Observation of a Stable Carbocation in a Consecutive Criegee Rearrangement with Trifluoroperacetic Acid

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Received November 9, 1999

Selective oxidative cleavage−cyclization of adamantane through the bridge carbon was developed in trifluoroperacetic acid (TFPAA). The methyl group in the bridge position was found to be the substituent that directs consecutive oxygen insertion into the cage structure during the course of a Criegee rearrangement. The formation of stable 5-methyl-4,6-dioxabishomoadamant-5-yl cation at −25 °C was observed. Stable carboxonium ion formation allows control of the selectivity of further transformations. Hydrolysis leads to the stereospecific formation of *endo,endo*-3-hydroxy-7-acetoxybicyclo[3.3.1]nonane. Its single-crystal X-ray structure was obtained. An increase in temperature results in deprotonation of the 5-methyl-4,6-dioxabishomoadamant-5-yl cation to *endo*-3-trifluoroacetoxybicyclo[3.3.1]non-6-ene, which undergoes further epoxidation with TFPAA and acidic transannular cyclization in trifluoroacetic acid (TFAA). The described reactions can be used as a convenient method for the synthesis of bicyclo[3.3.1]nonane and oxaadamantane derivatives. The proposed mechanism for each transformation, as well as supporting ab initio theoretical calculations of the strain energy and the stabilization energy of the relevant oxacage structures, are discussed.

Introduction

Criegee[1] proposed the ionic rearrangement of alkyl and aryl hydroperoxy esters long after the discovery of the Baeyer−Villiger reaction.[2] Peroxy esters, as the key intermediates in the Criegee rearrangement, can be usually synthesized from the corresponding hydroperoxides.[3] The hydroperoxides could also be formed from ketones[4] or aldehydes,[4] as well as from alcohols,[5] acetals,[6] and ketals.[7−9] (i.e., from any reaction involving the formation an intermediate carbocation in the presence of a peracid as nucleophile.) Although carboxonium ions[10]are well-known species in the Criegee rearrangement, such cations were obtained only in superacids.[11] It has also been shown[12] that carboxonium ions could be synthesized from ortho esters in trifluoroacetic acid (TFAA). However, the literature[10] has not revealed any examples of carboxonium ion formation during consecutive oxygen insertion in Criegee rearrangements. Sequential O-insertion[13−15] for ketones or aldehydes in the Baeyer−Villiger reaction has never been reported (Scheme 1). Nevertheless, the reaction of ketals[9] with peracids indicates the possibility of sequential O-insertion (it is more accurate to refer to the O-insertion to ketals as a double Criegee rearrangement, rather than "double Baeyer−Villiger oxidation"[9a,b]) in the Criegee rearrangement.

The motivation to develop a new option for observing consecutive Criegee (Scheme 1) rearrangements of alcohols emerged from our previous studies on adamantane oxidation with trifluoroperacetic acid.[16] The formation of oxaadamantanes (Scheme 2) from 2-methyl-2-hydroxyadamantane (**1**) could be considered a result of at least two O-insertions, with a consecutive cleavage−cyclization to oxaadamantane **2** and 2-oxa-*exo*-adamantan-4-ol (**3**).

The mechanism of this complex reaction is not well understood. A review of the literature suggested that the most probable pathway included the intermediate formation of an orthocarbonate (i.e., a triple insertion product). This would parallel the known double Criegee rearrangement of ketals,[9] which proceeds through the corresponding ortho esters and, ultimately, to oxacycloalkanes. If

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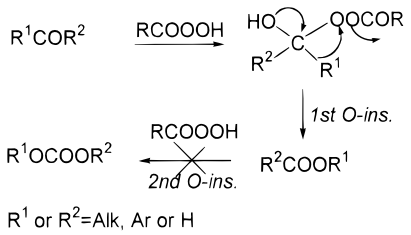
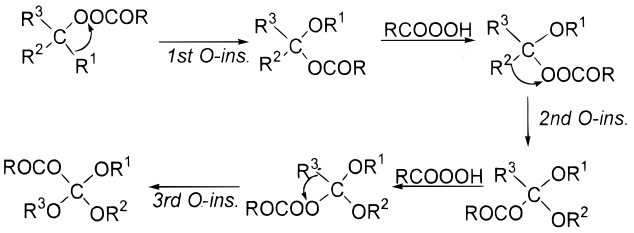
10.1021/jo991745u CCC: $19.00
Published on Web 05/26/2000

Scheme 1

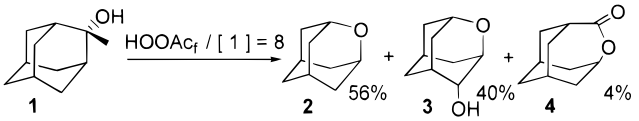


Baeyer-Villiger reaction



Sequential Criegee rearrangements

Scheme 2



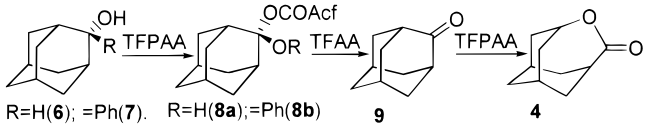
the web of O-insertion reactions from **1** to **2** and **3** could be untangled, a new controllable pathway of bicyclo[3.3.1]-nonane[17] and oxaadamantane[18] synthesis could be achieved.

It is noteworthy that, despite extensive research on the Baeyer−Villiger reaction with trifluoroperacetic acid (TFPAA),[15,19,20] a detailed understanding of Criegee rearrangements in trifluoroacetic acid (TFAA) is very limited. This situation remains despite the well-recognized electronegative character of the trifluoroacetyl group and the highly acidic conditions that should facilitate consecutive O-insertion.[15] Historically, the experiments were mostly performed with TFPAA[15] in the presence of phosphates. These conditions severely restricted the multiple insertions of oxygen by decreasing acidity and, thereby, reducing the possibility of carbocation formation, and minimal peroxy ester formation. The current use of TFPAA in TFAA offers promise for more extensive O-insertion.

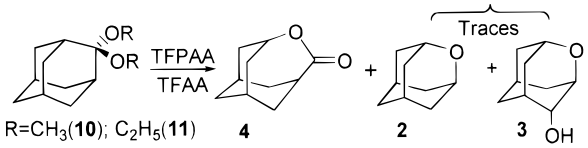
Results and Discussion

When adamantan-2-ol (**6**) and 2-phenyladamantan-2-ol (**7**) reacted with TFPAA in TFAA, lactone **4**[16] was formed in a good yield. This observation indicated that the first O-insertion was directed to the C^2−H bond in **6** and to the C^2−Ph bond in **7**. The intermediate hemiketals **8a** and **8b** do not survive under these acidic conditions, and the resulting adamantanone (**9**) undergoes a Baeyer−Villiger reaction to the stable lactone **4** (Scheme 3). Similar behavior of **9** and its derivatives has been repeatedly described.[20,21] No further O-insertion (except

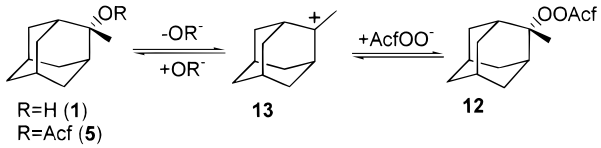
Scheme 3



Scheme 4



Scheme 5



C−H-oxidation) was observed, even in an excess of TFPAA.

An attempt to achieve an analogous double Criegee insertion through the dimethylketal **10** and diethylketal **11** using a procedure previously described for diethylketals[9] was unsuccessful (Scheme 4). It was shown that the ketals **10** and **11** are not stable in pure TFAA or in CH_2Cl_2 (with phosphate) due to ketal collapse to adamantanone (**9**) and further oxidation to the lactone **4**. Nevertheless, traces of oxaadamantanes **2** and **3** (from diethylketal **11**) were observed.

To avoid adamantanone (**9**) formation and to direct the O-insertion process into the cage structure, 2-methyladamantan-2-ol (**1**) and its trifluoroacetate **5** were used as model compounds. The CH_3-group was found to "block" the undesired Baeyer−Villiger reaction. Previous studies on the migratory ability of alkyl and aryl groups in acid-catalyzed Baeyer−Villiger reactions[15,22a,b] and in Criegee rearrangements[15, 22c]suggest the use of a methyl as the group least subject to rearrangement.

Trifluoroperacetate **12,** which could be formed from alcohol **1** and trifluoroacetate **5** through the intermediate carbocation **13**, is the obvious intermediate for O-insertion[15,22c] (Scheme 5). It was also found that the trifluoroacetate **5** is more reactive than alcohol **1**.

Reactions of 2-Methyladamantan-2-ol (1) and 2-Methyladamantan-2-ol Trifluoroacetate (5) with TFPAA. After the alcohol **1** was oxidized with an 8-fold excess of TFPAA in TFAA, the reaction mixture was analyzed by GC/MS. The structures and distribution of products are outlined in Scheme 2. Oxaadamantanes **2** and **3** are clearly products of sequential O-insertion into the cage structure. The formation of small amounts of **4** was evidence for a parallel O-insertion into the C^2−CH_3

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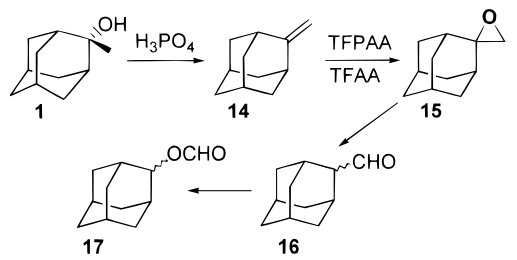
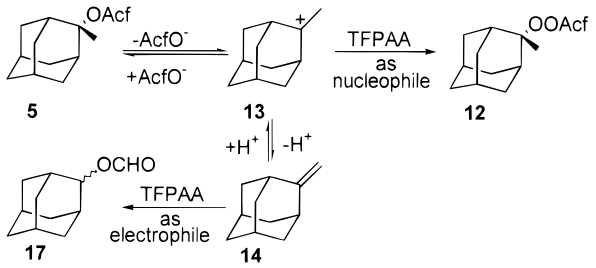
Scheme 6



Scheme 7



bond, with subsequent ketal hydrolysis to the intermediate ketone **9**. When this reaction was conducted at a 1:8 molar ratio of trifluoroacetate **5** to TFPAA, the only difference from the previous experiment was the formation of traces (2%) of 2-adamantyl formate (**17**).

^{1}H NMR analysis of the trifluoroacetate **5**/TFAA reaction mixture indicated the presence of terminal methylene protons ($\delta = 4.2$) and revealed 2-methyleneadamantane (**14**) as an intermediate. Independently prepared olefin **14**[23] and oxirane **15**,[24]when treated with TFPAA in TFAA, also gave formate **17** in good yields (Scheme 6). The intermediate formation of aldehyde **16** was also detected by GC/MS analysis of the crude reaction mixture. Similar oxirane isomerization has been the subject of an independent investigation.[25]

Despite only traces of olefin **14** in the reaction mixture at any time, the entire sequence can pass through this route (Scheme 7) by reaction with TFPAA. The optimal environment for this diversion is to maintain a low concentration of TFPAA. Under these conditions, the concentration of TFPAA is insufficient to generate the Criegee perester **12** and deprotonation to **14** can occur. TFPAA leads to a rapid epoxidation of olefin **14** on the pathway to the formate **17** (Scheme 7). It was found that by lowering the temperature and increasing of the concentration of TFPAA, the diversionary process can be avoided and the reaction redirected to generate the Criegee perester **12**. For example, when trifluoroacetate **5** was reacted at −25 °C with a 20-fold excess of TFPAA, the quantitative formation of carbocation **21** (as a result of the double O-insertion) was observed in situ by ^{1}H NMR and ^{13}C NMR (Scheme 8). The experimental chemical shifts of **21** were in good agreement with the ab initio calculations. Cation **21** is stable for 24 h at −25 °C in TFAA/TFPAA, but when the reaction temperature is increased, a rearrangement occurred to generate the final oxacage compounds **2** and **3** within 2 h at 0 °C or within 1 h at 20 °C. In contrast, the removal of TFPAA and TFAA at −25 °C in vacuo led to the *endo*-3-acetoxybicyclo-[3.3.1]non-6-ene (**18**) (i.e., cation **21** is stable only in the solution under strong acidic conditions). It is, therefore, necessary to remove the TFPAA and TFAA from the reaction to isolate the intermediate **18** (i.e., on the pathway from **21** to the final products **2** and **3**). The isolation of the olefin **18** was successfully achieved in good yield by adding Na_2HPO_4 to the reaction mixture and reducing the peroxides with $(CH_3)_2S$ in CH_2Cl_2. The reaction of olefin **18** with TFPAA in TFAA led to the formation of **2** and **3** with the same ratio as observed in the original reaction. Ab initio computations indicate that the direct rearrangement of **21** to **20** has about a 28 kcal/mol barrier (at B3LYP/6-31G*), which makes this an improbable process. This is consistent with the experimentally observed olefin **18** formation.

Elimination of $\mathbf{Ac}^+$ from cation **20**, as well as from the cation generated on the pathway from **19** to **3**, was supported by ^{19}F NMR and ^{1}H NMR analysis of the reaction products formed after the generation of the oxacage compounds **2** and **3**. The CH_3 ($\delta = 2.3$ ppm) and the CF_3 ($\delta = -71.8$ ppm) singlets observed in NMR spectra of the reaction mixture match acyltrifluoroacylperoxide $CH_3(CO)OO(CO)CF_3$. The latter was independently prepared by the reaction of acetyltrifluoroacetyl anhydride with TFPAA. This peroxide could be formed only by the reaction of $\mathbf{Ac}^+$ with TFPAA. This also negates the possible formation of an intermediate **29** from a triple O-insertion. The decomposition of **29** should produce methyltrifluoroacetate or methyltrifluoroperacetate (Scheme 9), which were not detected in the reaction mixture.

This observed pathway distinguishes the described approach from the earlier reaction of ketals with *m*-chloroperbenzoic acid[9] in dichloromethane. The polar, and acidic, reaction medium in the current study apparently stabilized the intermediate double O-insertion carbocation **21**, which explains the resistance to subsequent orthocarbonate formation. It is apparent that carbocation stability decreases the possibility of a further oxygen insertion through the perester **25**.

The presence of carbocation **21** allows transformation to other products. For example, quenching of **21** with water led to the stereoselective formation of *endo,endo*-3-hydroxy-7-acetoxybicyclo[3.3.1]nonane (**27**) in 90% yield.

The stereochemistry of **27** was proved by X-ray structure analysis (Figure 1). The observed stereochemistry of **27** can be explained by the intermediate formation of hydroxyorthoacetate **26**, which could be specifically cleaved by protonation on the ether oxygen. Acetates **27** and **28**, as well as **18** (Scheme 8), were easily transformed to oxadamantane in sulfuric acid.[18,26]

It is useful to identify the synthetic opportunities. Stabilization of the intermediate carbocation **21** at low temperature provides the possibility to guide the reaction toward alternative pathways. For example, the olefin **18** could be obtained selectively when the reaction mixture was quenched with Na_2HPO_4 and $(CH_3)_2S$. If the reaction mixture was added to a suspension of Na_2HPO_4 in CH_2Cl_2 the alcohol **3** could be obtained in a good yield. When the reaction mixture was treated with water the acetate **27** was formed, which can be selectively transformed to the oxaadamantane **2**.

Structure of the 5-Methyl-4,6-dioxabishomoadamant-5-yl Cation (21). Theoretically, three double O-

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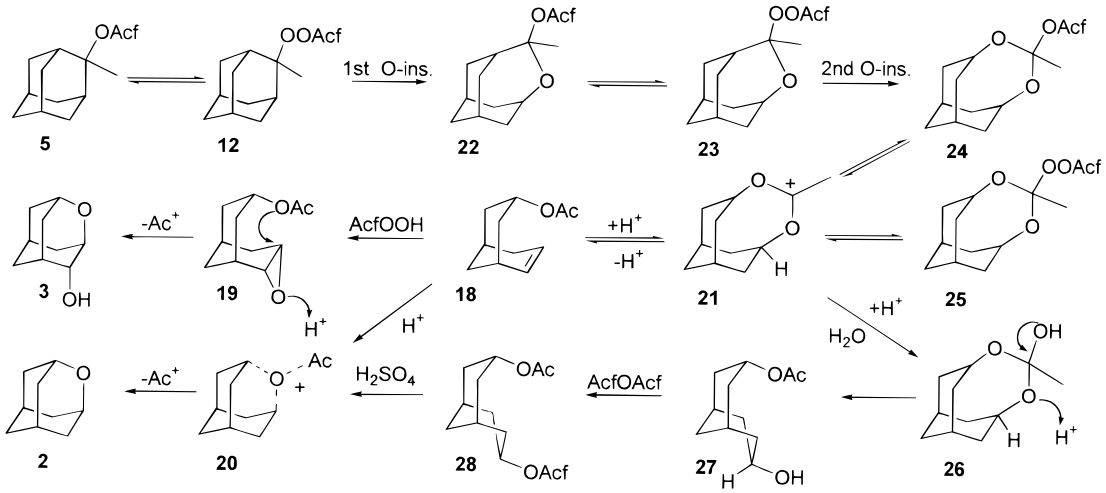
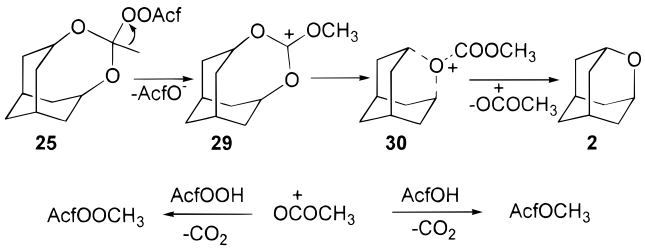
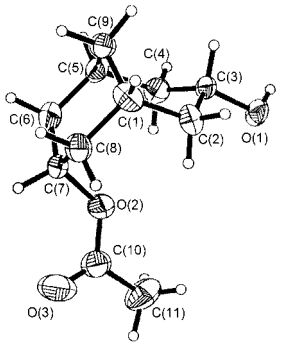
Scheme 8



Scheme 9





Selected Bonds Lengths [A]:

C(1)-C(2)	1.547(4)	C(1)-C(9)	1.525(5)
C(2)-C(3)	1.511(4)	C(5)-C(9)	1.521(5)
C(3)-C(4)	1.506(4)	C(3)-O(1)	1.436(4)
C(4)-C(5)	1.557(4)	C(7)-O(2)	1.469(4)
C(5)-C(6)	1.531(5)	C(10)-O(2)	1.333(4)
C(6)-C(7)	1.512(5)	C(10)-C(11)	1.496(5)
C(7)-C(8)	1.514(5)	C(10)-O(3)	1.199(4)
C(1)-C(8)	1.532(4)		

Selected Angles [0]:

C(9)-C(1)-C(8)	107.9(3)	C(9)-C1)-C2)	110.7(3)
C(8)-C(1)-C(2)	113.7(3)	C(3)-C(2)-C(1)	112.0(3)
C(2)-C(3)-O(1)	108.8(2)	C(4)-C(3)-C(2)	111.3(3)
C(3)-C(4)-C(5)	112.5(3)	C(9)-C(5)-C(4)	109.9(3)
C(7)-C(6)-C(5)	115.5(3)	O (2)-C(7)-C(6)	106.7(3)
C(7)-C(8)-C(1)	114.6(3)	C(5)-C(9)-C(1)	109.0(3)
O(3)-C(10)-C(11)	125.4(4)	C(10)-O(2)-C(7)	118.5(3)
C(9)-C(5)-C(6)	107.5(3)	O (2)-C(7)-C(8)	110.6(3)
C(4)-C(5)-C(6)	114.1(3)	C(6)-C(7)-C(8)	114.0(3)
O(1)-C(3)-C(4)	110.9(3)	O(3)-C(10)-O(2)	123.4(3)
C(3)-C(4)-C(5)	112.5(3)	O(2)-C(10)-C(11)	111.2(3)

Figure 1. Thermal ellipsoid plot of *endo,endo*-7-acetoxy-3-hydroxybicyclo[3.3.1]nonane (**27**).

insertion products (cation **21**, trifluoroacetate **24**, and trifluoroperacetate **25**) are possible intermediates on the way from the perester **23** to the final products (Scheme 8). The ^{13}C NMR spectra of the reaction mixture at −25 °C show only six high-field signals of the carbon atoms, which can be assigned to the C_{2v} symmetry of the cage fragment. However, this spectrum could result from the fast exchange of the trifluoroperacetate and trifluoroacetate groups in **24** and **25**. To further explain the ^{13}C NMR spectra, structures **21**, **24**, and **25** were computed at the GIAO-B3LYP/6-311+G(2d,p) level for B3LYP/6-31G*-optimized geometries[27] (Figure 2). The calculated ^{13}C NMR chemical shifts for cation **21** are in reasonable agreement with the experimental spectrum (Table 1).

The most characteristic shift is the C^5 carbon atom (experimental: δ 181.2 ppm, calculated: δ 191.1 ppm). Such a high-field shift in the ^{13}C NMR spectrum is evidence for the stable cation **21** (in trifluoroacetic acid at −25 °C). Previously described NMR data on carboxonium ions[12,28] are also in a good agreement with our NMR data.

Strain Destabilization Energy (DE). It is predictable that the O-insertion into the cage structure of the adamantane **31** would increase the strain due to ring enlargement.[29] To obtain a more accurate estimate for this assumption, ab initio (HF) and Becke's gradient-corrected hybrid 3-parameter exchange (B3LYP)[30] functionals as implemented in a Gaussian 94 program were employed.[27] Oxaadamantane (**2**), 4-oxahomoadamantane (**32**), and 4,6-dioxabishomoadamantane (**33**) served as a model oxacage compounds. Since only unstrained reference compounds were involved, eqs 1−5 gave the strain energies directly. The strain energy of adamantane (**31**) and homoadamantane (**34**) are close to the values obtained earlier via an increment scheme[31]or via isodesmic equations at the BLYP level.[32] Replacing the methylene group in adamantane (**31**) and homoadamantane (**34**) by oxygen does not increase the strain energy significantly (5.7 vs. 6.4 kcal/mol for adamantanes and 14.8 vs. 12.6 for homoadamantanes). Thus, it can be assumed that CH_2 and O contribute about the same to the strain energies in this model.

While oxaadamantane **2** is more strained than adamantane (**31**), homoadamantane (**34**) is more strained then 4-oxahomoadamantane (**32**) due to a decrease in the bridge size in the latter. If the first O-insertion [(**31**) to (**32**)] resulted in DE1 = 6.9 kcal/mol, the second insertion

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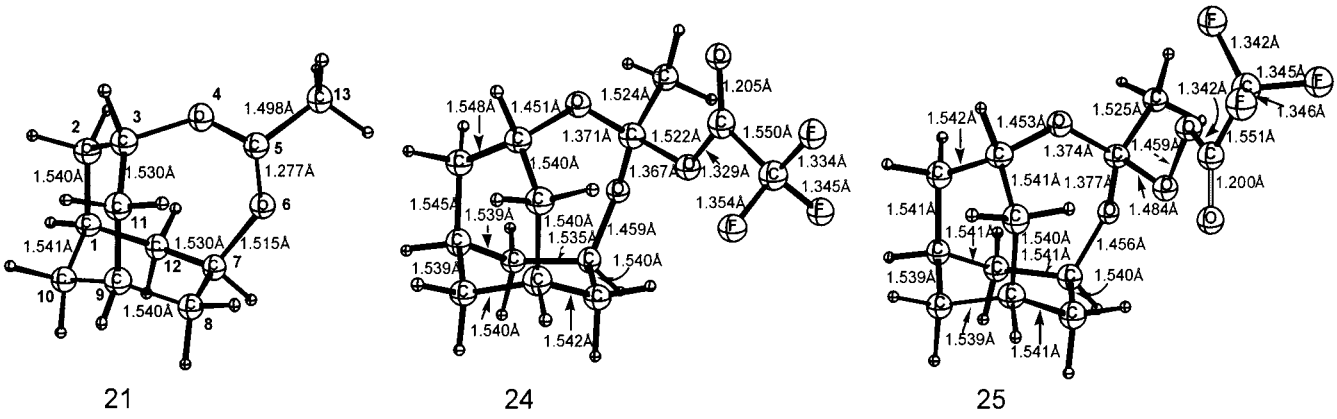
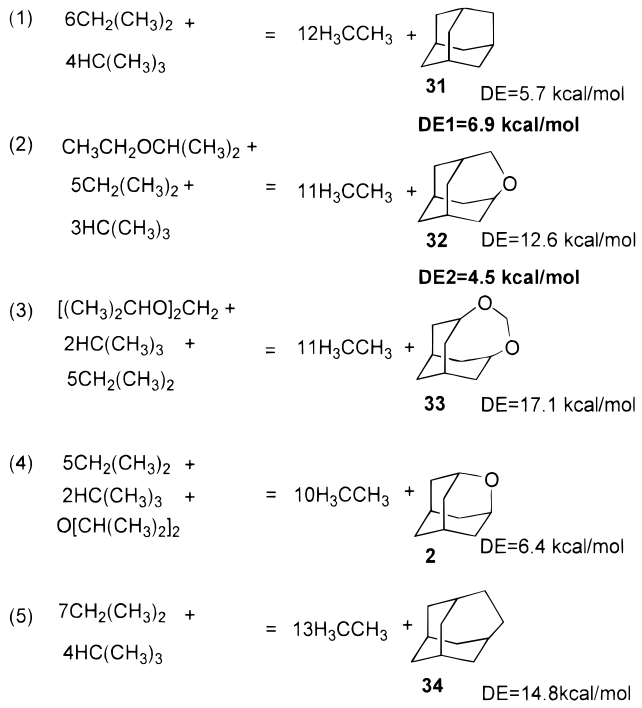


Figure 2. B3LYP/6-31G*-optimized geometries of 5-methyl-4,6-dioxabishomoadamant-5-yl cation (**21**), 5-methyl-4,6-dioxabishomoadamant-5-yl trifluoroacetate (**24**), and 5-methyl-4,6-dioxabishomoadamant-5-yl trifluoroperacetate (**25**).

Table 1. Experimental and Calculated ^{13}C NMR Shifts at GIAO B3LYP/6-311G+ (2d,p) Level

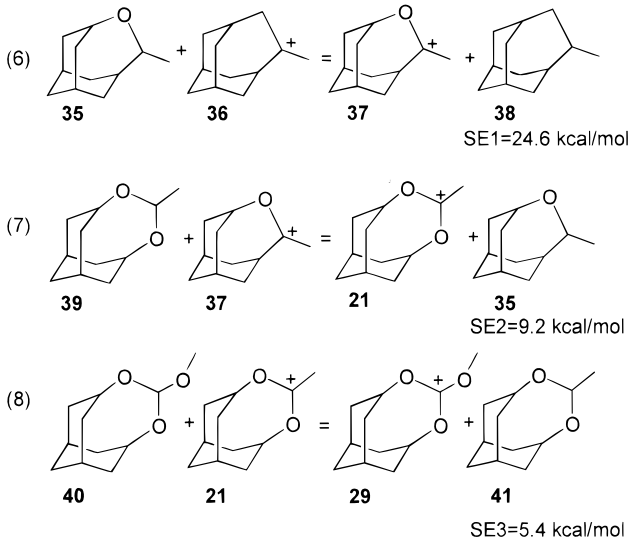
		calculated		
no. of carbons	observed	cation **21**	trifluoroacetate **24**	trifluoroperacetate **25**
1	28.4	25.7	30.7	30.6
2	33.1	39.3	40.5	42.2
3	89.6	98.8	75.0	75.7
5	181.2	191.1	128.3	127.8
7	89.6	98.8	78.3	76.7
8	33.1	39.3	36.6	39.5
9	28.4	25.7	30.7	30.7
10	22.9	33.2	38.8	38.6
11	33.1	39.3	43.3	41.9
12	33.1	39.3	37.8	36.4
13	19.1	27.1	31.1	30.1

[(**32**) to (**33**)] gives DE2 = 4.5 kcal/mol (eq 1−3). This supported the observation that monoinsertion intermediates **22** or **23** could not be isolated under stepwise oxygen insertion conditions (Scheme 8).



O-Electron Stabilization Energy (SE). It is apparent that the strain increase in the reactions of O-insertion into the adamantane structure is compensated by the additional stabilization of the carbocations SE by electrons on oxygen atoms attached to C^5-cation center. This stabilization is definitely apparent in the ab initio optimized geometry of the carboxonium ion **21** (Figure 2). The C^5−O,^{4} C^5−O^6 bond distances are 1.28 Å, which is close to a 1.5-bonded CO-group. The length of the C^3−O,^{4} C^7−O^6 bonds is 1.51 Å, which is 0.10 Å longer than the average C−O-bond for ethers.[33]

To get an estimate of the electronic SE for the three possible levels of O-insertion, the set of hydride exchange isodesmic reactions (eq 6−8) were computed at the B3LYP/6-31G* level. The reaction energies for these model reactions show a significant stabilization energy for carbocations, which have an attached oxygen atom. Equation 6 shows the additional stabilization by one oxygen atom, where eqs 7 and 8 reflect the additional incremental stabilization energy when a second and third oxygen atom are present. Calculations for these reactions indicate the rapid saturation of stabilization by consecutive O-insertion. Thus, the first O-insertion gives a higher SE (24.6 kcal/mol) stabilization effect than the second (9.2 kcal/mol). The third O-inserted carbocation intermediate has a much smaller SE (eq 8, 5.4 kcal/mol).



These calculations, as well as literature data on the

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aliphatic oxygen-stabilized carbocations,[34] show that the largest stabilization effect can be achieved during the first two O-insertion steps. This result explains the stability of the cation **21** (experimentally observed at −25 °C in TFAA). Despite the strain energy increase during the ring expansion in adamantane (DE1 + DE2 =10.7 kcal/mol), this is comparable compensation (SE1 + SE2 = 33.8 kcal/mol) obtained from the presence of two oxygen atoms. This also gives hope for the generalization of this method as a route to stable cations in TFAA via consecutive Criegee rearrangement processes.

Conclusions

Oxygen insertion into the adamantane structure with TFPAA in TFAA proceeds at −25 °C in TFAA via the intermediate formation of a stable 5-methyl-4,6-dioxabishomoadamant-5-yl cation (**21**). This is the first observation of a stable carbocation in the consecutive, and directed, Criegee rearrangement with trifluoroperacetic acid. Cation stabilization allows the selective straightforward transformation of a dioxabishomoadamantane structure to both bicyclo[3.3.1]nonane and oxaadamantane derivatives. The stabilization of carbocation **21** by attached oxygens (SE = 33.8 kcal/mol) exceeds the increase in strain during the ring expansion in adamantane to the dioxabishomoadamantane (DE = 11.4 kcal/mol). Our results demonstrate that consecutive oxygen insertions into 2-methyladamantan-2-ol in TFAA can be successfully directed into the cage because of the low migratory ability of the methyl group. Moreover, the process can be interrupted at the second insertion step because of the significant stabilization of carbocation **21**.

Experimental Section

General Methods. NMR spectra were recorded at 300 MHz (^{1}H NMR), 75 MHz (^{13}C NMR), and 282.2 MHz (^{19}F NMR). Chemical shifts are reported in parts per million (ppm); ^{1}H chemical shifts are referenced to TMS as internal standard; ^{19}F chemical shifts are given relative to external $CFCl_3$. ^{13}C NMR chemical shifts are referenced relative to $CDCl_3$ at δ 77.00. All geometry optimizations were performed at B3LYP[30] methods with 6-31G* basis set as implemented in Gaussian 94[27] program packages.

Materials. All commercial reagents were ACS reagent grade and used without further purification. H_2O_2 (95%) was prepared by one step distillation of 50% H_2O_2 in a vacuum 15−20 mm of Hg at 45−50 °C and stored at −10 °C in a Teflon bottle.[35] TFPAA (46−48%) in TFAA was prepared by a standard procedure from trifluoroacetic anhydride (TFAAn) and 95% H_2O_2. The concentration of TFPAA was verified by ^{19}F NMR (282 MHz, TFAA) δ −74.3 (c, CF_3, TFPAA), −77.7 (c, CF_3, TFAA). 2-Methyl-2-adamantanol (**1**) was purchased from Aldrich (cat. no. 32,310-1) and was used without purification.

2,2-Dimethoxyadamantane (10) was prepared by the usual literature procedure from adamantanone (**9**) and trimethylorthoformate with 98% yield (colorless liquid).[36] IR (film, cm^{-1}): 2840−2975, 1128. ^{1}H NMR ($CDCl_3$): δ 3.17 (s, 6H), δ 2.06 (s, 2H), δ 1.5−1.9 (m, 12H). ^{13}C NMR ($CDCl_3$): δ 101.9 (C−O), 46.6 (C−O), 37.4, 33.8, 32.9, 27.1. MS *m*/*z* (rel intensity): 196 (M^+, 0.52), 165 (100), 133 (2), 101(11), 91 (15). Anal. Calcd for $C_{12}H_{20}O_2$: C, 73.43; H, 10.27. Found: C, 73.12; H, 10.34.

2,2-Diethoxyadamantane (11) was prepared by the usual literature procedure from adamantanone (**9**) and triethylorthoformate with 98% yield (colorless liquid).[37] IR (film, cm^{-1}): 2840−2975, 1122. ^{1}H NMR ($CDCl_3$): δ 3.44 (q, 4H, J = 6.9 Hz), δ 1.5−2.05 (m, 14H), δ 1.18 (t, 3H, J = 6.9 Hz). ^{13}C NMR: δ 101.8 (C−O), 53.9 (C−O), 37.4, 33.9, 33.8, 27.2, 15.6. MS *m*/*z* (rel intensity): 224 (M^+, 0.6), 179 (100), 151 (88), 133 (6), 91 (18), 67 (15). Anal. Calcd for $C_{14}H_{24}O_2$: C, 74.95; H, 10.78. Found: C, 74.81; H, 10.67.

Oxidation of 2,2-Dimethoxyadamantane (10) with TFPAA. (a) A solution of ketal **10** (0.2 g, 1.02 mmol) in CH_2Cl_2 (0.3 mL) was added dropwise to a solution of TFPAA in TFAA (2.19 g, 8.17 mmol TFPAA) at 0 °C and stirred for 0.5 h. Then CH_2Cl_2 (20 mL) was added, and the reaction mixture was washed with H_2O and 5% Na_2SO_3 in water. After drying over Na_2SO_4 and evaporation of the solvent, 4-oxahomoadamantan-5-one (0.165 g, 97%) was obtained. **(b)** Anhydrous Na_2HPO_4 (1.4 g, 9.89 mmol) and anhydrous Na_3PO_4 (1.62 g, 9.89 mmol) were added to a solution of TFPAA in TFAA (2.19 g, 8.17 mmol TFPAA) and CH_2Cl_2 (10 mL). After 20 min of stirring, ketal **10** (0.2 g, 1.02 mmol) in CH_2Cl_2 (2 mL) was added, and reaction mixture was stirred for 1 h at 0 °C; 20 mL of CH_2Cl_2 was added, and then the solution was washed with H_2O and 5% aqueous Na_2SO_3. After drying over Na_2SO_4 and evaporation, 4-oxahomoadamantan-5-one (0.163 g, 96%) was obtained.

Oxidation of 2,2-Diethoxyadamantane (11) with TFPAA. Dry Na_2HPO_4 (0.923 g, 6.5 mmol) and dry Na_3PO_4 (1.066 g, 6.5 mmol) were added to a solution of TFPAA in TFAA (1.44 g, 5.36 mmol TFPAA) and 4 mL of CH_2Cl_2 at 0 °C and stirred 20 min. A solution of **11** (0.15 g, 0.669 mmol) in CH_2Cl_2 was then added dropwise. The mixture was stirred at 0 °C for 1 h, CH_2Cl_2 (20 mL) was added, and the solution was then washed with H_2O and 5% aqueous Na_2SO_3. After drying over Na_2SO_4 and solvent evaporation, the residue (0.136 g) was analyzed by GC/MS (peak areas): 97% 4-oxahomoadamantan-5-one (**4**), 1% of oxaadamantane **2**, 2% 2-oxaadaamantan-4-ol (**3**).

2-Methyladamant-2-yl Trifluoroacetate (5). Alcohol **1** (1 g, 6.02 mmol) was dissolved in TFAAn (2.54 g, 12.48 mmol) at 0 °C. After solvent evaporation, the oily residue was separated on silica. Traces of olefin **14** were eluted with hexane. The liquid ester **5** (1.51 g, 96%) was eluted with hexanes−ether (4:1). IR (Film, cm^{-1}): 2800−2950, 1776, 1169. ^{1}H NMR ($CDCl_3$): δ 2.36 (s, 2H), δ 1.6−2.03 (m, 15H). ^{13}C NMR ($CDCl_3$): δ 155.8 (q, CO, J_{CF} = 41 Hz), 114.5 (q, CF_3, J_{CF} = 285.8 Hz), 93.9, 37.8, 35.9, 34.5, 32.7, 27.1, 26.3, 21.9. MS *m*/*z* (rel intensity): 205 (0.06), 148 (100), 133 (15.9), 106 (75.1), 69 (15.8). Anal. Calcd for $C_{13}H_{17}F_3O_2$: C, 59.53; H 6.53. Found: C, 59.48; H, 6.49.

Oxidation of 2-methyladamantan-2-ol (1). 2-Methyladamantan-2-ol (**1**) (1 g, 6.02 mmol) was added to a solution of TFPAA in TFAA (13 g, 48.5 mmol TFPAA) at 0 °C. After being stirred for 15 min at 0 °C, the reaction mixture was allowed to warm to room temperature, stirred for 1 h, and then poured into a solution of 15% NaOH (50 mL) with ice. The mixture was extracted with CH_2Cl_2 (3 × 15 mL). The combined extract was washed with H_2O and 5% aqueous Na_2SO_3. The organic layer was dried over Na_2SO_4 and the solvent evaporated. The residue was separated on a silica column: 0.465 g (56%) oxaadamantane **2** was eluted with hexanes−ether (95:5); 0.371 g (40%) of 2-oxa-*exo*-adamantan-4-ol (**3**) and 0.04 g (4%) of lactone **5** were eluted with hexanes−ether (1:1).

Oxidation of 2-Methyladamant-2-yl Trifluoroacetate (5). A solution of trifluoroacetate **5** (1 g, 3.8 mmol) in TFAA (0.7 mL) was added to a solution of TFPAA in TFAA (8.3 g, 30.4 mmol TFPAA) at 0 °C. After being stirred for 15 min at 0 °C, the reaction mixture was allowed to warm to room temperature and stirred for 1 h. The reaction mixture was poured into a solution of 15% aqueous NaOH (50 mL) with ice and then extracted with CH_2Cl_2 (3 × 15 mL). The combined organic extracts were washed with H_2O and 5% aqueous Na_2SO_3 and dried over Na_2SO_4, and the solvent was evaporated.

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The residue was separated on a silica column: 0.283 g (54%) oxaadamantane **2** was eluted with hexanes−ether (95:5); 0.007 g (1%) formate **17**, 0.234 g (40%) of 2-oxa-*exo*-adamantan-4-ol (**3**), and 0.03 g (5%) of lactone **5** were eluted with hexanes−ether (1:1).

2-Adamantanyl Formate (17).[38] **(a)** The solution of TFPAA in TFAA (0.523 g, 1.81 mmol TFPAA) was added dropwise over 4 h to a stirred solution of **5** (0.158 g, 0.602 mmol) in TFAA (1.5 mL) at room temperature, and then CH_2Cl_2 (15 mL) was added. The mixture was then washed with H_2O and 5% aqueous Na_2SO_3 and dried over Na_2SO_4. The residue after solvent evaporation was purified on a silica column (10% ether in hexane). Formate **17** (0.095 g, 88%) was obtained. **(b)** The solution of 2-methyleneadamantane (**14**) (0.184 g, 1.24 mmol) in 0.5 mL of CH_2Cl_2 was added dropwise over 10 min at room temperature to the solution of TFPAA in TFAA (1 g, 3.73 mmol TFPAA) and was stirred for 0.5 h. Using the same purification procedure as in **(a)** formate **17** (0.203 g, 91% yield) was obtained. **(c)** A solution of oxirane **15** (0.2 g, 1.24 mmol) in 0.5 mL of CH_2Cl_2 was added dropwise over 10 min at room temperature to the solution of TFPAA in TFAA (1 g, 3.73 mmol TFPAA) and was stirred for 0.5 h. Using the same purification procedure as in **(a)**, formate **17** (0.21 g, 94% yield) was obtained. MS *m*/*z* (rel intensity): 180 (M^+, 1.5), 134 (100), 92 (63), 79 (18), 67 (6).

5-Methyl-4,6-dioxabishomoadamant-5-yl Cation (21). (a) Alcohol **1** (0.3 g, 1.8 mmol) was added at −25 °C to a solution of TFPAA in TFAA (9.8 g, 36.1 mmol TFPAA). After being stirred for 2 h at −25 °C, cation **21** was formed in the reaction mixture. The formation of **25** was monitored by the ^{1}H NMR spectra of reaction mixture at −25 °C. **(b)** A solution of trifluoroacetate **5** (0.3 g, 1.1 mmol) in TFAA (0.3 mL) was added at −25 °C to a solution of TFPAA in TFAA (6.17 g, 22.8 mmol TFPAA). After the mixture was stirred for 1 h 20 min at −25 °C, cation **21** was formed in the reaction. The formation of **21** was monitored by the ^{1}H NMR spectra of the reaction mixture at −25 °C. ^{1}H NMR (CF_3COOH): δ 5.2 (t, 2H, J = 6.2 Hz), δ 2.0 (s, 3H), 1.8 (dt, 4H, J_1 = 17.4 Hz, J_2 = 6.2 Hz), 1.5−1.7 (m, 6H), 1.1 (s, 2H). ^{13}C NMR (CF_3COOH): δ 181.2, 89.6, 33.1, 28.4, 22.9, 19.1.

Acidic Hydrolysis of 5-Methyl-4,6-dioxabishomoadamantyl Cation (21). A reaction mixture from the previous experiment (0.3 g of **1**, 1.8 mmol) was added dropwise over 10 min at 0 °C to a 10% solution of TFAA (100 mL). The solution was extracted with CH_2Cl_2 (4 × 10 mL), and the combined organic extracts were washed with water and dried over Na_2SO_4. The residue after solvent evaporation was purified on a silica column with ether−hexane (1:1). ***Endo,endo*-3-hydroxy-7-acetoxybicyclo[3.3.1]nonane (27)** (0.292 g, 82%) was obtained as white crystals, mp 81−82 °C. IR (Film, cm $^{-1}$): 3390, 2990−2960, 1724. ^{1}H NMR ($CDCl_3$): δ 5.06 (q, 1H, J = 5.4 Hz), δ 4.01 (tt, 1H, J_1 = 7.5 Hz, J_2 = 6.3 Hz), 1.6−2.2 (m, 14H), 1.52 (m, 1H). ^{13}C NMR ($CDCl_3$): δ 170.4 (C═O), 69.6, 65.9, 36.8, 36.2, 27.7, 24.6, 21.5. MS *m*/*z* (rel intensity) 154 (0.26), 138 (37), 120 (38), 79 (100), 43 (47). Anal. Calcd for $C_{14}H_{24}O_2$: C, 66.64; H, 9.15. Found: C, 66.52; H, 9.02. X-ray quality single crystals for **27** were obtained by slowly crystallizing a solution of **27** in hexane. Crystal data for **27** (173 K, MoKα-radiation, Siemens SMART Platform CCD diffractometer): $C_{11}H_{18}O_3$, FW = 198.25, a = 12.3109(7) Å, b = 19.4314(11) Å, c = 8.9908(5) Å, β = 97.973(2)°, monoclinic, $P2_1/c$, Z = 8, V = 2130.0(2) Å^3, D_c= 1.236 g/cm^3. R factor = 0.0706 for 2179 independent observed reflection (I>2σ(I)); weighted R2 factor = 0.1226. Selected bond lengths and bond angles of structure **27** are listed in Figure 2. Further details on crystal structure of **27** are available in the Supporting Information.

***Endo,endo*-3-Acetoxy-7-trifluoroacetoxybicyclo[3.3.1]nonane (28).** Alcohol **27** (0.1 g, 0.5 mmol) was added to TFAAn (2 g, 9.5 mmol) at 0 °C. After being stirred for 0.5 h, the reaction mixture was evaporated and purified on a silica column (40% ether/hexane). Trifluoroacetate **28** (0.144 g, 98%) was obtained as a colorless oil. IR (film, cm $^{-1}$): 2980−2960, 1781, 1735. ^{1}H NMR ($CDCl_3$): δ 5.31 (q, 1H, J = 6.3 Hz), 5.12 (q, 1H, J = 6.3 Hz), 2.28 (m, 2H), 2.2−1.9 (m, 9H), 1.82 (m, 2H), 1.2 (m, 2H). ^{13}C NMR ($CDCl_3$): δ 172.1 (C═O), 156.8 (q, $^2J_{CF}$ = 41.0 Hz), 114.4 (q, $^1J_{CF}$ = 284.2 Hz), 74.7, 69.8, 33.7, 33.6, 27.2, 24.1, 21.4. MS *m*/*z* (rel intensity): 191 (0.5), 180 (0.2), 138 (13), 120 (10), 69 (12), 43 (100). Anal. Calcd for $C_{13}H_{17}F_3O_4$: C, 53.06; H, 5.82. Found: C, 52.98; H, 5.84.

***endo*-7-Acetoxybicyclo[3.3.1]non-2-ene (18).** A solution of 5-methyl-4,6-dioxabishomoadamant-5-yl cation (**21**) prepared from alcohol **1** (0.3 g, 1.8 mmol) in TFPAA and TFAA was added dropwise to a well-stirred suspension of dry Na_2HPO_4 (25.6 g 180 mmol) in dry CH_2Cl_2 (200 mL) for 10 min at −25 °C and then stirred for 0.5 h more at this temperature. Dimethyl sulfide (3.35 g, 54 mmol) was added to the reaction mixture and stirred for 20 min at −25 °C. The temperature was then increased to room temperature and the reaction stirred for an additional 20 min. The reaction mixture was washed with water and dried over Na_2SO_4. The residue after evaporation of CH_2Cl_2 was purified on a silica column with ether−hexane (1:4), and olefin **18** (0.283 g, 87%) was obtained. IR (film, cm $^{-1}$): 3010−2960, 1726, 1624. ^{1}H NMR ($CDCl_3$): δ 5.82 (m, 1H), 5.65 (dt, J_1 = 9.9 Hz, J_2 = 3.6 Hz, 1H), 5.01 (m, 1H), 2.44−2.23 (m, 2H), 2.17 (m, 1H), 2.07−1.81 (m, 7H), 1.74 (m, 2H), 1.56 (m, 1H). ^{13}C NMR ($CDCl_3$): 170.7 (C═O), 131.3, 127.2, 68.9, 36.8, 33.4, 32.4, 30.8, 27.1, 25.3, 21.4. MS *m*/*z* (rel intensity): 180 (M^+, 1.0), 130 (0.9), 120 (20), 79 (100), 43 (28). Anal. Calcd for $C_{11}H_{16}O_2$: C, 73.30; H, 8.95. Found: C, 72,96; H, 8.87.

Acetyltrifluoroacetyl Peroxide. Trifluoroacetic anhydride (10 g, 47.6 mmol) was added to acetic acid (2.85 g, 47.5 mmol) at 20 °C and stirred for 0.5 h. The temperature was then decreased to 0 °C, and a solution of TFPAA in TFAA (12.9 g, 47.6 mmol) was added dropwise. The reaction mixture was stirred for 0.5 h, and the concentration of acetyltrifluoroacetyl peroxide was checked by ^{19}F NMR. ^{19}F NMR ($CDCl_3$): δ −71.8 (s, CF_3, acetyltrifluoroacetyl peroxide), −76.2 (s, CF_3, TFAA). ^{1}H NMR ($CDCl_3$): δ 2.3 (s, CH_3).

2-Oxa-*exo*-adamantan-4-ol (3).[39] **(a)** Dry Na_2HPO_4 (6.4 g, 45 mmol) was added to a dry CH_2Cl_2 (50 mL) solution of TFPAA in TFAA (2.4 g, 8.9 mmol TFPAA) at 0 °C. After 0.5 h of stirring, a CH_2Cl_2 (0.3 mL) solution of olefin **18** (0.2 g, 1.1 mmol) was added and stirred for another 0.5 h. The reaction mixture was then washed with water and 5% aqueous Na_2SO_3 solution and dried over anhydrous Na_2SO_4 and the CH_2Cl_2 evaporated. The residue was purified on a silica column (ether/hexane 1:1), and alcohol **3** (0.16 g, 94%) was obtained. **(b)** A solution of 5-methyl-4,6-dioxabishomoadamant-5-yl cation (**21**) prepared from alcohol **1** (0.3 g, 1.8 mmol) in TFPAA, and TFAA was added dropwise to a well stirred suspension of dry Na_2HPO_4 (25.6 g 180 mmol) in dry CH_2Cl_2 (200 mL) for 10 min at −25 °C and then stirred for 0.5 h at this temperature. The temperature was then increased to room temperature and stirred for additional 0.5 h. The reaction mixture was washed with H_2O and 5% aqueous Na_2SO_3 solution and then dried over anhydrous Na_2SO_4. The residue after evaporation of CH_2Cl_2 was purified on a silica column with ether−hexane (1:1) and alcohol **3** (0.248 g, 89%) was obtained. Mp: 267−269 °C (lit.[39] mp 268−273 °C). MS *m*/*z* (rel intensity): 154 (M^+, 100), 136 (9), 110 (79).

2-Oxaadamantane (2).[18,26,39] **(a)** Hydroxyacetate **27** (0.1 g, 0.5 mmol) was added to the 95% sulfuric acid (65 g) at 0 °C, and the reaction was stirred for 0.5 h and then poured into H_2O and extracted with CH_2Cl_2 (4 × 10 mL). The combined organic extracts were washed with 5% aqueous $NaHCO_3$ and dried over anhydrous Na_2SO_4. After removal of the solvent, oxaadamanatne **2** (0.067 g, 96%) was obtained. **(b)** Olefin **18** (0.2 g, 1.1 mmol) was added to 95% sulfuric acid (120 g) at 0 °C, and the reaction was stirred for 0.5 h and then poured into H_2O and extracted with CH_2Cl_2 (4 × 10 mL). The combined organic extracts were washed with 5% aqueous $NaHCO_3$ and dried over anhydrous Na_2SO_4. After removal of the solvent,

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oxaadamantane **2** (0.149 g, 97%) was obtained. MS *m*/*z* (rel intensity): 138 (M^+, 100), 94 (92), 79 (52), 41 (58).

Acknowledgment. This work was supported by an ISF grant (Reg No. NCCOOO). Special acknowledgment is made to Dr. Victor G. Young, Jr. and the X-ray Crystallographic Laboratory of the University of Minnesota for X-ray structural analysis of compound **27**. We also thank the Minnesota Supercomputer Institute and the UMD Digital Imaging Laboratory (DIL) for a generous allocation of computer resources. A.A.F. is grateful to Dr. Nico J. R. van Eikema Hommes (University Erlangen-Nurnberg) for "Molecule" program.

Supporting Information Available: ^{1}H and ^{13}C NMR spectra of all new compounds and ^{19}F NMR for a solution of TFPAA in TFAA. This material is available free of charge via the Internet at http://pubs.acs.org.

JO991745U