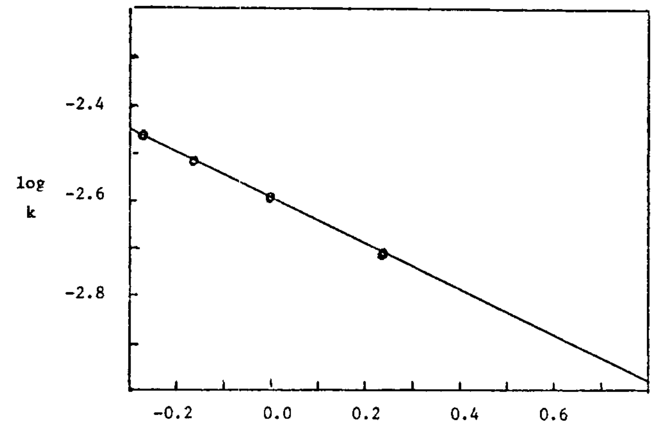

Figure 1. Log k vs. σ for N,N'-di-p-X-benzoyl-N,N'-dibenzyloxyhydrazines in chloroform at 30.1 ± 0.1 °C, $\rho = -0.47$.

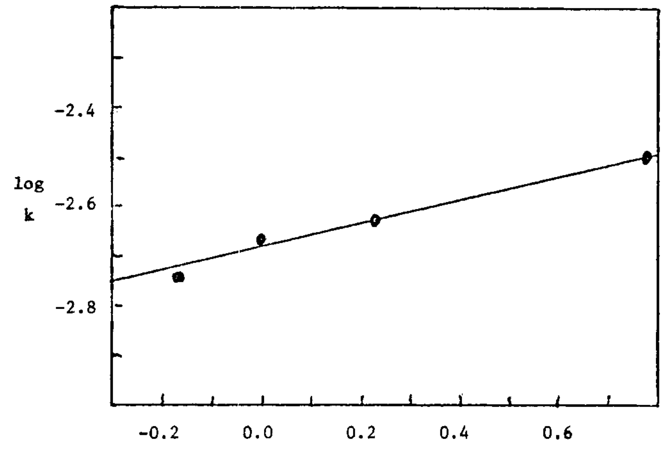

Figure 2. Log k vs. σ for N,N'-diacetyl-N,N'-di-p-X-benzyloxyhydrazines in chloroform at 59.4 ± 0.3 °C, $\rho = 0.22$.

Electron-donating substituents on R in **3b** with electron-withdrawing substituents on R′ in **3c** were found to accelerate the rates of reaction. Plots of log k vs. σ (Figures 1 and 2) for the two series of compounds **3b** and **3c** showed straight lines and ρ values of −0.47 and +0.22 were calculated, respectively. These indicate the expected stabilization of incipient alkoxide anions and acylium ions of the transition state.

Experimental Section

Melting points were determined using a Thomas-Hoover Uni-melt capillary apparatus and are corrected. Visible absorption spectra were measured with a Perkin-Elmer Model 202 ultraviolet–visible spectrophotometer or a Beckman DU spectrophotometer. Molecular weights were determined with a Hitachi Perkin-Elmer molecular weight apparatus, Model 115.

Preparation of Amides. Amides were prepared by the method of White.[4] Previously unknown amides included N-cyclohexyl-m-chlorobenzamide, mp 121 °C, N-cyclohexyl-m-methylbenzamide, mp 121 °C, and N-cyclohexyl-m-nitrobenzamide, mp 146 °C.[5]

N-Nitroso-N-cyclohexyl-Substituted Benzamides. The procedure described by Huisgen and Kraus[16] was used to prepare the nitroso amides. Solutions of these nitroso amides in carbon tetrachloride were prepared and held in a constant temperature bath at 25.0 ± 0.01 °C. Samples were withdrawn and changes in the absorption at 430 nm were recorded. From these data the rates shown in Table I were calculated. Similarly rates of decomposition of N-nitroso-N-cyclohexyl-substituted benzamides in acetic acid were measured and the results are in Table II.

Rate of Decomposition of N,N'-Diacyl-N,N'-dialkoxyhydrazines. These unstable compounds were prepared by lead tetraacetate oxidation of N-acyl-O-alkylhydroxylamines as described before.[3] Solutions of initial concentration in the range 5×10^{-2} to 5×10^{-3} m in chloroform were accurately prepared and kept in a constant temperature bath. Aliquots were withdrawn at 2-h intervals, and the molecular weights were measured using a Hitachi Perkin-Elmer molecular weight apparatus, Model 115. First-order rate constants were determined from the slope of the plot of $M_\infty - M_t$ against time.

Table I. Rate Constants for Decomposition of N-Nitroso-N-cyclohexyl-Substituted Benzamides in Carbon Tetrachloride

Substituent	Constant, s^{-1}	Substituent	Constant, s^{-1}
p-OCH_3	3.0×10^{-4}	m-CH_3	3.0×10^{-4}
m-Cl	3.5×10^{-4}	H	4.0×10^{-4}

Table II. Rate Constants for Decomposition of N-Nitroso-N-cyclohexyl-Substituted Benzamides in Acetic Acid

Registry no.	Substituent	Constant, s^{-1}
62250-57-1	m-CH_3	2.0×10^{-3}
62250-58-2	p-Nitro	5.36×10^{-4}
62250-59-3	m-Chloro	1.24×10^{-3}
62250-60-6	m-Nitro	9.39×10^{-4}
62250-61-7	p-Methoxy	1.39×10^{-3}
62250-62-8	None	1.73×10^{-3}

Registry No.—**3b** (X = p-CH_3), 62250-50-4; **3b** (X = H), 38636-07-6; **3b** (X = p-Cl), 62250-51-5; **3b** (X = p-OCH_3), 62250-52-6; **3c** (X = p-OCH_3), 53821-07-1; **3c** (X = H), 62250-53-7; **3c** (X = p-Cl), 62250-54-8; **3c** (X = p-NO_2), 62250-55-9; N-cyclohexyl-m-chlorobenzamide, 62250-56-0; N-cyclohexyl-m-methylbenzamide, 53205-66-6; N-cyclohexyl-m-nitrobenzamide, 2702-32-1.

References and Notes

(1) (a) R. Huisgen and G. Horeld, *Justus Liebigs Ann. Chem.*, **567**, 137 (1948); (b) R. Huisgen and L. Krause, *ibid.*, **574**, 157 (1951).
(2) D. H. Hey, J. Stuart-Webb, and G. H. Williams, *J. Chem. Soc.*, 4657 (1952).
(3) J. H. Cooley, M. W. Mosher, and M. A. Khan, *J. Am. Chem. Soc.*, **90**, 1867 (1968).
(4) E. H. White, *J. Am. Chem. Soc.*, **77**, 6011 (1955).
(5) Satisfactory microanalyses (0.3% absolute) were obtained on all new compounds.

Synthetic Methods and Reactions. 35.[1] Regioselective Oxidation of Alkyl (Cycloalkyl) Methyl Ethers to Carbonyl Compounds with Nitronium Tetrafluoroborate

Tse-Lok Ho and George A. Olah*

Department of Chemistry, Case Western Reserve University, Cleveland, Ohio 44106

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In our previous work we have shown that nitrosonium salts oxidize benzylic alcohols and the trimethylsilyl and tributylstannyl derivatives of secondary alcohols to carbonyl compounds,[2] and cleave benzylic esters[3] with ease. We now wish to report a related study on the reaction of alkyl (cycloalkyl) methyl ethers with nitronium tetrafluoroborate leading to a facile, regioselective oxidative cleavage.

Contrary to the nitrosonium ion, nitronium ion generally does not act as a hydride acceptor. However, it is a better electrophile toward π, n, and σ donors, as illustrated by, for example, aromatic nitration,[4] nitrate ester formation,[5] and

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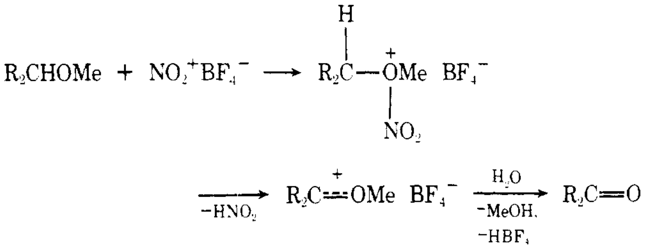
* Address correspondence to Institute of Hydrocarbon Chemistry, Department of Chemistry, University of Southern California, Los Angeles, Calif. 90007.

Table I. Oxidative Cleavage of Methyl Ethers ROMe with NO_2BF_4

R	Registry no.	Product	Registry no.	Yield, %
Benzyl	538-86-3	Benzaldehyde	100-52-7	89
p-Methylbenzyl	3395-88-8	*p*-Tolualdehyde	104-87-0	85
o-Methylbenzyl	15018-12-9	*o*-Tolualdehyde	529-20-4	82
p-Nitrobenzyl	1515-83-9	*p*-Nitrobenzaldehyde	555-16-8	93
2-Octyl	1541-09-9	2-Octanone	111-13-7	63
Cycloheptyl	42604-04-6	Cycloheptanone	502-42-1	57
Cyclohexyl	931-56-6	Methyl 5-oximinocaproate	62344-93-8	60
Cyclopentyl	5614-37-9	Methyl 4-oximinovalerate	62842-23-3	53

the nitration (nitrolysis) of alkanes,[6] respectively. Thus alkyl ethers are expected to react smoothly with nitronium salts to form oxonium ion intermediates which should decompose via nitrous acid elimination. The direction of proton loss is dictated by the stability of the incipient cation; therefore, in most methyl ethers the methoxycarbenium ions would ensue, and the net reaction (with hydrolytic workup) is then a formal demethanation.



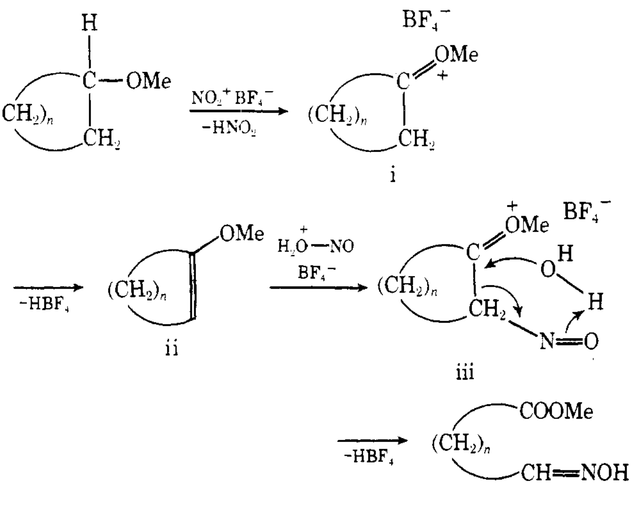
$$R_2CHOMe + NO_2^+BF_4^- \longrightarrow R_2\overset{H}{C}(NO_2)\text{—}\overset{+}{O}Me\ BF_4^- \xrightarrow[-HNO_2]{} R_2\overset{+}{C}\text{=}OMe\ BF_4^- \xrightarrow[-MeOH,\ -HBF_4]{H_2O} R_2C\text{=}O$$

Results summarized in Table I clearly show the generality of methyl ether oxidation. Interestingly, under the experimental conditions methyl ethers of cyclohexanol and cyclopentanol suffer ring fission which is readily accommodated by Scheme I.

It should be noted that cyclohexanone undergoes ring cleavage[7] on reaction with nitrosyl chloride in alcoholic solvents. A similar mechanism involving enol ether formation and nitrosation steps has been formulated. In our cases the enol ethers and the nitrosating agent are only inferred as intermediates. The different behaviors of the cycloalkyl ethers (e.g., cyclohexyl vs. cycloheptyl) can be correlated with the enolizabilities of the corresponding ketones. Thus tautomerization of the methoxycarbenium ions (i) to enol ethers (ii) by elimination of HBF_4 is more favorable when the ring size is either five or six membered.

Methods for oxidative cleavage of *simple* primary alkyl ethers are scarce. One addition is our recently reported process utilizing uranium(VI) fluoride.[8] Most of the existing procedures are concerned with fission of tertiary ethers[9] using trityl salts and silyl and stannyl derivatives of alcohols with various reagents.[2,10] The present method is complementary to others and suggests the feasibility of cleaving enol ethers with nitrosonium salts.

Scheme I



Experimental Section

Oxidative Cleavage of Methyl Ethers with Nitronium Tetrafluoroborate. To a suspension of nitronium tetrafluoroborate[11] (0.565 g, 5 mmol) in dry dichloromethane (5 mL) was added dropwise a solution of a methyl ether (5 mmol) in the same solvent (5 mL) with ice cooling and magnetic stirring. After the vigorous reaction subsided, the ice bath was removed and stirring was continued for 1 h at room temperature. The reaction mixture was quenched with water and extracted with dichloromethane (3 × 20 mL), and the dried ($MgSO_4$) extracts were rotary evaporated to give the product which was microdistilled or recrystallized, and identified by comparison with an authentic sample.

Acknowledgment. Support of our work by the National Institutes of Health is gratefully acknowledged.

Registry No.—Nitronium tetrafluoroborate, 13826-86-3.

References and Notes

(1) Part 34: T.-L. Ho and G. A. Olah, *Synthesis*, 170 (1977).
(2) G. A. Olah and T.-L. Ho, *Synthesis*, 609 (1976).
(3) T.-L. Ho and G. A. Olah, *Synthesis*, in press.
(4) G. A. Olah and S. Kuhn, *Chem. Ind.* (*London*), 98 (1956), and later papers.
(5) G. A. Olah, L. Noszkó, S. J. Kuhn, and M. Szelke, *Chem. Ber.*, **89**, 2374 (1956).
(6) G. A. Olah, and H. C. Lin, *J. Am. Chem. Soc.*, **93**, 1259 (1971).
(7) M. M. Rogić, J. Vitrone, and M. D. Swerdloff, *J. Am. Chem. Soc.*, **97**, 3848 (1975); **99**, 1156 (1977).
(8) G. A. Olah, J. Welch, and T.-L. Ho, *J. Am. Chem. Soc.*, **98**, 6717 (1976).
(9) M. P. Doyle, D. J. DeBruyn, and D. J. Scholten, *J. Org. Chem.*, **38**, 625 (1973); D. H. R. Barton, P. D. Magnus, G. Smith, G. Streckert, and D. Zurr, *J. Chem. Soc., Perkin Trans. 1*, 542 (1972).
(10) K. Saigo, A. Morikawa, and T. Mukaiyama, *Chem. Lett.*, 145 (1975); T. Ogawa and M. Matsui, *J. Am. Chem. Soc.*, **98**, 1629 (1976).
(11) Obtained from Cationics, Inc., Columbia, S.C.

Analysis of Reactivity of Alkenylidenecyclopropanes with Electrophilic Reagents

Daniel J. Pasto,* Michael F. Miles, and Shine-King Chou

Department of Chemistry, University of Notre Dame, Notre Dame, Indiana 46556

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In previous studies on the reactions of differently ring-substituted alkenylidenecyclopropanes with electrophilic reagents, differences in both mode of reaction and reactivity were noted.[1,2] Notably, the phenyl-substituted compound 1 reacted with chlorosulfonyl isocyanide (CSI),[1] acetic acid in the presence of *p*-toluenesulfonic acid (*p*-TS),[2] mercuric acetate,[2] and benzenesulfenyl chloride[2] exclusively at the p orbital on central allene carbon C(4) of the C(1)–C(4) double