30 min at −15 °C, about 60% of the SO_2 was removed. The liquid was stirred into diethyl ether, the ether was decanted, and acetone was added to yield upon filtration 29 g (85%) of **15**.

Preparation of 15 in CH_2Cl_2. To 70 g of CH_2Cl_2 and 20 g (0.23 mol) of THT at −30 °C was added 14 g (0.40 mol) of chlorine followed by addition of 18.1 g (0.17 mol) of styrene. After 30 min, the solution was stirred into ether, the ether was decanted, and acetone was added to give 4.2 g (9.2%) of **15**: 60-MHz ^{1}H NMR (D_2O) δ 7.5 (5 H, b, phenyl), 5.48 [1 H, t, J = 7 Hz, C(2) H], 3.96 [2 H, AB of ABX, J(AB) = 13 Hz, C(1) H2], 3.4 (4 H, m, width 20 Hz, THT^+ α H), 2.14 (4 H, m, width 14 Hz, THT^+ β H); 60-MHz ^{1}H NMR (CF_3COOH) δ 7.5 (5 H, b, phenyl), 5.45 (1 H, t, J = 7 Hz), 3.85 (2 H, t, J = 7 Hz), 3.55 (4 H, m, width 25 Hz), 2.36 (4 H, m, width 15 Hz). Anal. Calcd for $C_{12}H_{16}Cl_2S$: C, 54.76; H, 6.13; Cl, 26.94. Found: C, 54.80; H, 6.25; Cl, 25.80.

[2-Chloro-1-[(4-chlorobutyl)thio]ethyl]benzene (15Rb) and [1-Chloro-2-[(4-chlorobutyl)thio]ethyl]benzene (15Ra). The chloride salt **15** was heated gently in a test tube to 120 °C, causing it to melt and resolidify to a water-insoluble and acetone-soluble product: 60-MHz ^{1}H NMR (acetone-d_6) δ 7.35 (5 H, m, phenyl), 5.15 (0.7 H, t, J = 7.5 Hz), 4.00 (0.7 H, ABC pattern), 3.53 (2 H, t, J = 8 Hz), 3.21 (1.3 H, d, J = 7.5 Hz), 2.80 (0.4 H, t, J = 8 Hz), 2.50 (2 H, t, J = 8 Hz), 1.8 (4 H, m width 20 Hz).

1-(2-Hydroxytetrahydro-3-furanyl)tetrahydrothiophenium Picrylsulfonate (16). To 70 g of SO_2 and 20 g (0.23 mol) of THT at −30 °C was added 26.7 g (0.20 mol) of SO_2Cl_2 followed by addition of 14 g (0.20 mol) of 2,3-dihydrofuran. After 30 min at −15 °C about $^2/_3$ of the SO_2 was removed under vacuum, 50 mL of water was added, and the remaining SO_2 was removed. The aqueous solution was extracted with CH_2Cl_2 and picrylsulfonic acid was added, giving 18.2 g (19.5%) of **16**: 60-MHz ^{1}H NMR (Me_2SO-d_6) δ 8.82 (2 H, s, picrylsulfonate), 7.45 [1 H, d, J = 4 Hz, C(2) OH], 5.54, [1 H, t, J = 4 Hz, C(2) H], 3.98 [3 H, m, incl J = 0.6 Hz, C(3) H and C(5) H_2], 3.5 (4 H, m, width 15 Hz, THT^+ α), 2.18 [6 H, m, width 20 Hz, C(4) H_2 and THT^+ β]. Smaller absorptions at δ 7.7, 4.6, and 3 are attributed to another component. Adding D_2O caused the δ 7.45 signal to disappear and that at 5.54 to collapse to a 4.5 Hz d. Anal. Calcd for $C_{14}H_{17}N_3O_{11}S_2$: C, 35.97; H, 3.67; N, 8.99. Found: C, 36.24; H, 3.54; N, 8.96.

1-(2-Thienyl)tetrahydrothiophenium Picrate (17). To 75 g of SO_2 and 16 g (0.18 mol) of THT at −30 °C was added 21.7 g (0.16 mol) of SO_2Cl_2 followed by 13.96 g (0.16 mol) of thiophene. After 30 min at −5 °C 30 mL of H_2O was added and the SO_2 was removed. After extraction twice with both chloroform and hexanol, the material was converted to the picrate by the usual manner to give 9.3 g (14.6%) of **17**: 100-MHz ^{1}H NMR (Me_2SO-d_6) δ 8.61 (2 H, s, picrate), 8.22 [1 H, dd, J = 5.1 Hz, J' = 1.4 Hz, C(5) H], 8.00, [1 H, dd, J = 3.8 Hz, J' = 1.4 Hz, C(3) H], 7.34 [1 H, dd, J = 5.1 Hz, J' = 3.8 Hz, C(4) H], 3.88 (4 H, m, width 60 Hz, THT^+ α), 2.39 (4 H, m, width 18 Hz, THT^+ β). Coupling constants among thiophene ring protons: J(3,4) = 3.8 Hz, J(3,5) = 1.4 Hz, J(4,5) = 5.1 Hz. Placement of the THT^+ ring at the 2-position on the thiophene ring is established by similarity of the thiophene ring proton–proton coupling constants to the corresponding values reported[16] for unsubstituted thiophene, J(3,4) = 3.50 Hz, J(2,4;3,5) = 1.04 Hz, J(2,3;4,5) = 4.90 Hz, J(2,5) = 2.84 Hz. Anal. Calcd for $C_{14}H_{13}O_7N_3S_2$: C, 42.10; H, 3.28; N, 10.52. Found: C, 41.8; H, 3.33; N, 10.54.

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Dioxiranes: Synthesis and Reactions of Methyldioxiranes

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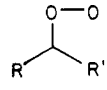
The peroxymonosulfate–acetone system produces dimethyldioxirane under conditions permitting distillation of the dioxirane from the synthesis vessel. The same conditions were used to prepare other methyldioxiranes. Solutions of dimethyldioxirane prepared in this manner were used to study its chemical and spectroscopic properties. The caroate–acetone system was also used to study the chemistry of in situ generated dimethyldioxirane.

Introduction

Dioxiranes (1) members of the smallest cyclic peroxide system, are isomeric with carbonyl oxides **2**, one of the



2

1a, R = R' = H
1b, R = R' = CF_3
1c, R = CF_3, R' = CF_2Cl
1d, R = R' = CH_3
1e, R = CH_3, R' = CH_3CH_2
1f, R = CH_3, R' = $CH_3CH_2CH_2$
1g, R = CH_3, R' = $CH_3CH_2CH_2CH_2$
1h, R = R' = CH_3CH_2

peroxidic intermediates involved in the ozonolysis process. Dioxirane **1a**, produced via ozonolysis of ethylene, has been characterized by both mass spectral and microwave methods.[1-3] In two cases, **1b** and **1c**, it has been reported[4] that dioxiranes have been isolated and characterized by physical and chemical methods. In these cases the dioxiranes were synthesized by oxidation of the corresponding dilithioalkoxides.

Dioxiranes have been postulated as intermediates in reactions involving peracids.[5-10] Edwards, Curci, and

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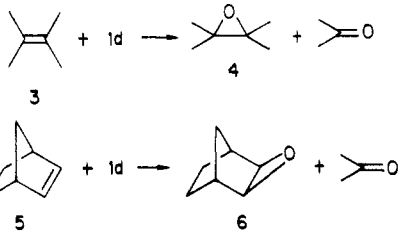
co-workers[5-9] used the peroxymonosulfate–acetone system for stereospecific epoxidation of alkenes. Furthermore Edwards and Curci used a combination of kinetic, stereochemical, and ^{18}O-labeling data to suggest that this system produced the dioxirane intermediate **1d**, which they felt was responsible for the oxygen atom transfer process. A second possible peracid source of a dioxirane was described by us[10a] and involves the use of peracetic acid and acetone.

We recently reported[10b] the use of the peroxymonosulfate–acetone system for the conversion of arenes to arene oxides as an extension of the reactions of dimethyldioxirane produced in situ[5-10] and in connection with our studies on the chemistry of carbonyl oxides and the isomeric dioxiranes.[10-18] The full experimental details of the production of arene oxides and other reactions of dimethyldioxirane in situ are given here along with a description of a modification to the procedure which permits isolation of solutions of the volatile dioxiranes. The solutions can be used to study the chemical and spectroscopic properties of the dioxiranes. For example, we have shown that the use of dimethyldioxirane produced in this manner provides an efficient method of epoxide synthesis which is not only stereospecific and results in high yields[5-9] but is unencumbered by the presence of acid, base, high-boiling solvents, and other drawbacks of some of the commonly used epoxidation methods.

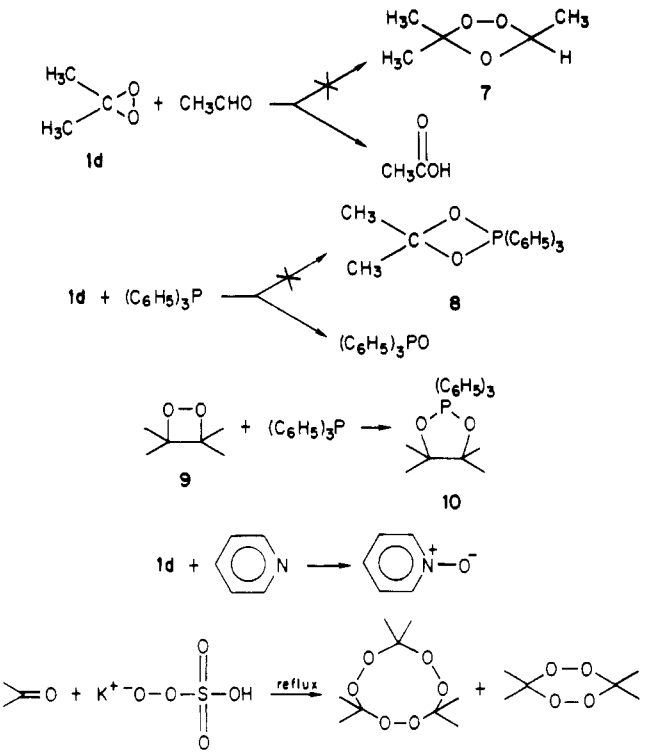
Results and Discussion

Reactions of in Situ Generated Dimethyldioxirane. As part of an on-going program designed to distinguish, if possible, the chemistries of carbonyl oxides and the corresponding dioxiranes, we investigated the use of the caroate–acetone system as a dioxirane source. The initial work was done following in general the procedures used by Edwards and Curci and co-workers[5-9] in which dimethyldioxirane (**1d**) is generated in situ.

Tetramethylethylene (**3**) was converted to the corresponding epoxide (**4**) in 90% yield. In this case the caroate–acetone system was used without water or phase-transfer catalyst. In contrast the conversion of norbornene (**5**) to the exo epoxide **6** (95% yield) did require an aqueous system, phase-transfer catalyst, and pH control (7.5–8.0).



Scheme I



Thus we confirm the earlier observations of Edwards and Curci[5-9] that the use of in situ generated dimethyldioxirane provides an excellent synthetic method for epoxides. At the same time these results suggest that a possible distinguishing test for dioxiranes and carbonyl oxides is their reaction with olefins. We had earlier reported[18] that carbonyl oxides, generated from diazo compounds and singlet oxygen, can epoxidize olefins, but in a stereoselective rather than stereospecific manner and in relatively low yields. Edwards and Curci and co-workers have suggested[5,6] that the chemistry of the isomeric peroxides could be distinguished since carbonyl oxides would be expected to add to olefins to give 1,2-dioxolanes. Such behavior for carbonyl oxides has only recently been observed experimentally.[19] At the same time dioxiranes apparently do not add to olefins to give the analogous 1,3-dioxolanes. The choice of norbornene (**5**) as a substrate in this work was made in order to encourage the 1,3-dioxolane possibility, but we found instead that epoxide **6**, in high yield, is the only product.

The caroate–acetone reaction was carried out in the presence of a large excess of acetaldehyde. Under these conditions it was at least possible that **1d** could react with acetaldehyde to give trimethylethylene ozonide (**7**) (Scheme I). However the acetaldehyde was converted to acetic acid and a trace of peracetic acid only. This experiment, combined with those using acetone solutions of **1d** (vide infra), suggests that dioxiranes do not react with aldehydes to give ozonides. This possibility has long been a nettlesome concern to those studying the mechanism of ozonolysis, particularly when ^{18}O tracer studies are used. At the same time the results indicate that the aldehyde reaction could be an important one in distinguishing the chemistries of the peroxide isomers.

The acetone–caroate reaction was next carried out in aqueous solution with phosphate buffer, in the presence of triphenylphosphine. In this case the reaction temper-

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ature was not allowed to rise above 0 °C. We anticipated that such temperature control would permit isolation of any phosphorane, 8, resulting from reaction of the triphenylphosphine with dimethyldioxirane (**1d**). No evidence for the formation of 8 could be obtained, however. Formation of 8 would be analogous to the reaction reported[20] by Bartlett et al. in which triphenylphosphine inserts into tetramethyl-1,2-dioxetane (**9**) to give phosphorane **10**. The reaction of **1d** with triphenylphosphine gives only the reduction product, triphenylphosphine oxide. Similarly reaction of an acetone solution of **1d** with triphenylphosphine failed to give any evidence of phosphorane formation.

Similar reaction conditions were used to study the reaction of **1d** with pyridine. In this case pyridine oxide was produced in 93% yield. Our results confirm those of Gallopo and Edwards,[7] who have also shown that pyridine oxide yield is a function of pH. At the pH used here (7.5–8.0) the yield is the highest, as demonstrated by Gallopo and Edwards. While the pyridine reaction is not particularly surprising, it is important to include it in these studies inasmuch as Griesbaum and co-workers[21] have shown that the reaction of carbonyl oxides with pyridine does not give the oxide, as once believed,[22] but instead leads to intractable materials.

When solid oxone is added to acetone and the mixture refluxed for 16 h, acetone triperoxide is formed along with acetone diperoxide (ratio 97:2.4; total yield = 66%). This observation is interesting in that the use of "dry Caro's reagent", i.e. caroate, has been described[23] as the best way of preparing ketone diperoxides including acetone diperoxide. Indeed such syntheses are described[23] as giving the diperoxide, but not the triperoxide. The only difference in procedure that we can detect is that the procedure cited by Schulz and Kirschke[23] uses ether solvent and was done at lower temperature (15 °C). On the other hand use of H_2O_2[24] or a combination of H_2O_2 and $KHSO_4$[25] is reported to give only the triperoxide. At any rate our procedure is a useful one for preparing the triperoxide.

Ketone peroxides have long been recognized[26] as products of the ozonolysis of some olefins. In general these olefins are either tetrasubstituted or at least capable of giving ketones and ketone oxides. In many cases no ozonides are formed in these ozonolyses. In one case, tetramethylethylene, some ketone triperoxide formation has also been reported.[27] As a result of some recent work[28] in our laboratory we have become interested in the possibility that these di- and triperoxides might have their origin, at least in part, in dioxiranes instead of carbonyl oxides as is generally accepted[26] to be the case. It is interesting that while most recent versions of the ozonolysis mechanism invoke the intermediacy of a carbonyl oxide,[29] some earlier versions[30] of the mechanism described the same peroxidic intermediate as a dioxirane. Indeed in a relatively recent study of the ozonization of alkynes Hamilton and Keay[31] suggest a dioxirane structure for one of several intermediates involved. Also Adam and Rodriguez[32] considered both carbonyl oxide and dioxirane structures for an O atom transfer species formed in the thermal decomposition of some furan endoperoxides.

We have found that the caroate–acetone system can be used to convert arenes to arene oxides.[10b] In some cases the yields obtained are such that the procedure may be the preferable one for such conversions. There is considerable interest in the synthesis of arene oxides because of their relationship to mutagenesis/carcinogenesis in certain polycyclic aromatic hydrocarbons (PAH).[33-37] A number of such syntheses have been described in the literature.[38-54] The use of hypochlorite, as described by Hamilton and co-workers,[38] appears to be the simplest of these procedures. In some cases the caroate–acetone method described here may be the method of choice.

It has been suggested recently[1] that certain gas-phase ozonolyses could be sources of dioxiranes. In the case of ethylene, dioxirane has been identified[1-3] as an ozonolysis product. The demonstration that dimethyldioxirane can convert arenes to arene oxides may be highly significant in that it is now well established that PAH must undergo metabolic activation prior to displaying carcinogenic activity and that such active metabolites contain the arene oxide functionality. Thus reactions of olefins and ozone in the atmosphere could lead to the conversion of particulate-bound PAH to arene oxides.

Preparation and Use of Dioxirane Solutions. The stereochemical, kinetic, and ^{18}O tracer data presented by Edwards and Curci[5-9] in support of dimethyldioxirane as the O atom transfer agent produced in situ in the caroate–acetone system are both elegant and convincing. Nevertheless we felt that isolation of the dioxirane was desirable in order to complete the case for its existence as

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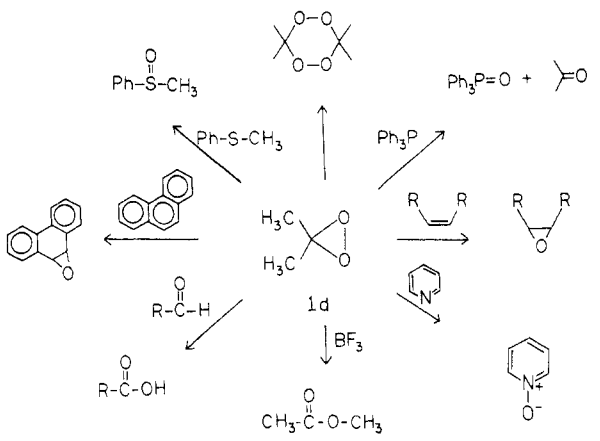
Scheme II



well as to open up new avenues for its use. We have modified (Experimental Section) the in situ procedure so as to permit distillation of methyldioxiranes from the generation vessel containing caroate and methyl ketone. The dioxirane is obtained as a solution in the precursor ketone. The dioxirane content of the ketone solution was assayed by triphenylphosphine or phenyl methyl sulfide reduction of an aliquot. Solutions of dioxirane obtained in this manner could be stored for several days in the freezer with little or no decomposition. The highest yield was obtained in the case of **1d** (0.04–0.185 M solution), but ketone solutions of **1e–1h** were also obtained. Increasing bulk in the alkyl substituents leads to decreasing yield of dioxirane.

Dimethyldioxirane is yellow in solution and has UV absorption with λ_{max} 335 nm (ϵ 263). Both **1b** and **1c** have been reported to be yellow. In addition **1b** is reported[4] to have a UV absorption with λ_{max} 306 nm. We also measured the UV spectrum of **1e** and found it to have λ_{max} 333 nm (ϵ 126). When the decomposition of **1d** in acetone is followed by using the UV absorption band at 335 nm, then the half-life was found to be 48 ± 1 h at ca 25 °C; i.e., $k_1 = 4.0 \pm 0.1 \times 10^{-6}$ s^{-1}. The proton NMR spectrum of dimethyldioxirane shows a single absorption at δ 1.65. The ^{13}C NMR spectrum (360 MHz, $CDCl_3$) consists of absorptions at 22.72 and 214.04 ppm (relative to Me_4Si) which are assigned to the methyl and ring carbons, respectively, of **1d**. In the proton-coupled spectrum the peak at δ 22.72 becomes a quartet while that at 214.04 remains a singlet. On standing absorptions due to acetone diperoxide, ca. 22.5 and 102 ppm for methyl and ring carbons, respectively, began to appear. The infrared spectrum of **1d** (acetone solution) has absorptions at 3012, 3005, 2999, 1209, 1094, 899, and 784 cm^{-1} (only strong absorptions shown).

Solutions of dimethyldioxirane in acetone, prepared as described above, were used to carry out a variety of reactions (Scheme II). The reactions were performed by adding freshly prepared solutions of the dioxirane to solutions of the desired substrate in acetone and stirring at room temperature. With use of this procedure ethyl *trans*-cinnamate, *cis*-stilbene, and *trans*-stilbene were all converted to the corresponding epoxides in 75–95% yield (glpc determination). In all cases the reactions were stereospecific with retention of configuration. Phenanthrene was converted to its 9,10-oxide (83% yield) and phenyl methyl sulfide to phenyl methyl sulfoxide (84% yield) in a similar manner. When an acetone solution of **1d** was treated with BF_3–ether at 0 °C, the dioxirane was converted to methyl acetate as the sole product. Addition of **1d** to acetone solutions of acetaldehyde or propionaldehyde led only to formation of the corresponding acids; i.e., no ozonides were formed. As indicated earlier this result is of particular interest to the ozonolysis mechanism problem and suggests a way of distinguishing carbonyl oxide and dioxirane chemistry. When allowed to stand dilute solutions of **1d** in acetone are slowly converted to the dimerization product, acetone diperoxide.

The procedure described above was used to convert 2-butanone to ethylmethyldioxirane (**1e**), which was collected in 2-butanone solution. The solutions were used to convert phenanthrene to its 9,10-oxide (82% yield) and *trans*-stilbene to *trans*-stilbene oxide (58% yield).

Summary and Significance

We have confirmed the earlier reports[5–9] of Edwards and Curci that the caroate–acetone system generates dimethyldioxirane in situ. In addition the procedure has been modified so as to permit distillation of a number of methyldioxiranes from the generation vessel to receivers where the dioxiranes are available as solutions in the parent ketone. Solutions of dimethyldioxirane so obtained have been used to carry out a variety of oxygen atom transfer reactions as well as to obtain spectroscopic data on the dioxirane. The use of these dioxirane solutions is a useful synthetic procedure which gives products in high yields and, in the case of epoxides, in a stereospecific manner.

The work described here, combined with the earlier work of ourselves and others, also indicates a set of criteria which can be used to distinguish carbonyl oxides and their isomeric dioxiranes. While additional examples need to be studied, the work to date reveals the following contrasts. Carbonyl oxides react with olefins to give epoxides in low yields and a stereoselective manner while dioxiranes give the epoxides in a high yield and stereospecific reaction. Carbonyl oxides react with some nucleophiles, e.g., pyridine, to give largely polymeric products while dioxiranes give the *N*-oxide in a simple, O atom transfer reaction. Carbonyl oxides react with aldehydes to give ozonides while it appears that dioxiranes give only the acid derived from the aldehyde. In addition the work reported here raises additional questions concerning chemistry long associated with carbonyl oxides produced in the ozonolysis process, i.e., rearrangement reactions leading to esters or acids, and dimerization and trimerization reactions leading to di- and tripoxides, e.g. acetone diperoxide and triperoxide. One must now speculate that such products could arise, at least in part, from dioxiranes rather than carbonyl oxides.

The observation that dioxiranes can convert arenes to arene oxides may be highly significant to the environmental chemistry of urban atmospheres. Dioxirane itself has been identified as a product of the gas-phase ozonolysis of ethylene.[1–3] Urban atmospheres frequently contain relatively high concentrations of ozone as well as of olefins and arenes, the latter in the form of particulate matter. This combination of factors could lead to arene oxide production in such atmospheres, thereby increasing the risk of mutagen/carcinogen formation.

On the basis of a suggestion made by Hamilton[55] the carbonyl oxide isomers of dioxiranes have been studied as models for the oxygen atom transfer intermediates in the flavin-dependent monooxygenase enzymes. Alternatively Dolphin and Orf have suggested[56] that this intermediate could be an oxaziridine. Both oxaziridines[56–62] and car-

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bonyl oxides[10-17,63-69] show oxygen atom transfer ability. The results described here suggest that the 4α-hydroperoxyflavin precursor, proposed for the carbonyl oxide or the oxaziridine, might alternatively be converted to a dioxirane. The high yield and stereospecificity displayed by dioxiranes in their oxygen atom transfer reactions would seem to increase the eligibility of a dioxirane structure for the intermediate in the enzyme-mediated oxidation. At any rate we suggest that such a possibility deserves further consideration.

Experimental Section

Instrumentation. Gas chromatography was performed on a Perkin-Elmer Sigma 2000 gas chromatograph or a Varian-Aerograph Model A-700 gas chromatograph interfaced with a Model 3390-A Hewlett-Packard integrator. ^{1}H NMR spectra were recorded with a Varian T-60 NMR spectrometer. ^{13}C NMR spectra were obtained with a Bruker 360-MHz NMR spectrometer. Deuterated chloroform containing 1% tetramethylsilane (Aldrich) was used as solvent. UV spectra were recorded with a Perkin-Elmer Model 202 UV-visible spectrophotometer. IR spectra were recorded with a Beckmann FT IR instrument or Perkin-Elmer 337 instrument. Mass spectra were obtained using an Associated Electronics Industries Model MS-1201 B mass spectrometer at a 70-eV ionizing voltage.

Chromatography. Gas chromatography was performed with a Supelco column, SPB-5 (SE-54), 15 m × 0.25 mm, with a liquid-phase thickness of 0.25 m, or with a 7% β,β′-oxypropionitrile on Chromosorb G-AW (60–80 mesh, 6 ft × $^1/_4$ in. or 18 ft × $^3/_4$ in.) column. For HPLC a MCH-5 reverse-phase column (30 cm × 4 mm), purchased from Varian Aerograph, Palo Alto, CA, was used. Preparative thin-layer chromatography plates (20 × 20 cm) precoated with 1.00 mm thickness silica were obtained from Mallinckrodt Chemical Co.

The GC conditions were as follows: (A) FID: temperature 1, 130 °C; time 1, 10 min; rate, 20 °C/min; temperature 2, 200 °C; time 2, 2–10 min; injection temperature, 150 °C; detector temperature, 250 °C. (B) FID: temperature 1, 200 °C; time 1, 2 min; rate, 10 °C/min; temperature 2, 220 °C; time 2, 10–15 min; injection temperature, 200 °C; detector temperature, 270 °C. (C) TCD: temperature column 50 °C; injection temperature 50 °C, detector temperature 50 °C; flow 60–180 mL/min. (D) FID: temperature 1, 50 °C; time 1, 1 min; rate, 10 °C/min; temperature 2, 150 °C; time 2, 5–10 min; injection temperature, 150 °C; detector temperature, 200 °C.

Materials. Oxone (Du Pont), $2KHSO_5 \cdot KHSO_4 \cdot K_2SO_4$, was obtained from Aldrich Chemical Co. and used as such. Acetone (Aldrich reagent grade) and 2-butanone (Fisher) were distilled from dry potassium carbonate prior to use. Triphenylphosphine, triphenylphosphine oxide, phenanthrene, pyrene, chyrsene, and *trans*-stilbene (all obtained from Aldrich), naphthalene (Fisher), and anthracene (Fisher) were recrystallized, and the purity was confirmed by melting point, NMR, and GC or HPLC data. Ethyl cinnamate (Eastman), *cis*-stilbene (Aldrich), and thioanisole (Mathieson, Coleman & Bell) were distilled in vacuo, and the purity was verified by GC and NMR data. Acetaldehyde (Eastman), propionaldehyde (Eastman), and pyridine (Aldrich, Gold label) were distilled prior to use. Lead tetraacetate, 18-crown-6, 1-methylphenanthrene, and 2-acetylphenanthrene were purchased from Aldrich Chemical Co. and used as such. Tetra-*n*-butylammonium hydrogen sulfate was obtained from Sigma Chemical Co. Boron trifluoride in ether (45% solution) was obtained from Eastman.

Dioxirane Formation in Situ. Formation of Acetone Triperoxide and Diperoxide.[70] Oxone (28 g, 45 mmol) was added to acetone (100 mL) and the mixture stirred at 52 °C for 16 h. The mixture was filtered and the solution evaporated. A white solid (4.4 g) containing acetone triperoxide and acetone diperoxide (ratio = 97:2.4, combined yield = 66%) was obtained. The triperoxide was obtained in pure form (mp 92–93 °C) by fractional crystallization of the mixture from hexane. The diperoxide (mp 130–132 °C) was separated by preparative GC and identified by comparison with an authentic sample: ^{1}H NMR spectrum: δ 1.0–2.0 ppm (broad).

Reaction of a Mixture of Acetone and Acetaldehyde with Oxone. A mixture of acetone (35 mL) and acetaldehyde (35 mL) was stirred at 25 °C, and Oxone (12 g, 0.0195 mol) was added in four portions. After stirring the mixture for 5 h, it was filtered and the filtrate worked up. It contained acetic acid, a trace of peracetic acid, acetone triperoxide (2% yield), and the trimer of acetaldehyde (1%). GC analysis under various conditions showed the absence of an ozonide.

Reaction of Triphenylphosphine with the Oxone–Caroate System. A neutral solution of potassium caroate was prepared by carefully adding a KOH solution (0.05 N) to a cold solution of Oxone (6.2 g, 10 mmol) in phosphate buffer (50 mL). The solution was dropped into a well-stirred solution of triphenylphosphine (2.0 g, 0.76 mmol) in acetone (100 mL). After stirring for 10 min the mixture was extracted with methylene chloride and washed with cold water. The solvent was evaporated keeping the temperature below 0 °C. NMR, GC analysis, and TLC separation indicated that the triphenylphosphine has been converted completely to the oxide. No other product was obtained.

Reaction of Pyridine with the Oxone–Acetone System. Oxone (18.3 g, 0.0298 mol) in water (100 mL) was added in drops to the mixture of pyridine (1.00 g, 0.0126 mol), acetone (5 mL, 0.068 mol), and phosphate buffer (50 mL). KOH solution was added simultaneously to keep the pH at 7.5–8.0. After stirring for 2 h the mixture was extracted with methylene chloride and analyzed. Only pyridine oxide (1.1 g, yield 93%) was obtained. It was identified by comparison with an authentic sample prepared by *m*-chloroperbenzoic acid oxidation. A portion of the oxide, after recrystallization from methylene chloride–hexane, melted at 64–65 °C (lit.[71] mp 65–66 °C); ^{1}H NMR δ 8.5–8.3 (m), 7.5–7.3 (m).

When a mixture of pyridine (3 mL, 0.037 mol), Oxone (10 g, 0.0163 mol), and acetone (50 mL) was heated and stirred at 50 °C for 16 h, acetone triperoxide (4%) was formed in addition to pyridine oxide (63%, based on Oxone). Some of the pyridine adhered to the solid Oxone, forming a pasty mass.

When pyridine (5 mL) was used in the absence of water in the reaction with oxone (10 g) in acetone (50 mL), then diacetone alcohol was formed in addition to pyridine oxide (70–80% based on Oxone).

Reaction of Norbornylene with the Acetone–Caroate System. A solution of Oxone (18 g, 29 mmol) in water (100 mL) was added slowly to a stirred mixture of acetone (50 mL), water (50 mL), methylene chloride (50 mL), 18-crown-6 (0.3 g), and norbornylene (1.9 g, 0.02 mol) with the temperature controlled at 0–5 °C and the pH controlled at 7.5–8.0. Workup of the reaction mixture gave a solid which was more than 95% pure *exo*-nor-

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(70) Dimethyldioxirane is a very volatile peroxide. Reactions should be carried out in the hood and behind a shield.

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bornene oxide. Recrystallization of a portion of the product from methylene chloride–hexane yielded the oxide melting at 125–126 °C (lit.[72] mp 125.5–126.5 °C); ^{1}H NMR δ 3.0 (s), 2.4 (s), 1.6–0.5 (m). TLC, GC, and NMR analyses showed the absence of a cycloaddition product.

Reaction of Aromatic Hydrocarbons with Dimethyldioxirane Produced in Situ. Control reactions in the absence of acetone indicated no oxide formation except in the cases of 1-methylphenanthrene and 2-acetylphenanthrene where traces of oxide were found.

(a) 9,10-Phenanthrene Oxide. To a mixture of acetone (100–250 mL), phosphate buffer (50 mL), methylene chloride (50–100 mL), tetra-*n*-butylammonium hydrogen sulfate (0.200 g), and phenanthrene (0.900 g, 0.0050 mol) was added, in drops, a solution of potassium peroxymonosulfate (46.0 g, 0.075 mol) in water (225 mL) while the mixture was stirred vigorously and the pH was maintained between 7.5 and 8.5 and the temperature at 0–10 °C. The addition required about 1.5 h. The mixture was stirred for an additional period of 4 h and then mixed with an equal volume of ice-cold water and extracted with ether. The ether extract was repeatedly washed with cold water to remove the phase-transfer catalyst completely. The ether solution was dried over anhydrous potassium carbonate and the solvent stripped off in a rotatory evaporator. TLC analysis of a portion of the solid residue indicated the presence of phenanthrene and phenanthrene oxide as the nearly exclusive components.

The amount of the arene oxide present in the reaction mixture was determined by adding a known weight of diglyme (0.0401 g) to a solution ($CDCl_3$–CCl_4–Me_4Si) which contained 0.4160 g of the mixture and making up to 5 mL in a standard flask. From the areas of the ^{1}H NMR signals for the 9,10-hydrogens of the arene oxide and those of diglyme the mixture was found to contain a minimum of 65% phenanthrene oxide.

The oxide was isolated from the reaction mixture, obtained in a duplicate run, using preparative TLC and employing methylene chloride and hexane (50:50) as the eluent. The yield was 60%. The oxide was recrystallized from methylene chloride and hexane to give shining white flakes, mp 127–128 °C. Another sample of the oxide obtained from a different run melted at 145–147 °C. However, both samples were found to be identical in all other respects, including HPLC retention times and spectral data. Similar melting point behavior has been reported in the literature; i.e., mp 124–125[73] and 148 °C[74] have been reported.

(b) A similar procedure was used to prepare the other arene oxides in yields reported earlier.

Preparation of Dioxirane Solutions. (a) Dimethyldioxirane (1d). A 500-mL, three-necked round bottom flask, containing a mixture of water (20 mL), acetone (12 mL, 0.163 mol), sodium bicarbonate (24 g), and a magnetic stirring bar, was equipped with a solid addition flask containing peroxymonosulfate (Oxone, 50 g, 0.0813 mol) and a pressure-equalized dropping funnel containing a mixture of water (20 mL) and acetone (14 mL, 0.191 mol). An air condenser, loosely packed with glass wool, was attached to the reaction vessel. The top of the air condenser was connected to a dry ice (CH_3CN–dry ice) condenser which was attached to a receiving flask (100 mL) cooled in ice water. The receiving flask was connected to a series of cold traps (dry ice–acetone, acetone–liquid N_2, ethanol–liquid N_2, pentane–liquid N_2, and liquid N_2). Helium was passed through the reaction flask while the solid Oxone was added in small portions and simultaneously adding the acetone–H_2O mixture dropwise. The mixture was stirred vigorously at room temperature throughout the reaction period. After 15 min of reaction time a slight vacuum was applied to the reaction assembly. The yellow-colored dimethyldioxirane–acetone solution collected primarily in the receiving flask with some material found in the first three attached traps. The solution was stirred briefly with $MgSO_4$, filtered, and stored in the freezer for subsequent use. Solutions obtained in this manner were assayed for dioxirane content using triphenylphosphine. The concentrations obtained were in the range of 0.04 to 0.185 M.

(b) Ethylmethyldioxirane (1e). The general procedure as described for **1d** was used. Thus Oxone (50 g, 0.0813 mol) was added to a mixture of water (20 mL), 2-butanone (12 mL, 0.134 mol), and sodium bicarbonate in the generation flask while a mixture of 2-butanone (14 mL, 0.157 mol) and water (20 mL) was added dropwise. The solution of ethylmethyldioxirane in 2-butanone was dried with $MgSO_4$ and then filtered. The triphenylphosphine reduction assay showed the solution to be 0.056 M in dioxirane.

(c) Methyl-*n*-propyldioxirane (1f). Oxone (40 g, 0.065 mol) was added in small portions to a well-stirred mixture of 18-crown-6 (0.20 g), 2-pentanone (24 mL, 0.227 mol), water (50 mL), and sodium bicarbonate (30 g). Helium was passed through the generation flask and a slight vacuum applied. The organic layer was separated from the two-layer mixture obtained and dried ($MgSO_4$), and the concentration of **1f** determined to be 0.008 M by using phenyl methyl sulfide reduction.

Methyl-*n*-butyldioxirane (1g). The procedure used was the same as for **1f** except that 2-hexanone was used as the ketone. The concentration of the solution of **1g** in 2-hexanone was found to be 0.002 M.

Diethyldioxirane (1h). The same procedure as for **1f** was used with 3-pentanone as the ketone. The concentration of **1h** obtained was determined to be 0.006 M.

Reactions with Dimethyldioxirane Solutions. (a) Triphenylphosphine. A freshly prepared solution of **1d** (0.5 mL) was mixed with a solution of triphenylphosphine in acetone (0.500 mL, 0.20 M). The amount of triphenylphosphine oxide formed was determined by capillary GC by injecting 0.001 mL of the reaction mixture at intervals of 15–30 min and extrapolating the areas of the triphenylphosphine and phosphine oxide peaks to complete reaction. The yield of phosphine oxide was virtually quantitative. The oxide was identified by comparing its properties with those of an authentic sample. The concentration of the dioxirane was calculated from a correlation line for standard triphenylphosphine–phosphine oxide mixtures under the same GC conditions (B). The concentration of **1d** so determined was found to be in the range 0.085–0.185 M.

(b) Ethyl *trans*-Cinnamate. Freshly prepared dimethyldioxirane solution (10 mL, 0.063 M) was added to a solution of ethyl *trans*-cinnamate in acetone (10 mL; 0.20 M) and the mixture stirred at 25 °C. The mixture was analyzed periodically by GC (conditions A), and the conversion of alkene to the corresponding epoxide in 22 h was found to be 85%. This reaction mixture was then added to an excess of **1d** (50 mL; 0.08 M) and stirring continued overnight. After evaporation of acetone, the paste remaining was dissolved in methylene chloride (5 mL), dried, and separated by preparative TLC (1 mm, silica gel, CH_2Cl_2–hexane, 1:1). The epoxide was collected (0.252 g). Its NMR spectrum showed absorptions at δ 7.4 (m, aryl H), 4.5–4.1 (quartet for CH_2 and doublet for 1 oxirane proton), 3.6 (d, oxirane proton), 1.5–1.2 (t, CH_3). The isolated yield was 63%. This material was identified as the oxide of ethyl *trans*-cinnamate by comparing its properties with those of an authentic sample prepared using *m*-chloroperbenzoic acid oxidation.

(c) *cis*-Stilbene. A solution of **1d** (3.0 mL, 0.118 M) was mixed with an equal volume of *cis*-stilbene in acetone (0.239 M) at 22 °C. After 2 h the reaction mixture was analyzed by GC (conditions A) and found to contain only *cis*-stilbene oxide and unreacted *cis*-stilbene. The solvent was evaporated, the residue dissolved in $CDCl_3$ (Me_4Si), and the ^{1}H NMR recorded. The oxirane NMR has absorptions at δ 4.2 (s, 2 H, oxirane protons) and 7.1–7.2 (s, 10 H, aryl protons). With use of the ratio of integrated absorptions of the aromatic and olefinic protons in the mixture of olefin plus oxide the conversion to oxide was found to be 73.4%. The oxide was isolated by preparative TLC and identified by comparison with an authentic sample prepared by *m*-chloroperbenzoic acid oxidation.

(d) *trans*-Stilbene. With use of the same procedure as for *cis*-stilbene, a solution of *trans*-stilbene was converted to *trans*-silbene oxide (72.9% conversion). The product was identified by comparing its properties with those of an authentic sample prepared by *m*-chloroperbenzoic acid oxidation of *trans*-stilbene.

(e) Phenanthrene. A freshly prepared solution of **1d** in acetone (20 mL, 0.043 M) was mixed with a solution of phenan-

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threne in acetonitrile (20 mL, 0.10 M) and the mixture stirred at 26 °C. The reaction was followed by withdrawing aliquots and analyzing by reverse-phase HPLC (30 cm MCH-5 column and CH_3CN–H_2O, 20:30). The solvent was evaporated and the mixture dissolved in $CDCl_3$. The yield of phenanthrene oxide was determined by NMR by comparing peak integrations for aromatic and oxirane ring protons. The oxide (83.1% yield) was identified by comparison with an authentic sample.

(f) Phenyl Methyl Sulfide. A solution of **1d** (0.5 mL, 0.189 M) was mixed with an acetone solution of phenyl methyl sulfide (0.5 mL, 0.22 M). The solution was stirred at room temperature. The yield of phenyl methyl sulfoxide formed was determined by GC using previously determined correlation factors (conditions D). The yield was 98%. In a separate experiment under identical conditions the sulfoxide was separated by preparative TLC and identified by comparison with a sample prepared by *m*-chloroperbenzoic acid oxidation of the sulfide. The isolated yield was 0.199 g (65%).

(g) Treatment of 1d with Boron Trifluoride–Ether. To a freshly prepared solution of **1d** in acetone, cooled to 0 °C, was added a solution of boron trifluoride in ether (1.0 mL, 45%) and stirring continued for 10 min. GC analysis (7% β,β'-oxypropionitrile on Chrom G-AW, DMCS column, T = 25 °C) indicated the presence of methyl acetate, acetone, and ether only. The yield was not determined.

(h) Acetaldehyde and Propionaldehyde. A freshly prepared solution of **1d** in acetone (25 mL, 0.06 M) was added to freshly distilled acetaldehyde and propionaldehyde (10 mL, 0.10 M) in separate experiments. The solutions were stirred at room temperature for 2 h and then analyzed by GC with a 7% β,β'-oxypropionitrile column at 40 °C and a flow rate of 60–180 mL/min. In the case of propionaldehyde the exclusive product was propionic acid. In the case of acetaldehyde the major product was acetic acid accompanied by a trace of acetaldehyde trimer. No ozonides could be detected in either case. In a separate experiment **1d** was condensed into 4 mL of propionaldehyde. Again propionic acid was the exclusive product.

(i) Formation of Acetone Diperoxide. A solution of **1d**, prepared as described above, was allowed to stand in the freezer (ca. 5 °C), protected from light, for 3 days. Under these conditions the epoxidizing power of the solution was largely retained. When the solution was allowed to stand at room temperature, then the epoxidizing power was lost completely in 5–10 days. The resulting solution was analyzed by GC and found to contain only acetone diperoxide.

(j) Pyridine. A solution containing **1d** (0.5 mL, 0.116 M), pyridine (in acetone, 0.5 mL, 0.2 M), and decane (in hexane, 0.5 mL, 0.1 M) was stirred briefly at room temperature. Analysis of the solution indicated that pyridine *N*-oxide was the only product. The solvent was evaporated to give solid pyridine *N*-oxide, which was dried in vacuo for 1 h. The yield was 0.084 g (75%). The oxide was identified by comparing it with an authentic sample obtained by *m*-chloroperbenzoic acid oxidation of pyridine.

(k) Low-Temperature Reaction with Triphenylphosphine. A freshly prepared solution of **1d** in acetone was cooled to −50 to −70 °C and then mixed with a cold solution of triphenylphosphine in acetone. The ^{31}P NMR spectrum of the reaction mixture was measured at 0 °C with phosphoric acid as external standard. No signals and corresponding to phosphorane formation could be detected.

(l) Control Reactions. Solutions of acetone diperoxide and acetone triperoxide were used instead of solutions of dimethyldioxirane in attempted reactions with olefins. No epoxides were formed under these conditions.

A freshly prepared solution of **1d** was treated with lead tetraacetate. No oxygen liberation was detected; i.e., no hydroperoxide compounds were present.

Reactions with Ethylmethyldioxirane Solutions. (a) Phenanthrene. Ethylmethyldioxirane in 2-butanone (5 mL, 0.056 M) was mixed with a solution of phenanthrene in acetonitrile (5 mL, 0.10 M). After stirring at room temperature the reaction mixture was analyzed by HPLC using a MCH-5 column. Only phenanthrene and phenanthrene oxide could be detected. The solvent was evaporated and the residue dissolved in $CDCl_3$. With use of NMR and integration of the peaks corresponding to aromatic and oxirane protons it was determined that there was an 82% conversion of phenanthrene to the 9,10-oxide.

(b) *trans*-Stilbene. A solution of **1e** in acetone (0.5 mL, 0.056 M) was mixed with an acetone solution of *trans*-stilbene (0.5 mL, 0.1 M). After the mixture had stirred for 3 h at room temperature, GC analysis indicated that the *trans*-stilbene had been converted exclusively to *trans*-stilbene oxide (58% conversion).

Spectroscopic Measurements on Dimethyldioxirane. (a) Ultraviolet. The UV spectrum of **1d** was measured by using 1-cm quartz cells and acetone as reference solvent. The λ_{max} was at 335 nm (ϵ 263) with a tail extending into the visible. A similar measurement using **1e** showed a λ_{max} at 333 nm (ϵ 126).

(b) Infrared. The infrared spectrum of 1d was measured in acetone as reference. Absorptions were observed at (cm^{-1}) 3012 (s), 3005 (s), 2999 (s), 1209 (s), 1196 (w), 1094 (s), 1080 (w), 1059 (w), 1034 (w), 899 (s), and 784 (s).

(c) NMR. The ^{13}C NMR spectrum of a freshly prepared solution of **1d** in acetone was recorded with Me_4Si as internal standard and $CDCl_3$ (10%) lock. The proton-decoupled spectrum was recorded over 15 h at 4 °C. Absorptions at 22.725 (CH_3) and 214.044 (>$\overline{C-O-O}$) were observed for **1d**. Strong acetone absorptions were also observed at δ 30.718 (CH_3) and 207.08 (carbonyl C). Additional absorptions at δ 22.5 and 102 were observed to arise in time and were assigned to acetone diperoxide. In the proton-coupled spectrum the singlet assigned to the methyl carbon was observed as a quartet while the absorption assigned to the ring carbon remained a singlet.

The ^1H NMR spectrum of **1d** (both 60 MHz and 100 MHz) in acetone solution (0.18 M) showed a single absorption at δ 1.65.

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Registry No. **1d**, 74087-85-7; **1e**, 58272-12-1; **1f**, 96964-30-6; **1g**, 96964-31-7; **1h**, 96964-32-8; **6**, 3146-39-2; acetone, 67-64-1; acetone triperoxide, 17088-37-8; acetone diperoxid , 1073-91-2; acetaldehyde, 75-07-0; acetic acid, 64-19-7; triphenylphosphine, 603-35-0; triphenylphosphine oxide, 791-28-6; pyridine, 110-86-1; pyridine oxide, 694-59-7; norbornylene, 498-66-8; phenanthrene, 85-01-8; phenanthrene oxide, 585-08-0; 2-butanone, 78-93-3; 2-pentanone, 107-87-9; 2-hexanone, 591-78-6; 3-pentanone, 96-22-0; ethyl *trans*-cinnamate, 4192-77-2; ethyl *trans*-cinnamate oxide, 2272-55-1; *cis*-stilbene, 645-49-8; *cis*-stilbene oxide, 1689-71-0; *trans*-stilbene, 103-30-0; *trans*-stilbene oxide, 1439-07-2; phenyl methyl sulfide, 100-68-5; phenyl methyl sulfoxide, 1193-82-4; methyl acetate, 79-20-9; propionaldehyde, 123-38-6; propionic acid, 79-09-4.