydride shifts to give the bicyclo[4.4.0]-decan-1-yl cation (**10**).

We have subsequently turned our attention to expectedly more stable secondary and tertiary cyclobutylmethyl cations. The ionization of 1-cyclobutylethanol (**16**), cyclobutylphenylmethanol (**17**), and cyclobutylcyclopropylmethanol (**18**) using SbF_5/SO_2ClF gave again only the corresponding ring-expanded cations, 1-methylcyclopentylium (**19**), 1-phenylcyclopentylium (**20**), and 1-cyclopropylcyclopentylium (**21**) carbocations. Persistent secondary cyclobutylmethyl cations could not be observed under the reaction conditions employed, apparently due to the large driving force for ring expansion associated with neighboring group participation of the cyclobutyl ring. The reaction of cyclobutyldimethylmethanol (**22**) in superacidic media also resulted in the clean formation of the rearranged carbocation, the 1,2-dimethylcyclopentylium cation (**23**) (Scheme 3). The NMR spectra are consistent with those reported for the cyclopentyl cations.[10]

Scheme 3. Attempted Preparation of Some Secondary and Tertiary Cyclobutylmethyl Cations



Scheme 4. Preparation of the Cyclobutyldicyclopropylmethylium Cations



To overcome ring expansion to thermodynamically preferred cyclopentyl cations, we next considered more stabilized examples, such as the cyclobutyldicyclopropylmethyl cation (**26**) which was, indeed, formed without competing ring expansion. Cyclobutyldicyclopropylmethanol (**25**, δ ^{13}C 70.5 (C−OH), 46.1 (C1-cb), 23.3 (C2, C4-cb), 17.8 (C3-cb), 16.6 (Cα-cp), −0.2 and −1.0 (Cβ-cp)) was synthesized through the reaction of ethylcyclobutanecarboxylate (**24**) with cyclopropyllithium. The alcohol was transformed into the tertiary carbocation **26** using fluorosulfuric acid (FSO_3H) in sulfuryl chloride fluoride at −90 °C (Scheme 4).

The ^{13}C NMR spectrum of ion **26**, obtained at −80 °C, shows the following absorptions: δ ^{13}C 275.9 (C+), 44.3 (d, J = 139.2 Hz, C1), 39.6 (d, J = 177 Hz, Cα), 36.6 (t, J = 170.8 Hz, Cβ), 32.2 (d, J = 172.0 Hz, Cα'), 31.5 (t, J = 171.8 Hz, Cβ'), 29.3 (t, J = 142.0 Hz, C2, C4), 17.1 (t, J = 137.4 Hz, C3). The carbocationic center (at δ ^{13}C 275.9) is strongly deshielded and is very similar to that of the tricyclopropylmethylium cation (δ ^{13}C 280.5) and dicyclopropylmethyl cation (δ ^{13}C 253.0). Ion **26**, in analogy with these and other related static tertiary

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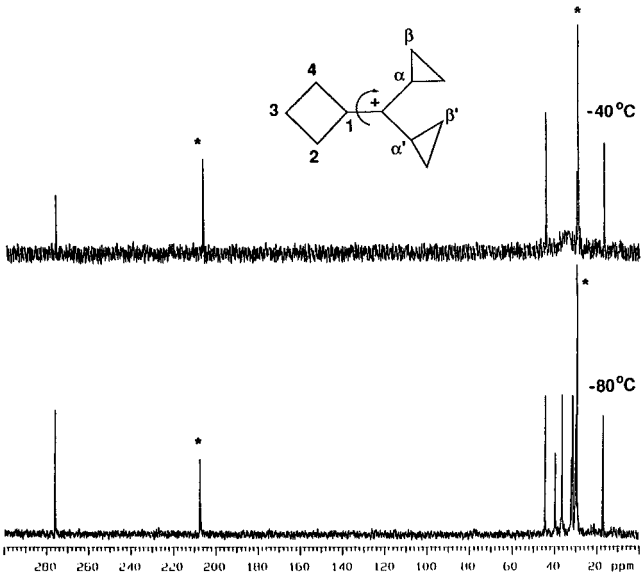

Figure 1. 75 MHz proton decoupled ^{13}C NMR spectra of cyclobutyldicyclopropylmethyl cation (**26**) in FSO_3H/SO_2ClF at −40 and −80 °C; * denotes acetone-d_6 signals.

carbocations,[10] is substantially trivalent (classical) in nature, with the expected delocalization into the cycloalkyl rings. The classical nature of the carbocation **26** is also inferred from the ^{13}C NMR chemical shift additivity criterion.[11] The summation of the chemical shifts for all the carbons of **26** is 611.3. The sum of the chemical shifts for the parent hydrocarbon, cyclobutyldicyclopropylmethane (estimated from that of its alcohol by subtraction of 50 ppm, a usual increment for an OH substitution), is 161.8. The difference in chemical shift, 449.5 ppm, is similar in magnitude, for example, to that of the static nortricyclylmethyl cation ($\Delta\delta = 470$) and is substantially greater than that for the σ-delocalized cyclopropylmethyl cation ($\Delta\delta = 283$). The ^{13}C NMR data also show that the carbocation exists in solution mainly as the C_s symmetric bisected conformer (**27**). The perpendicular conformation of the cation would show identical chemical shifts for the Cα and Cα′ carbons, as well as the Cβ and Cβ' carbons of the cyclopropyl ring, whereas the bisected conformer, being C_s symmetric, would show distinct chemical shifts for the Cα and Cα′ carbons and the Cβ and Cβ' carbons, as observed in the present work. Theoretical calculations are also consistent with this assignment (vide infra).

The distinct chemical shifts for the cyclopropyl methine and methylene carbons at −80 °C is indicative of the absence of the C1−C$^+$ free rotation on the NMR time scale.[12] To estimate the rotational barrier, we have carried out variable-temperature NMR studies of the carbocation. When the solution was warmed from −80 to −40 °C, the signals for the cyclopropyl methine (Cα and Cα′) and methylene (Cβ and Cβ') carbons merged into the baseline (Figure 1). The carbocation was not stable at higher temperatures and new unidentified absorptions appeared at −10 °C. Considering −40 °C to correspond to the coalescence temperature of the signals, the free energy of activation ($\Delta G^{\ddagger}$) for the rotational barrier around the C1−C$^+$ bond was calculated as 11.0 ± 0.5 kcal/mol at −40 °C.[13] The barrier is comparable to that of the α,α-dimethylcyclopropylmethyl cation (13.7 kcal/mol at −21 °C)[14] and suggests that although the carbocation **26** is a trivalent (classical) ion, it involves significant σ-participation from the adjacent cycloalkyl rings.

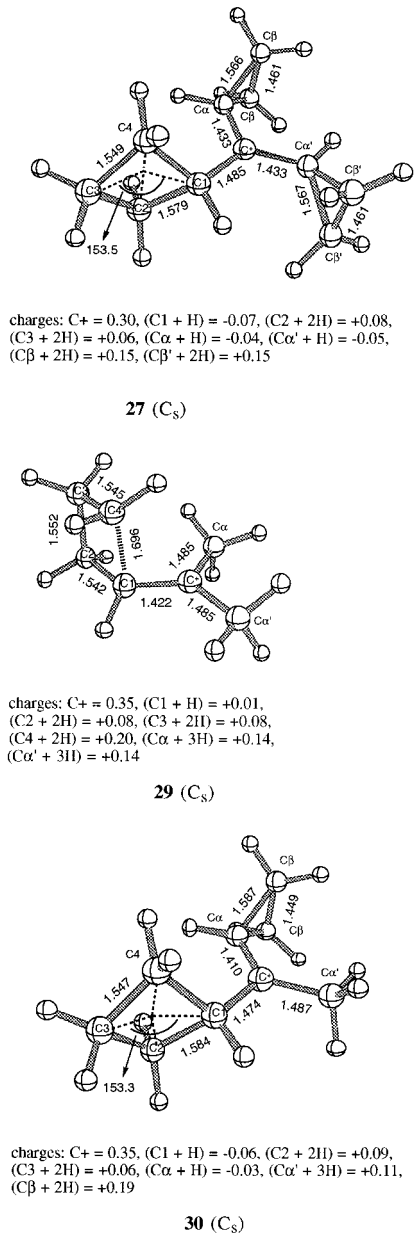

Figure 2. B3LYP/6-31G* optimized structures and NBO charges (given as sum of the charges at the carbon and pendant hydrogens) of **27**, **29**, and **30**.

We have also calculated the structures of the α,α-dimethylcyclobutylmethyl cation (**29**), the α-methyl α-cyclopropylcyclobutylmethyl cation (**30**), and the perpendicular (**28**) and bisected (**27**) conformations of the cyclobutyldicyclopropylmethyl cations using the ab initio Hartree−Fock (HF)[15] and density functional theory (DFT) methods.[16] The calculated structures for **27** and **29** are shown in Figure 2. The parent cyclobutylmethyl cation is not a minimum on the potential energy surface at the B3LYP[17]/6-31G* levels and spontaneously

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Table 1. Calculated (at the IGLO DZ//B3LYP/6-31G* level) and Experimental ^{13}C NMR Data for **27** and **29**

ion		C1	C2	C3	C4	C^+	Cα	Cα′	Cβ	Cβ′
27	IGLO	34.8	27.4	15.5	27.4	300.0	32.4	25.0	34.0	30.7
	exptl	44.3	29.3	17.1	29.3	275.9	39.6	32.2	36.6	31.5
29	IGLO	64.7	14.0	10.7	37.8	280.6	30.7	35.2		
30	IGLO	44.6	29.7	14.7	29.7	310.1	39.3	31.5	42.6	42.6

rearranged to the cyclopentyl cation. The α,α-dimethylcyclobutylmethyl cation (**29**) and the α-methyl α-cyclopropylcyclobutylmethyl cation (**30**) are stationary points at the B3LYP/6-31G* level. The B3LYP/6-31G* optimized geometry of **29** shows that the C1−C4 bond is elongated to 1.696 Å. Thus, a partially charge-delocalized system is indicated for this system. Atomic charges of **27**, **29**, and **30** were also calculated (Figure 2) using the natural bond orbital analysis (NBO)[18] method. The charge calculations show that the cyclobutyl group of **29** (+0.37 au) bears significantly more positive charge than that of **27** (+0.15 au) or **30** (+0.18 au).

The bisected conformation of the cyclobutyldicyclopropylmethyl cation **27** (C_s symmetry) is a stationary point at the B3LYP/6-31G* level. The calculated structure shows a C1−C2 bond length of the cyclobutyl ring of 1.579 Å, slightly elongated as compared to the C2−C3 bond (1.549 Å). The Cα−Cβ and Cα′−Cβ′ bond lengths of the cyclopropyl rings are 1.566 and 1.567 Å, respectively. The Cα−C^+ and Cα′−C^+ bond lengths (both 1.433 Å) are slightly shorter than the C1−C^+ bond length (1.485 Å). The carbocation adopts a propellar conformation, which is ideal for the partial delocalization of the charge into the cyclopropyl and cyclobutyl rings. The IGLO calculated ^{13}C NMR chemical shifts for the bisected conformer **27** (IGLO DZ//B3LYP/6-31G*) are in accord with the experimental values, and they facilitate the ready assignment of the ^{13}C NMR chemical shifts for the carbocation. Table 1 summarizes the experimental and/or theoretical ^{13}C NMR data for the carbocation **26** (in the bisected conformation **27**), **29**, and **30**. Carbocation **29** involves significant charge delocalization into the cyclobutyl ring, as revealed by its structure and its IGLO calculated ^{13}C NMR chemical shifts. The carbocation center is slightly shielded compared with that of **27**, and the C1 and C4 carbons are much deshielded, implying charge delocalization into the cyclobutyl ring. The carbocation center of **30** is slightly deshielded compared with that of **27**.

The perpendicular conformation of the cyclobutyldicyclopropylmethyl cation (**28**) is not a minimum on the potential energy surface at the B3LYP/6-31G* level, and it collapsed into the bisected conformation **27** spontaneously. The perpendicular conformation is, however, a minimum at the Hartree−Fock HF/3-21G level. At this level, the bisected (**27**) conformer was found to be 3.43 kcal/mol more stable than the perpendicular (**28**) conformer. However, the experimentally estimated barrier for the interconversion of these conformers, 11.0 ± 0.5 kcal/mol at −40 °C, is significantly high, which explains the observation of only one conformer at −80 °C.

Conclusions

In summary, it was found that cyclobutylmethyl cations readily undergo ring expansion−rearrangement to give the corresponding cyclopentyl cations. Attempts to observe persistent (long-lived) cyclobutylmethyl cations in superacidic media even at low temperature were not successful. The more stabilized (delocalized) cyclobutyldicyclopropylmethyl cation (**26**), however, was found stable at −80 °C. From the ^{13}C NMR data (experimental and the IGLO calculated values) the carbocation was shown to exist in the C_s symmetric bisected conformation. The observed rotational barrier around the C−C^+ bond of 11.0 ± 0.5 kcal/mol at −40 °C implies that there is significant charge delocalization into the cycloalkyl rings, but the carbocation is predominantly of trivalent (classical) carbocationic nature, as revealed by the NMR data and the theoretical calculations.

Experimental Section

Diethyl ether was distilled from sodium−benzophenone ketyl immediately before use. Lithium metal, cyclopropyl bromide, ethylcyclobutane carboxylate, methyllithium, $LiAlH_4$, and phenyllithium were obtained from Aldrich Chemical Co. and were used as received. SbF_5 and FSO_3H were freshly distilled before use. ^1H and ^{13}C NMR spectra were recorded on a Varian Unity-300 instrument equipped with a variable-temperature probe. ^1H and ^{13}C NMR spectra were obtained with respect to tetramethylsilane (TMS) by using an acetone-d_6 capillary as external standard.

Preparation of Cyclobutyldicyclopropylmethanol. Lithium wire (sodium content 1%, 0.4 g, 57 mmol) was hammered into shiny plates and was placed into 50 mL of ether contained in a 100-mL three-necked round-bottom flask equipped with a magnetic stirrer, reflux condenser, an addition funnel, and a nitrogen inlet. The flask was cooled to 0 °C, and cyclopropyl bromide (2.3 g, 19 mmol, 1.2 equiv) was added dropwise to the contents at such a rate as to maintain gentle reflux. The solution was stirred at this temperature for 30 min. Ethylcyclobutane carboxylate (1.02 g, 8 mmol) dissolved in 10 mL of ether was then added dropwise, and the reaction mixture was stirred for 2 h at room temperature. After it was quenched with 100 mL of water, the mixture was extracted with ether (2 × 50 mL). The ether layers were washed with saturated sodium bicarbonate (50 mL) and dried ($MgSO_4$), and the solvents were rotary evaporated. Cyclobutyldicyclopropylmethanol (1.33 g, 80%) was obtained after purification of the residue by column chromotography (silica gel), eluting with 1:1 dichloromethane and ether. ^{13}C NMR: δ 70.5 (s), 46.1 (d), 23.3 (t), 17.8 (t), 16.6 (d), −0.2 (t) and −1.0 (t). ^1H NMR: δ 2.5 (m, 1H), 1.6−2.2 (m, 6H), 0.9 (s, 1H), 0.7 (m, 2H) and 0.2−0.5 (m, 8H).

Preparation of Ion. To a slurry of the appropriate precursor (ca. 30 mg) in SO_2ClF (ca. 0.5 mL) in a 5 mm NMR tube cooled to −80 °C (dry ice/acetone slurry) was added the needed quantity of neat FSO_3H in SO_2ClF (see text). The ensuing mixture was vigorously stirred (Vortex agitator) while cooled prior to transfer to a precooled NMR probe.

Calculational Methods. Ab Initio calculations were performed with the GAUSSIAN-94[19] package of programs. Atomic charges were obtained using the natural bond orbital analysis (NBO)[18] method (Figure 2). IGLO calculations were performed according to the reported method[20] at IGLO DZ level.

Acknowledgment. Support of our work by the National Science Foundation is gratefully acknowledged.

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