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Oxidation of Cyclic Amines with Ruthenium Tetroxide

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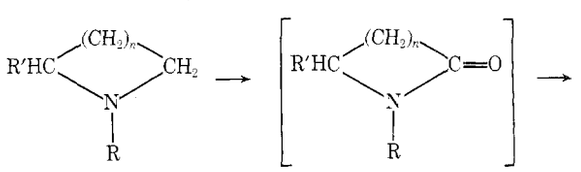
Treatment of 1,2-di-*tert*-butylaziridine with ruthenium tetroxide gave *N*-*tert*-butyl-2,2-dimethylpropionamide. The reaction involves several successive oxidations and intermediates, one of which could be an α-lactam. Treatment of acylated cyclic amines with ruthenium tetroxide gives lactams and/or imides.

The use of ruthenium tetroxide in the oxidation of organic compounds is becoming increasingly more popular. It has been used primarily in the oxidation of alkenes to aldehydes, acids, or ketones,[1] alkynes to α-diketones,[2] primary alcohols to acids,[1,3] secondary alcohols to ketones,[1,4] acyclic ethers to esters, and cyclic ethers to lactones.[1] Ruthenium tetroxide readily oxidizes aromatic systems, but is unreactive toward hydrocarbons.[1,5] Unusual oxidation insertion reactions have been reported in the oxidation of osuloses[6] and in the oxidation of a sterically hindered cyclopropanol to a β-lactone in low yield.[7]

Berkowitz and Rylander[1] applied ruthenium tetroxide oxidations to nitrogen-containing compounds. Unsubstituted amines produced only intractable mixtures under the reaction condition. Acyclic and cyclic amides were oxidized to imides in good yield. Prompted by these workers, we treated a series of cyclic amines from aziridine to piperidine with ruthenium tetroxide. Essentially similar results were obtained as those reported.[1]

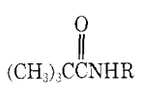
Since ruthenium tetroxide does not oxidize the nitrogen atom directly, it should be possible to influence the oxidation of amines by suitable substitution on nitrogen.

The results of N-alkylation were first determined. Treatment of **1a** with 1 equiv of ruthenium tetroxide gave a low yield (10%) of *N*-*tert*-butyl-2,2-dimethylpropionamide (**3**). It appeared that several successive oxidations were occurring and this was confirmed when a higher yield of **3** was obtained with 4 equiv of oxidant.



1a **2a**

R = R′ = *tert*-butyl
$n = 0$

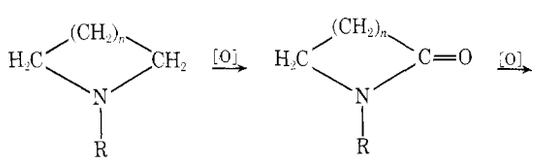


3

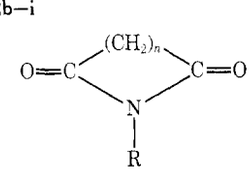
A carbon atom is lost during the reaction. Carbon dioxide can be detected as a by-product of the oxidation. Carbon monoxide is oxidized by ruthenium tetroxide only very slowly and in very low yield, indicating that the carbon atom of the aziridine is lost as carbon dioxide.

A possible intermediate in the oxidation of aziridine **1a** is 1,3-di-*tert*-butylaziridinone (**2a**). When compound **2a** was treated with 1 equiv of RuO_4, an 11% yield of amide **3** was obtained. This yield is increased to 77% with 4 equiv of oxidant. Carbon dioxide was isolated in 91% yield. Thus it appears that the α-lactam **2a** is an intermediate in the oxidation of aziridine **1a**.

The effects of N-acylation and N-sulfonation were determined next. The results are shown in Table I for the following reaction.



1b–i **2b–i**



5d,e only

The reaction is more likely to succeed the larger the ring size and seems to be effected by the electronegativity of the N substituent. It was also noted that the rate of reaction decreases as ring size decreases and electronegativity increases.

Different classes of compounds were oxidized preferably in a single-phase rather than a double-phase system. The single-phase system requires stoichiometric amounts of the oxidant. The major disadvantage of this procedure is that a large amount of solid ruthenium dioxide must be filtered from the solution and the desired product may become occluded in the solid, thereby decreasing the

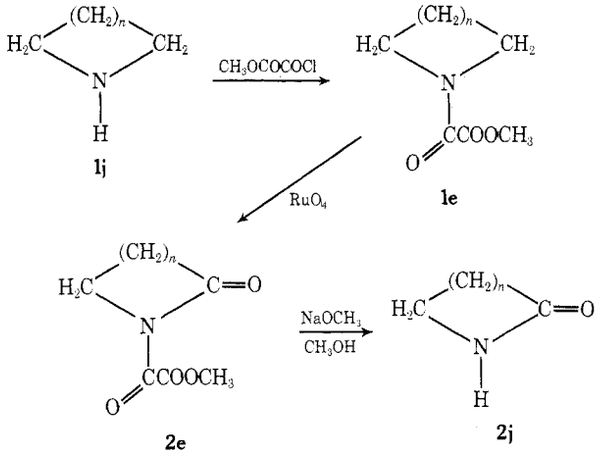
Table I
Per Cent Yields of Lactams[a,b] or Imides[c,d] Obtained from the Oxidation of Cyclic Amines with Ruthenium Tetroxide

R	n = 0	n = 1	n = 2	n = 3	ROH pK_a
b *p*-$MePhSO_2$	*e*	*e*	46[a]	3–5[a]	≪0
c CH_3SO_2	*e*	*e*	90[a]	85[a]	−1.20
d CF_3CO		*e*	34[d]	74[d]	−0.26
			21[c]	33[c]	
e CH_3OCOCO		22[b]	68[b]	59[b]	<3.07
		1[a]	71[c]	57[c]	
f HCO		*e*	34[a]	*e*	3.75
g CH_3CO	*e*	13[b]	45[b]	42[b]	4.75
		9[a]	69[a]	60[a]	
i EtOCO	5[b]	33[b]	65[a]	63[a]	
		15[a]			

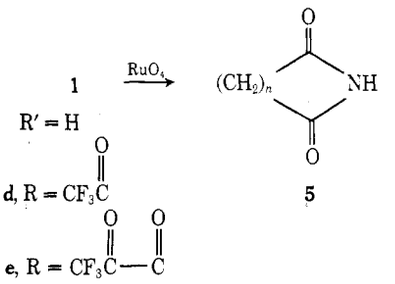
[a] Lactam isolated from double-phase oxidation system. [b] Lactam isolated from single-phase system. [c] Imide isolated from double-phase system. [d] Imide isolated from single-phase system. [e] No product could be isolated.

yield.[8] The major advantage is the shorter reaction time compared to the two-phase method which requires that the starting material and the products be stable to hydrolysis; the major advantage of this procedure is the relatively small amount of ruthenium dioxide hydrate which must be filtered from the solution.

With the methyloxalyl protecting group and a one-phase system it is possible to obtain the unsubstituted lactam after oxidation. The methyloxalyl group can be cleaved with sodium methoxide in methanol.[9] This procedure was successful with all ring sizes except the three-membered aziridine. The results are shown in Table II for the following reaction scheme.



When a two-phase system was employed, the methyloxalyl and trifluoroacetyl derivatives yielded cyclic imides, which were isolated in only the five- and six-membered ring cases. In the four-membered ring case (**1e**, $n = 1$) a 22% yield of 3-(*N*-methyloxalyl)aminopropionic acid and a 1% yield of *N*-methyloxalyl-2-azetidinone were isolated. The propionic acid derivative undoubtedly resulted from hydrolysis of the azetidinone. No lactams were detected in the oxidation of **1d** ($n = 2, 3$). Presumably water formed



as a by-product in the oxidation and/or associated with the oxidant[10] cleaved the labile trifluoroacetyl group from the intermediate *N*-trifluoroacetyl lactam and the unsubstituted lactam was then further oxidized to the imide. The oxidation of 1-trifluoroacetylazetidine was unsuccessful; the reaction rate was very slow and most of the starting material was recovered.

The oxidation of *N*-carboethoxy derivatives of azetidine (**1i**, $n = 1$) and aziridine (**1i**, $n = 0$) afforded very low yields of ethyl carbamate (2 and 5%, respectively), which indicates that complete oxidation of the ring may be competing in the smaller ring cases. Although such compounds were sought, no similar amides were detected in the oxidation of other derivatives of aziridine and azetidine.

Experimental Section

General Procedures. Melting points were determined on a Fisher-Johns hot-stage apparatus and are uncorrected. Infrared spectra were taken in sodium chloride cells or potassium bromide pellets as noted using a Perkin-Elmer 237 spectrophotometer. Nuclear magnetic resonance spectra were obtained on a Varian T-60, with tetramethylsilane as internal standard. Mass spectra were determined on a Hitachi Perkin-Elmer RMU-6D mass spectrometer at 70 eV. Product mixtures were analyzed by gas–liquid chromatography on an F & M Model 810 flame ionization instrument; also, products were analyzed and collected for mass spectra by gas–liquid chromatography using an F & M Model 720 thermal conductivity instrument. Microanalyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn. Thin layer chromatography was performed on Baker-flex silica gel IB-F or IB.

General Methods for Ruthenium Tetroxide Oxidations. Two-Phase System. A mixture of the compound to be oxidized (4–8 mmol) and 0.10–0.30 g of ruthenium dioxide hydrate (Engelhard Minerals & Chemicals Corp.) in an appropriate chlorinated solvent was stirred at room temperature in a stoppered flask with 10 equiv of a 10% aqueous solution of sodium metaperiodate. If chloroform is used as a solvent, it must be free of alcohol.[11] When the oxidation was complete (2–6 days), the layers were separated; the aqueous layer was extracted with 3 × 75 ml each of methylene chloride and chloroform. These extracts were combined with the original organic solution and a minimum amount of methanol or 2-propanol was added to destroy excess oxidant. The mixture was filtered and the filtrate was washed with 5 ml of 10% aqueous sodium thiosulfate. After drying, the filtrate was stripped of solvent and the product was isolated and purified in the appropriate manner.

Single-Phase System. A solution of the required number of equivalents of ruthenium tetroxide in a chlorinated solvent was generated by treating an equimolar amount of ruthenium dioxide hydrate suspended in the solvent with 10 equiv of a 10% aqueous solution of sodium metaperiodate. After vigorous stirring, the layers were separated when the reaction was completed and the aqueous layer was extracted with 3 × 15 ml of the appropriate chlorinated solvent. The extracts were combined with the original

Table II
Per Cent Yields of Products Obtained in the Overall Conversion of a Cyclic Amine to a Lactam

n	1e	Registry no.	2e	Registry no.	2j	Registry no.	Overall yield from 1j
3	92	20173-02-8	59	51599-65-6	95	675-20-7	51
2	98	41600-21-9	68	51599-66-7	92	616-45-5	61
1	68	51599-64-5	22	51635-69-9	91	930-21-2	14

solution of the tetroxide. This solution of the oxidant was added to a solution of the compound to be oxidized and the mixture was stirred at room temperature in a stoppered flask, which was occasionally unstoppered to relieve internal pressure. After the reaction was complete, methanol or 2-propanol was added to destroy excess oxidant. The mixture was filtered and the filtrate was dried (Na_2SO_4 or $MgSO_4$). After evaporation of the solvents, the residue was purified in the appropriate manner.

The following compounds were prepared according to published procedures: 1,3-di-*tert*-butylaziridinone;[12] 1-*p*-toluenesulfonylpiperidine;[13] 1-*p*-toluenesulfonylpyrrolidine;[14] 1-*p*-toluenesulfonylazetidine;[15] 1-*p*-toluenesulfonylaziridine;[16] 1-methanesulfonylpiperidine;[17] 1-methanesulfonylpyrrolidine;[18] 1-methanesulfonylazetidine;[15] 1-methanesulfonylaziridine;[19] 1-trifluoroacetylpiperidine;[20] 1-trifluoroacetylpyrrolidine;[21] 1-carboethoxypiperidine;[22] 1-carboethoxypyrrolidine;[23] 1-carboethoxyaziridine.[19]

1,2-Di-*tert*-butylaziridine. A mixture of 1.33 g (35.0 mmol) of lithium aluminum hydride (Alfa Inorganics) and 9.00 g (53.3 mmol) of α-lactam **2a** in 80 ml of dry tetrahydrofuran was refluxed for 3.5 hr and then allowed to cool to room temperature. To this mixture was added dropwise 4 ml of distilled water, 1.3 ml of 5% aqueous sodium hydroxide, 1.3 ml of distilled water, and finally 15 ml of tetrahydrofuran. This mixture was refluxed for 20 min. Filtration and fractionation of the filtrate yielded 7.10 g (77%) of 2-(*tert*-butylamino)-3,3-dimethyl-1-butanol: bp 48.5° (0.5 mm); ir (neat) 3400 (m, broad), 2960 (s), and 1070 cm^{-1} (m); nmr ($CDCl_3$) δ 3.80–3.16 (m, 2 H), 2.53–1.36 (m, 1 H), 1.10 (s, 9 H), 0.93 (s, 9 H); mass spectrum (70 eV) *m/e* (rel intensity) M^+ 173 (1), 155 (11), 140 (55), 98 (61), 57 (82), 41 (100).

Anal. Calcd for $C_{10}H_{23}NO$: C, 69.31; H, 13.38; N, 8.08. Found: C, 69.44; H, 13.52; N, 8.17.

A mixture of 3.9 g (38 mmol) of 95% sulfuric acid and 5.5 g (32 mmol) of 2-(*tert*-butylamino)-3,3-dimethyl-1-butanol in 4 ml of distilled water was stirred at room temperature for 90 min, heated on a steam bath under water aspirator pressure for 8 hr, and dried at 105° (160 mm). The solid was pulverized and added slowly to 28 g (700 mmol) of sodium hydroxide in 3.5 ml of distilled water heated in an oil bath at 200° and at water aspirator pressure. A mixture of aziridine **1a** and water was collected in a Dry Ice–acetone trap. The basic water layer was separated from **1a** and 1.8 g (36%) of pure **1a** was obtained after distillation from potassium hydroxide: bp 59° (45 mm); ir (neat) 3015 (w), 2950 (s), 1485 (s), and 1370 cm^{-1} (s); nmr ($CDCl_3$) δ 1.43–1.15 (ABC pattern, 3 H), 0.95 (s, 9 H), 0.85 (s, 9 H); mass spectrum (70 eV) *m/e* (rel intensity) M^+ 155 (22), 98 (100), 84 (91), 57 (75), 41 (72), 30 (58).

Anal. Calcd for $C_{10}H_{21}N$: C, 77.35; H, 13.63; N, 9.02. Found: C, 77.16; H, 13.75; N, 9.11.

1-Trifluoroacetylazetidine (1d, *n* = 1). To 1.25 g (8.80 mmol) of ethyl trifluoroacetate (Aldrich) in 5 ml of chloroform at −10° was added slowly 500 mg (8.76 mmol) of azetidine in 5 ml of chloroform. The mixture was stirred vigorously at room temperature overnight. Fractionation of the mixture afforded 810 mg (61%) of 1-trifluoroacetylazetidine: bp 38° (0.9 mm); ir ($CHCl_3$) 3960 (w), 1687 (vs), 1480 (m), and 1160 cm^{-1} (s); nmr ($CDCl_3$) δ 4.37 (p, 4 H, *J* = 8 Hz), 2.44 (p, 2 H, *J* = 8 Hz); mass spectrum (70 eV) *m/e* (rel intensity) M^+ 153 (144), 126 (11), 96 (19), 84 (30), 69 (60), 56 (100), 42 (14), 41 (14), 28 (43).

Anal. Calcd for $C_5H_6NOF_3$: C, 39.23; H, 3.95; N, 9.15; F, 37.23. Found: C, 39.47; H, 3.93; N, 9.21; F, 37.44.

1-Methyloxalylpiperidine (1e, *n* = 3). A mixture of 2.75 g (22.5 mmol) of methyloxalyl chloride (Aldrich), 1.79 g (21.0 mmol) of piperidine, and 2.23 g (22.0 mmol) of triethylamine in 100 ml of anhydrous benzene was stirred at room temperature for 30 min. The mixture was filtered and the filtrate was fractionally distilled to yield 3.32 g (92%) of **1e** (*n* = 3): bp 104° (1 mm); ir ($CHCl_3$) 2940 (s), 2860 (s), 1738 (s), 1655 (vs), and 1455 cm^{-1} (m); nmr ($CDCl_3$) δ 3.89 (s, 3 H), 3.57 (t, broad, 2 H), 3.33 (t, broad, 2 H), 1.80–1.53 (m, 6 H); mass spectrum (70 eV) *m/e* (rel intensity) M^+ 171 (31), 116 (11), 112 (100), 98 (9), 84 (8), 83 (15), 71 (19), 70 (12), 69 (66), 56 (19), 42 (17), 41 (43), 30 (10), 29 (35), 28 (32), 15 (9).

All other methyloxalyl derivatives were prepared analogously.

1-Methyloxalylpyrrolidine (1e, *n* = 2): 98%; bp 112° (0.7 mm); ir ($CHCl_3$) 2970 (m), 2870 (w), 1735 (s), 1655 (vs), and 1455 cm^{-1} (m); nmr ($CDCl_3$) δ 3.89 (s, 3 H), 3.80–3.33 (m, 4 H), 2.12–1.78 (m, 4 H); mass spectrum (70 eV) *m/e* (rel intensity) M^- 157 (39), 98 (100), 71 (11), 70 (11), 69 (11), 59 (11), 56 (48), 55 (89), 42 (18), 41 (15), 30 (15), 29 (22), 15 (18).

Anal. Calcd for $C_7H_{11}NO_3$: C, 53.49; H, 7.06; N, 8.91. Found: C, 53.29; H, 7.18; N, 9.03.

1-Methyloxalylazetidine (1e, *n* = 1): 68%; bp 97.5–98.5° (1.2 mm); ir ($CHCl_3$) 2980 (w), 1735 (s), 1655 (vs), and 1435 cm^{-1} (w); nmr ($CDCl_3$) δ 4.60 (t, 2 H, *J* = 8 Hz), 4.20 (t, 2 H, *J* = 8 Hz), 3.90 (s, 3 H), 2.40 (p, 2 H); mass spectrum (70 eV) *m/e* (rel intensity) M^- 143 (22), 112 (4), 98 (10), 84 (69), 59 (21), 56 (100), 42 (17), 41 (22), 28 (20), 15 (18).

Anal. Calcd for $C_6H_9NO_3$: C, 50.35; H, 6.34; N, 9.79. Found: C, 50.26; H, 6.38; N, 9.85.

Methanolysis of 1-Methyloxalyl Derivatives. A mixture of 1.0 mmol of imide **2e** and 0.04 mmol of sodium methoxide in 3 ml of methanol was stirred at room temperature for 5 hr. Fractionation of the mixture, followed by distillation or sublimation gave the lactam **2j,** identical with authentic materials.

1-Formylazetidine (1f, *n* = 1). A mixture of 1.30 g (17.5 mmol) of ethyl formate (Eastman) and 1.00 g (17.5 mmol) of azetidine was stirred at room temperature for 2 days. Distillation afforded 1.29 g (87%) of 1-formylazetidine: bp 43° (0.65 mm); ir ($CHCl_3$) 3450–3320 (w), 2970 (m), 2830 (w), 1655 (s), 1420 (s), and 1370 cm^{-1} (s); nmr ($CDCl_3$) δ 7.90 (s, 1 H), 4.13 (q, 4 H, *J* = 8 Hz), 2.37 (p, 2 H, *J* = 8 Hz); mass spectrum (70 eV) *m/e* (rel intensity) M^+ 85 (65), 56 (24), 42 (21), 30 (27), 29 (100), 28 (88).

Anal. Calcd for C_4H_7NO: C, 56.45; H, 8.29; N, 16.46. Found: C, 56.70; H, 8.40; N, 16.40.

1-Acetylazetidine (1g, *n* = 1). Excess ketene[24] was bubbled into 100 ml of diethyl ether at 0° as 0.76 g (13 mmol) of azetidine (Eastman) was added slowly by syringe during 7 min. The mixture was stirred at 0° for 15 min after addition of the amine was complete. The solvent was carefully distilled from the reaction mixture below 41°. Distillation of the crude residue afforded 0.96 g (74%) of 1-acetylazetidine: bp 46° (1 mm); ir (neat) 2950 (s), 2880 (s), 1645 (s), and 1430 cm^{-1} (s); nmr ($CDCl_3$) δ 4.10 (q, 4 H, *J* = 8 Hz), 2.26 (p, 2 H, *J* = 8 Hz), 1.85 (s, 3 H); mass spectrum (70 eV) *m/e* (rel intensity) M^+ 99 (26), 56 (38), 43 (100), 30 (17), 15 (17).

Anal. Calcd for C_5H_9NO: C, 60.58; H, 9.17; N, 14.13. Found: C, 60.48; H, 9.23; N, 13.94.

1-Carboethoxyazetidine (1i, *n* = 1). A mixture of 1.01 g (17.7 mmol) of azetidine, 6.24 g (61.7 mmol) of triethylamine, and 1.95 g (18.0 mmol) of ethyl chloroformate in 145 ml of anhydrous benzene was stirred overnight at room temperature. The mixture was filtered and the filtrate was fractionated to afford 1.47 g (63%) of urethane **17:** bp 78° (15 mm); ir ($CHCl_3$) 2960 (m), 1685 (s), and 1430 cm^{-1} (m); nmr ($CDCl_3$) δ 4.13 (q, 2 H, *J* = 7 Hz), 4.07 (t, 4 H, *J* = 8 Hz), 2.26 (p, 2 H, *J* = 8 Hz), 1.26 (t, 3 H, *J* = 7 Hz); mass spectrum (70 eV) *m/e* (rel intensity) M^+ 129 (31), 114 (2), 100 (26), 84 (25), 56 (62), 42 (50), 29 (100), 28 (44), 15 (4).

Anal. Calcd for $C_6H_{11}NO_2$: C, 55.80; H, 8.59; N, 10.85. Found: C, 55.61; H, 8.48; N, 11.00.

Acknowledgment. We wish to thank the Sloan Basic Research Fund for support of this work.

Registry No.—**1a** (*n* = 0), 51599-67-8; **1b** (*n* = 2), 6435-78-5; **1c** (*n* = 2), 51599-68-9; **1c** (*n* = 3), 3989-48-8; **1d** (*n* = 1), 51599-69-0; **1d** (*n* = 2), 6442-87-1; **1d** (*n* = 3), 340-07-8; **1f** (*n* = 1), 51599-70-3; **1f** (*n* = 2), 3760-54-1; **1g** (*n* = 1), 45467-31-0; **1g** (*n* = 2), 4030-18-6; **1g** (*n* = 3), 618-42-8; **1i** (*n* = 1), 51599-71-4; **1i** (*n* = 2), 5470-26-8; **1i** (*n* = 3), 5325-94-0; **2a** (*n* = 0), 14387-89-4; **2b** (*n* = 2), 10019-95-1; **2c** (*n* = 2), 51599-72-5; **2c** (*n* = 3), 51599-73-6; **2f** (*n* = 2), 40321-44-6; **2g** (*n* = 1), 51599-74-7; **2g** (*n* = 2), 932-17-2; **2g** (*n* = 3), 3326-13-4; **2i** (*n* = 1), 51599-75-8; **2i** (*n* = 2), 4036-03-7; **2i** (*n* = 3), 33485-71-1; **5d** (*n* = 2), 51599-76-9; **5d** (*n* = 3), 51745-67-6; **5e** (*n* = 2), 51599-77-0; **5e** (*n* = 3), 51599-78-1; 2-(*tert*-butylamino)-3,3-dimethyl-1-butanol, 51599-79-2.

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Allylic Substituent Effects in the Peracid Oxidation of Cyclopropenes to Enones

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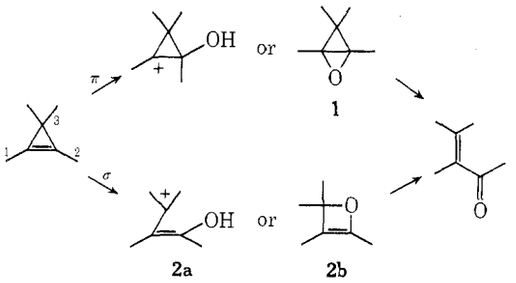
The second-order rate constants ($\times 10^3\ M^{-1}\ sec^{-1}$) for *m*-chloroperbenzoic acid oxidation in CCl_4 at 0° have been measured for the following 1,2-diphenyl-substituted cyclopropenes: 3-unsubstituted, 3.4; 3-methyl, 1.24; 3,3-dimethyl, 0.40; 3-phenyl, 0.122. These values were compared to those for epoxidation of the following cyclopentenes: unsubstituted, 9.1; 3-methyl, 10.6, 64:36 ratio of cis:trans epoxides; 3-phenyl, 1.93, 25:75 ratio of cis:trans epoxides. These results are discussed in an attempt to determine whether peracid oxidation of cyclopropenes occurs with σ- or π-bond attack.

The reaction of electrophilic reagents with strained σ bonds has been extensively studied in recent years. Since these reagents also react with π systems of olefins, the interesting question is raised of σ *vs.* π reactivity.[2] The question becomes operationally acute when an exceptionally strained σ bond is incorporated in a molecule that possesses a π system with possibly normal reactivity.

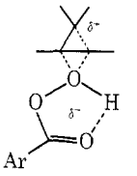
The cyclopropene system is an especially good example of this class of molecules. Fragmentation of the $C_{1,3}$ or $C_{2,3}$ σ bond of cyclopropenes thermodynamically releases *ca.* 55 kcal/mol of strain.[3] In cyclopropene and related systems, there are numerous literature postulates concerning reactions which occur preferentially with strained σ bonds.[4]

Our work concerns the detailed mechanism by which cyclopropenes are electrophilically oxidized to enones by peracids. At present, product studies provide the major evidence that peracid oxidation of cyclopropenes to enones proceeds *via* oxabicyclobutane intermediates.[5]

The evidence, however, is equally consistent with mechanisms which involve electrophilic cleavage of a cyclopropene σ bond. Such cleavage would preclude intermediates such as oxabicyclobutane **1** in favor of species such as **2a, 2b,** or other variants formed from electrophilic oxidation of a σ bond. On the other hand, if cleavage of a σ bond is



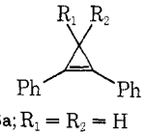
occurring simultaneously with reaction of the π bond to produce a transition state like **2c**, the overall electronic effect of allylic substituents would be expected to mimic that produced by **2a** or **2b.**



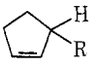
2c

Unfortunately, there is a dearth of kinetic data on the electrophilic oxidation of strained σ bonds with peracids. Oxidation of the strained σ bonds of methylbicyclobutane 1-carboxylate with peracid is reported to be slow and to lead to polymer.[6] It is unclear, however, to what extent the ester functionality retards oxidation. Oxidation of the strained σ bonds of cyclopropenes to form, after $C_{1,3}$ bond rotation, the highly stabilized allylic cation **2a** could conceivably occur in competition with electrophilic addition to the π system. This possibility becomes especially important since we know that the rate of cyclopropene oxidations with peracid is more than a power of ten times slower than epoxidations of analogous cyclopentenes.[7] Whatever the oxidation mechanism, the reactivity of the π double bond is clearly not so great to preclude competitive reaction with the σ bonds of cyclopropenes.

As a result, we have studied the C-3 allylic substituent effects on oxidations of cyclopropenes **3a–d.** We judge that



3a; $R_1 = R_2 = H$
b; $R_1 = H$; $R_2 = Me$
c; $R_1 = R_2 = Me$
d; $R_1 = H$; $R_2 = Ph$



4a; R = H
b; R = Me
c; R = Ph

a rate-determining π oxidation process should produce small allylic substituent effects similar to that in the true epoxidation of C-3 substituted cyclopentenes, **4a–c.** Contrastingly, electrophilic cleavage of a cyclopropene strained