Chemistry of Dioxiranes. 21. Thermal Reactions of Dioxiranes[1,†]

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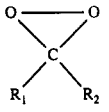
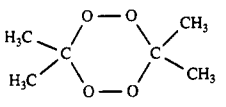
Received March 2, 1992

Thermolysis of dioxiranes in solutions of their parent ketones or in mixtures of the parent ketone and a foreign ketone leads to the formation of esters. The results are explained by postulating a free-radical mechanism involving H atom abstraction from the ketones. The resulting radicals are converted to the observed esters by reaction with acyloxy radicals derived from homolysis of the dioxiranes. Autodecomposition of dimethyldioxirane in acetone solution at room temperature gives methyl acetate at a very slow rate. When catalyzed by BF_3 etherate the same decomposition proceeds much more rapidly and is accompanied by acetol formation.

Introduction

Dioxiranes have proven to be very powerful and versatile oxygen atom transfer reagents.[2] Their potential was more fully realized after it was shown that they could be isolated in solution.[3] To date the chemistry of dioxiranes is best described as that of electrophilic oxidants. Despite the fact that dioxiranes are peroxides most of their reported chemistry is not that of typical peroxides. The oxygen atom transfer reactions which have been studied take place at room temperature or below. Until quite recently the literature contained but a single report[4] of any radical character in these reactions. In that case the substrate was benzaldehyde which contains a readily abstractable hydrogen atom. Recently, Curci et al.[5] have described the oxidation of catechol and hindered phenols with dioxiranes **1a** and **1b**. The products obtained led the authors to





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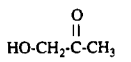
1a, $R_1 = R_2 = CH_3$

1b, $R_1 = CH_3$, $R_2 = CF_3$

1c, $R_1 = CH_3$, $R_2 = Et$

1d, $R_1 = CH_3$, $R_2 = iPr$



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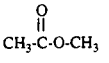

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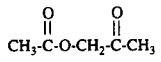

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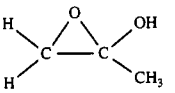

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suggest radical pathways in these oxidations. In other cases kinetic isotope,[6] reactivity,[2] and stereochemical data[6,7] argue against radical character. During the course of our studies of the autodecomposition of dimethyldioxirane (**1a**), we became interested in the fate of **1a** when it is heated, that is, when it is encouraged to participate in radical chemistry. In this paper we report that the thermolysis of dioxiranes in ketone solution gives new reaction pathways leading in most cases to non-Baeyer–Villiger esters. These esters are believed to arise from hydrogen abstraction reactions between a radical and the parent ketone. It is also of interest that some of the ester products obtained are used as flavoring ingredients in foods[8] and some have been identified[9] as contributing to the aromas of some red wines. Adam, Curci, et al. have described[10] the thermolysis of dioxirane **1b**. In that work, however, the thermolyses were conducted in ketone-free solutions of the dioxirane which leads to different fates for the analogous intermediates.

The situation in the literature with respect to the autodecomposition reaction of **1a** is a somewhat confused one. Adam et al. have reported[3b] that the decomposition of **1a** at room temperature did not follow first-order kinetics but had a pronounced inhibition period. Baumstark et al.[4] have also observed this inhibition period and found that the decomposition did not follow either first- or second-order kinetics. In recent experiments we have confirmed[11] these observations and found that the decomposition follows a complex rate law at higher concentrations of **1a**. At lower concentrations, e.g., 0.03 M, a first-order plot can be obtained. The reported lifetimes of solutions of **1a** at room temperature are also quite varied with Adam et al.[3a] finding ca. 7 h and Baumstark et al.[4] finding a slow decomposition requiring 18–24 h. It is interesting that Curci et al. found[12] that the thermal decomposition of methyl(trifluoromethy)dioxirane (**1b**) follows a mixed first-order and second-order rate law.

Literature reports on the product(s) of the decomposition of **1a** also are at some variance. We originally reported[3a] that the slow decomposition gave acetone diperoxide **2**. We have not been able to repeat this observation. It may be that the **2** found in the earlier experiment was formed in the reaction flask and carried over into the

† Dedicated to Professor John O. Edwards (Brown University) on the occasion of his 70th birthday.

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dioxirane collector. At any rate, we do not find it under the conditions used now in our laboratory. A similar situation exists with respect to the production of methyl acetate from the decomposition of **1a**. Baumstark et al.[4] find varying amounts of methyl acetate in the decomposed solutions. They also have found some of the ester in the solution prior to decomposition and speculate that it was formed in the reaction flask and carried over during the distillation of **1a**. On the other hand methyl trifluoroacetate had reported[12] to be the product of the thermal decomposition of methyl(trifluoromethyl)dioxirane. A subsequent study[10] revealed, however, that the decomposition is a complex free-radical process which also gives methyl acetate, trifluoromethyl acetate, and trifluoromethyl trifluoroacetate. Baumstark et al.[4] report that acetol (**3**) is the major product of the decomposition of **1a** under their conditions.

Results and Discussion

Autodecomposition of Dimethyldioxirane. Prior to beginning our work on thermal decompositions of dioxiranes, we have attempted to further clarify the situation with respect to the autodecomposition of **1a** and describe here the results of additional experiments on this process. A fresh solution of **1a** was prepared and dried with anhydrous sodium sulfate and its NMR spectrum examined immediately. The spectrum indicated the presence of **1a** as well as a small peak for methyl acetate (**4**) (3.6 ppm). This small amount of methyl acetate may have been formed from **1a** or it may have been formed in the generation flask and carried over in the distillation. No NMR peaks were present for acetone diperoxide, acetol, or acetol acetate (**5**). This solution was kept at room temperature for 26 days with periodic examination of its NMR spectrum. This analysis indicates that at room temperature the peak due to methyl acetate grows at the expense of those due to **1a**. This process is a slow one, however. After 26 days **1a** is almost completely converted to the acetate. Amazingly enough there is still a small amount of the dioxirane remaining at this time. The latter conclusion is based on the NMR of the solution as well as by an experiment in which an aliquot of the solution is treated with dimethyl sulfide. This treatment leads to the disappearance of the peaks due to **1a** and the apparance of peaks due to dimethyl sulfoxide and dimethyl sulfone. Under the conditions used in this experiment the only product of the decomposition of **1** is methyl acetate.

When a similar solution is kept in the freezer (ca. −25 °C) for 70 days no loss in **1a** can be observed by NMR. Likewise, the small peak for methyl acetate does not increase in size. A similar experiment was carried out over a 14-month period. Again the NMR spectrum indicates only the presence of **1a** and a small amount of methyl acetate.

Acetone solutions of **1a** are frequently treated with molecular sieves as well as with a drying agent such as sodium sulfate. This step is advisable when epoxides with particularly high sensitivities to water are being prepared. We have noticed that such treatment also appears to decrease the lifetime of **1a**. We have examined this point more closely by storing a freshly prepared solution of **1a** in acetone over molecular sieves and following the concentration of **1a** by NMR. The sample had also been previously dried twice with sodium sulfate. The concentration of **1a** decreases at a rate that is significantly faster than in a sample (vide supra) which had not been exposed to molecular sieves. The amount of methyl acetate is also observed to increase as before. In addition an absorption due to acetol, **3** is present and also slowly increases with time. After 48 h the yellow color of the dioxirane is absent which is in great contrast to the solution not exposed to the molecular sieves. The total of the amounts of **3** and **4** do not account for all of the consumed **1a**, however. The NMR spectrum does not indicate the presence of any other products. The best explanation that we can give for this observation is that some of the dioxirane may be trapped in the molecular sieves or was decomposed by the sieves to give products that are not detected in our analysis. We believe that the acetol was formed in the manner suggested by Baumstark;[4] that is, **1a** reacts with the enol of acetone to give the hydroxy epoxide **6**, which rapidly rearranges to **3**. These observations, as well as the earlier ones of Baumstark, indicate that acetone solutions of **1a** are very sensitive to any conditions which promote enol formation. Epoxidation to give **6** will occur rapidly and lead to a decrease in the concentration of **1a**. The varying estimates reported for the lifetime of **1a** in acetone solution may, in fact, be due to this interfering process.

With these results in hand we then reinvestigated our earlier observation[3a] that boron trifluoride increases the rate of conversion of **1a** to methyl acetate. A freshly prepared solution of **1a** in acetone, which had been dried with sodium sulfate, but not with molecular sieves, was treated with a drop of BF_3-ether complex in an NMR tube. The NMR spectrum of the solution was followed with time. In 15 min the peak (4.16) due to acetol (**3**) was readily observable. At the same time the peak due to methyl acetate (**4**) was observed to increase. Continued NMR measurements indicated that the amounts of **3** and **4** were increasing as the amount of **1a** decreased. In 90 min the yellow color of **1a** had disappeared. Repetition of this experiment four times led to the same results. The NMR spectrum of the spent sample indicated that **3** is the major product. Thus, while BF_3 increases the rate of conversion of **1a** to methyl acetate, as previously reported, its major role is to increase the amount of **3** presumably by increasing the amount af acetone enol present.

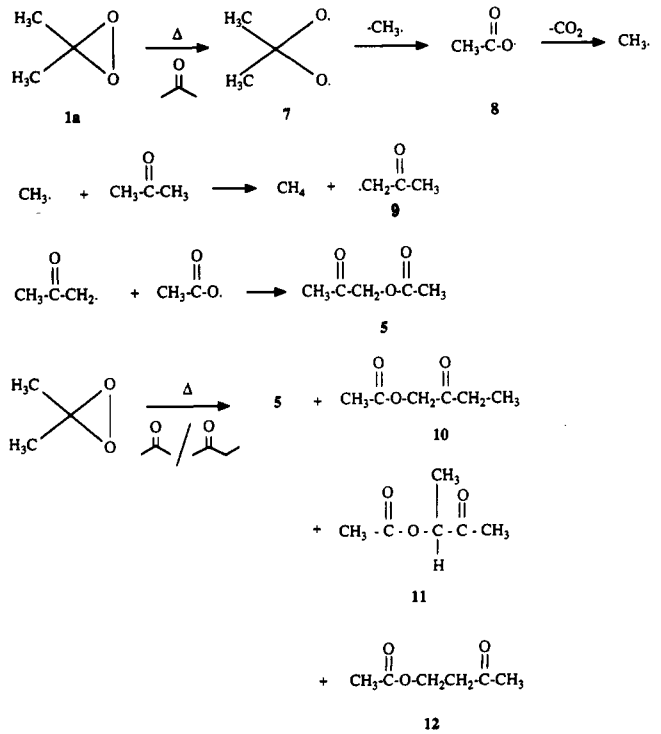
Thermolysis of Dioxiranes. We have thermolyzed dioxiranes in the parent ketone as well as in solutions containing a foreign ketone. The results are shown in Table I. The reactions are carried out by refluxing the solution of the dioxirane in the parent ketone or, in the case of **1a**, in a mixture of the parent ketone and foreign ketone. This process leads to the formation of ester products as shown in Table I. These esters are derived from the ketone or ketones present. The structures of the esters suggest the radical mechanism shown in Scheme I. The process is believed to proceed through formation of the dioxyl diradical formed from the dioxirane used. Thus, **1a** would give **7**. This diradical then may undergo a β-scission reaction to give an acetyloxy radical **8**. The acetyloxy radical **8** may lose CO_2 to also generate a methyl radical. The acetyloxy radical, or more likely, the methyl radical produced in the β-scission, then apparently abstracts hydrogen atoms from the ketone or ketones present. The resulting radical, **9** in the acetone case, then couples with the acetyloxy radical to give the product ester, such as 1-(acetyloxy)-2-propanone (**5**). The ester products formed in the other thermolyses summarized in Table I can be rationalized on the basis of this basic scheme. The ester products formed reflect the types of abstractable hydrogens in the ketone substrate. Thus, when **1a** is thermolyzed in acetone alone then **5** is the sole ester product. However, when **1a** is thermolyzed in a 50:50 (v/v) mixture of acetone and 2-butanone then the esters formed include **5** as well as **10**, **11**, and **12** (Table I). The latter three esters are those derived from hydrogen atom ab-

Table I. Thermal Reactions of Dioxiranes in Ketone Solutions

dioxirane	ketones (1:1)[a]	products (relative %)	total yield of esters[b,c] (%)
1a	2-propanone	1-(acetyloxy)-2-propanone (100)	26.1
1a	2-propanone/2-butanone	3-(acetyloxy)-2-butanone (86.90)	52.3
		1-(acetyloxy)-2-butanone (5.00)	
		1-(acetyloxy)-2-propanone (6.54)	
		4-(acetyloxy)-2-butanone (1.55)	
1a	2-propanone/3-pentanone	2-(acetyloxy)-3-pentanone (94.86)	64.6
		1-(acetylox)-2-propanone (5.13)	
1a	2-propanone/2-pentanone	3-(acetyloxy)-2-pentanone (70.83)	35.9
		4-(acetyloxy)-2-pentanone (15.85)	
		1-(acetyloxy)-2-pentanone (3.71)	
		1-(acetyloxy)-2-propanone (9.61)	
1a	2-propanone/3-methyl-2-butanone	3-(acetyloxy)-3-methyl-2-butanone (94.91)	43.6
		1-(acetyloxy)-3-methyl-2-butanone (1.93)	
		1-(acetyloxy)-2-propanone (3.16)	
1a	2-propanone/3,3-dimethyl-2-butanone	1-(acetyloxy)-2-propanone (40.87)	8.8
		1-(acetyloxy)-3,3-dimethyl-2-butanone (31.02)	
		4-(acetyloxy)-3,3-dimethyl-2-butanone (28.10)	
1a	2-propanone/2,4-dimethyl-3-pentanone	2-(acetyloxy)-2,4-dimethyl-3-pentanone (92.73)	32
		1-(acetyloxy)-2-propanone (7.27)	
1a	2-propanone/4-methyl-2-pentanone	4-(acetyloxy)-4-methyl-2-pentanone (30.23)	46.5
		3-(acetyloxy)-4-methyl-2-pentanone (35.70)	
		1-(acetyloxy)-4-methyl-2-pentanone (3.53)	
		1-(acetyloxy)-2-propanone (9.30)	
		4-hydroxy-4-methyl-2-pentanone (21.37)	
1a	2-propanone/cyclopentanone	2-(acetyloxy)cyclopentanone (96.45)	54.3
		1-(acetyloxy)-2-propanone (3.54)	
1a	2-propanone/cyclohexanone	2-(acetyloxy)cyclohexanone (84.73)	57.6
		1-(acetyloxy)-2-propanone (15.27)	
1c	2-butanone	3-(acetyloxy)-2-butanone (68)	nd[d]
		1-(acetyloxy)-2-butanone (6)	
		3-(1-oxopropoxy)-2-butanone (26)	
1d	3-methyl-2-butanone	3-(acetyloxy)-3-methyl-2-butanone (80)	nd
		1-(acetyloxy)-3-methyl-2-butanone (5)	
		3-(1-oxo-2-methylpropoxy)-3-methyl-2-butanone (15)	

[a] Vol/Vol ratios. [b] Does not include methyl acetate which is formed in all cases. [c] Determined by GLC. [d] Not determined.

Scheme I



stractions from 2-butanone to give radicals which combine with 8 to give the observed esters. When dioxirane 1c is thermolyzed in its parent ketone, 2-butanone, then esters 10 and 11 are formed. The reaction mixture in this case also includes 3-(1-oxopropoxy)-2-butanone which presumably is derived from a propionyloxy radical. This radical can be produced by a β-scission process in the dioxyl diradical derived from 1c. The major product, however, is the one arising from reaction of the acetyloxy radical with 2-butanone. When methylisopropyldioxirane (1d) is thermolyzed in its parent ketone the major product again is that derived from the reaction of the acetyloxy radical with the most readily abstractable hydrogen in the ketone solvent. The reaction mixture also contains the ester corresponding to the reaction of the acyloxy radical derived from the isopropyl group with the tertiary hydrogen in the ketone. The results in the cases of 1c and 1d both indicate that the dioxyl diradical derived from the dioxirane has a greater tendency to choose the β-scission reaction in which the most stable of the two possible radicals is lost, i.e., isopropyl versus methyl in the case of 1d. This result is in keeping with the known selectivity[13] in β-scissions in which there are several possible options. It should be noted that not all possible esters arising from application of the mechanism shown in Scheme I are realized. The distribution of the esters reflects the ease of abstraction of the appropriate hydrogen atom. In some cases the hydrogen atoms have such low abstraction tendencies that they do not provide competitive reaction paths to esters.

Two other product results require comment. When 1a is thermolyzed in a ketone mixture containing 3,3-dimethyl-2-butanone then an ester product is formed which corresponds to reaction of the acetyloxy radical with one of the methyl groups in the *tert*-butyl group. The other interesting product is formed when 1a is thermolyzed in 4-methyl-2-pentanone. The product mixture (Table I) contains a product, 4-hydroxy-4-methyl-2-pentanone,

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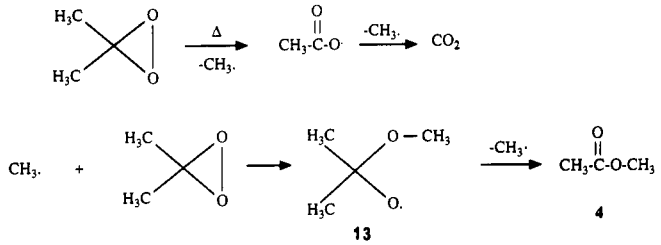
Scheme II



which apparently arises from insertion[2] of O atom into the tertiary C–H bond of the ketone. In a separate experiment it was shown that **1a** reacts with 4-methyl-2-pentanone at room temperature to give this insertion product.

A solution of **1a** was carried into a flash vacuum pyrolysis (FVP) apparatus at reduced pressure (0.2 mmHg) and a temperature of 150–180 °C in the heated portion of the apparatus. The exit gases were collected in a receiver cooled with dry ice/acetone. The contents of the receiver were analyzed by GLC and NMR. The major product was methyl acetate. Amazingly enough, some of the dioxirane survived the FVP conditions. Similar results were obtained when He was used to carry **1a** into the pyrolysis apparatus at atmospheric pressure. In contrast to the solution thermal reactions described above the FVP conditions do not give acetol acetate which is a major product of the solution reactions. Under the conditions of the FVP experiment the dioxirane apparently decomposes to the diradical **7** which then rapidly undergoes unimolecular rearrangement to give methyl acetate. These results are similar to those obtained by Adam, Curci, and co-workers[10] in the case of **1b**. The results of the FVP experiments support the mechanism shown in Scheme I. Thus, in the gas-phase experiments, the low concentration of acetone present effectively shuts off the reaction paths to esters shown in Scheme I.

We have also carried out variations of the basic thermolyses based on some recent work of Adam, Curci, and co-workers.[10] When the thermolyses are conducted in an oxygen atomsphere then the rate of decomposition of the dioxirane is markedly retarded. When **1a** is thermolyzed in refluxing acetone and under an oxygen atmosphere then only 27% of the **1a** is decomposed in 2 h. In contrast, when the same experiment is conducted in an argon atmosphere then the dioxirane is completely decomposed in 10–15 min. The latter results are essentially those obtained in the earlier thermolysis experiments conducted in air (Table I). These observations are nicely explained by the mechanism given by Adam, Curci, et al.;[10] that is, the decomposition of the dioxirane is probably occurring by a chain process (Scheme II). In the presence of oxygen the chain-carrying radical, $^{\bullet}CH_3$, for example, is scavenged by oxygen. Operation of the radical chain mechanism and, in particular, the involvement of radical **13** should lead to more methyl acetate in the thermolyses carried out in air or under argon than in those in which an oxygen atmosphere was used. We have examined this point by carrying out quantitative NMR measurements. These experiments indicate that the thermolysis in an oxygen atmosphere gave no detectable increase in the amount of methyl acetate present over that contained in the starting solution of **1a**. In contrast, when the thermolysis is carried out in an argon atmosphere the methyl acetate amount at the end of the experiment was three times that at the beginning. The thermolyzed solution also shows the presence of acetol acetate in this case. In the thermolysis reactions involving **1a** summarized in Table I the reaction mixtures also contained methyl acetate in an amount that exceeded that present in the initial solutions. This additional methyl acetate is presumed to arise from operation of the process shown in Scheme II in competition with that shown in Scheme I.

Experimental Section

Materials. Acetone (Fisher, reagent grade) was fractionally distilled over potassium carbonate. 2-Butanone (Fisher), 3-methyl-2-butanone, 2-pentanone, 4-methyl-2-pentanone, 3-pentanone, 2,4-dimethyl-3-pentanone, cyclopentanone (all obtained from Aldrich), 3,3-dimethyl-2-butanone, and cyclohexanone (both from Eastman) were distilled prior to use. Dimethyl sulfide, phenyl methyl sulfide, and 3-hydroxy-2-butanone (Aldrich) were of the highest purity and were used as such after verifying their purity by GLC. Anhydrous sodium sulfate, sodium dihydrogen phosphate, sodium monohydrogen phosphate, KOH, and phosphate buffer (pH 7.41) were obtained from Fisher Scientific. Oxone (DuPont), 2 $KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$, was obtained from Aldrich and used as such. All dioxirane solutions were assayed for dioxirane content using phenyl methyl sulfide and the GLC[3] method. Elemental analyses were performed by the Atlantic Microlab, Inc. (Atlanta, GA).

Instrumentation. ^1H and ^{13}C NMR spectra were obtained on a 300-MHz spectrometer with $CDCl_3$ as solvent unless stated otherwise. All NMR data are reported in ppm or δ values downfield from TMS. The multiplicities of the ^{13}C signals were determined by use of the attached proton test (APT) or the distortionless enhancement by polarization transfer (DEPT) pulse sequence. Electron impact mass spectra (at 70 eV ionizing voltage) were recorded on a twin EI and CI quadrupole mass spectrometer connected to a gas chromatograph fitted with a 12-m × 0.2-mm × 0.33-μm cross-linked methyl silicone column. Infrared spectra were determined as thin films between NaCl or KBr disks on an FT-IR spectrophotometer.

Chromatography. Gas chromatography was performed on a gas chromatograph equipped with a flame ionization detector and interfaced with an integrator. The columns used were a fused silica capillary column (30 m × 0.318 mm, film thickness 0.5 μm) or a fused silica capillary column (30 m × 0.254 mm, film thickness 0.25 μm). Helium was used as the carrier gas. Preparative GLC was performed on a gas chromatograph equipped with TC detector and using He as carrier. The columns used were a 12-ft × $^3/_8$-in. aluminum column packed with 8% SF-96 methyl silicone on Chromosorb G 60/80 mesh or an 18-ft × $^1/_4$-in. steel column packed with OV-25 on Chromosorb Q 80/100 mesh or a 15% SE-30 (Chromosorb G, 30/60 mesh, 20-ft by $^3/_8$-in.) column.

Preparation of Dimethyldioxirane Solution. Solutions of dimethyldioxirane in acetone were prepared according to the literature[3] procedure with the following modifications. A 2-L, three-necked, round-bottom flask containing a mixture of water (80 mL), acetone (50 mL, 0.68 mol), sodium bicarbonate (96 g), and a magnetic stirring bar was equipped with a pressure-equalized dropping funnel containing water (60 mL) and acetone (60 mL, 0.82 mol). A solid addition flask containing the granular peroxymonosulfate (Oxone (DuPont), 180 g, 0.29 mol) was attached to the reaction vessel via a rubber tube. An air condenser (length 20 cm) loosely packed with glass wool was attached to the second neck of the reaction vessel. The outlet of the air condenser was connected to a large acetone–dry ice condenser, which was connected to a receiving flask (100 mL) cooled in an acetone–dry ice bath. The receiving flask was connected to an acetone–dry ice cold trap which was connected in succession to a potassium iodide solution trap. A gas inlet tube extending into the reaction mixture was connected to the neck of the reaction flask to which the dropping funnel is also attached. Helium gas was bubbled through the reaction mixture while the granular Oxone was added in 10–15-g portions with simultaneous dropwise addition of the acetone–water mixture. The mixture was stirred vigorously at room temperature throughout the addition of the Oxone and acetone–water mixture which generally takes about 30 min. A yellow solution of dimethyldioxirane in acetone starts collecting slowly in the receiving flask. Vigorous stirring was continued for an additional 15–20 min. A slight vacuum (ca. 30 mmHg) was applied to the cold trap until most of the remaining acetone from the reaction flask had been collected in the cooled receiving flask

(2–3 min). The yellow dimethyldioxirane solution (80–90 mL) was dried over sodium sulfate (50 g), filtered, and stored in the freezer (–25 °C) over sodium sulfate (30 g). The dioxirane content of the solutions were assayed using phenyl methyl sulfide and the GLC method. The concentrations of dimethyldioxirane solutions in acetone obtained in this manner were in the range of 0.05 to 0.12 M.

Ethylmethyldioxirane was prepared as described for **1a** except using 2-butanone.

Isopropylmethyldioxirane. Isopropylmethyldioxirane in 3-methyl-2-butanone was prepared using the in situ[1] method. A mixture of 3-methyl-2-butanone (50 mL), phosphate buffer (pH 7.4, 50 mL), and crushed ice (10–20 g) was stirred at 0 °C (ice–salt bath). Cooled Oxone (90 g) was added as a slurry in 200 mL of water over 5 min. A KOH solution (15%), cooled to 0–5 °C, was added simultaneously to maintain the pH at 7–8.5. A yellow color appeared immediately upon combining the reagents. The mixture was stirred vigorously for 2–3 min and then poured into a beaker containing a cooled mixture of anhydrous Na_2SO_4, $NaH_2PO_4{\cdot}H_2O$, and $Na_2HPO_4{\cdot}7H_2O$ (2:1:1), and the combined mixture was stirred vigorously in an ice–salt bath. The liquid phase was transferred rapidly to a cooled separatory funnel, and the aqueous phase was separated out. The dark yellow organic phase was dried with cold anhydrous Na_2SO_4 (50 g), filtered (40 mL), dried again with cold Na_2SO_4 (50 g), and stored in the freezer (–25 °C). The concentration of isopropylmethyldioxirane solution obtained in this method was found to be 0.074 M.

General Procedure for the Thermolysis of Dioxiranes in Ketones. A solution of dimethyldioxirane in acetone (0.06–0.085 M, 50–150 mL) was placed in a round-bottom flask equipped with a dry ice–acetone condenser. The solution used contained either acetone alone or a mixture of acetone and another ketone (see Table I). The reaction mixture was heated to reflux which caused the yellow color of the dioxirane to begin to disappear. The color was gone completely in 5–15 min. The colorless solution was refluxed for another 15–30 min. GLC analysis of the reaction mixture indicated that it contained one or more components in addition to the ketone(s). Acetone and excess ketones were removed by fractional distillation. Analysis of the distillation fractions indicated that only minor amounts of products were contained in these fractions. Products in the pale yellow residue (2–5 mL) were separated by preparative GLC. All of the reaction products were collected and the samples analyzed further to ensure purity. The products were characterized using ^1H ^{13}C NMR, infrared, and mass spectroscopy and by comparison of their spectral and chromatographic properties with those of authentic samples or with literature values. Yields of the products were determined by GLC using an internal standard and measured response factors.

Decomposition of Dimethyldioxirane in Acetone. The general procedure was followed to give a residue which GLC analysis indicated contained a single product. This material was identified as 1-(acetyloxy)-2-propanone (acetol acetate) by comparing its IR,[14] ^1H,[15] ^{13}C,[16] and mass spectral[17] data with the literature values. Preparative GLC conditions: column, SF-96 (12 ft × $^3/_8$ in.), column temperature (temp), 100 °C, injector temp, 140 °C, detector temp, 140 °C, collector temp, 50 °C, He flow, 60 mL/min, current, 150 mA. Retention time, 5 min.

Decomposition of Dimethyldioxirane in Acetone/2-Butanone. The general procedure was followed. The residue contained four products which were collected by preparative GLC. One of these products was 1-(acetyloxy)-2-propanone, identified as described previously. The major product was a colorless liquid which was identified as 3-(acetyloxy)-2-butanone. This material had a ^1H NMR spectrum which was the same as that given in the literature.[15,18] ^{13}C NMR ($CDCl_3$): δ 15.9 (CH_3CH–), 20.67 (CH_3COO–), 25.69 (CH_3CO–), 74.84 (–CH–), 170.3 (CH_3COO–), 205.56 (CH_3CO–). Mass (EI, 70 eV): m/z 130 (M^+, 3.5), 88 (2), 87 (26.4), 86 (3.4), 70 (1), 55 (1.5), 45 (5), 43 (100). Calcd for $C_6H_{10}O_3$: 130.14. A smaller quantity of a third colorless liquid was identified as 1-(acetyloxy)-2-butanone. This material had ^1H NMR[18] and mass spectral[19] data which were the same as the literature values.[18,19] ^{13}C NMR ($CDCl_3$): δ 7.12 (CH_3CH_2–), 20.47 (CH_3CO–), 32.04 (CH_3CH_2–), 67.70 (–CH_2O–), 170.26 (–COO), 204.38 (CH_3CH_2CO–). Traces of a fourth ester product were identified as 4-(acetyloxy)-2-butanone on the basis of a comparison of ^1H NMR[20] and mass spectral[19] data with the literature values.

Analytical GLC conditions: column, DB-210, temp 1, 60 °C, time 1, 5 min; temp 2, 200 °C, time 2, 5 min, injector temp 250 °C, detector temp 250 °C, inlet P, 24 psi. Retention times: acetol acetate, 8.3 min; 3-(acetyloxy)-2-butanone, 8.4 min; 1-(acetyloxy)-2-butanone, 9.0 min; 4-(acetyloxy)-2-butanone, 9.6 min. Preparative GLC conditions: column, OV-25 (18 ft × $^1/_4$ in. SS); column temp, 90 °C, injector temp, 70 °C, detector temp, 105 °C, collector temp, 50 °C, He flow 60 mL/min, current 145 mA. Retention times: acetol acetate, 8 min; 3-(acetyloxy)-2-butanone, 20 min; 1-(acetyloxy)-2-butanone, 36 min; 4-(acetyloxy)-2-butanone, 45 min. The fraction containing 3-(acetyloxy)-2-butanone was contaminated with acetol acetate and required further separation as follows: column, 8% SF-96 (12 ft × $^3/_8$ in.), column temp, 60 °C, injector temp, 70 °C, detector temp, 100 °C, collector temp, 80 °C, He flow 80 mL/min, current 145 mA. Retention times: acetol acetate, 5 min, 3-(acetyloxy)-2-butanone, 7 min.

Decomposition of Dimethyldioxirane in Acetone/3-Pentanone. The general procedure was used to give a pale yellow residue. GLC analysis indicated the presence of two products which were separated by preparative GLC. One of these was identified as acetol acetate as before. The second product was identified as 2-(acetyloxy)-3-pentanone. This material had a ^1H NMR spectrum that was the same as that given in the literature.[18a] IR (neat, NaCl): 2984, 2942, 1750, 1732, 1451, 1412, 1372, 1235, 1096, 1034, 976, 932, 866, and 802 cm^{-1}. ^{13}C NMR ($CDCl_3$): δ 7.17 (CH_3CH_2–), 16.24 (CH_3CH–), 20.69 (CH_3COO–), 31.39 (–CH_2CO–), 74.49 ($CHCH_3$), 170.35 (–COO–), 208.29 (–CH_2COCH–). MS (EI, 70 eV): m/z 144 (M^+, 2), 115 (2), 101 (16), 100 (8), 87 (22), 57 (65), 43 (100). Calcd for $C_7H_{12}O_3$ 144.17. Analytical GLC conditions: column DB-210, temp 1, 60 °C, time 1, 5 min, rate 1, 20 °C/min, temp 2, 200 °C, time 2, 5 min, injector temp, 250 °C, detector temp, 250 °C, inlet P 24 psi. Retention times: acetol acetate, 8.3 min; 2-(acetyloxy)-3-pentanone, 8.9 min. Preparative GLC: column, 15 % OV-25 (18 ft × $^1/_4$ ft, SS), column temp, 130 °C, injector temp, 100 °C, detector temp, 175 °C, collector temp, 70 °C, current 145 mA, flow rate 40 mL/min. Retention times: acetol acetate, 6 min; 2-(acetyloxy)-3-pentanone, 10 min.

Decomposition of Dimethyldioxirane in Acetone/2-Pentanone. The general procedure was followed to give a pale yellow residue. Analytical GLC analysis of the residue indicated that it contained acetol acetate and three other materials. The major reaction product was identified as 3-(acetyloxy)-2-pentanone[21] on the basis of the following data. IR (neat, KBr): 2975, 1740, 1720, 1458, 1432, 1375, 1236, 1103, 1059, 1023, 973, and 897 cm^{-1}. ^1H NMR ($CDCl_3$): δ 0.98 (t, J = 7.4 Hz, 3 H, CH_3CH_2–), 1.65–1.98 (complex m, 2 H, –CH_2–), 2.16 (s, 3 H, CH_3COO–), 2.16 (s, 3 H, CH_3COCH–), 4.95 (dd, J = 7.7 Hz, J = 4.6 Hz, 1 H, –CH_2CHCO–). ^{13}C NMR ($CDCl_3$): δ 9.44 (CH_3CH_2–), 20.56 (CH_3COO–), 23.57 (CH_2–), 26.10 (CH_3COCH–), 79.63 (–CH–), 170.55 (–COO–), 205.22 (–$CHCOCH_3$). MS (EI, 70 eV): m/z 144 (M+, 1), 116 (2.3), 101 (39), 84 (2.5), 69 (3.5), 59 (5), 43 (100). Calcd for $C_7H_{12}O_3$: 144.17. The two minor products were identifed as 1-(acetyloxy)-2-propanone and 4-(acetyloxy)-2-propanone by comparison of their ^1H NMR spectra with the respective[22] and[23] literature spectra and the following data. 4-(Acetyloxy)-2-pentanone. IR (neat,

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KBr): 2984, 2938, 1735, 1717, 1371, 1247, 1172, 1143, 1072, 1019, 957, and 912 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.27 (d, J = 6.3 Hz, 3 H, CH_3CH–), 2.01 (s, 3 H, CH_3COO–), 2.16 (s, 3 H, CH_3COCH–), 2.68 (double AB q, J = 16.3, 5.9 Hz and J = 16.3, 7.0 Hz, each 1 H, –$CHCH_2CO$–), 5.28 (two overlapped q, J = 6.3 Hz, 1 H, CH_3CHCH_2–). ^{13}C NMR ($CDCl_3$): δ 20.02 (CH_3CH–), 21.20 (CH_3COO–), 30.43 (CH_3COCH_2–), 49.40 (–$COCH_2CH$–), 66.95 (CH_3CH–), 170.06 (CH_3COOCH–), 205.20 (CH_3COCH–). MS (EI, 70 eV): m/z 129 ($M^+ - CH_3$, 0.7), 103 (24), 101 (12), 84 (8), 69 (22), 61 (7), 43 (100). Calcd for $C_7H_{12}O_3$: 144.17. 1-(Acetyloxy)-2-pentanone. IR (neat, KBr): 2966, 2937, 1750, 1733, 1418, 1375, 1234, 1166, 1132, 1091, 1053, 1029, and 896 cm^{-1}. ^{13}C NMR ($CDCl_3$): δ 1374 (CH_3CH_2–), 16.92 ($CH_3CH_2CH_2$–), 20.56 (CH_3COO–), 40.73 (–CH_2CH_2CO–), 67.99 (–$COCH_2OCO$–), 170.05 (CH_3COO–), 203.58 (–CH_2COCH_2–). MS (EI, 70 eV): m/z 144 (M^+, 2), 116 (8), 102 (7), 73 (8), 71 (75), 55 (2), 43 (100). Calcd for $C_7H_{12}O_3$, 144.17. Analytical GLC conditions: column, DB 210, temp 1, 60 °C, time 1, 5 min, rate 1, 20 °C/min, temp 2, 200 °C, time 2, 5 min, injector temp, 250 °C, detector temp, 250 °C, inlet P, 24 psi. Retention times: acetol acetate, 8.3 min, 3-(acetyloxy)-2-pentanone, 9.2 min, 4-(acetyloxy)-2-pentanone, 9.7 min, 1-(acetyloxy)-2-pentanone, 9.8 min. Preparative GLC conditions: column, 15 % OV-25 (18 ft × $^1/_4$ in., SS), column temp, 130 °C, injector temp, 110 °C, detector temp, 175 °C, collector temp, 70 °C, He flow, 60 mL/min, current 150 mA. Retention times: acetol acetate, 10 min; 3-(acetyloxy)-2-pentanone, 20 min; 4-(acetyloxy)-2-pentanone, 23 min; 1-(acetyloxy)-2-pentanone, 29 min.

Decomposition of Dimethyldioxirane in Acetone/3-Methyl-2-butanone. The general procedure was followed to give a pale yellow residue which analytical GLC analysis indicated was composed of three products. The products were collected using preparative GLC. One of these products was identified as acetol acetate as before. The major product was identified as 3-(acetyloxy)-3-methyl-2-butanone. The identification was based on a comparison of its ^{1}H NMR spectrum with that in the literature[18] as well as the following data. IR (neat, NaCl): 2989, 2942, 1733 (–COO–), 1724 (–CO–), 1372, 1256 (–COO–), 1155, 1123, 1020, 957, 894, 845 cm^{-1}. ^{13}C NMR ($CDCl_3$): δ 21.10 (CH_3COO–), 23.30 (–$(CH_3)_2C$–), 23.50 (CH_3CO–), 83.59 (–$(CH_3)_2C$–), 170.21 (CH_3COO–), 206.77 (CH_3CO–). Mass (EI, 70 eV): m/z 144 (M^+, 2), 102 (3), 101 (44), 69 (3), 59 (40), 57 (5), 43 (100). Calcd for $C_7H_{12}O_3$: 144.17. A minor product was identified as 1-(acetyloxy)-3-methyl-2-butanone by comparing its ^{1}H NMR spectrum with that in the literature[18] as well as on the basis of the following data. Mass (EI, 70 eV): m/z 144 (M^+, 1), 101 (16.5), 74 (7), 73 (8.7), 71 (57.2), 43 (100). Calcd for $C_7H_{12}O_3$: 144.17. Analytical GLC conditions: column DB-210, temp 1, 60 °C, time 1, 5 min, rate 1, 20 °C/min; temp 2, 200 °C, time 2, 5 min, injector temp, 250 °C, detector temp, 250 °C, inlet P, 24 psi. Retention times: acetol acetate, 8.4 min, 3-(acetyloxy)-3-methyl-2-butanone, 8.7 min, 1-(acetyloxy)-3-methyl-2-butanone, 9.4 min. Preparative GLC conditions: column, 8% SF-96 (12 ft × $^3/_8$ in.), column temp, 100 °C, injector temp, 140 °C, detector temp, 140 °C, collector temp, 50 °C, He flow, 60 mL/min, current 150 mA. Retention times: acetol acetate, 5 min, 3-(acetyloxy)-3-methyl-2-butanone, 7 min, 1-(acetyloxy)-3-methyl-2-butanone, 10 min.

Decomposition of Dimethyldioxirane in Acetone/2,4-Dimethyl-3-pentanone. The general procedure was followed to give a residue which analytical GLC indicated contained acetol acetate and one other product. The products were collected using preparative GLC. The major product was identified as 2-(acetyloxy)-2,4-dimethyl-3-pentanone by comparing its ^{1}H NMR spectrum with that in the literature[26] as well as from the following data. IR (neat, NaCl): 2978, 2939, 2875, 1740, 1718, 1471, 1367, 1257, 1148, 1044, 1020, 964, 844, 831 cm^{-1}. ^{13}C NMR ($CDCl_3$): δ 20.03 ($(CH_3)_2CH$–), 21.19 (CH_3COO–), 23.93 (–$C(CH_3)_2O$–), 34.04 ($(CH_3)_2CH$–), 83.70 (–$C(CH_3)_2O$–), 170.13 (–COO), 213.62 ($(CH_3)_2CHCO$–). Mass (EI, 70 eV): m/z 172 (M^+, 1), 129 (47), 101 (58), 85 (4), 71 (49), 69 (10), 59 (57), 43 (100). Calcd for $C_9H_{16}O_3$: 172.22. These data compare favorably with those in the literature.[27] Analytical GLC conditions: column, DB-5, temp 1, 60 °C, time 1, 5 min, rate 1, 20 °C/min; temp 2, 200 °C, time 2, 5 min, injector temp, 250 °C, detector temp, 250 °C, inlet P, 24 psi. Retention times: acetol acetate, 3.9 min, 2-(acetyloxy)-2,4-dimethyl-3-pentanone, 8.0 min. Preparative GLC conditions: column, 15 % OV-25 (18 ft × $^1/_4$ in., SS), column temp, 100 °C, injector temp, 115 °C, detector temp, 180 °C, collector temp, 100 °C, He flow, 60 mL/min, current, 135 mA. Retention times: acetol acetate, 8 min, 2-(acetyloxy)-2,4-dimethyl-3-pentanone, 16 min.

Decomposition of Dimethyldioxirane in Acetone/3,3-Dimethyl-2-butanone. The general procedure was followed to give a pale yellow residue. Analytical GLC showed the presence of acetol acetate and two other products. The products were collected using preparative GLC. The major product was identified as 1-(acetyloxy)-3,3-dimethyl-2-butanone on the basis of the following data. IR (neat, KBr): 2971, 2878, 1753, 1725, 1480, 1417, 1370, 1233, 1049, 1010, 987, and 842 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 1.20 (s, 9 H, $(CH_3)_3C$–), 2.16 (s, 3 H, CH_3COO–), 4.87 (s 2 H, –$COOCH_2$–). These data compare well with the literature[24] values. ^{13}C NMR ($CDCl_3$): δ 20.52 (CH_3COO–), 26.21 ($(CH_3)_3C$–), 42.84 ($(CH_3)_3C$–), 64.42 (–CH_2O–), 170.14 (CH_3COO–), 207.59 ($(CH_3)_3CCO$–). MS (EI, 70 eV): m/z 158 (M^+, 0.9), 101 (15), 85 (12), 73 (3), 57 (100), 43 (45). Calcd for $C_8H_{14}O_3$: 158.17.

Of the two minor products acetol acetate was identified as previously described. The second minor product was identified as 4-(acetyloxy)-3,3-dimethyl-2-butanone by comparing its ^{1}H NMR spectrum with that given in the literature[25] and the following data. IR (neat, KBr): 2974, 2876, 1746, 1710, 1474, 1376, 1241, 1134, and 1041 cm^{-1}. ^{13}C NMR ($CDCl_3$): δ 20.83 (CH_3COO–), 21.79 (–$C(CH_3)_2$–), 25.47 (CH_3COC), 47.60 (–$C(CH_3)_2$–), 69.86 (–OCH_2C–), 170.62 (CH_3COO–), 210.84 (CH_3COC–). MS (EI, 70 eV): m/z 115 ($M^+ - CH_3 - CO$–, 1.4), 103 (14), 98 (8), 86 (7), 71 (7), 56 (35), 43 (100). Calcd for $C_8H_{14}O_3$: 158.17.

Analytical GLC conditions: column, DB 210, temp 1, 60 °C, time 1, 5 min, rate 20 °C/min, temp 2, 200 °C, time 2, 5 min, injector temp, 250 °C, detector temp, 250 °C, inlet P, 24 psi. Retention times: acetol acetate, 8.2 min, 1-(acetyloxy)-3,3-dimethyl-2-butanone, 9.5 min, 4-(acetyloxy)-3,3-dimethyl-2-butanone, 10.3 min. Preparative GLC conditions: column, 15% SE-30 (Chrom G (30/60), 20 ft × $^3/_8$ in.), column temp, 100 °C, injector temp, 110 °C, detector temp, 120 °C, collector temp, 100 °C, He flow rate, 50 mL/min, current 145 mA. Retention times: acetol acetate, 8 min, 1-(acetyloxy)-3,3-dimethyl-2-butanone, 23 min, 4-(acetyloxy)-3,3-dimethyl-2-butanone, 24 min.

Decomposition of Dimethyldioxirane in Acetone/4-Methyl-2-pentanone. The general procedure was followed, and the residue was analyzed by analytical GLC which indicated the presence of acetol acetate and four other compounds. The products were collected using preparative GLC. Two of the products were present in larger quantity. One of these was identified as 4-(acetyloxy)-4-methyl-2-pentanone by comparing its ^{1}H NMR with that in the literature[28] as well as by the following data. IR (neat, KBr): 2982, 2940, 1732, 1717, 1474, 1428, 1368, 1257, 1173, 1120, 1020, 946, 831, and 763 cm^{-1}. ^{13}C NMR ($CDCl_3$): δ 22.38 (CH_3COO–), 26.51 (–$C(CH_3)_2$–), 31.73 (CH_3COCH_2–), 52.25 (–CH_2–), 80.04 (–$C(CH_3)_2$–), 170.31 (CH_3COO–), 205.67 (CH_3COCH_2–). MS (EI, 70 eV): m/z 143 (0.2), 115 (2.5), 98 (11), 83 (18), 59 (7), 56 (6), 43 (100). Calcd for $C_8H_{14}O_3$, 158.17.

The next most abundant compound was identified as 3-(acetyloxy)-4-methyl-2-pentanone on the basis of the following data. IR (neat, KBr): 2970, 2937, 2879, 1747, 1732, 1467, 1428, 1373, 1267, 1236, 1185, 1128, 1112, 1036, 963, and 905 cm^{-1}. ^{1}H NMR ($CDCl_3$): δ 0.93 (d, J = 6.8 Hz, 3 H, $(CH_3)_2CH$–), 1.01 (d, J = 6.8 Hz, 3 H, $(CH_3)_2CH$–), 2.15 (s, 3 H, CH_3COO–), 2.20 (double septet, J = 6.8 and 4.4 Hz, 1 H, $(CH_3)_2CHCH$–), 4.86 (d, J = 4.4 Hz, 1 H, $(CH_3)_2CHCH$–). ^{13}C NMR ($CDCl_3$): δ 16.85 and 19.19 ($(CH_3)_2CH$–), 20.63 (CH_3COO–), 27.02 ($(CH_3)_2CH$–), 29.46 (CH_3COCH–), 82.79 ($CH_3COOCHCH$–), 170.57 (–COO–), 205.11 (–$CHCOCH_3$). MS (EI, 70 eV): m/z 158 (M^+, 1), 116 (4), 115 (25), 98 (3), 73 (5), 55 (4), 43 (100). Calcd for $C_8H_{14}O_3$: 158.17. Anal. Calcd for $C_8H_{14}O_3$: C, 60.74; H, 8.92. Found: C, 60.58; H, 8.94.

One of the minor components was identified as 1-(acetyloxy)-4-methyl-2-pentanone on the basis of a comparison of its ^{1}H NMR spectrum with that in the literature[23] as well as the

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following data. ^{13}C NMR ($CDCl_3$): δ 22.57 (-CH(CH_3)$_2$), 24.56 (CH_3COO-), 30.47 (-CH(CH_3)$_2$), 47.61 (-$CHCH_2$-), 68.33 (-CH_2O-), 170.07 (CH_3COO-), 207.34 (-CH_2COCH_2-). MS (EI, 70 eV): m/z 158 (M^+, 1.5), 116 (12), 101 (7), 86 (5), 85 (96), 73 (11), 57 (100), 43 (86). Calcd for $C_8H_{14}O_3$: 158.17. The second minor component was identified as 4-hydroxy-4-methyl-2-pentanone by comparing its mass spectral data with those in the literature[19] and the following data. ^1H NMR ($CDCl_3$): δ 1.25 (s, 6 H (CH_3)$_2$C-), 2.18 (s, 3 H, CH_3COCH_2-), 2.63 (s, 2 H, CH_2CO-), 3.79 (s, 1 H, (CH_3)$_2$C(OH)-). ^{13}C NMR ($CDCl_3$): δ 29.26 ((CH_3)$_2$C-), 31.73 (CH_3COCH_2-), 53.80 (-CH_2-), 69.44 ((CH_3)$_2$$C$-), 210.51 ($CH_3COCH_2$-). In a separate experiment 4-methyl-2-pentanone was treated with dimethyldioxirane at room temperature for 30 h. Preparative GLC on the residue obtained by fractional distillation of acetone and 4-methyl-2-pentanone afforded 4-hydroxy-4-methyl-2-pentanone.

Analytical GLC conditions: column, DB 210, temp 1, 60 °C, time 1, 5 min, rate 20 °C/min, temp 2, 200 °C, time 2, 5 min, injector temp, 250 °C, detector temp, 250 °C, inlet P, 24 psi. Retention times: 4-hydroxy-4-methyl-2-pentanone, 7.0 min, acetol acetate 8.2 min, 4-(acetyloxy)-4-methyl-2-pentanone, 9.2 min, 3-(acetyloxy)-4-methyl-2-pentanone, 9.5 min, 1-(acetyloxy)-4-methyl-2-pentanone, 9.9 min. Preparative GLC conditions: column 15% SE-30 (Chrom G (30/60), 20 ft × $^3/_8$ in.), column temp, 100 °C, injector temp, 110 °C, detector temp, 120 °C, collector temp, 100 °C, He flow, 50 mL/min, current, 145 mA. Retention times: 4-hydroxy-4-methyl-2-pentanone, 10 min, acetol acetate, 12 min, 4-(acetyloxy)-4-methyl-2-pentanone, 26 min, 3-(acetyloxy)-4-methyl-2-pentanone, 28 min, 1-(acetyloxy)-4-methyl-2-pentanone, 38 min.

Decomposition of Dimethyldioxirane in Acetone/Cyclopentanone. The general procedure was followed to give a pale yellow residue. Analytical GLC indicated the presence of acetol acetate and a second compound. The second compound was the major component and was collected using preparative GLC. This material was identified as 2-(acetyloxy)cyclopropanone by comparing its ^1H NMR with that given in the literature[18a] and the following data. IR (neat): 2975 (m), 1757 (sh), 1741 (vs), 1373 (m), 1234 (s), 1100 (m), 1033 (m) cm^{-1}. ^{13}C NMR ($CDCl_3$): δ 17.08 (C-4, -CH_2-), 20.71 (CH_3COO-), 28.36 (C-3, -CH_2-), 34.81 (C-5, -CH_2-), 75.67 (C-2, -CH-), 170.18 (-$OCOCH_3$-), 212.39 (C-1, CO). MS (EI, 70 eV): m/z 142 (M^+, 5), 99 (51), 82 (29), 71 (16), 55 (16), 43 (100). Calcd for $C_7H_{10}O_3$: 142.15. Analytical GLC conditions: column, DB 210, temp 1, 60 °C, time 1, 5 min, rate 1, 20 °C/min, temp 2, 200 °C, time 2, 5 min, injector temp, 250 °C, detector temp, 250 °C, inlet P, 24 psi. Retention times: acetol acetate, 8.4 min, 2-(acetyloxy)cyclopropanone, 11 min. Preparative GLC conditions: column, 15 % OV-25 (18 ft × $^1/_4$ in., SS), column temp, 140 °C, injector temp, 120 °C, detector temp, 190 °C, collector temp, 110 °C, He flow, 50–60 mL/min. Retention times: acetol acetate, 4 min, 2-(acetyloxy)cyclopentanone, 9 min.

Decomposition of Dimethyldioxirane in Acetone/Cyclohexanone. The general procedure was followed to give a pale yellow residue. Analytical GLC of the residue indicated the presence of acetol acetate and one other compound. The latter was collected using preparative GLC. This material was identified as 2-(acetyloxy)cyclohexanone by comparing its ^1H NMR with that given in the literature[18a,29] and on the basis of the following data. IR (neat, KBr): 2944, 2868, 1745 (sh), 1726 (s), 1431, 1374, 1237 (s), 1071, 912, 879 cm^{-1}. ^{13}C NMR ($CDCl_3$): δ 20.66 (CH_3COO-), 23.70 (C-4, -CH_2), 27.09 (C-5, -CH_2-), 33.01 (C-3, -CH_2-), 40.62 ((C-6, -CH_2-), 76.49 (C-2, -CH-), 169.96 (-$OCOCH_3$), 204.47 (C-1, CO). MS (EI, 70 eV): m/z 156 (M^+, 3.3), 114 (22), 113 (45), 96 (19), 85 (10), 67 (30), 57 (10), 43 (100). Calcd for $C_8H_{12}O_3$: 156.17. Analytical GLC conditions: column, DB 210, temp 1, 60 °C, time 1, 5 min, rate 1, 20 °C/min, temp 2, 200 °C, time 2, 5 min, injector temp, 250 °C, detector temp, 250 °C, inlet P, 24 psi. Retention times: acetol acetate, 8.4 min, 2-(acetyloxy)cyclohexanone, 11.8 min. Preparative GLC conditions: column, 15 % OV-25 (18 ft × $^1/_4$ in., SS), column temp, 180 °C, injector temp, 120 °C, detector temp, 190 °C, collector temp, 110 °C, He flow, 70 mL/min, current, 150 mA. Retention times: acetol acetate, 4 min, 2-(acetyloxy)cyclohexanone, 12 min.

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Decomposition of Ethylmethyldioxirane in 2-Butanone. The general procedure was followed. Excess 2-butanone was removed to give a residue which was found to contain three products using analytical GLC. The products were collected using preparative GLC. The major product was identified as 3-(acetyloxy)-2-butanone by comparing its ^1H NMR spectrum with that in the literature[15,18] as well as on the basis of the following data. ^{13}C NMR ($CDCl_3$): δ 15.90 (CH_3CH-), 20.66 (CH_3COO-), 25.58 (CH_3CO-), 74.85 (-CH-), 170.30 (CH_3COO-), 205.54 (CH_3CO-). MS (EI, 70 eV): m/z 130 (M^+, 3.7), 87 (26), 86 (3.5), 55 (1.1), 43 (100). Calcd for $C_6H_{10}O_3$: 130.14. The minor product was identified as 1-(acetyloxy)-2-butanone by comparing its ^1H NMR spectrum with that in the literature.[18] The measured mass spectrum also agrees with that in the literature.[19] Additional support for the structure comes from the following data. ^{13}C NMR ($CDCl_3$): δ 7.12 (CH_3CH_2-), 20.47 (CH_3CO-), 32.04 (CH_3CH_2-), 67.70 (-CH_2O-), 170.26 (CH_3COO-), 204.38 (CH_3CH_2CO-). The second most abundant compound was identified as 3-(1-oxopropoxy)-2-butanone on the basis of the following data. IR (neat, NaCl): 2987, 2944, 1743, 1732, 1463, 1424, 1363, 1273, 1182, 1098, 1000, 875, 808 cm^{-1}. ^1H NMR ($CDCl_3$): δ 1.17 (t, J = 7.5 Hz, 3 H, CH_3CH_2-), 1.39 (d, J = 7 Hz, 3 H, CH_3CH-), 2.17 (s, 3 H, CH_3CO-), 2.42 and 2.43 (two q, J = 7.5 Hz, 2 H, CH_3CH_2COO-), diastereotopic -CH_2- protons), 5.08 (q, J = 7 Hz, -CH-). ^{13}C NMR ($CDCl_3$): δ 8.95 (CH_3CH_2-), 15.96 (CH_3CH-), 25.63 (CH_3COCH-), 27.33 (CH_3CH_2COO-), 74.73 ($CH_3CHCOCH_3$), 173.80 (CH_3CH_2COO-), 205.75 (CH_3CO-). MS (EI, 70 eV): m/z 144 (M^+, 1), 115 (1), 101 (18), 100 (5), 55 (1), 45 (5), 43 (19). Calcd for $C_7H_{12}O_3$: 144.17. Anal. Calcd for $C_7H_{12}O_3$: C, 58.31; H, 8.39. Found: C, 57.60; H, 8.27. An authentic sample of this material was prepared by heating a mixture of 3-hydroxy-2-butanone, propionic anhydride, and amberlite-IR-120. Excess reactants were removed by distillation. The residue was subjected to Kugelrohr distillation (oven temp, 70–80 °C (5 mmHg)) to give a colorless liquid. Preparative GLC was used to obtain a pure sample whose properties were the same as those for the sample obtained in the dioxirane thermolysis. Analytical GLC conditions: column, HP-1 (GC-MS column), temp 1, 40 °C, time 1, 2 min, rate 1 10 °C/min, temp 2, 200 °C, time 2, 2 min, injector temp, 250 °C, detector temp, 250 °C. Retention times: 3-(acetyloxy)-2-butanone, 4.1 min, 1-(acetyloxy)-2-butanone, 5.3 min, 3-(1-oxopropoxy)-2-butanone, 5.7 min. Preparative GLC conditions: column, 8% SF-96 (12 ft × $^3/_8$ in.), column temp, 100 °C, injector temp, 140 °C, detector temp, 140 °C, collector temp, 50 °C, He flow, 60 mL/min, current, 150 mA. Retention times: 3-(acetyloxy)-2-butanone, 5 min, 1-(acetyloxy)-2-butanone, 7 min, 3-(1-oxopropoxy)-2-butanone, 8 min.

Decomposition of Isopropylmethyldioxirane in 3-Methyl-2-butanone. The general procedure was used except that the total reflux time was 15 min. Analytical GLC analysis of the residue obtained by removing excess 3-methyl-2-butanone showed the presence of one major and two minor products. The products were collected by preparative GLC. The major product was identified as 3-(acetyloxy)-3-methyl-2-butanone by comparing its ^1H NMR spectrum with that given in the literature[18] and the following data. IR (neat, NaCl): 2989, 2942, 1733 (-COO-), 1724 (-CO-), 1372, 1256 (-COO-), 1155, 1123, 1020, 957, and 845 cm^{-1}. ^{13}C NMR ($CDCl_3$): δ 21.10 (CH_3COO-), 23.30 ((CH_3)$_2$C-), 23.50 (CH_3CO-), 83.59 (-C(CH_3)$_2$-), 170.21 (CH_3COO-), 206.77 (CH_3CO-). MS (EI, 70 eV): m/z 144 (M^+, 2), 102 (3), 101 (44), 69 (3), 59 (40), 57 (5), 43 (100). Calcd for $C_7H_{12}O_3$: 144.17. The next most abundant compound was identified as 3-(1-oxo-2-methylpropoxy)-3-methyl-2-butanone by comparing its ^1H NMR with that in the literature[30] and by the following data. IR (neat, KBr): 2979, 2939, 1732 (-COO-), 1720 (-CO-), 1470, 1385, 1354, 1279, 1205, 1151, 1118, 1068, 967, 950, 903, 860, and 757 cm^{-1}. ^{13}C NMR ($CDCl_3$): δ 18.76 ((CH_3)$_2$CH-), 23.30 (-C(CH_3)$_2$-), 23.45 (CH_3CO-), 33.95 ((CH_3)$_2$CH-), 83.23 (-OC(CH_3)$_2$-), 176.13 (-COO-), 206.59 (-$COCH_3$). MS (EI, 70 eV): m/z 172 (M^+, 0.2), 130 (2), 129 (27), 85 (5), 72 (3), 71 (82), 59 (31), 57 (10), 43 (100). Calcd for $C_9H_{16}O_3$: 172.21. The minor component was identified as 1-(acetyloxy)-3-methyl-2-butanone by comparing its ^1H NMR spectrum with that in the literature[18] and the following data. MS (EI, 70 eV):

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m/z 144 (M^+, 1), 101 (17), 74 (7), 73 (9), 71 (57), 43 (100). Calcd for $C_7H_{12}O_3$: 144.17. Analytical GLC conditions: column, DB 210, temp 1, 60 °C, time 1, 5 min, rate 20 °C/min, temp 2, 200 °C, time 2, 5 min, injector temp, 250 °C, detector temp, 250 °C, inlet P, 24 psi. Retention times: 3-(acetyloxy)-3-methyl-2-butanone, 8.5 min, 1-(acetyloxy)-3-methyl-2-butanone, 9.2 min, 3-(1-oxo-2-methylpropoxy)-3-methyl-2-butanone, 9.4 min. Preparative GLC conditions: column 5% SE-30 (10 ft × $^3/_8$ in.), column temp, 85 °C, injector temp, 100 °C, detector temp, 100 °C, collector temp, 60 °C, He flow, 45 mL/min, current, 150 mA. Retention times: 3-(acetyloxy)-3-methyl-2-butanone, 7 min, 1-(acetyloxy)-3-methyl-2-butanone, 11 min, 3-(1-oxo-2-methylpropoxy)-3-methyl-2-butanone, 17 min.

Flash Vacuum Pyrolysis of Dimethyldioxirane. A solution of dimethyldioxirane (60 mL, 0.068 M) was placed in a round-bottom flask which was attached to a FVP apparatus. A vacuum (0.2 mmHg) was applied in order to carry the vapors of acetone and **1a** into the pyrolysis zone. The pyrolysis zone consisted of a glass tube packed with glass beads which was enclosed in a tube furnace at 150–180 °C. Vapors leaving the heated zone were condensed by passing them through a double trap (liquid N_2 and dry ice–acetone). A pale yellow condensate was collected and dried with Na_2SO_4. NMR analysis of this material indicated that the major component was methyl acetate. No peaks due to acetol or acetol acetate were present. Amazingly the NMR indicated that some of the dioxirane had survived exposure to the pyrolysis zone.

Treatment of Dimethyldioxirane with BF_3·Etherate. A solution of **1a** (freshly prepared, dried with Na_2SO_4) in acetone (0.5 mL) in an NMR tube was treated with a small drop of BF_3·etherate (3–4 μL). After 15 min the NMR of the solution indicated the presence of acetol (peak at δ 4.16). The peak due to methyl acetate (δ 3.59) was observed to increase while, simultaneously, the absorption due to the methyl groups in **1a** (δ 1.65) was observed to decrease in height. This absorption disappears in 90–100 min while the peaks due to acetol and methyl acetate cease to increase in intensity. At this point the solution was colorless. Repetition of this experiment four times always gave the same results. Upon completion of the experiment the acetone was evaporated off. The residue was dissolved in CH_2Cl_2 and dried with Na_2SO_4. Examination of this solution by NMR indicated that acetol and methyl acetate were present in the ratio of 5:1.

Acknowledgment. We gratefully acknowledge support of this work by the National Institute of Environmental Health Sciences (Grant No. ES01984). The Varian XL-300 NMR Spectrometer was purchased with support from the National Science Foundation. Acknowledgment is also made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this work.

Registry No. **1a**, 74087-85-7;)1c, 58272-12-1; **1d**, 138629-57-9; **3**, 58272-12-1; **4**, 79-20-9; boron trifluoride etherate, 109-63-7; 2-propanone, 67-64-1; 2-butanone, 78-93-3; 3-pentanone, 96-22-0; 3-methyl-2-butanone, 563-80-4; 3,3-dimethyl-2-butanone, 75-97-8; 2,4-dimethyl-3-pentanone, 565-80-0; 4-methyl-2-pentanone, 108-10-1; cyclopentanone, 120-92-3; cyclohexanone, 108-94-1; 1-(acetyloxy)-2-propanone, 592-20-1; 3-(acetyloxy)-2-butanone, 4906-24-5; 1-(acetyloxy)-2-butanone, 1575-57-1; 4-(acetyloxy)-2-butanone, 10150-87-5; 2-(acetyloxy)-3-pentanone, 2983-05-3; 3-(acetyloxy)-2-pentanone, 20510-66-1; 4-(acetyloxy)-2-pentanone, 55577-75-8; 1-(acetyloxy)-2-pentanone, 7137-27-1; 3-(acetyloxy)-3-methyl-2-butanone, 10235-71-9; 1-(acetyloxy)-3-methyl-2-butanone, 36960-07-3; 1-(acetyloxy)-3,3-dimethyl-2-butanone, 38559-25-0; 4-(acetyloxy)-3,3-dimethyl-2-butanone, 72816-02-5; 2-(acetyloxy)-2,4-dimethyl-3-pentanone, 21980-75-6; 4-(acetyloxy)-4-methyl-2-pentanone, 1637-25-8; 3-(acetyloxy)-4-methyl-2-pentanone, 135274-69-0; 1-(acetyloxy)-4-methyl-2-pentanone, 141665-39-6; 4-hydroxy-4-methyl-2-pentanone, 123-42-2; 2-(acetyloxy)cyclopentanone, 52789-75-0; 2-(acetyloxy)cyclohexanone, 17472-04-7; 3-(1-oxopropoxy)-2-butanone, 141665-40-9; 3-(1-oxo-2-methylpropoxy)-3-methyl-2-butanone, 76777-46-3; oxygen, 7782-44-7; 3-hydroxy-2-butanone, 513-86-0; propionic anhydride, 123-62-6.

Conformational Analysis and Configurational Assignment of 3-(Alkylsulfenyl)-, 3-(Alkylsulfinyl)-, and 3-(Alkylsulfonyl)-*N*-methylpiperidinium Chlorides

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Received November 20, 1991

^1H, ^{13}C NMR, DEPT, and two-dimensional ^1H–^{13}C heteronuclear correlation spectra of 3-(alkylsulfenyl)-, 3-(alkylsulfinyl)- (its two epimeric sulfoxides), and 3-(alkylsulfonyl)-*N*-methylpiperidinium chlorides (alkyl = methyl, ethyl, isopropyl) have been recorded and fully interpreted. Magnetic resonance parameters (chemical shifts of ^1H and ^{13}C, and geminal and vicinal coupling constants) of these compounds are described for the first time. Conformational analysis has been carried out on conformations selected by a molecular mechanics force field (MMX). In all compounds there is a single ring conformation, the undistorted chair with *N*-methyl and SO_nR (n = 0, 1, 2; R = Me, Et, Pr^i) in the equatorial orientation. These conclusions are supported by the observed vicinal coupling constants. Configurational assignment of ring nitrogen and carbon C_3 has been carried out from observed vicinal axial–axial coupling constants, and the relative configurations of the diastereomeric sulfoxide pairs have been established from observed ^{13}C chemical shifts for ring carbons C_2 and C_4.

The substitution of a ring methylene unit in cyclohexane by a heteroatom provides a system with a rich variety of conformational properties. Among six-membered saturated heterocycles, the piperidine ring is one of the most important ones because of its occurrence in many alkaloids as well as in compounds of pharmacological importance.[1–4] These piperidyl derivatives have been also widely used in synthesis of metallic complexes,[5–9] which are useful sub-

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