standard. Carbon-13 spectra were run in the same solvent on a Bruker CXP-100 spectrometer. Mass spectra were run on a Varian MAT CH5-DF spectrometer in either the electron impact (EI) or field ionization (FI) mode, and only the most intense peaks are reported. Gas chromatographic analyses were performed on a F&M Model 720 instrument using a 10 ft × 0.375 in., 20% SE-30 on Chromosorb W column.

General Reaction Procedure. A mixture of aqueous sodium hydroxide solution, 30 mL of dichloromethane, and 0.1 g of catalyst was cooled to 0 °C under nitrogen. To this mixture was added, dropwise with stirring and cooling, a solution of **1** (0.02 mol) or, in the case of crossed condensations, a mixture of 0.02 mol of each reactant, in 20 mL of dichloromethane. The addition required 20 min. Stirring was continued at 0 °C for 2.5 h, and then the mixture was refluxed for 20 min. The organic phase was separated, diluted with 100 mL of ether, washed with water, and dried over sodium sulfate. Evaporation of the solvents gave the product which was analyzed by GLC. The yields quoted in Tables I and II were obtained by multiplying the weight of crude product by the integrated (disk integrator) area of the peak in the GLC analysis. In each case, the NMR spectrum of the crude product showed no significant extraneous peaks. Variations in the time of cooling or reflux did not significantly affect the product yields.

6-Methylcyclohexa-1,3-dienecarboxaldehyde (4)[5] was obtained as a clear oil: IR 3050, 2800, 1675, 700 cm^{-1}; NMR 9.47 (s, 1 H), 6.69 (t, 1 H, J = 5 Hz), 6.15 (m, 2 H), 2.79 (m, 1 H), 2.30 (m, 2 H), 0.94 (d, 3 H, J = 7 Hz); mass spectrum (FI), m/z 122 (M$^+$), 120, 92, 58, 52, 29.

5,6-Dihydro-2,6-dimethyl-2*H*-pyran-3-carboxaldehyde (3)[6,7] was obtained as a clear oil: IR 2960, 1695, 1255, 865 cm^{-1}. GLC analysis showed the presence of two isomers, **3a** and **3b**, in a ratio of 45:55. These were separated by preparative GLC to give **3a** [NMR 9.57 (s, 1 H), 6.90 (m, 1 H), 4.77–4.33 (m, 1 H), 3.80–3.37 (m, 1 H), 2.43–2.08 (m, 2 H), 1.41 (d, 3 H, J = 7 Hz), 1.30 (d, 3 H, J = 7 Hz); mp (2,4-DNP) 178–179 °C (lit.[6a] mp 180 °C)] and **3b** [NMR 9.60 (s, 1 H), 6.92 (m, 1 H), 4.90–4.50 (m, 1 H), 4.16–3.63 (m, 1 H), 2.53–2.15 (m, 2 H), 1.42 (d, 3 H, J = 7 Hz), 1.23 (d, 3 H, J = 7 Hz); mp (2,4-DNP) 200–201 °C (lit.[6a] 204 °C)]. The mass spectra (EI) of the two isomers were identical: m/z 140 (M$^+$), 125, 111, 83.

4-Ethylidenecyclohex-2-enone[14] **(10)** was obtained with **4** when the condensation of **1** and **9** was effected. These were separated by preparative GLC to give **10** as an oil: IR 1675, 1635, 910, 845 cm^{-1}; NMR 6.95 (d, 1 H, J = 10 Hz), 6.85 (m, 2 H), 2.57 (m, 4 H), 1.82 (d, 3 H, J = 6 Hz); ^{13}C NMR 199.4 (s), 149.4 (d), 133.9 (d), 132.4 (d), 125.3 (d), 36.5 (t), 23.3 (t), 14.3 (q); mass spectrum (FI), m/z 122 (M$^+$), 107, 94, 79, 66, 51. Anal. Calcd for $C_8H_{10}O$: C, 78.65; H, 8.25. Found: C, 78.82; H, 8.37. Hydrogenation of **10** over a palladium catalyst at 1 atm led to the uptake of 2 equiv of hydrogen. The product gave a semicarbazone melting point of 173–174 °C (the literature[15] value for the semicarbazone of 4-ethylcyclohexanone is 171 °C).

Ethyl 3-ethoxypropanoate (12): IR 2995, 1730, 1195, 1110 cm^{-1}; NMR 4.10 (q, 2 H, J = 8 Hz), 3.70 (t, 2 H, J = 6 Hz), 3.48 (q, 2 H, J = 8 Hz), 2.55 (t, 2 H, J = 6 Hz), 1.30 (t, 3 H, J = 8 Hz), 1.15 (t, 3 H, J = 8 Hz); mass spectrum (FI), m/z 146 (M$^+$), 100, 58, 29 [identical with an authentic sample (Aldrich)].

4-Methoxy-2-butanone (13): IR 2930, 1705, 1160, 1110 cm^{-1}; NMR 3.62 (t, 2 H, J = 6 Hz), 3.32 (s, 3 H), 2.65 (t, 2 H, J = 6 Hz), 2.15 (s, 3 H); mass spectrum (FI), m/z 102 (M$^+$), 87, 58, 43.

Methyl 3-methoxypropanoate (14): IR 2850, 1720, 1240, 1050 cm^{-1}; NMR 3.70 (s, 3 H), 3.65 (t, 2 H, J = 6 Hz), 3.35 (s, 3 H), 2.55 (t, 2 H, J = 6 Hz); mass spectrum (FI), m/z 118 (M$^+$), 103, 87, 43.

Preparation of Trimethylbenzylammonium Fluoride (TMBAF). The catalyst TMBAF was prepared by neutralizing commercial Triton B solution with 48% hydrofluoric acid to the phenolphthalein end point. The solvents were evaporated, and the residue was dried at 100 °C (0.1 mm) for 24 h. The solid was finely pulverized, dried at 120 °C (0.1 mm) for a further 24 h, and transferred under an inert atmosphere in a drybox.

2-Ethylidine-3-methylglutaraldehyde (5). Crotonaldehyde (0.35 g, 5 mmol), THF (5 mL), and TMBAF (0.3 g) were stirred together under nitrogen at room temperature for 48 h. Hexane (15 mL) was added, the mixture was stirred for 10 min and filtered, and the filtrate was evaporated to leave a yellow oil which GLC analysis showed to be a mixture of **5** and unreacted **1**. The yield of **5**[10] was 60%. A GLC-collected sample of **5** showed the following: $n^{25}{}_{D}$ 1.4961; IR 2720, 1725, 1685, 1645 cm^{-1}; NMR 9.71 (s, 1 H), 9.37 (m, 1 H), 6.55 (q, 1 H, J = 6.5 Hz), 2.85 (m, 3 H), 2.10 (d, 3 H, J = 6.5 Hz), 1.20 (d, 3 H, J = 6.5 Hz).

2-Ethylidineglutaraldehyde (6). In a similar manner a mixture of 5 mmol of **1**, 7 mmol of acrolein, 5 mL of dry THF, and 0.3 g of TMBAF at reflux for 10 h led to **6**: 57% yield; $n^{25}{}_{D}$ 1.4620; IR 2730, 1725, 1685, 1650 cm^{-1}; NMR 9.79 (s, 1 H), 9.40 (s, 1 H), 6.65 (q, 1 H, J = 6.5 Hz), 2.51 (s, 4 H), 2.05 (d, 3 H, J = 6.5 Hz). Anal. Calcd for $C_7H_{10}O_2$: C, 66.65; H, 7.99. Found: C, 66.51; H, 7.92.

2-Ethylidine-5-oxohexanal (7). With the same amounts of reactants and the same conditions as in the acrolein reaction but with substitution of methyl vinyl ketone for acrolein, a 78% yield of **7** was obtained: $n^{25}{}_{D}$ 1.3972; IR 2720, 1715, 1685, 1650 cm^{-1}; NMR 8.38 (s, 1 H), 6.51 (q, 1 H, J = 6.5 Hz), 2.40 (s, 4 H), 2.01 (s, 3 H), 1.90 (d, 3 H, J = 6.5 Hz). Anal. Calcd for $C_8H_{12}O_2$: C, 68.54; H, 8.63. Found: C, 68.41; H, 8.87.

2-Ethyl-2-hexenal (8). A stirred mixture of butanal (7.2 g, 10 mmol), dry THF (30 mL), TMBAF (0.5 g), and 0.3 g of no. 4 molecular sieves was refluxed under a nitrogen atmosphere for 6 h. Workup as usual gave **8** in quantitative yield.

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Registry No. **1**, 4170-30-3; **3a**, 20831-01-0; **3b**, 20831-00-9; **4**, 4748-86-1; **5**, 74128-78-2; **6**, 74128-79-3; **7**, 74128-80-6; **8**, 645-62-5; **9**, 78-94-4; **10**, 74128-81-7; **10** semicarbazone, 74128-82-8; **11**, 107-86-8; **12**, 763-69-9; **13**, 6975-85-5; **14**, 3852-09-3; acrolein, 107-02-8; butanol, 123-72-8; ethyl 2-propenoate, 140-88-5; methyl 2-propenoate, 96-33-3; Ethylene glycol, 107-21-1.

Reaction of Saturated Organic Compounds with Acetyl and Trifluoroacetyl Nitrate

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The reaction of selected hydrocarbons with trifluoroacetyl nitrate in trifluoroacetic acid results in hydride ion abstraction and formation of alkyl trifluoroacetate. The reaction of reactive alkyl halides and alkyl methyl ethers with protonated acetyl nitrate in acetic acid affords the corresponding alkyl acetates in good yield. The oxidizing reagent in both reactions is ammonium nitrate which is converted in situ to the nitronium acetate by reaction with an anhydride.

Although the numerous addition reactions of electrophilic nitronium compounds to unsaturated substrates containing reactive π electrons have received a considerable amount of attention in the literature, there have only re-

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cently been reports of electrophilic reactions with saturated σ-donor hydrocarbons and molecules with nonbonding (n) electrons. With NO_2PF_6 in aprotic solvents, substitution (nitration) has been observed[2] with saturated hydrocarbons while reactions of NO_2BF_4 in acetonitrile resulted in hydride abstraction with subsequent formation of acetamides.[3] The reaction of nascent nitronium ion, generated in situ by the action of protic acid upon HNO_3, with isobutane[4] and alkyl iodides[5] has been reported. Nitronium tetrafluoroborate in dichloromethane solvent has been employed to good advantage in the oxidation of alkyl methyl ethers to carbonyl compounds (eq 1).[6]

$$R_2CHOMe + NO_2BF_4 \xrightarrow{CH_2Cl_2} \xrightarrow{H_2O} R_2C{=}O + CH_3OH \quad (1)$$

More recently, we have found that selected saturated alkyl halides and alkyl ethers are readily converted to their corresponding acetamides by treatment with NO_2BF_4[7a,b] and $NOBF_4$[7c] in acetonitrile. Mechanistic studies have demonstrated that both σ-donor hydrocarbons[3] and n-donor alkyl halides[7a] react by heterolytic C–X bond cleavage to form carbenium ion intermediates which are efficiently trapped by the CH_3CN solvent (eq 2).

$$R_3CX \xrightarrow{NO_2BF_4} R_3C^+ + NO_2X \xrightarrow{CH_3CN} R_3CN^+{\equiv}CCH_3 \xrightarrow{H_2O} R_3CNHC(O)CH_3 \quad (2)$$

$$X = H, I, Br, Cl, F, OR$$

We now report our results on the related reactions of saturated molecules with acetyl and trifluoroacetyl nitrate. The active oxidant is prepared in situ by the reaction of ammonium nitrate with an anhydride.

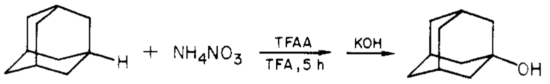
Results and Discussion

Hydrocarbon Oxidation with Trifluoroacetyl Nitrate. Under certain circumstances the nitronium ion (NO_2^+) can be a powerful oxidizing agent as evidenced by the fact that NO_2ClO_4 reacts violently even with saturated hydrocarbons. We attributed the success of our prior studies[3,7] to the relative stability of NO_2BF_4 in acetonitrile solvent where further oxidation of the "Ritter type"[8] nitrilium ion intermediate (eq 2) was minimized. Although NO_2BF_4 is commercially available and readily prepared in the laboratory,[9] it was the primary objective of the present study to generate the active nitronium reagent in situ from common laboratory reagents. With variation of the anion in $NO_2^+X^-$, it is to be anticipated that an increase in the nucleophilicity of X^- will be attended by a decrease in the overall reactivity of the reagent. Our success with the tetrafluoroborate anion prompted us to examine the selectivity of trifluoroacetyl nitrate.

Trifluoroacetyl nitrate (**1**) is conveniently prepared by the reaction of the nitrate anion with trifluoroacetic anhydride (TFAA).

$$NH_4NO_3 + (CF_3CO)_2O \rightleftarrows \underset{\textbf{1}}{CF_3CO_2NO_2} + CF_3CO_2NH_4 \quad (3)$$

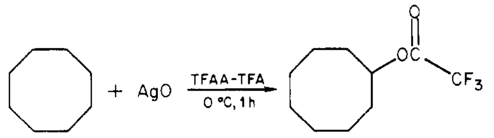
This equilibrating system (eq 3) has been reported[10] to be a cooxidant when used with catalytic amounts of Ag(I) salts. The reaction of adamantane with 3 equiv of NH_4NO_3 and TFAA in trifluoroacetic acid solvent (eq 4) readily afforded 1-adamantyl trifluoroacetate, isolated (53%) as the alcohol after saponification with KOH.



(4)

In a similar manner cyclooctane (2 h) and norbornane (4 h) were oxidatively functionalized, affording cyclooctyl trifluoroacetate (50%) and *exo*-2-trifluoroacetoxynorbornane (52%). Oxidation of the latter hydrocarbon was accompanied by the formation *exo*-2-norbornyl nitrate (23%). We suggest that these reactions involve electrophilic attack at the more reactive σ C–H bond with formal hydride abstraction and capture of the incipient carbenium ion by either solvent or nitrate anion. A similar mechanism has been established for hydrocarbon oxidation with NO_2BF_4 in acetonitrile.[3] The active oxidant in the present case is presumably protonated (vide infra) trifluoroacetyl nitrate ($CF_3CO_2NO_2H^+$).

We also briefly examined the direct oxidation of hydrocarbons with higher oxidation states of silver.[10] We treated a variety of hydrocarbons with argentic oxide[11,12] in a 20% solution of TFAA in trifluoroacetic acid solvent and found that the principal product isolated was the alkyl trifluoroacetate. However, the yields were disappointing when based upon the actual conversion of hydrocarbon to product instead of the reduction of Ag(III) to Ag(I).[10] For example, gas chromatographic analysis revealed a maximum of 17% conversion of cyclooctane to its trifluoroacetate when hydrocarbon and oxidant were used in stoichiometric quantities (eq 5).



(5)

We obtained better results using silver(I) trifluoroacetate and 2 equiv of NO_2BF_4 as a cooxidant in methylene chloride. Adamantane was oxidized to 1-adamantyl trifluoroacetate (60%), but there is some question as to whether the active oxidant was Ag(III) or NO_2BF_4. These experiments were abandoned in favor of oxidation employing NH_4NO_3 as the oxidizing agent.

Reactions with Acetyl Nitrate. Acetyl nitrate has been the subject of a number of investigations involving

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(1) (a) Lubrizol Fellow, 1975–1976. (b) Wayne State University Fellow, 1975–1977.

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(8) Ritter, J. J.; Minieri, P. P. *J. Am. Chem. Soc.* **1948**, *70*, 4045.

(9) Nitronium tetrafluoroborate may be purchased from Aldrich Chemical Co., Inc., or prepared according to the procedure of Olah: Olah, G. A.; Kuhn, S. J. *Org. Synth.* **1967**, *47*, 56.

(10) Crivello, C. V. *Synth. Commun.* **1976**, *6*, 543. It was claimed in this report that NH_4NO_3 served as an oxidant capable of oxidizing Ag(I) to Ag(III). However, the reaction with adamantane proceeds at the same rate in the absence of silver salts, and we therefore suggest that the effective oxidant is trifluoroacetyl nitrate.

(11) Hammer, R. N.; Kleinberg, J. *Inorg. Synth.* **1953**, *4*, 12.

(12) Analysis of the AgO showed it to contain 82–91% silver(II) oxide. Lloyd, C. P. *Anal. Chim. Acta* **1968**, *43*, 95.

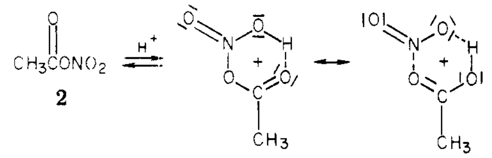
the nitration of aromatic compounds[13] and alkenes.[14] Both the nitronium ion and protonated acetyl nitrate have been implicated as the reactive electrophile in these reactions.[15] As anticipated, this reagent is not highly dissociated in the relatively nonpolar solvent acetic acid, and its reactivity is substantially decreased. This reagent exhibits the desired selectivity and does not readily oxidize carbon–hydrogen σ bonds.

Acetyl nitrate was prepared in situ by the facile reaction of NH_4NO_3 with acetic anhydride. This reagent offers several advantages over NO_2BF_4 such as increased solubility in organic solvents and its latent generation from the inexpensive and relatively safe oxidizing agent ammonium nitrate. The problem with the reduced reactivity of $CH_3CO_2NO_2$ was circumvented by addition of fluoroboric acid. Although 1-bromoadamantane is essentially inert to $CH_3CO_2NO_2$, in the presence of 1 equiv of HBF_4 1-adamantyl acetate was produced in 95% yield (eq 6).

$$RX + NH_4NO_3 \xrightarrow[CH_3COOH,\ HBF_4]{(CH_3CO)_2O} ROAc + NO_2X + NH_4OAc \qquad (6)$$

$$X = I, Br, Cl, OCH_3$$

The necessity for an acid catalyst infers either that protonation of acetyl nitrate (**2**) increases the effective concentration of nitronium ions in solution due to dissociation or that the actual oxidizing species is protonated acetyl nitrate (eq 7). We prefer to think that a tightly


2 **3a** **3b** (7)

solvated nitronium ion, represented by resonance structure **3b**, is the reactive electrophilic reagent in acetic acid and also in the case of protonated **1** in trifluoroacetic acid. A similar suggestion was presented earlier by Bordwell[14] to account for the stereospecific formation of *cis*-β-nitroacetates in reactions of **2** with alkenes.

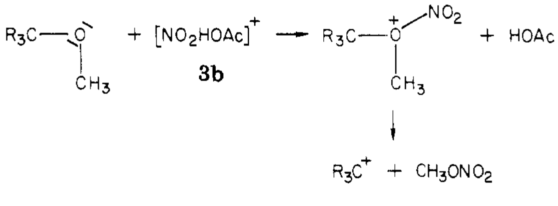
In order to ascertain the overall utility of this reaction with n-donor substrates, we have examined the reactivity of a variety of alkyl halides and ethers with $CH_3CO_2NO_2/HBF_4$ (1:1) in glacial acetic acid. The reactions were usually carried out at room temperature with a 100% excess of oxidant. The results are given in Table I. As noted previously, the overall reactivity paralleled the stability of the carbenium ion resulting from C–X bond rupture. In general, alkyl chlorides and primary and secondary alkyl bromides were found to react very slowly. For example, adamantyl chloride gave only a 44% yield of 1-adamantyl acetate with 50% of the starting material being unconsumed after 48 h. However, *exo*-2-norbornyl bromide afforded the exo acetate in high yield (84%) due to σ-bond participation resulting in Wagner–Meerwin rearrangement concomitant with C–Br bond heterolysis.[7a] Alkyl iodides and tertiary alkyl bromides react with protonated **2** to afford the corresponding alkyl acetates in respectable yields. The reaction with cyclohexyl iodide was accompanied by the formation of considerable amounts of an intractable oil, presumably due to competing polymerization reactions.

Table I. Reaction of Alkyl Halides and Alkyl Methyl Ethers with $CH_3CO_2NO_2$ in Acetic Acid[a]

structure (RX)				
R	X	*t*, h	product	yield,[c] %
1-adamantyl	I	2	ROAc	95[b]
	Br	2	ROAc	95
	Cl	48	ROAc	44 (50)
	OMe	2	ROAc	88
exo-2-norbornyl	Br	2	ROAc (exo)	84
	Cl	96	ROAc (exo)	2 (78)
	OMe	2	ROAc (exo)	80
endo-2-norbornyl	OMe	2	ROAc (exo)	15
			2-norbornanone	32
cyclohexyl	I	2	ROAc	28
	Br	2	ROAc	14 (84)
2-octyl	OMe	7	ROAc	13 (41)
			2-octanone	13
1-octyl	OMe		no reaction	(78)

[a] All reactions utilized a twofold excess of oxidizing reagent. [b] Yields were determined by GLC using do-, tri-, and pentadecane as internal standards. [c] Numbers in parentheses are the percent recovered starting material.

The increased selectivity of acetyl nitrate is further exemplified in its reactions with alkyl methyl ethers. 1-Adamantyl methyl ether, as predicted on the basis of the stability of the resulting tertiary carbenium ion, gave 1-adamantyl acetate in high yield (88%). Similarly, *exo*-2-norbornyl methyl ether reacted cleanly to afford the *exo*-2-acetate. However, 2-octyl methyl ether afforded only minor amounts of 2-octanone (see eq 1) and 2-octyl acetate, with an appreciable amount (41%) of unreacted starting material being recovered. *endo*-2-Norbornyl methyl ether also exhibited competitive hydride abstraction and C–O bond cleavage, with 2-norboranone being the major product. We suggest a mechanism for acetate formation involving initial complexation of a nitronium ion with the nonbonding electrons on the oxygen with ionization, giving the norbornyl cation and CH_3ONO_2. A similar mechanism was established for halide cleavage.[7a] The weakly nucleophilic n electrons should be capable of displacing acetic acid from **3b** (eq 8). It is interesting to note that reaction



(8)

of the endo ether with NO_2BF_4/CH_3CN afforded only 2-norbornanone (83%) resulting from α-hydride abstraction and hydrolysis of the resulting oxonium ion. In a control experiment the *endo*-methyl ether gave only *exo*-2-acetoxynorbornane in the absence of NH_4NO_3. Therefore, at least part of the product derived from the *exo*-methyl ether arises by acid-catalyzed solvolysis of the methoxyl group.

In summary, we have provided a novel procedure for the direct introduction of an oxygen functionality into selected hydrocarbons. We have provided a highly selective economical procedure for the conversion of fairly reactive alkyl halides to their acetates which complements the compa-

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rable reaction employing NO_2BF_4/CH_3CN where nitrogen substitution is achieved. Finally, we present an ether cleavage reaction under relatively mild conditions. The experimental procedures are very easy to execute, and product isolation is not complicated by formation of side products. In principle this reaction may be extended to include reactions with other molecules containing nonbonding electrons that upon C–X bond cleavage will afford a stable carbenium ion.

Experimental Section

Oxidation of Adamantane with Ammonium Nitrate and Trifluoroacetic Anhydride in Trifluoroacetic Acid. To 1.36 g (10 mmol) of adamantane and 2.4 g (30 mmol) of ammonium nitrate, suspended in 20 mL of trifluoroacetic acid, was added dropwise 6.5 g (31 mmol) of trifluoroacetic anhydride. The rate of addition was controlled so as to maintain a temperature of 25–40 °C. After being stirred an additional 5 h at room temperature, the reaction was quenched with 50 mL of distilled water. The aqueous mixture was extracted with pentane (3 × 20 mL), and the combined organic extracts were washed successively with 10 mL of distilled water and 10 mL of saturated aqueous sodium bicarbonate. After the extract was dried (Na_2SO_4), the volatiles were removed. The crude reaction mixture was dissolved in 20 mL of ethanol and 1 mL of distilled water. Potassium hydroxide (2 g, 0.035 mol) was added, and the reaction was allowed to proceed for 0.5 h at 25 °C. After dilution with 20 mL of water, the aqueous solution was extracted with ethyl ether (4 × 20 mL). The combined ether layers were washed with saturated aqueous sodium chloride (2 × 20 mL) and dried (Na_2SO_4). Concentration of the solution afforded 0.88 g of a white solid. Dissolution of this material in 9:1 ether–pentane and cooling to −15 °C afforded 0.80 g (52.6%) of 1-adamantanol: mp >220 °C (sublimes). The infrared spectrum of this alcohol was identical with that of an authentic spectrum of 1-adamantanol.

Oxidations of Alkyl Halides and Alkyl Methyl Ethers with Ammonium Nitrate in Acetic Anhydride–Acetic Acid. General Procedure. To 0.80 g (10 mmol) of ammonium nitrate in 15 mL of glacial acetic acid was added 15 mL of acetic anhydride. The mixture was cooled to 0 °C, and then 1.5 mL of 48% aqueous HBF_4 was added. The resulting mixture was stirred for 15 min at 0 °C, and then 5 mmol of the alkyl halide (in ether) was added. The reaction was warmed to room temperature and stirred for the additional time denoted in each specific run. After the oxidation was quenched by the addition of 20 mL of ice–water, the mixture was extracted with pentane (3 × 20 mL). The combined organic layers were washed with 10 mL of water and 10 mL of saturated aqueous sodium bicarbonate solution and then dried ($MgSO_4$). The solvent was removed by rotary evaporation and the resulting material analyzed via gas–liquid phase chromatography (4-ft, 20% Carbowax 20-M on 60/80 Chromosorb P). The resulting alkyl acetates all had physical and spectral properties identical with those of authentic samples.

Quantitative Determination of Silver(II) Oxide. By use of the method of Lloyd,[12] a 0.1–0.3-g sample of silver(II) oxide was dissolved in 5 mL of saturated aqueous sodium iodide. The liberated iodine was titrated with 0.02 M sodium thiosulfate by using a starch indicator. The oxide analyzed in this manner was found to be 82–91% silver(II) oxide.

Attempted Oxidations of Hydrocarbons with Silver(II) Reagents. To a solution of 1 mL of trifluoroacetic anhydride and 4 mL of trifluoroacetic acid at 0 °C were added 0.112 g (1 mmol) of cyclooctane and 0.123 g (1 mmol) of silver(II) oxide. After being stirred at 0 °C for 1 h, the colorless mixture was diluted with water, and the aqueous solution was extracted with chloroform. After the extract was dried ($MgSO_4$), removal of the solvent afforded 1.36 g of an oil. Analysis by gas chromatography (15 ft × 0.25 in. column of 10% SE-30 at 110 °C) showed a 17% conversion to cyclooctyl trifluoroacetate. An analytical sample of the ester obtained by preparative gas chromatography had an infrared spectrum identical with that of authentic cyclooctyl trifluoroacetate prepared by the reaction of cyclooctanol with trifluoroacetic anhydride.

A similar series of experiments with a variety of alkanes also afforded only minor amounts of alkyl trifluoroacetates as products.

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Registry No. 1-Adamantyl iodide, 768-93-4; 1-adamantyl bromide, 768-90-1; 1-adamantyl chloride, 935-56-8; 1-methoxyadamantane, 6221-74-5; *exo*-2-norbornyl bromide, 2534-77-2; *exo*-2-norbornyl chloride, 765-91-3; *exo*-2-methoxynorbornane, 10395-53-6; *endo*-2-methoxynorbornane, 10395-55-8; cyclohexyl iodide, 626-62-0; cyclohexyl bromide, 108-85-0; 2-methoxyoctane, 1541-09-9; 1-methoxyoctane, 929-56-6; 1-adamantyl acetate, 22635-62-7; *exo*-2-norbornyl acetate, 36914-56-4; 2-norbornanone, 497-38-1; cyclohexyl acetate, 622-45-7; 2-octyl acetate, 2051-50-5; 2-octanone, 111-13-7; adamantane, 281-23-2; 1-adamantanol, 768-95-6; cyclooctane, 292-64-8; cyclooctyl trifluoroacetate, 1478-73-5; 1-adamantyl trifluoroacetate, 58652-54-3; norbornane, 279-23-2; *exo*-2-trifluoroacetoxynorbornane, 31024-13-2; *exo*-2-norbornyl nitrate, 54894-23-4; trifluoroacetyl nitrate, 66693-89-8; acetyl nitrate, 591-09-3.