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Peracid Oxidation of Imino Ethers[1]

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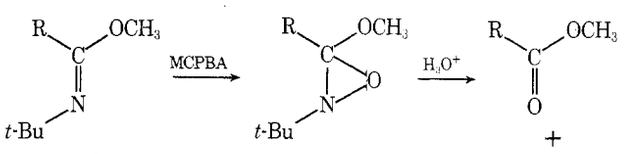
Peracid oxidation of imino ethers results in the formation of 3-alkoxyoxaziranes. The oxidation of the 2-alkoxyazetines **15**, **18**, and **22** leads to unstable 1-aza-5-oxabicyclo[2.1.0]pentanes and Baeyer–Villiger products, 2-alkoxy-2-oxazolines. The product distribution depends upon the substitution at the migrating center. These 2-alkoxy-2-oxazoline products represent the first examples of Baeyer–Villiger type oxidation of imines. The oxaziranes **9** and **10** derived from the cyclic imino ethers **7** and **8** can be isolated, but readily rearrange to imino esters **11** and **12** thermally. The hydrolysis of alkoxyoxaziranes yields esters and hydroxylamines, but hydrolysis of the bicyclic oxaziranes **9** and **10** leads to cyclic hydroxamic acids as well. Further oxidation of alkoxyoxaziranes gives esters and nitroso compounds. The nitroso compounds dimerize if tertiary or tautomerize to oximes if secondary. Oxidation of 2-alkoxyoxazoline **19** (an imino carbonate) results in the formation of a nitroso carbonate **29**, by a double oxidation sequence. Oxidation of imino ethers with 2 equiv of peracid provides a convenient synthetic method for cleavage of the C=N bond.

The oxazirane ring system was first synthesized in 1956 by peracid oxidation of imines.[3–8] Since then, many oxaziranes have been prepared by this method as well as new ones.[9–30] The ring strain and electronegative elements of the oxazirane ring make it unique in its physical and chemical properties. Oxaziranes, for example, have an unusually high barrier to nitrogen inversion (ref 4, 16, 17, 26, 27, 31, 32). Thermally, oxaziranes rearrange to nitrones (ref 3, 4, 6, 8, 11, 15, 26–28) (as low as −8°),[12] amides (generally above 150°) (ref 4, 9, 10b, 26–28, 30), or a carbonyl compound plus an imine (ref 4, 12, 13, 26, 27). Photochemically, oxaziranes open to give nitroxides,[28,33a] nitrenes,[28] or amides.[28,33b,c] Hydrolytically, oxaziranes can decompose to carbonyl compounds, hydroxylamines, and ammonia or imines, the products dependent upon the pH and the substituents of the oxazirane (ref 3, 4, 6, 9, 10b, 26, 27, 30, 34a,b, 35a,b). Some interesting cycloaddition reactions with heterocumulenes have recently been investigated by Agawa and coworkers.[36,37]

While many imines have been oxidized to oxaziranes, no imino ethers have been oxidized before.[1,22] Imino ethers are readily available by alkylation of amides and lactams[38–41] and other methods.[42] Of particular interest are the alkoxyazetines derived from alkylation[43,44a,b] of β-lactams available from addition of chlorosulfonyl isocyanate to olefins.[45,46] This constitutes nearly the only entry into the azetine ring system.[47] We describe here the oxidation of some cyclic and acyclic imino ethers and some properties of the derived alkoxyoxaziranes.

Results and Discussion

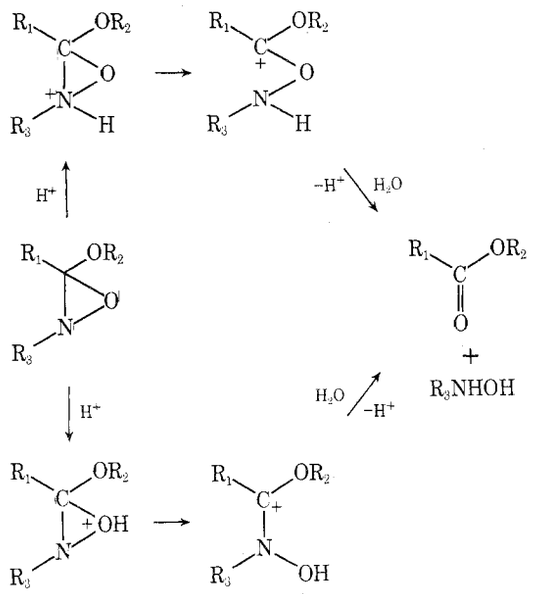
Oxidation of Acyclic Imino Ethers. Oxidation of imino ethers **1** and **2** using *m*-chloroperbenzoic acid (MCPBA) gives the oxaziranes **4** and **5** in good yields. Oxazirane **4** is stable to aqueous base, but treatment with aqueous acid results in the formation of methyl formate (95% by nmr) and *N-tert*-butylhydroxylamine (87% by nmr). This reaction sequence can be used to synthesize hydroxylamines from the corresponding amides in two steps.[4,27] The acid hydrol-



1, R = H
2, R = *t*-Bu
3, R = CH_3

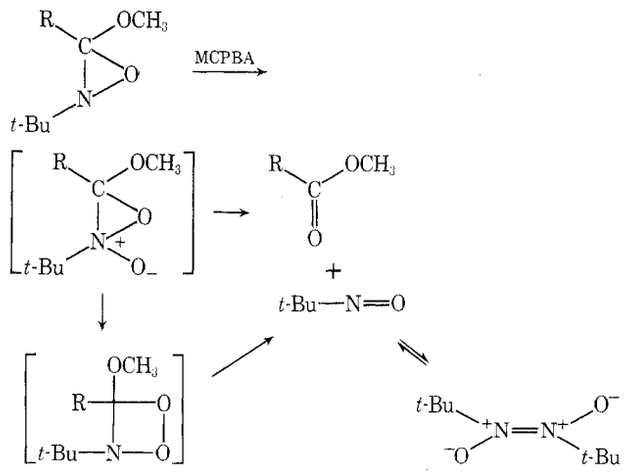
4, R = H
5, R = *t*-Bu
6, R = CH_3

ysis of 3-alkoxyoxaziranes yields products analogous to those obtained from 3-phenyloxaziranes.[3,4,10b,34a,b,35a] Two routes are possible, considering alkoxyoxaziranes as cyclic amide acetals.[48] Protonation on oxygen with C–O bond cleavage has been suggested for this process with most oxaziranes,[4,34a,b,35a] although protonation on nitrogen with C–N bond cleavage is the preferred mode for cleavage of acyclic amide acetals in acid.[48] The C–O cleavage is favored only in neutral hydrolysis of amide acetals.[48] Apparently no N–O cleavage occurs. If it had occurred, a simultaneous

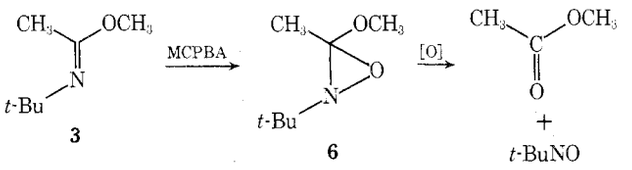


migration from carbon to nitrogen of the 3 substituent would be expected, giving an amine and two carbonyl compounds as observed with some oxaziranes.[4,34a,35a,b] The methoxy substituent probably directs ring cleavage to the ring C–O bond rather than the N–O bond, while ring strain directs cleavage to the ring C–O bond rather than the external C–O bond.

The oxazirane **4** can be oxidized further with MCPBA to give methyl formate (76% by nmr), 2-methyl-2-nitrosopropane (17.5% by nmr) as-a blue liquid, and the solid *trans*-nitroso dimer (58.5% by nmr). The nitroso compounds were independently synthesized by oxidation of *tert*-butylamine using MCPBA.[49] Nitroso compounds have previously been found to result from the peracid oxidation of oxaziranes[4,5,9,14,26,27] and aziridines.[50a] Such reactions were postulated to involve an *N*-oxide which undergoes elimination of the nitrosoalkane,[50b] apparently nonstereospecifically in the case of the aziridine *N*-oxides.[50a] The reaction

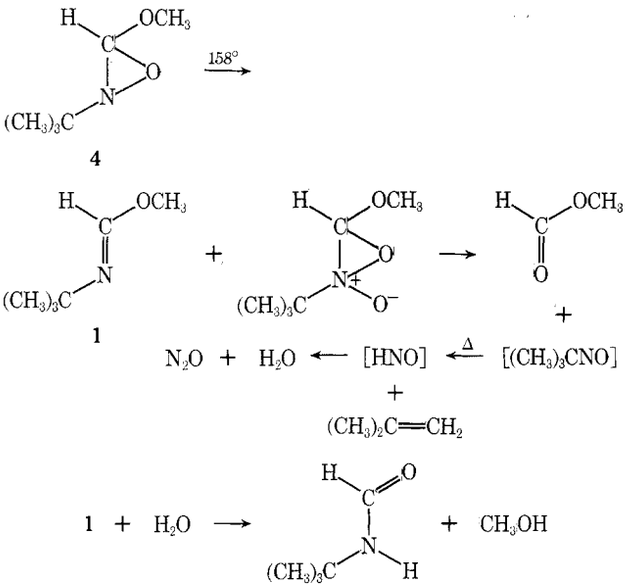


may also go by ring expansion to the unknown dioxazetidine ring system, which would probably cleave readily to the nitrosoalkanes.[51] Curiously, oxidation of the imino ether **3** gives only 5% of the oxazirane **6** along with recovered starting material when a 1:1 ratio of MCPBA and



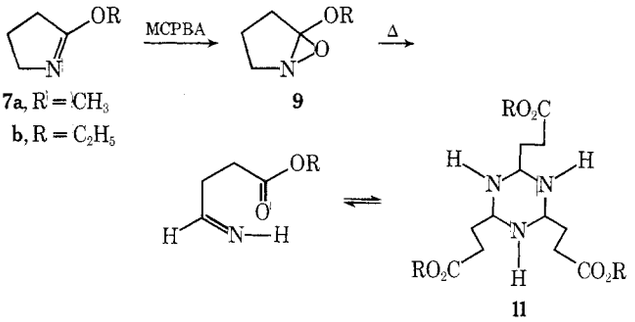
imino ether is used. The oxazirane **6** is especially sensitive to overoxidation and the major products formed are methyl acetate and 2-methyl-2-nitrosopropane.

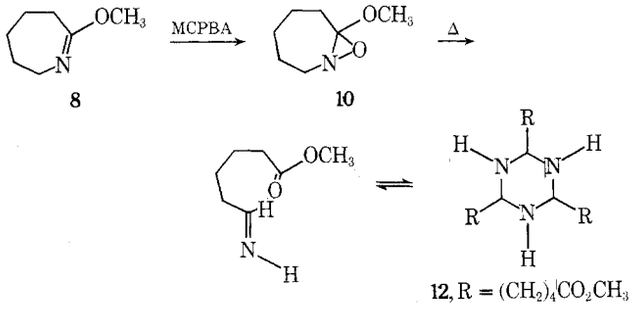
Oxazirane **4** was subjected to vacuum pyrolysis at 158°. The observed products were isobutene (10%), methyl formate (11%), *N-tert*-butylformamide (7%), imino ether **1** (6%), and methanol (18%). Approximately 4% recovered oxazirane **4** and a nonvolatile residue comprise the remainder of the material. Apparently the primary reaction occurring in this pyrolysis is disproportionation of **4** to **1** and the cyclic *N*-oxide, followed by secondary decomposition and hydrolysis of **1**. Analogous products have been characterized in the thermolysis of 2-*tert*-butyl-3-phenyloxazirane,[4,32]



which gives parent imine, benzaldehyde, 2-methyl-2-nitrosopropane, isobutene, and nitrous oxide along with nitrone. Oxaziranes without 3-phenyl substituents normally give amides[4,9,26–28] and oxaziranes with abstractable protons on the 2 substituent normally give a carbonyl compound plus an imine.[4,13,32]

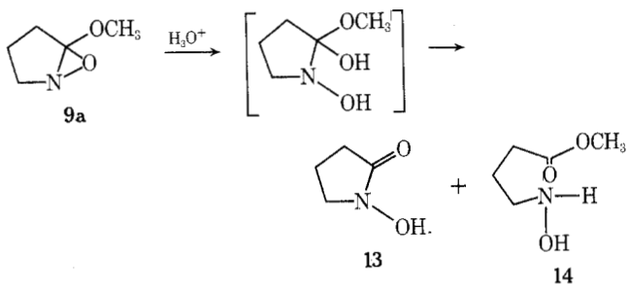
Oxidation of Cyclic Imino Ethers. Oxidation of imino ethers **7** and **8** gives oxaziranes **9** and **10**. In contrast to **4**, oxaziranes **9** and **10** are unstable thermally. The best conditions for formation of **9** and **10** are oxidation in dichloro-





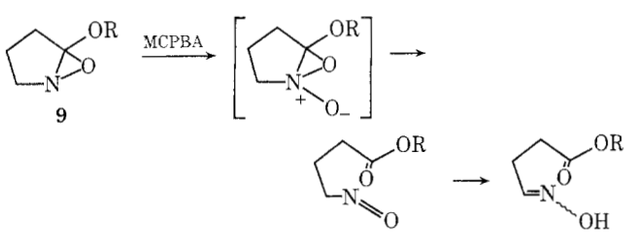
methane[18] at low temperature (−40°) with added solid potassium carbonate. Under these conditions and after careful work-up, yields of **9** are *ca.* 60%. These oxaziranes can decompose violently when concentrated at room temperature. The decomposition of these oxaziranes in dilute solution requires an induction period. Decomposition of oxazirane **9b** results in the formation of ethyl 4-iminobutanoate, isolated as its trimer **11b.** The trimer **11b** was further characterized by conversion to the 2,4-dinitrophenylhydrazone and semicarbazone of ethyl 4-oxobutanoate. The formation of imine esters appears to proceed by a radical chain mechanism analogous to other oxaziranes.[4,26,27] This decomposition for **7** and **8** takes place much more readily and at lower temperatures than for other oxaziranes. The mechanism requires an abstractable hydrogen atom on the carbon next to nitrogen.

Hydrolysis of the above bicyclic oxaziranes was studied using oxazirane **9a.** Treatment of **9a** with aqueous acid results in the formation of methyl 3-hydroxyaminobutanoate (**14**) (17%), *N*-hydroxypyrrolidone (**13**) (27%), and methanol. The hydroxamic acid **13** yields a characteristic dark violet solution upon treatment with ferric chloride solution.[52] Hydrolysis of the oxazirane **10** has been found to yield an analogous hydroxamic acid in 3% yield.[22] Isolated yields of hydroxamic acids are low possibly because of their water solubility. With the isolation of hydroxamic acids from the bicyclic oxaziranes, it is of interest to know if any hydroxamic acids are formed at all from the acyclic oxaziranes upon hydrolysis. Following the same procedure for hydrolysis of oxazirane **9a,** oxazirane **4** gives an essentially quantitative yield of *tert*-butylhydroxylamine with no evidence of hydroxamic acid formation. Testing the reaction mixture with ferric chloride solution was negative for the presence of hydroxamic acids. Hydroxamic acid **13** could be formed from the intermediate shown below along with hydroxylamine **14,** or be the product of cyclization of hydroxylamine

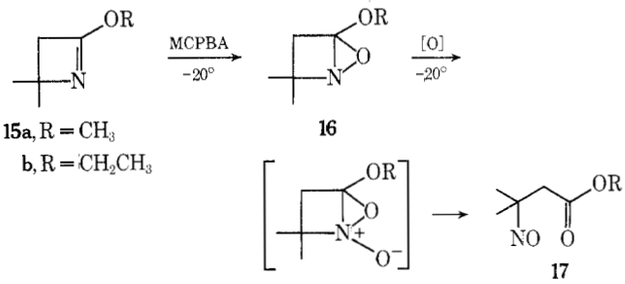


14. Cyclic hydroxamic acids have been obtained by reduction of nitro esters, presumably by cyclization of the hydroxylamino esters.[53,54]

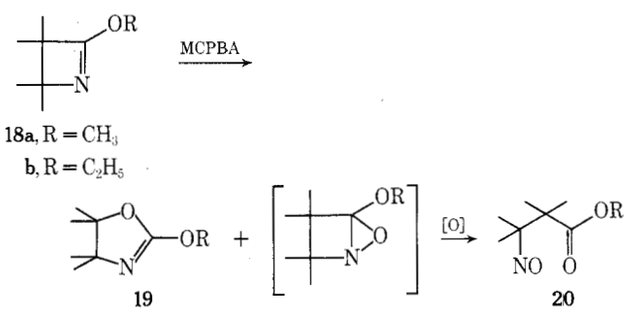
Oxidation of **9** with MCPBA gives methyl alkyl isonitrosobutanoates. Such oxime esters are also isolated as overoxidation products in the preparation of oxaziranes **9** and **10.** These oximes must be derived from tautomerization of the initially formed nitroso compounds. Oxidation of **8** also gives some methyl 5-cyanopentanoate,[22] perhaps by dehydration of the oxime.

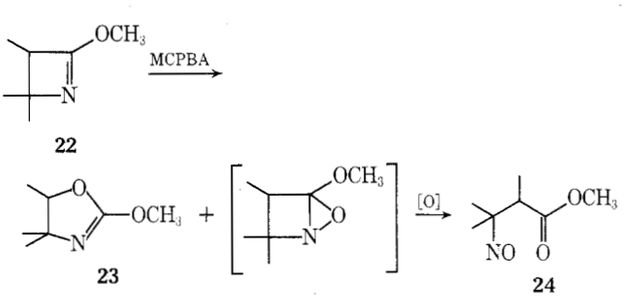


Because of the radical induced rearrangement of oxaziranes **9** and **10** to imines, azetines lacking abstractable hydrogens next to nitrogen were chosen as a source for synthesis of the unknown 1-aza-5-oxabicyclo[2.1.0]pentane ring system. Reaction of 2-methoxy-4,4-dimethylazetine **15a** with 1 equiv of MCPBA results in a 50% conversion of **15a** into methyl 3-methyl-3-nitrosobutanoate **17a,** a bright blue liquid. The novel 2,2-dimethyl-4-methoxy-1-aza-5-oxabicyclo[2.1.0]pentane (**16**) was detected as an intermediate in the reaction by observation of characteristic nmr signals at low temperature. An AB pattern for the ring methylene group, the nonequivalent methyl groups, and the upfield methoxy group strongly support the oxazirane structure **16** for this intermediate. It could not be isolated,



however, because of its rapid oxidation on to the nitroso ester, **17a.** In contrast, the reaction of 2-methoxy-3,3,4,4-tetramethylazetine (**18a**) with 1 equiv of MCPBA yields 2-methoxy-4,4,5,5-tetramethyloxazoline (**19a**) with only a trace of methyl 2,2,3-trimethyl-3-nitrosobutanoate (**20**). Following the reaction by low-temperature nmr showed the buildup of **19a** at the expense of azetine **18a,** with no detectable intermediate. Oxidation of 2-methoxy-3,4,4-trimethylazetine (**22**) with an excess of MCPBA results in a mixture of 2-methoxy-4,4,5-trimethyloxazoline (**23**) and methyl 2,3-dimethyl-3-nitrosobutanoate (**24**). A 53% yield of products containing 73% of **23** and 27% of **24** is obtained.

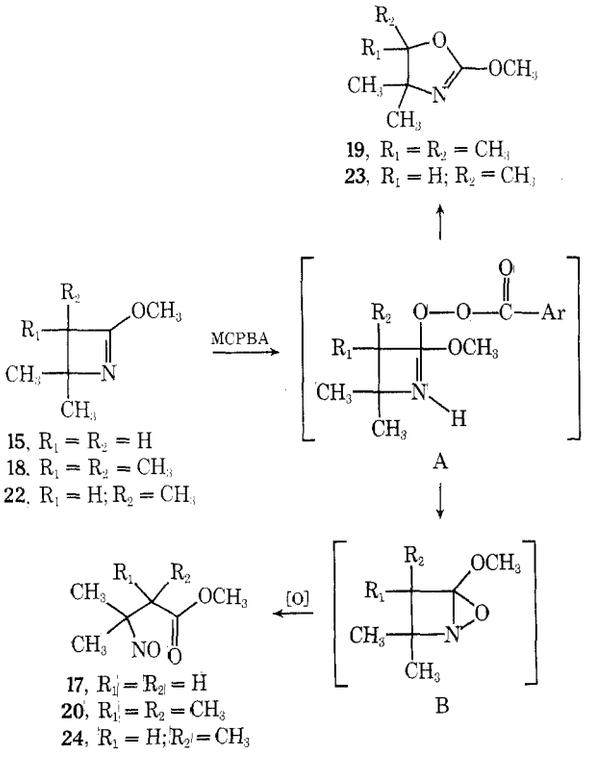




Again, no intermediate oxazirane could be detected by low-temperature nmr. The distribution of oxidation products changes in regular fashion with increasing substitution at C-3. Ring expansion (giving oxazolines) becomes less competitive compared to oxidation to bicyclic oxaziranes (giving nitroso esters) with decreasing substitution at C-3 of the alkoxyazetines. Not only is the bicyclic oxazirane **16** the first reported 1-aza-5-oxabicyclo[2.1.0]pentane ring system, but the oxazolines **19** and **23** represent the first isolated products attributable to a Baeyer–Villiger oxidation of

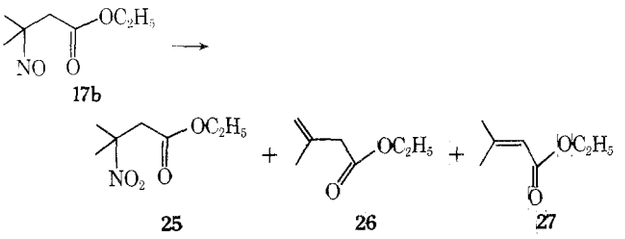
an imine. The migratory aptitude of C-3 in forming the oxazolines is tertiary > secondary > primary.

Unlike the one-step mechanism of oxidation of olefins to epoxides,[55] the mechanism of peracid oxidation of imines has recently been proposed to be a two-step mechanism similar to the Baeyer–Villiger reaction.[29] Addition to the carbon nitrogen double bond is normally the rate-determining step. Previous support for this mechanism comes from isolation of intermediates that decompose to oxaziranes[23,24] and products attributable to hydrolysis of Baeyer–Villiger intermediates.[30] The peracid oxidation of azetines **18** and **22** supports this mechanism since the Baeyer–Villiger rearrangement products **19** and **23** are well explained by the intermediacy of the tetrahedral addition product A. The Baeyer–Villiger intermediate A can then decompose competitively to B or **19** (**23**) depending upon the migratory aptitude of C-3.



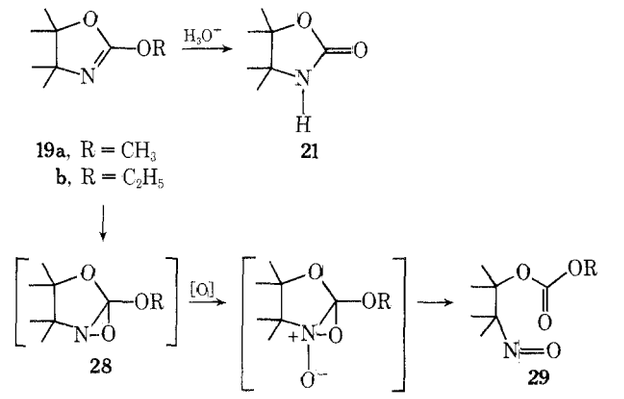
To check for the possibility of Baeyer–Villiger reactions with other imino ethers with tertiary migrating groups, imino ether **2** was oxidized (*vide supra*). No indication of a Baeyer–Villiger product could be found by nmr, however. Apparently migration is dependent on ring strain as well as the availability of a good migrating group. As a point of interest, oxidation of **3** proceeds without the filterable precipitate characteristic of all other peracid oxidations. It could be that a relatively stable Baeyer–Villiger intermediate forms and remains in solution.

The isolated tertiary nitroso esters encountered in this work decompose on standing. The decomposition was studied using ethyl 3-methyl-3-nitrosobutanoate (**17b**) obtained by double oxidation of azetine **15b.** The nitroso ester **17b** decomposes to a mixture composed of 24% ethyl 3-methyl-3-nitrobutanoate (**25**), 32% of ethyl 3-methyl-3-butenoate (**26**), and 44% of ethyl 3-methyl-2-butenoate (**27**). The formation of nitro compounds from oxaziranes is not unprecedented. Emmons[4] obtained 7% of 2-methyl-2-nitroheptane as the only isolated product from acid hydrolysis of 2-*tert*-octyloxazirane. Also, nitroso compounds are known to form nitroxides plus nitric oxide upon irradiation,[28] to generate olefins plus nitric acid upon thermolysis



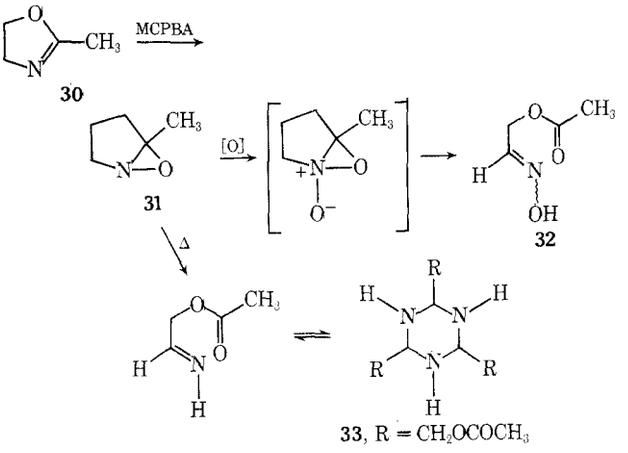
with nitric oxide,[56] and to form nitro compounds by disproportionation.[51a] The details of the decomposition pathways of nitroso compounds, however, are unknown. For the above decomposition mixture, a 45 to 55% ratio of **26** to **27** was found. No change in the ratio of products occurred when the unsaturated ester mixture was subjected to experimental conditions.[57]

The oxazolines **19a** and **b** formed from oxidation of the azetines are comparable to the imino ethers in reactivity. They were found to undergo hydrolysis and oxidation reactions characteristic of cyclic imino ethers. Acid hydrolysis of **19a** results in the formation of 4,4,5,5-tetramethyl-2-oxazolidinone (**21**). Oxidation of **19b** with 1 equiv of MCPBA results in a 50% conversion of **19b** into the nitroso carbonate **29b,** by a mechanism analogous to that for the oxidation of **15a** to **17a.** The extra alkoxy substituent in **19b**



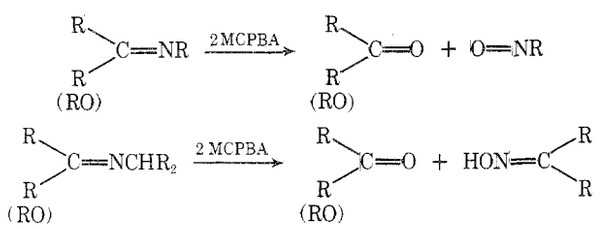
makes it less reactive than imino ether **7**; **19b** is oxidized only at 25° while **7** reacts with MCPBA below 0°. No intermediate oxazirane was detected in the nmr spectrum at 25° as **19b** was oxidized to **29b.**

To test the effect of constraining the ether group of an imino ether within a rigid ring, the oxidation of oxazoline **30** was explored. Using 1 equiv of MCPBA, oxidation of **30** followed by vacuum distillation gave a mixture of **30** and 5-methyl-1-aza-4,6-dioxabicyclo[3.1.0]hexane (**31**). No conditions were found, however, where **30** could be completely oxidized to **31** without concurrent formation of 2-acetoxy-



acetaldoxime (**32**). The oxazirane **31** decomposes in solution to the trimer of 2-acetoxyacetaldimine (**33**) in a reaction analogous to the other bicyclic oxaziranes with abstractable hydrogens.

For all of the imino ethers studied, the further oxidation of oxaziranes to give cleavage products is possible. For the imino ethers and the oxazolines **19a,b** the oxidation rates of the oxaziranes and the starting imines are comparable. Whether the oxidation rate of the oxazirane is slow enough to permit its isolation varies rather unpredictably. Imino ethers **1, 2, 3, 7, 8, 15a,** and **30** give isolable (or detectable) oxaziranes but **22** and **19a** give oxidative cleavage products. Such oxidative cleavages appear to be general for imines,[4,5,9,14] imino ethers, and oxazolines. They provide a specific, mild, and nonhydrolytic method for the cleavage of C=N bonds which could be useful synthetically.



Experimental Section

All boiling points and melting points are uncorrected. Vpc analyses were performed with a Varian Aerograph (A-700) gas chromatograph equipped with a thermal conductivity detector. Ir spectra were obtained in solution with a matched reference cell on a Perkin-Elmer 337 grating infrared spectrophotometer. Uv spectra were recorded on a Cary 15 spectrophotometer. Nmr spectra were obtained on a 60-MHz Varian Associates T-60 or a Jeolco C-60H spectrometer. Where indicated, 100-MHz spectra were obtained on a Varian HA-100 spectrometer. Mass spectra were obtained on a MS-902 spectrometer or on a Finnigan 1015 quadrupole spectrometer where indicated.

Materials. The *m*-chloroperbenzoic acid (MCPBA), 1-aza-2-methoxycycloheptene (**8**), 2-methyloxazoline (**30**), chlorosulfonyl isocyanate (CSI), and methyl fluorosulfonate were purchased from Aldrich Chemical Co. The amide precursors were either available commercially or made from the corresponding acid chloride and amine for the acyclic amides or chlorosulfonyl isocyanate addition to olefins followed by reduction to the corresponding β-lactams.[45,46]

General Procedure for Preparation of Imino Ethers. To a solution of 1 equiv of trialkyloxonium tetrafluoroborate[40] in dichloromethane was added a solution of amide in dichloromethane at room temperature. After a minimum of 1 hr, this solution was dripped into ice-cold aqueous sodium hydroxide solution, separated, and dried over sodium hydroxide pellets. The solvent was removed by distillation followed by distillation of the imino ether.

O-**Methyl-***N-tert*-**butylformimidate (1):** 70% yield; bp 90–100°; ir (CH_2Cl_2) 2960, 1670, 1370, 1190, 1170, 690 cm^{-1}; nmr (CCl_4) δ 1.15 (s, 9 H), 3.50 (s, 3 H), 7.33 (s, 1 H); mass spectrum (70 eV) *m/e* 115.0997 (calcd for $C_6H_{13}NO$, 115.0997), *m/e* (rel intensity) 115 (M^+, 84), 101 (5), 100 (10), 86 (4), 4 (3), 72 (10), 68 (15), 60 (12), 57 (30), 56 (11), 43 (4), 42 (15), 41 (40), 39 (10), 30 (4), 29 (18), 28 (12), 27 (8), 18 (9), 15 (9).

O-**Methyl-***N-tert*-**butylacetimidate (3):** 80% yield; bp 60° (100 mm); ir (CH_2Cl_2) 2960, 1690, 1370, 1200, 1065 cm^{-1}; nmr (CH_2Cl_2) δ 1.17 (s, 9 H), 1.88 (s, 3 H), 3.44 (s, 3 H); mass spectrum (70 eV) *m/e* 129.1154 (calcd for $C_7H_{15}NO$ 129.1154), *m/e* (rel intensity) 129 (M^+, 15), 115 (6), 114 (100), 82 (6), 74 (17), 73 (11), 72 (9), 58 (5), 57 (32), 56 (11), 55 (5j, 43 (31), 42 (53), 41 (32), 39 (11), 29 (19), 28 (9), 27 (9), 15 (13).

1-Aza-2-methoxycyclopentene (7a): 69% yield; bp 118–120° (lit. bp 118–120°).[58]

1-Aza-2-ethoxycyclopentene (7b): 81% yield; bp 137–142° (lit. bp 135–140°).[59]

2-Methoxy-4,4-dimethylazetine (15a): 78% yield; bp 50° (75 mm) (lit. bp 112–114°).[43]

2-Ethoxy-4,4-dimethylazetine (15b): 81% yield; bp 137–142° [lit. bp 82° (100 mm)].[43]

2-Methoxy-3,3,4,4-tetramethylazetine (18a): 58% yield; bp 54° (28 mm); ir (CH_2Cl_2) 2960, 1630 cm^{-1}; nmr (CCl_4) δ 1.07 (s, 6 H), 1.12 (s, 6 H), 3.66 (s, 3 H); mass spectrum (70 eV) *m/e* 141.1158 (calcd for $C_8H_{15}NO$, 141.1154), *m/e* (rel intensity) 141 (M^+, 49), 140 (14), 127 (34), 99 (15), 85 (18), 84 (44), 83 (13), 73 (13), 70 (45), 69 (70), 68 (18), 58 (20), 57 (18), 56 (33), 55 (26), 43 (30), 42 (70), 41 (100), 39 (36), 29 (18), 28 (30), 27 (25), 18 (31), 15 (27).

2-Ethoxy-3,3,4,4-tetramethylazetine (18b): 80% yield; bp 68° (80 mm) [lit. bp 82° (50 mm)].[43]

2-Methoxy-3,4,4-trimethylazetine (22): 50% yield; bp 50° (50 mm); ir (CCl_4) 2960, 1630 cm^{-1}; (CCl_4) δ 1.05 (d, J = 7.4 Hz, 3 H), 1.13 (s, 3 H), 1.22 (s, 3 H), 1.65 (q, J = 7.4 Hz, 1 H), 3.72 (s, 3 H); mass spectrum (70 eV) *m/e* 127.0992 (calcd for $C_7H_{13}NO$, 127.0997), *m/e* (rel intensity) 127 (M^+, 20), 126 (6), 112 (32), 98 (20), 84 (38), 82 (6), 71 (26), 70 (16), 58 (38), 57 (8), 56 (100), 55 (44), 54 (18), 43 (12), 42 (34), 41 (54), 39 (28), 29 (20), 28 (40), 27 (34), 18 (6), 15 (28).

O-**Methyl-***N-tert*-**butylpivalimidate (2).** No alkylation took place using oxonium salts and *N-tert*-butylpivalamide. The amide and methyl fluorosulfonate were heated to 90° neat. Upon cooling, crystals developed. The solid was identified as the fluorosulfonic acid salt of imino ether **2:** mp 131–133°; ir (CH_2Cl_2) 2950, 1610 cm^{-1}; nmr (CH_2Cl_2) δ 1.45 (s, 9 H), 1.50 (s, 9 H), 4.50 (s, 3 H). The salt was dissolved in dichloromethane and mixed with concentrated aqueous sodium hydroxide at room temperature for 1 hr. The organic layer was separated and dried over sodium hydroxide pellets, and solvent removed. Distillation gave imino ether **2:** bp 75° (45 mm); ir (CH_2Cl_2) 2960, 1660 cm^{-1}; nmr (CCl_4) δ 1.17 (s, 9 H), 1.20 (s, 9 H), 3.67 (s, 3 H); mass spectrum (70 eV) *m/e* 171.1625 (calcd for $C_{10}H_{21}NO$, 171.1623), *m/e* (rel intensity) 171 (M^+, 1), 157.1466 ($M^+ - CH_2$, 2), 156 (4), 102.0919 ($M^+ - C_5H_9$, 0.7), 100 (2), 95 (4), 84 (2), 82 (3), 73 (9), 68 (32), 67 (11), 57 (26), 56 (29), 55 (12), 42 (74), 41 (100), 39 (28), 32 (20), 31 (21), 29 (22), 28 (36), 27 (17), 18 (11), 15 (15); stereochemistry not established.

General Procedure for Oxidation of Imino Ethers. 2-*tert*-Butyl-3-methoxyoxazirane (4). To a mixture of 2.654 g (0.013 mol)[60] of MCPBA, 500 mg of anhydrous potassium carbonate, and 10 ml of dichloromethane at −40° was added 1.326 g (0.012 mol) of **1** in 3 ml of dichloromethane. After 30 min the solution was filtered at −70°. The residue was rinsed with 2 ml of dichloromethane at −70°. The cold filtrates were poured into cold aqueous sodium bicarbonate containing a small amount of sodium sulfite. The organic layer was separated, washed with saturated sodium chloride solution, and dried over anhydrous potassium carbonate. The solvent was removed by careful distillation through a 10-cm Vigreux column. Vacuum distillation gave 979 mg (65%) of **4:** bp 52° (45 mm); ir (neat) 2970, 1480, 1410, 1370, 1280, 1150, 790 cm^{-1}; nmr (CCl_4) δ 1.08 (s, 9 H), 3.15 (s, 3 H), 5.17 (s, 1 H); mass spectrum (70 eV) *m/e* 131.0946 (131.0946 calcd for $C_6H_{13}NO_2$), *m/e* (rel intensity) 131 (M^+, 0.4), 130 (0.6), 129 (0.8), 116 (2.6), 115 (1.6), 114 (1.8), 101 (8), 100 (14), 76 (16), 75 (11), 56 (90), 55 (90), 43 (10), 42 (27), 41 (100), 40 (9), 39 (30).

Hydrolysis of 4. (a) To a solution of 162 mg (1.24 mmol) of **4** in 0.5 ml dichloromethane were added 266 mg (1.55 mmol) of *p*-toluenesulfonic acid, 23 mg (1.28 mmol) of water, and 9.0 mg of benzene. Integration of the nmr spectrum of the homogeneous solution indicated the presence of 95% methyl formate using benzene as an internal standard. Enough aqueous sodium hydroxide solution was added so that the system was basic. Nmr integration on the organic layer showed 87% of *tert*-butylhydroxylamine to be present. (b) A mixture of 498 mg of **4** and 5 ml of 10% aqueous sulfuric acid was stirred at 0°. Within a few minutes a homogeneous solution was obtained. The acidic solution was evaporated to remove methyl formate identical with an authentic sample: ir (CH_2Cl_2) 1730 cm^{-1}; nmr (CCl_4) δ 3.74 (s, 3 H), 8.04 (s, 1 H). The solution was made basic with sodium hydroxide, extracted two times with 3 ml of dichloromethane, and dried over anhydrous potassium carbonate. The solvent was evaporated *in vacuo* leaving behind 76 mg (23%) of *tert*-butyl hydroxylamine: mp 58–59.5° [lit. mp 64–65°];[4] nmr (CCl_4) δ 1.07 (s).

Oxidation of 4. To a solution of 48.8 mg (0.372 mmol) of **4** in 0.5 ml of dichloromethane was added a solution of 83.5 mg (0.412 mmol)[60] of MCPBA in 1.0 ml of dichloromethane at 0°. Integration of the nmr spectrum after 12 hr at 25° gave 76% of methyl formate, 17.5% of 2-methyl-2-nitrosopropane, and 58.5% of the nitroso dimer using benzene as an internal standard.

Oxidation of *tert*-Butylamine. To 92 mg (1.26 mmol) of frozen (−78°) *tert*-butylamine was added 511 mg (2.52 mmol)[60] of MCPBA. The mixture was slowly allowed to come to room temperature. Vacuum distillation gave a blue liquid, bp <25° (1 mm),

that slowly turned into a white solid. The blue liquid was 2-methyl-2-nitrosopropane:[49] ir (CH_2Cl_2) 1540 cm^{-1}; nmr (CH_2Cl_2) δ 1.20 (s). The white solid was the trans dimer of 2-methyl-2-nitrosopropane: mp 75° (sublimation) [lit. mp 83°,[61] and 76° (sublimation)[62]]; nmr (CH_2Cl_2) δ 1.57 (s).

Thermolysis of 4. A 100-ml evacuated (10^{-3} mm) bulb containing 68 mg of **4** was heated at 158° for 2 hr. Integration of the nmr spectrum using chloroform as an internal standard gave 6% imino ether, 10% isobutylene, 11% methyl formate, 18% methanol, 7% *N-tert*-butylformamide, and 4% recovered oxazirane **4**. The remaining material was unidentified residue.

2,3-Di-*tert*-butyl-3-methoxyoxazirane (5). Following the procedure for **4**, treatment of 130 mg (0.76 mmol) of **2** with 155 mg (0.70 mmol)[60] of MCPBA gave 68 mg (36%) of **5**: bp <50° (2 mm); ir (CH_2Cl_2) 2950, 1120 cm^{-1}; nmr (CH_2Cl_2) δ 0.97 (s, 9 H), 1.13 (s, 9 H), 3.47 (s, 3 H); mass spectrum (70 eV) *m/e* 157.1459 (calcd for $C_9H_{19}NO$, 157.1466, $M^+ - CH_2O$), *m/e* (rel intensity) 187 (0.008), 172 (0.016), 171 (0.034), 170 (0.034), 157 (1.9), 116 (6.4), 73 (9), 57 (100), 56 (64), 42 (18), 41 (64), 39 (23).

Oxidation of 3. A mixture of 372 mg (1.83 mmol)[60] of MCPBA in 5 ml of dichloromethane containing 1.5 g of anhydrous potassium carbonate was cooled to −50°. To this solution was added 212 mg (1.64 mmol) of **3** in 1 ml of dichloromethane. After 30 min the solution was filtered at −50°. Filtration of the solution was difficult, taking over 1 hr, leaving little *m*-chlorobenzoic acid behind. The blue colored solution was distilled at <25° (2 mm) removing some methyl acetate and 2-methyl-2-nitrosopropane along with dichloromethane. Distillation at <25° (0.1 mm) showed the presence of 5% of 2-*tert*-butyl-3-methyl-3-methoxyoxazirane (**6**), 17% of methyl acetate, 8% of 2-methyl-2-nitrosopropane, and 5% of imino ether **3**. The nmr spectrum of **6** in CH_2Cl_2 showed peaks at δ 1.13 (s, 9 H), 1.75 (s, 3 H), and 3.10 (s, 3 H).

5-Methoxy-1-aza-6-oxabicyclo[3.1.0]hexane (9a). Following the procedure for **4**, treatment of 708 mg (3.48 mmol)[60] of MCPBA with 310 mg (3.13 mmol) of **7a** gave 75% of **9a** in dichloromethane (from integration of nmr spectrum using benzene as an internal standard): bp <25° (0.1 mm); ir (CH_2Cl_2) 2940 cm^{-1}; nmr (CH_2Cl_2) δ 1.40–2.40 (m, 6 H), 2.70–3.20 (m, 2 H), 3.12 (s, 3 H); mass spectrum (Finnigan) (70 eV), *m/e* (rel intensity) 115 (M^+, 0.4), 100 (1.1), 94 (0.9), 88 (1.8), 85 (1.5), 84 (0.9), 59 (1.5), 57 (2.9), 56 (3.3), 55 (2.2), 54 (0.9), 44 (27), 40 (100). The mass spectral sample contained some of the trimer, **11**.

The oxazirane **9a** decomposed to the imine trimer **11a** of methyl 4-iminobutanoate upon standing: ir (CH_2Cl_2) 3300, 2940, 1750 cm^{-1}; nmr (CH_2Cl_2) δ 0.80 (br s, 1 H), 1.60 (m, 2 H), 2.30 (m, 2 H), 3.30 (m, 1 H), 3.48 (s, 3 H); mass spectrum (70 eV) *m/e* (rel intensity) 329 ($M^+ - 16$, 0.06), 312 (0.1), 298 (0.08), 269 (0.08), 255 (0.4), 241 (1.2), 228 (0.8), 214 (16), 182 (8), 154 (17), 150 (9), 122 (40), 116 (17), 100 (59), 94 (42), 84 (100), 59 (32), 57 (43), 56 (78), 55 (40), 54 (39), 41 (77). The imine trimer **11a**, an oil, decomposed upon attempted purification *via* distillation or column chromatography.[63]

5-Ethoxy-1-aza-6-oxabicyclo[3.1.0]hexane (9b). Following the procedure for **4**, treatment of 487 mg (2.40 mmol)[60] of MCPBA with 263 mg (2.33 mmol) of **7b** gave 47.5% (by nmr) of **9b** in dichloromethane: bp <25° (0.1 mm); ir (CH_2Cl_2) 2970 cm^{-1}; nmr (CCl_4) δ 1.12 (t, J = 7.4 Hz, 3 H), 1.30–2.30 (m, 4 H), 2.80–3.30 (m, 2 H), 3.52 (q, J = 7.4 Hz, 2 H); mass spectrum (Finnigan) (10 eV) *m/e* (rel intensity) 129 (M^+, 0.9), 115 (0.6), 114 (1.1), 113 (1.1), 112 (1.4), 102 (6.4), 101 (100), 100 (13), 86 (27), 85 (68), 84 (52), 74 (29), 73 (70), 58 (22), 57 (41), 56 (67), 46 (55), 45 (27), 44 (27), 42 (22).

The oxazirane **9b** decomposed in acid-free dichloromethane solution to the trimer of ethyl 4-iminobutanoate (**11b**) in quantitative yield by nmr: mp 70–72°; ir (CH_2Cl_2) 3400, 2970, 1740, 1180 cm^{-1}; nmr (CH_2Cl_2) δ 0.80 (br s, 1 H, N–H), 1.22 (t, J = 8.5 Hz, 3 H), 1.80 (m, 2 H), 2.30 (m, 2 H), 3.55 (m, 1 H), 4.10 (q, J = 8.5 Hz, 2 H) (*ca.* 7.8, br s, N–H unknown, trace);[63] mass spectrum (70 eV) *m/e* (rel intensity) 387 (M^+, 0.003), 362 (0.01), 343.2175 ($M^+ - C_2H_5O$, 0.003), 326.1851 ($M^+ - C_2H_7NO$, 0.13), 325 (0.3), 297 (0.1), 283.1657 ($M^+ - C_4H_{10}NO_2$, 0.9), 270.1617 ($M^+ - C_5H_9NO_2$, 0.9), 269 (1.3), 256 (0.8), 242 (4), 212 (1.4), 196 (6), 168 (12), 150 (3), 130 (4), 129 (4), 122 (17), 102 (20), 100 (79), 94 (28), 85 (42), 84 (100), 74 (36), 73 (20), 57 (22), 56 (86), 55 (28), 54 (20), 45 (28), 41 (42). The imine trimer **11b** was further characterized by conversion to the 2,4-dinitrophenylhydrazone, mp 113–115° (lit. mp 110–111°),[64a,b] and the semicarbazone, mp 133–135° (lit. mp 135°),[64a,b,65] of ethyl 4-oxobutanoate. The imine trimer **11b** was also converted to its oxime, ethyl 4-isonitrosobutanoate, upon treatment with hydroxylamine (identical ir and nmr with the compound isolated below).

Ethyl 4-Isonitrosobutanoate from Oxidation of 7b. Aqueous sodium bicarbonate solution and dichloromethane were added to the residue from oxidation of **7b** after filtration. The dichloromethane extract was dried over potassium carbonate and evaporated *in vacuo* leaving an oil. Vacuum distillation gave 10 mg of oxime: bp 60–80° (0.3 mm) [lit. bp 139° (14 mm)[65] and 149–152° (11 mm)[66]]; ir (CH_2Cl_2) 3590, 3300, 2970, 1740, 1175 cm^{-1}; nmr (HA-100) (CCl_4) δ 1.27 (t, J = 7.0 Hz, 3 H), 2.49 (m, 4 H), 4.09 (q, J = 7.0 Hz, 2 H), 6.67 (m, 0.39 H, syn), 7.37 (m, 0.61 H, anti), 8.95 (br s, 1 H); mass spectrum (70 eV) *m/e* (rel intensity) 128 (M^+ − 17.5), 115 (2), 100 (20), 99 (7), 82 (23), 72 (11), 55 (14), 54 (16), 44 (13), 29 (30), 28 (32), 27 (21), 18 (100), 17 (29). The oxime was further characterized by conversion to 2,4-dinitrophenylhydrazone of ethyl 4-oxobutanoate, mp 108–109° (lit. mp 110–111°).[64a,b] Oxidation of **9b** using MCPBA also produced some ethyl 4-isonitrosobutanoate.

Ethyl 4-Oxobutanoate from the Oxidation Products of 7b. Some traces of aldehyde have been observed from neutral hydrolysis of oxazirane **9b**, or acid hydrolysis of the oxime and imine trimer **11b**. The data for the aldehyde are bp 60° (1–2 mm) [lit. bp 84–85° (12 mm)[65]]; ir (CH_2Cl_2) 2940, 2900, 2830, 2730, 1730 cm^{-1}; nmr (CH_2Cl_2) δ 1.16 (t, J = 7.3 Hz, 3 H), 2.64 (four-peak m, 4 H), 4.12 (q, J = 7.3 Hz, 2 H), 9.70 (t, J < 1 Hz, 1 H); mass spectrum (70 eV) *m/e* (rel intensity) 115 (M^+, 1.2), 114 (2), 101 (10), 73 (3), 59 (3), 57 (2), 56 (2.5), 55 (6), 45 (4), 44 (2.5), 43 (2.5), 29 (7), 28 (18), 27 (4), 18 (100), 17 (24).

Hydrolysis of Oxazirane 9b. A mixture of 120 mg (1.05 mmol) of oxazirane **9b**, 1 ml of dichloromethane, and 1 drop (19 mg, 1.05 mmol) of water was saturated with hydrogen chloride gas. A water soluble oil remained after removal of volatiles *in vacuo*. The oil was dissolved in deuterium oxide and made basic (pH 8) with sodium hydroxide. The nmr spectrum of the aqueous solution showed the presence of both methyl 4-hydroxyaminobutanoate (**14**) and *N*-hydroxypyrrolidone (**13**). The aqueous material was extracted with dichloromethane. The dichloromethane solution was separated and evaporated *in vacuo*. Water was added (for hydrogen exchange) and reevaporated *in vacuo* leaving 24 mg (17%) of ester hydroxylamine **14**: ir (CH_2Cl_2) 3670, 3570, 3440, 3270, 2940, 1735, 1185 cm^{-1}; nmr (CH_2Cl_2) δ 1.92 (m, $J \simeq$ 6.8 Hz, 2 H), 2.34 (m, 2 H), 2.90 (J = 6.6 Hz, 2 H), 3.64 (s, 3 H), 6.37 (br s, 2 H); mass spectrum (70 eV) *m/e* 130.0873 (calcd for $C_6H_{12}NO_2$, 130.0868), *m/e* (rel intensity) 130 ($M^+ - OH$, 1.8), 115.0759 ($M^+ - NHOH$, 1.8), 100 (4.4), 99 (1.8), 55 (3.3j, 54 (3), 45 (3.3), 44 (3.7), 43 (3.7), 42 (3), 41 (3.3), 31 (2.6), 29 (10), 28 (11), 27 (6), 18 (100), 17 (26). The ester hydroxylamine **14** decomposed within hours either neat or in solution. The basic aqueous (D_2O) layer above was evaporated *in vacuo* and water was added (for hydrogen exchange), and the mixture reevaporated *in vacuo*, leaving a solid behind. Recrystallization of the solid from carbon tetrachloride–dichloromethane solution gave 28 mg (27%) of hydroxamic acid **13**: mp 80–81° (lit. mp 68–69°);[67] ir (CH_2Cl_2) 3650, 3100, 2900, 1690 cm^{-1}, nmr (CH_2Cl_2) δ 1.67–2.67 (m, 4 H), 3.57 (t, J = 7.0 Hz, 2 H), 8.75 (s, 1 H); mass spectrum (70 eV) *m/e* 101.0470 (calcd for $C_4H_7NO_2$, 101.0476), *m/e* (rel intensity) 101 (M^+, 42), 85 (15), 73 (9), 56 (23), 55 (15), 46 (66), 45 (21), 42 (23), 41 (17), 30 (15), 29 (11), 28 (70), 27 (19), 18 (100), 17 (21).

Oxidation of 8. A mixture of 280 mg (1.38 mmol)[60] of MCPBA, 100 mg of potassium carbonate, and 2 ml of dichloromethane was cooled to −40°. To this mixture was added 143 mg (1.0 mmol) of **8** in 1 ml of dichloromethane. After 30 min the solution was filtered at −78°. The nmr spectrum of this solution indicated approximately 50% formation of 7-methoxy-1-aza-8-oxabicyclo[5.1.0]octane **10** and 50% of a mixture of esters. Distillation afforded 15 mg (1%) of **10**: bp <50° (0.03 mm) [lit. bp 110–120° (0.27 mm)[22]]; ir (CCl_4) 2940, 1480, 1450, 1395, 1320, 1245, 1110 cm^{-1}; nmr (CCl_4) δ 1.15–2.50 (m, 10 H], 3.10 (s, 3 H); mass spectrum (25 eV) *m/e* (rel intensity) 143 (M^+, 0.09), 142 (0.14), 127 (0.9), 126 (1.1), 113 (5), 112 (2), 96 (5), 85 (10), 84 (29), 83 (5), 70 (5), 69 (20), 68 (8), 67 (9), 60 (3), 59 (8), 57 (12), 56 (100), 55 (83), 54 (12), 45 (4), 44 (6), 43 (26), 42 (57), 41 (86). Cyclohexane was an impurity in the mass spectrum. Aqueous sodium bicarbonate–sodium sulfite solution and dichlormethane were added to the residue from distillation of **10**. The dichloromethane extract was dried over potassium carbonate and evaporated *in vacuo* leaving an oil. Distillation afforded 124 mg (78% based on oxime), bp <120° (0.1 mm), of a mixture of methyl 5-cyanopentanoate (**35**) (~35% by nmr) and methyl 6-isonitrosohexanoate (**36**) (~65% by nmr). Redistillation resulted in an early fraction composed of **35** and a late fraction composed of **36**. The data for **35** are bp 60° (0.3 mm) [lit. bp 87–89° (2 mm)[68]]; ir (CCl_4) 2950, 2250, 1750 cm^{-1}; nmr (CCl_4) δ 1.50–2.00 (m, 4 H), 2.00–2.50 (m, 4 H), 3.68 (s, 3 H); mass spectrum (70 eV) *m/e* (rel

intensity) 141 (M^+, 0.4), 139 (1), 110 (24), 83 (5), 82 (60), 81 (8), 74 (90), 69 (8), 68 (24), 59 (87), 55 (100), 54 (33), 53 (12), 43 (40), 42 (29), 41 (78), 39 (33). The data for **36** are bp 120° (0.1 mm); ir (CCl_4) 3580, 3250, 2930, 2850, 1745 cm^{-1}; nmr (CCl_4) δ 1.40–2.00 (m, 4 H), 2.00–2.50 (m, 4 H), 3.65 (s, 3 H), 6.67 (t, J = 5.5 Hz, 0.42 H, anti), 7.36 (t, J = 6.0 Hz, 0.57 H, syn), 8.70 (br s, 1 H); mass spectrum (70 eV) m/e (rel intensity) 143 (M^+ − 16,0.2), 110 (22), 82 (25), 74 (41), 68 (9), 59 (28), 55 (31), 54 (9), 43 (38), 42 (22), 41 (25), 39 (13), 29 (16), 28 (22), 27 (16), 18 (100), 17 (22), 15 (19).

The oxazirane **10** decomposed in acid-free dichloromethane solution to methyl 6-iminohexanoate **12**,[22] apparently a mixture of monomer and trimer from nmr data. The spectral data for **12** are ir (CCl_4) 3300, 2930, 2850, 1745, 1650 cm^{-1}; nmr (CCl_4) δ 1.33–2.00 (m, 6 H), 2.00–2.60 (m, 2 H), 3.06–3.42 (m, 1 H), 3.64 (s, 3 H), 1.20 and 5.40 (two br s, 1 H, N–H, trimer and monomer[63]).

Oxidation of 30. To a solution of 647 mg (3.18 mmol)[60] of MCPBA in 15 ml of dichloromethane was added 239 mg (2.81 mmol) of **30** in 5 ml of dichloromethane; the mixture was left at room temperature for several hours. Removal of solvent *in vacuo* and distillation at <25° (1 mm) gave approximately 100 mg of a mixture of **30** (60% by nmr) and 5-methyl-1-aza-4,6-dioxabicyclo-[3.1.0]hexane **31** (40% by nmr) [nmr (CH_2Cl_2) δ 1.77 (s, 3 H), 2.83–4.00 (m, 4 H)]. The oxazirane **31** decomposed in the above solution to the imine trimer of 2-acetoxyacetaldimine **33.** The volatile imino ether **30** was removed *in vacuo* leaving the imine trimer **33** behind: ir (CH_2Cl_2) 3410, 3300, 2940, 2870, 1740, 1500, 1370, 1230, 1045 cm^{-1}; nmr (CCl_4) δ 1.40 (br s, 1 H), 2.04 (s, 3 H), 3.50–3.84 (m, 1 H), 3.95 (br s, 2 H); mass spectrum (70 eV) m/e 230.1141 (calcd for $C_9H_{16}N_3O_4$, 230.1141), m/e (rel intensity) 230 (M^+ − CH_2OCOCH_3, 1), 215 (3), 186 (1), 173 (1), 144 (5), 129 (15), 119 (2), 117 (2), 114 (2), 113 (1), 112 (1), 102 (9), 84 (8), 83 (16), 72 (20), 71 (6), 70 (8), 60 (18), 59 (7), 57 (8), 45 (11), 44 (8), 43 (100), 42 (17), 41 (6).

Aqueous sodium bicarbonate (containing some sodium sulfite) and dichloromethane were added to the residue from the distillation of oxazirane **30.** The organic layer was separated, dried over potassium carbonate, and evaporated *in vacuo.* The oil residue was distilled, giving 36 mg of 2-acetoxyacetaldoxime **32:** bp ~85° (5 mm); ir (CCl_4), 3575, 3320, 2940, 1750, 1445, 1380, 1230, 1050, 950 cm^{-1}; nmr (CCl_4) δ 2.05 (s, 3 H), 4.57 (d, J = 5.8 Hz, 2 H), 7.37 (t, J = 5.8 Hz, 1 H) for the syn isomer (57%); δ 2.07 (s, 3 H), 4.80 (d, J = 3.8 Hz, 2 H), 6.68 (t, J = 3.8 Hz, 1 H) for the anti isomer (43%); *ca.* 8.0 (br s, 1 H, OH); mass spectrum (70 eV) m/e 100.0397 (calcd for $C_4H_6NO_2$, 100.0398), m/e (rel intensity) 100 (M^+ − OH,0.3), 99.0320 (M^+ − H_2O,0.5), 75 (3), 61 (2), 60 (3), 58 (3), 57 (42), 45 (1.7), 44 (5), 43 (100), 42 (6), 41 (4), 40 (8), 39 (1), 31 (2.5), 30 (2.5), 29 (5), 28 (22), 27 (8), 26 (1.5), 18 (35), 17 (7), 15 (23).

Oxidation of 15a. Some carbon tetrachloride was frozen above a solution of 50 mg (0.44 mmol) of **15a** in 0.3 ml of dichloromethane in an nmr tube. A solution containing 90 mg (0.44 mmol)[60] of MCPBA in 0.5 ml of dichloromethane was placed above the frozen carbon tetrachloride (nmr tube in −78° bath). The nmr tube was placed in a low-temperature nmr probe at −56° and scanned after the sample was removed from the probe to warm to *ca.* −20° briefly. In successive warmings the concentration of 2,2-dimethyl-4-methoxy-1-aza-5-oxabicyclo[2.1.0]pentane (**16**) reached a maximum of 30% of the total mixture as analyzed by nmr (HA-100) [δ 1.11 (s, 3 H), 1.29 (s, 3 H), 2.16 and 2.34 (AB, J = 11 Hz, 2 H), 3.19 (s, 3 H)]. The concentration of **16** decreased and the concentration of methyl 3-methyl-3-nitrosobutanoate **17a** increased as the sample was warmed further. At the completion of the reaction 50% (by nmr) of the imino ether **15a** had been converted to the nitroso ester **17a:** bp <25° (0.1 mm); ir (CH_2Cl_2) 2950, 1740, 1560 cm^{-1}; nmr (CH_2Cl_2) δ 1.25 (s, 6 H), 2.94 (s, 2 H), 3.58 (s, 3 H); mass spectrum (Finnigan) (12 eV) m/e (rel intensity) 129 (M^+ − 16, 2.3) 115 (M^+ − 30, 23), 114 (17), 98 (9), 83 (39), 73 (100), 59 (27), 56 (19), 55 (27), 43 (14), 42 (23), 30 (6), 29 (9), 18 (12), 15 (5). The ion at M^+ − 16 may be due to the parent molecular ion of oxazoline.

Ethyl 3-Methyl-3-nitrosobutanoate (17b). Following the procedure for **4,** treatment of 217 mg (1.72 mmol) of **15b** with 708 mg (3.46 mmol)[60] of MCPBA gave 55 mg (20%) of nitroso ester **17b:** bp <25° (0.1 mm); ir (CCl_4) 2950, 1740, 1560 cm^{-1}; nmr (CCl_4) δ 1.22 (t, J = 7.2 Hz, 3 H), 1.27 (s, 6 H), 2.75 (s, 2 H), 4.07 (q, J = 7.2 Hz, 2 H); mass spectrum (70 eV) m/e (rel intensity) 143 (M^+ − 16, 0.07), 129 (M^+ − 30, 2), 128 (3), 114 (2), 110 (2),3 (9), 59 (8), 57 (7), 56 (12), 43 (12), 42 (8), 41 (9), 39 (7), 31 (11), 28 (8), 27 (13), 18 (100), 17 (23), 15 (6). The nitroso ester **17b** decomposed in carbon tetrachloride at room temperature to 24% (by nmr) of ethyl 3-methyl-3-nitrobutanoate **25,** 3 (by nmr) of ethyl 3-methyl-3-butenoate **26,**[69] and 44% (by nmr) of ethyl 3-methyl-2-butenoate **27.** The data for **25** are bp 60–70° (1 mm); ir (neat) 2980, 1745, 1550, 1380, 1360, 1210 cm^{-1}; nmr (CCl_4) δ 1.27 (t, J = 7.3 Hz, 3 H), 1.68 (s, 6 H), 2.90 (s, 2 H), 4.15 (q, J = 7.3 Hz, 2 H); mass spectrum (70 eV) m/e 130.0504 (calcd for $C_5H_8NO_3$, 130.0504), m/e (rel intensity) 130 (M^+ − OC_2H_5, 8), 129.0917 (M^+ − NO_2, 20), 128.0832 (M^+ − HNO_2, 14), 87 (29), 83.0490 (M^+ − HNO_2 and OC_2H_5, 38), 82 (9), 59 (46), 57 (14), 56 (35), 55 (46), 44 (15), 43 (40), 42 (14), 41 (30), 39 (24), 30 (52), 29 (100), 28 (38), 27 (35), 18 (46), 17 (10), 15 (10). The data for **26** are: bp <25° (1 mm); ir (CCl_4) 1740, 1630 cm^{-1}; nmr (CCl_4) δ 1.20 (t, J = 7.2 Hz, 3 H), 1.75 (s, 3 H), 2.90 (s, 3 H), 4.00 (q, J = 7.2 Hz, 2 H), 4.85 (m, 2 H). The data for **27** are: bp <25° (1 mm); ir (CCl_4) 2950, 1720, 1660, 1450, 1230, 1150 cm^{-1}; nmr (CCl_4) δ 1.20 (t, J = 7.2 Hz, 3 H), 1.83 (d, J = 1.3 Hz, 3 H), 2.08 (d, J = 1.3 Hz, 3 H), 4.00 (q, J = 7.2 Hz, 2 H), 5.50 (heptet, J = 1.3 Hz, 1 H). The α,β-unsaturated ester **27** was independently synthesized from acid hydrolysis of 1-ethoxy-3-methyl-3-hydroxybutyne[70] with 10% sulfuric acid at 25° and shown to have identical nmr and ir spectra.

Attempted Equilibration of Unsaturated Esters 26 and 27. A carbon tetrachloride–dichloromethane solution containing 55% α,β-unsaturated ester **27** and 45% β,γ-unsaturated ester **26** was treated with aqueous hydrochloric acid and sodium nitrite. No change in ester ratio or decomposition occurred during a 2-week test period.

2-Methoxy-4,4,5,5-tetramethyl-2-oxazoline (19a). Following the procedure for **4,** treatment of 200 mg (1.42 mmol) of **18a** with 292 mg (1.44 mmol)[60] of MCPBA gave 100 mg (45%) of oxazoline **19a:** bp 40–60° (0.1 mm); ir (CH_2Cl_2) 2960, 1660, 1350, 1160, 1120 cm^{-1}; nmr (CCl_4) δ 1.08 (s, 6 H), 1.27 (s, 6 H), 3.75 (s, 3 H); mass spectrum (70 eV) m/e 157.1105 (calcd for $C_8H_{15}NO_2$, 157.1103), m/e (rel intensity) 157 (M^+, 2.2), 142 (4.4), 126 (1.2), 110 (4), 99 (12), 98 (12), 85 (8), 84 (100), 73 (3), 69 (6), 56 (16), 43 (9), 42 (14), 41 (22), 39 (10), 28 (9), 27 (10), 26 (7), 18 (5), 15 (24). A trace amount of methyl 2,2,3-trimethyl-3-nitrosobutanoate **20a** was also formed and came over in the distillation of **19a.** The spectral data for **20a** are ir (CH_2Cl_2) 1740 and 1560 cm^{-1}; nmr (CCl_4) δ 0.83 (s, 6 H), 1.55 (s, 6 H), 3.60 (s, 3 H).

Hydrolysis of 19a. Treatment of 111 mg (0.71 mmol) of **19a** in 0.5 ml of dichloromethane with 0.5 ml of 10% sulfuric acid, followed by separation, drying, and evaporation of the organic layer resulted in 15 mg (15%) of 4,4,5,5-tetramethyl-2-oxazolidinone **21:** mp 111–112°; ir (CH_2Cl_2) 3230, 2970, 1760 cm^{-1}; nmr (CCl_4) δ 1.22 (s, 6 H), 1.33 (s, 6 H), (N–H not visible); mass spectrum (70 eV) m/e 143.0948 (calcd for $C_7H_{13}NO$, 143.0946), m/e (rel intensity) 143 (M^+, 1.5), 128 (2.5), 115 (10), 100 (2.5), 84 (13), 59 (29), 57 (14), 43 (9), 42 (28), 41 (10), 39 (5), 29 (4), 28 (6), 27 (4), 18 (100), 17 (25).

2-Ethoxy-4,4,5,5-tetramethyloxazoline 19b. Following the procedure for **4** at −20°, treatment of 168 mg (1.08 mmol) of **18b** with 222 mg (1.09 mmol)[60] of MCPBA gave 103 mg (56%) of oxazoline **19b:** bp 36–38° (0.4 mm); ir (CH_2Cl_2) 2960, 1660, 1380, 1340, 1165, 1130, 1020, 830 cm^{-1}; nmr (CH_2Cl_2) δ 1.18 (s, 6 H), 1.30 (t, J = 7.2 Hz, 3 H), 1.33 (s, 6 H), 4.32 (q, J = 7.2 Hz, 2 H); mass spectrum (70 eV) m/e 171.1264 (calcd for $C_9H_{17}NO_2$, 171.1259) (10 eV), m/e (rel intensity) 171 (M^+, 11), 156 (8), 141 (2), 128 (4), 113 (22), 98 (48), 84 (100), 59 (3), 58 (7), 49 (3), 43 (2). Hydrolysis of oxazoline **19b** also produced oxazolidinone **21.**

Oxidation of 19b. A mixture of 427 mg (2.10 mmol)[60] of MCPBA, 100 mg of potassium carbonate, and 3 ml of dichloromethane was cooled to −30°. To this mixture was added 300 mg (1.75 mmol) of oxazoline **19b** in 3 ml of dichloromethane. After 30 min the solution was allowed to come to room temperature, filtered, and added to an aqueous sodium bicarbonate–sodium sulfite solution. The organic layer was separated and dried over anhydrous potassium carbonate. The nmr spectrum of this solution indicated 40% of ethyl 2-(2,3-dimethyl-3-nitroso)butylcarbonate **29** and 60% starting oxazoline **19b.** Removal of solvent and oxazoline **19b** *in vacuo* followed by bulb-to-bulb distillation, bath 50–100° (0.03 mm), gave 23 mg (16%) of carbonate **29:** ir (CCl_4) 2970, 1740, 1560, 1375, 1280 cm^{-1}; nmr (CCl_4) δ 0.83 (s, 6 H), 1.27 (t, J = 7.2 Hz, 3 H), 2.00 (s, 6 H), 4.07 (q, J = 7.2 Hz, 2 H); mass spectrum (70 eV) m/e 173.1181 (calcd for $C_9H_{17}O_3$, 173.1178), m/e (rel intensity) 173 (M^+ − NO, 2.3), 158 (4), 129 (4), 114 (5), 101 (30), 86 (7), 85 (16), 84 (64), 83 (68), 82 (45), 69 (59), 67 (36), 59 (54), 58 (30), 57 (14), 56 (9), 55 (55), 46 (18), 45 (36), 44 (55), 43 (100), 42 (21), 41 (100), 39 (30), 31 (71), 30 (38), 29 (97), 28 (50), 27 (43), 18 (30), 15 (34).

Oxidation of 22. Following the procedure for **4,** treatment of 288 mg (2.26 mmol) of **22** with 510 mg (2.52 mmol)[60] of MCPBA gave 175 mg (53%) of a mixture of 2-methoxy-4,4,5-trimethyl-oxazoline (**23**) (73% by nmr) and methyl 2,3-dimethyl-3-nitrosobu-

tanoate (**24**) (27% by nmr). The products were separated by vpc on a 0.25 in. × 6 ft column of 5% SE-30 on 60–80 Chromosorb W. The data for **23** are $T_R(140°)$ = 7.75 min; bp 70° (20 mm); ir (CH_2Cl_2) 2950, 1670, 1470 cm^{-1}; nmr (CH_2Cl_2) δ 1.08 (s, 3 H), 1.21 (s, 3 H), 1.27 (d, J = 6.7 Hz, 3 H), 3.78 (s, 3 H), 4.32 (q, J = 6.7 Hz, 1 H); mass spectrum (70 eV) *m/e* 143.0942 (calcd for $C_7H_{13}NO_2$, 143.0946), *m/e* (rel intensity) 143 (M^+, 9), 129 (5), 128 (60), 100 (6), 85 (8), 84 (100), 73 (10), 71 (8), 70 (5), 69 (7), 59 (10), 58 (22), 56 (25), 55 (11), 49 (7), 43 (19), 42 (21), 41 (26), 39 (12), 30 (8), 29 (13), 28 (25), 27 (16). The data for **24** are: $T_R(140°)$ = 8.50 min; bp <25° (0.1 mm); ir (CH_2Cl_2) 2950, 1735, 1560, 1205 cm^{-1}; nmr (CH_2Cl_2) δ 1.00 (s, 3 H), 1.10 (s, 3 H), 1.18 (d, $J \simeq 7$ Hz, 3 H), 3.64 (s, 3 H), methine hydrogen not detected; mass spectrum (70 eV) *m/e* 129.0909 (calcd for $C_7H_{13}O_2$, 129.0915), *m/e* (rel intensity) 129 ($M^+ - NO$, 21), 128 (14), 113 (14), 100 (6), 97 (11), 88 (21), 83 (7), 74 (7), 73 (100), 71 (7), 70 (36), 69 (50), 68 (7), 67 (7), 59 (50), 58 (7), 57 (13), 56 (21), 55 (43), 53 (14), 45 (9), 44 (21), 43 (36), 42 (28), 41 (79), 40 (11), 39 (28).

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Registry No.—**1**, 49680-36-6; **2**, 49680-48-0; 2 fluorosulfonic acid salt, 52855-94-4; **3**, 52855-95-5; **4**, 49680-37-7; **5**, 49680-50-4; **6**, 52906-79-3; **7a**, 5264-35-7; **7b**, 931-46-4; **8**, 2525-16-8; **9a**, 52855-96-6; **9b**, 49680-39-9; **10**, 35009-23-5; **11a**, 52855-97-7; **11b**, 49680-40-2; **12** monomer, 52855-98-8; **12** trimer, 38167-93-0; **13**, 52928-63-9; **14**, 52855-99-9; **15a**, 23974-38-1; **15b**, 23974-43-8; **16**, 49680-45-7; **17a**, 49680-44-6; **17b**, 52856-00-5; **18a**, 49680-46-8; **18b**, 23974-48-3; **19a**, 49680-47-9; **19b**, 52856-01-6; **20a**, 52856-02-7; **21**, 52856-03-8; **22**, 52856-04-9; **23**, 52856-05-0; **24**, 52856-06-1; **25**, 52856-07-2; **26**, 1617-19-2; **27**, 638-10-8; **29** (R = Et), 52856-08-3; **30**, 1120-64-5; **31**, 52856-09-4; *anti*-**32**, 52856-11-8; *syn*-**32**, 52856-12-9; **33**, 52856-10-7; **35**, 3009-88-9; *anti*-**36**, 42586-30-1; *syn*-**36**, 42586-29-8; MCPBA, 937-14-4; CSI, 1189-71-5; methyl fluorosulfonate, 421-20-5; *N-tert*-butylpivalamide, 686-96-4; methyl formate, 107-31-3; *tert*-butylhydroxylamine, 16649-50-6; *tert*-butylamine, 75-64-9; 2-methyl-2-nitrosopropane, 917-95-3; trans dimer of 2-methyl-2-nitrosopropane, 52856-13-0; ethyl 4-isonitrosobutanoate, 52856-14-1; ethyl 4-oxobutanoate, 10138-10-0; 1-ethoxy-3-methyl-3-hydroxybutyne, 20411-76-1.

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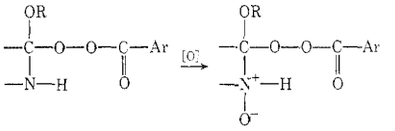

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