CF_3SCl with a group of alkanes show that the preference of attack by various alkyl radicals on sulfur vs. chlorine is best ordered on a steric basis, assuming that alkyl radicals intrinsically prefer to attack sulfur, but increasingly settle for attack on the more accessible chlorine as they become more bulky.[2] The same trend is evident in the reactions of 1 with alkyl radicals (Table I), but the shift to preference for chlorine by the more bulky radicals appears to be less pronounced than in the CF_3SCl reactions. The extremely high preference for attack on sulfur by benzylic radicals suggests that factors other than steric, e.g., reactivity of the radical, can be important in determining the pattern of attack by hydrocarbon radicals upon sulfenyl chlorides.

Experimental Section

I. Free-Radical Reactions of 1 with Hydrocarbons. A stirred solution of 1 dissolved in excess hydrocarbon contained in a quartz tube (7 × 1.5 in.) was irradiated under nitrogen with a sunlamp until the characteristic color of 1 was gone and the evolution of gas ceased. The reaction mixture was analyzed quantitatively by gas chromatography, and the principal products were identified by (1) comparison of retention times with materials of known structure, (2) mass spectroscopic examination of peaks in the gas chromatogram, or (3) isolation by distillation followed by elemental and proton NMR analyses. Details of the experiment are tabulated in Table I. Characterization of all new compounds is given in Tables IV and V.[6]

II. Free-Radical Reactions of Pentafluorobenzenethiol with Olefins. A stirred solution of the thiol and olefin contained in a quartz tube (7 × 1.5 in) fitted with a dry ice condenser and a magnetic stirrer was irradiated under nitrogen with a spiral-shaped, low-pressure mercury resonance lamp fitted around the reactor. The adducts were isolated by distillation, and structures were established by ^1H NMR spectroscopy. The details of these reactions are tabulated in Table II.

III. Determination of the Ratio of Pentafluorophenyl Cyclohexyl Sulfide (13) to Chlorocyclohexane at Various Conversions in the Photoreaction of 1 with Cyclohexane. A solution of 2.0 mL of 1 and 30 mL of cyclohexane (both freshly distilled) was placed in a small Pyrex flask fitted with a magnetic stirrer, a reflux condenser, and a syringe adapter. The mixture was irradiated with a sunlamp placed 5–6 in from the reactor. Samples (0.5 mL) were withdrawn periodically via syringe. Each sample was placed in a test tube containing 0.2 mL of *p*-methylacetophenone and shaken until colorless. A 5-μL sample was then examined by GC. The results of the measurements are given in Table III.

IV. Reaction of 1 with *p*-Methylacetophenone. A 5-mL amount of 1 was added in small portions to 80 mL of freshly distilled *p*-methylacetophenone with stirring. The color of 1 faded quickly after each addition. GC analysis showed the presence of one product. Distillation through a small Vigreux still gave 8.40 g (70%) of pentafluorophenyl *p*-methylphenacyl sulfide (**14**), distilling at 116–122 °C (0.20 mm). Elemental analysis and a ^1H nmr spectrum data are given in Tables IV and V.[6]

V. Reaction of 1 with Cyclohexane in the Presence of 6. A mixture of 0.2 mL (0.31 g, 0.00132 mol) of 1, 0.53 g (0.00133 mol) of **6**, and 3 mL of cyclohexane was irradiated as described above for 21 min. The color of the reaction mixture remained pale yellow during the last 5 min of the irradiation period. The mixture was analyzed by GC, and the ratio of the peak areas corresponding to **13** and chlorocyclohexane was found to be 7.38 (average of two determinations).

For comparison, a mixture of 0.2 mL of 1 and 3 mL of cyclohexane was similarly irradiated for 13 min, after which the mixture was essentially colorless. The peak area ratio of **13** to chlorocyclohexane was found to be 6.31.

VI. Preparation of 1. Compound 1 was prepared by the chlorination of pentafluorobenzenethiol (Peninsular Chem. Research) in carbon tetrachloride as described by Sheppard and Foster.[13]

VII. Gas Chromatography. The GC analyses were done primarily with a 6 ft × 0.25 in column packed with 20% SE-30 on 60–80 mesh WAWDMCS. Temperatures varied from 50 to 200 °C. The helium flow rate was about 100 mL/min.

VIII. Mass Spectroscopy/Gas Chromatography. A Du Pont Model 21-490 mass spectrometer interfaced to a Varian Model 1440 gas chromatograph and a VG 2040 data system was used.

Registry No.—14, 65015-61-4; *p*-methylacetophenone, 122-00-9.

Supplementary Material Available: Tables IV and V of elemental analyses and ^1H NMR spectral data for the new pentafluorophenyl alkyl and aralkyl sulfides (8 pages). Ordering information is given on any current masthead page.

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Peracid Oxidations of Cyclopropenes and Cyclopropenones[1a]

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The reactions of cyclopropenes **1a–c** with peracid yield isomeric conjugated ketones **2a–c** and **3a,b**. These conversions are interpreted in terms of an oxabicyclobutane intermediate. The peracid oxidation of cyclopropenones **11** and **21** were shown to initially produce CO_2 and an acetylene. The latter is converted to other products under the reaction conditions.

Considerable recent effort has been directed toward the synthesis and chemical characterization of novel small-ring heterocyclic systems. 2-Oxabicyclo[1.1.0]butane is the parent of one such class of highly strained heterocycles. Although no authentic example of this elusive structure has yet been described in the literature, species of this type have been considered as reactive intermediates in photochemical isomerizations of conjugated carbonyl compounds[2] and from peracid oxidations of cyclopropenes.[3–8] In this report, we detail our results concerning potential approaches to oxabicyclobutanes.

Concurrently with published studies, we too have explored the peracid oxidation of cyclopropenes. Thus, oxidation of 1,2-diethyl-3-carbethoxycyclopropene (**1a**) with an excess of

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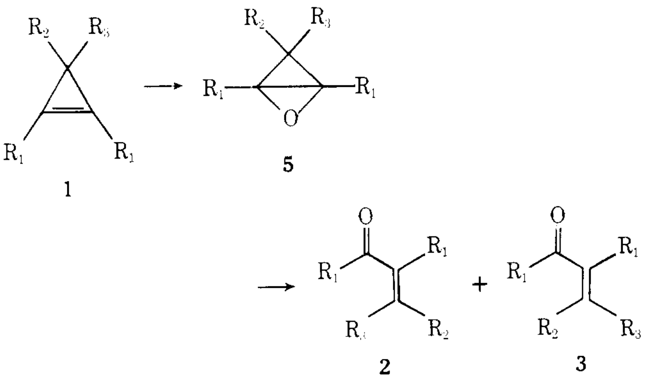
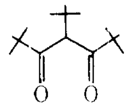
m-chloroperbenzoic acid (MCPBA) in CH_2Cl_2 solution resulted in an 85:15 mixture of isomeric conjugated enones **2a** and **3a**. The use of methanol as solvent gave a 91:9 ratio of **2a**/**3a**, whereas a 90:10 mixture was obtained in cyclohexane. However, neither peracetic acid nor peroxybenzimidic acid[9] promoted appreciable conversion of **1a**. The structures of the enones follow from their spectral characteristics which are detailed in the Experimental Section. The NMR data permit assignments of double-bond configurations, since the olefinic proton should be at lower field for the *E* isomer relative to the *Z* form.[10] The isomeric relationship of **2a** and **3a** was readily confirmed by photochemical equilibration. However, these enones did not interconvert under the reaction conditions, indicating that the observed ratios reflect kinetic product distributions.

The reaction of **1b** (in which a hydroxymethyl group is present at C-3) with MCPBA in CH_2Cl_2 produced a 65:35 mixture of **2b** and **3b**. In methanol the product ratio was 70:30 and in cyclohexane it was 60:40. Product stereochemistry is again assigned by NMR. Photoequilibration experiments interrelated the two enones, which were stable to interconversion under the reaction conditions.

Sterically hindered cyclopropene **1c** was examined with the idea that its bulky substituents might permit the isolation of an unstable intermediate. This strategy has been successfully employed in a number of similar situations. However, in the case of **1c** only conjugated ketone **2c** was produced by MCPBA oxidation, even when the reaction product was examined at 0 °C. Since certain hindered olefins are epoxidized by ozone,[11] the ozonolysis of 1,2,3-tri-*tert*-butylcyclopropene (**1d**) was studied at low temperatures in the absence of protic materials. Unfortunately, diketone **4**, derived from normal ozone double-bond cleavage, was the only important product.



a, R_1 = Et; R_2 = CO_2Et; R_3 = H
b, R_1 = Et; R_2 = CH_2OH; R_3 = H
c, R_1 = *t*-Bu; R_2 = R_3 = Me
d, R_1 = R_2 = *t*-Bu; R_3 = H
e, R_1 = Ph; R_2 = CH_2OH; R_3 = H
f, R_1 = Ph; R_2 = CH_2OMe; R_3 = H



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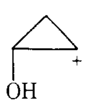
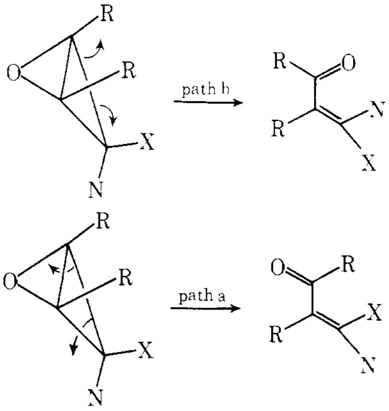


6

Although concrete evidence has still not been obtained for the intermediacy of oxabicyclobutanes **5** in the peracid oxidation of cyclopropenes, the production of conjugated carbonyl compounds is most readily rationalized in terms of the formation and spontaneous rearrangement of such species.[3-8] The latter transformation is formally analogous to the bicyclobutane–butadiene isomerization, which has received considerable attention.[12] If similar concerted mechanisms obtain in these structurally related systems, the proposed oxabicyclobutanes must be much more susceptible to thermal rearrangement than their hydrocarbon analogues. In fact, the isomerization of the parent oxabicyclobutane to acrolein is predicted[2,13] to be ca. 20 kcal/mol more exothermic than the bicyclobutane to butadiene conversion when equivalent strain energies are assumed for the two strained-ring systems.[14] Nonetheless, estimates of the expected kinetic behavior of oxabicyclobutane suggest that it might be an observable species.[13]

The heterocyclic system is more likely to react by acid-catalyzed mechanisms, but kinetic[8] and product studies[7] have been used to argue persuasively against intermediates of type **6** anywhere in the overall conversion of cyclopropenes to conjugated carbonyl compounds. However, protonation of oxabicyclobutanes could well hasten *concerted* decomposition to protonated enones.[4]

Friedrich has calculated that the parent oxabicyclobutane should display a preference for "disrotatory" over "conrotatory" ring opening.[4] He has also inferred from product studies on **1e** and **1f** that the disrotatory mode leading initially to a *transoid* enone conformer (path a) is preferred over the alternate disrotatory process which gives the *cisoid* enone (path b). [5]These transformations result in geometrical isomers of the enone product when $R_2 \neq R_3$ in oxabicyclobutane **5**. The above hypothesis does not appear to satisfactorily accommodate our results.



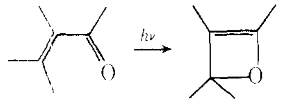
5_X, X = R_2, N = H; 5_N, X = H, N = R_2

In order to follow the stereochemistry of the oxabicyclobutane ring opening, a knowledge of the structure of this reactive intermediate is required. In the case of **1a** this can be predicted to be predominately the exo isomer 5_X with some confidence. This conclusion is based on the known stereochemistry of attack of other sterically demanding reagents on cyclopropenes[15] and the usual propensity for peracid to approach a cyclic olefin bearing a proximate ester function from the side of the molecule away from this polar group.[16] The rules given above predict **3a** as the major enone product from 5_X, whereas experimentally **2a** is observed to predominate. Note also that the **2a**/**3a** product ratio is not significantly different in the three solvents utilized (cyclohexane, CH_2Cl_2, and methanol).

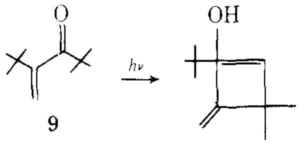
The stereochemistry of the intermediate from **1b** is less certain, although there is ample precedence for expecting peracid attack cis to the hydroxymethyl group owing to association by hydrogen bonding prior to reaction.[16] This line of reasoning predicts preferential formation of the *endo*-oxabicyclobutane 5_N in inert solvents. Rearrangement of 5_N is predicted to yield **2b** as the major enone product in agreement with the experimental results. However, hydrogen bonding between peracid and **1b** will not be important in methanol and the exo intermediate 5_X should predominate in this solvent. Accordingly, a reversal in the enone stereochemistry would be anticipated. In fact, the **2b**/**3b** product distribution is not greatly affected by the nature of the solvent. Thus, either the neighboring hydroxy group is not functioning as anticipated or the product ratio is not dependent on the stereochemistry of the oxabicyclobutane intermediate. In any event, the predominance of the *E* enone for both **1a** and **1b** contrasts markedly with the results for the pair **1e** and **1f** which give major enones of opposite stereochemistry (*Z* and *E*, respectively).

We conclude that the currently available data do not present a consistent pattern for the **2**/**3** ratios which can be rationalized in terms of a preferred decomposition mode for the intermediate oxabicyclobutanes. Rather, if such species are indeed formed, their product ratios are probably determined by subtle substituent interactions. In fact, typical product distributions correspond to rather similar energies for the competitive kinetic pathways to isomeric enone products; i.e., the reactions are not very stereoselective.

The possibility of photochemically isomerizing conjugated enones to oxabicyclobutanes has been considered. However, ketone **7** does not so react, preferring transformation to the isomeric oxetene **8** instead,[2] probably from a cisoid conformation of the starting enone. Consequently, the photochemistry of **9**, an enone which cannot readily achieve a planar cisoid conformation, was examined with the hope that the alternate cycloaddition mode to an oxabicyclobutane might be favored by this conformational distortion. No reaction was observed upon prolonged irradiation of **9** through Pyrex, but a facile photoconversion occurred upon irradiation through quartz. Disappointingly the photoisomer thus obtained was shown to be cyclobutanol **10**. Such photochemical transformations are, of course, amply precedented.[17]



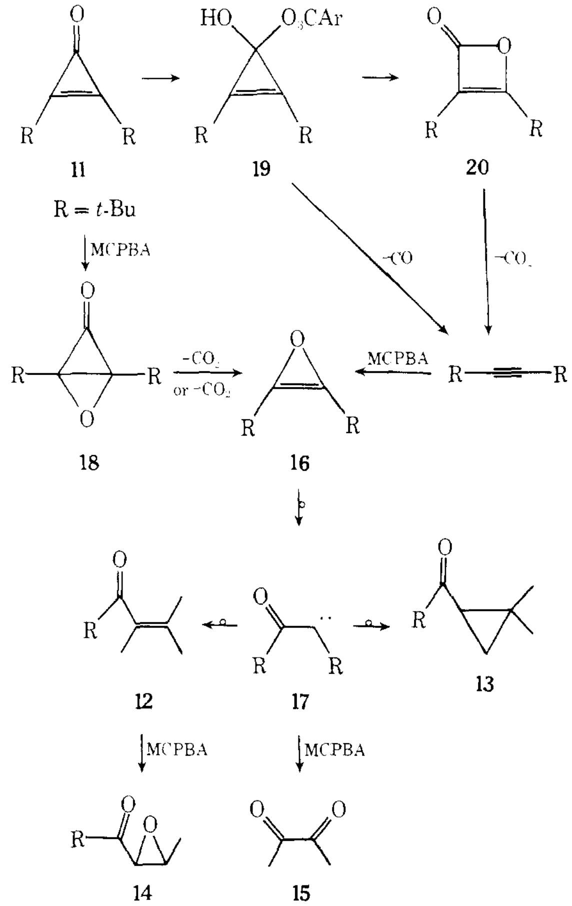
7 8



9 10

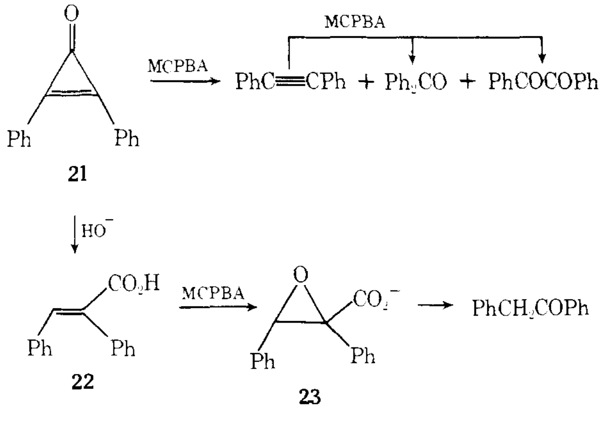
Peracid oxidations were also performed on several cyclopropenones, a rather special class of cyclopropenes.[15,18] Thus, di-*tert*-butylcyclopropenone (**11**) reacted slowly with an excess of MCPBA to yield di-*tert*-butylacetylene and ketones **12**, **13**, **14**, and **15** in a 1:2:5:90:2 ratio. One equivalent of CO_2 was also produced. The carbonyl products suggest the intermediacy of oxirene **16**, a highly reactive, antiaromatic species which is expected to yield stable products via the isomeric ketocarbene **17**.[19] A pathway to oxirene **16** proceeding by way of the oxabicyclobutanone **18** was considered prior to the identification of di-*tert*-butylacetylene as a minor product from **11**. However, the reaction of this acetylene with peracid is known to yield ketones **12**–**15** in a process postulated to involve the oxirene intermediate **16**.[19] Repeating the oxidation of the acetylene under the reaction conditions used for the cyclopropenone gave ketones **12**, **13**, **14**, and **15** in a 3:5:90:2 ratio. The identity of the product distributions in the two oxidation reactions establishes with virtual certainty that the acetylene is a key intermediate in the cyclopropenone reaction. Furthermore, this description is more in accord with the characteristic behavior of cyclopropenones, which are likely to suffer nucleophilic attack at the carbonyl group.[16] Adduct **19**, formed by addition of peracid to cyclopropenone **11**, can fragment to CO_2 and di-*tert*-butylacetylene either concertedly or by first rearranging to lactone **20**. Cyclopropanones are reputed to undergo a related conversion to olefin and CO_2.[20] Acetylenes are also produced as side products during the peracid oxidation of certain highly hindered cyclopropenes by a process which appears to involve an intermediate cyclopropenyl cation.[7] (Interestingly cyclopropenone **11** did not react with ozone, an electrophilic reagent.)

The MCPBA oxidation of diphenylcyclopropenone (**21**) resulted in a 40:10:50 mixture of diphenylacetylene, benzophenone, and benzil. Identical treatment of the acetylene resulted in partial conversion to the two ketones in a 1:5 ratio, essentially as described in the literature.[21] An intermediate oxirene is again postulated as the key intermediate.



11 19 20 18 16 12 17 13 14 15

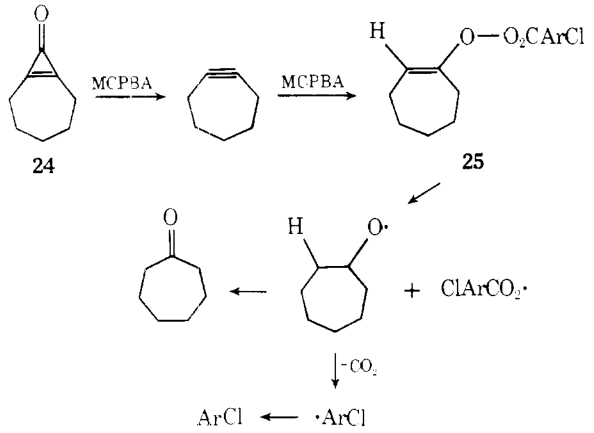
The absence of benzyl phenyl ketone in the product mixture from **21** and MCPBA was puzzling in view of a report that the oxidation of **21** with basic hydrogen peroxide gave this ketone as the major product.[22] In fact, duplication of this experiment led to a 30:10:40:20 mixture of diphenylacetylene, benzophenone, benzil, and benzyl phenyl ketone more in agreement with the MCPBA results. Submitting cyclopropanone **19** to the basic reaction conditions in the absence of hydrogen peroxide gave *cis*-1,2-diphenylacrylic acid **22** as anticipated.[23]



21 22 23

Acid **22** was readily converted to benzyl phenyl ketone in high yield by basic hydrogen peroxide. These results account for the experimental discrepancies and demonstrate part of the route to this ketone. The salt of acid **22** is undoubtedly epoxidized to give the glycidic acid salt **23** which decarboxylates to benzyl phenyl ketone.

Finally, cycloheptenocyclopropenone (**24**) was transformed by excess MCPBA to a complex mixture containing a 51% yield of chlorobenzene and 6% of cycloheptanone as the major components. These unanticipated results were not further investigated, but the observed products can be rationalized in terms of initial acetylene formation. In this instance, the very unstable cycloheptyne is postulated to nucleophilically add peracid to give the vinyl perester **25** which can proceed to the observed products by plausible free-radical processes.



Experimental Section

General. NMR spectra were recorded for CCl_4 solutions on a Varian HR-220 spectrometer; infrared spectra were obtained on a Perkin-Elmer IR-7 prism spectrophotometer. Commercial *m*-chloroperbenzoic acid was recrystallized from CH_2Cl_2 after which it analyzed as >98% peracid.[24] Sodium sulfate was used as a drying agent. Analyses were performed by Spang Microanalytical Laboratory.

1,2-Diethyl-3-carbethoxycyclopropene (1a). To a mixture of 10 g of 3-hexyne and 0.1 g of electrolytic Cu at reflux temperature was added 50 g of ethyl diazoacetate over a 12-h period. After gas evolution ceased, the mixture was distilled to give 7.5 g (55%) of 1,2-diethyl-3-carbethoxycyclopropene of >95% purity by GLPC: bp 90–95 °C (30 mm); IR 5.28, 5.81, 7.35, 8.10, and 8.48 μm; NMR δ 1.14 (t, 6, J = 7 Hz), 1.19 (t, 3, J = 7 Hz), 1.96 (s, 1), 2.42 (q, 4, J = 7 Hz), and 4.01 (q, 2, J = 7 Hz).

Anal. Calcd for $C_{10}H_{16}O_2$: C, 71.39; H, 9.59. Found: C, 71.2; H, 9.5.

Peracid Oxidation of 1a. A mixture of 0.5 g of **1a** and 2 g (4 equiv) of MCPBA in 25 mL of CH_2Cl_2 was stirred at 0 °C for 3 h, washed successively with solutions of $NaHCO_3$, $NaHSO_3$, $NaHCO_3$, and dried. Solvent removal under vacuum at 0 °C gave 2.1 g (96%) of a mixture of two products in a 85:15 ratio by GLPC. Inspection of the crude reaction mixture by NMR indicated that the GLPC isolated products were the only components. The major component was ethyl (*E*)-3-ethyl-4-keto-2-hexenoate (**2a**): IR 5.80, 5.92, 6.11, and 8.28 μm; NMR δ 0.98 (t, 3, J = 7 Hz), 1.09 (t, 3, J = 7 Hz), 1.29 (t, 3, J = 7 Hz), 2.63 (q, 2, J = 7 Hz), 2.75 (q, 2, J = 7 Hz), 4.17 (q, 2, J = 7 Hz), and 6.33 (s, 1).

Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.3; H, 8.9.

The minor component was ethyl (*Z*)-3-ethyl-4-keto-2-hexenoate (**3a**); IR 5.82 (br), 6.08, 8.3, and 8.8 μm; NMR δ 1.10 (br t, 6, J = 7 Hz), 1.25 (t, 3, J = 7 Hz), 2.51 (br q, 2, J = 7 Hz), 2.57 (q, 2, J = 7 Hz), 4.11 (q, 2, J = 7 Hz), and 5.56 (t, 1, J = 2 Hz).

Anal. Calcd for $C_{10}H_{16}O_3$: C, 65.19; H, 8.75. Found: C, 65.3; H, 8.7. Reaction of **1a** with peracetic acid at 0 °C for 24 h resulted in recovery of starting material, as did reaction with peroxybenzimidic acid.[9]

Peracid Oxidation of 1a in Methanol. A mixture of 0.5 g of **1a** and 2 g (4 equiv) of MCPBA in 25 mL of methanol was stirred at 0 °C for 6 h. Addition of 25 mL of CH_2Cl_2 and workup as described above gave **2a** (91%) and **3a** (9%).

Peracid Oxidation of 1a in Cyclohexane. A mixture of 0.5 g of **1a** and 2 g (4 equiv) of MCPBA in 25 mL of cyclohexane was stirred at 0 °C for 6 h. After workup as described above the solvent was removed under vacuum to give a 90:10 ratio of **2a**/**3a**.

Photoequilibration of 2a and 3a. Pure samples of **2a** and **3a** were independently irradiated in a Rayonet reactor with 3100-Å bulbs until an identical ratio of 91:9 of **2a**/**3a** was obtained (6 h).

Acid Stability of 2a and 3a. Pure samples of **2a** and **3a** were stirred with a mixture of 0.5 g of *m*-chlorobenzoic acid and 0.5 g of MCPBA in 25 mL of CH_2Cl_2 at 0 °C for 24 h. Workup as described above followed by GLPC analysis indicated no interconversion of isomers under these reaction conditions.

1,2-Diethyl-3-hydroxymethylcyclopropene (1b). To a slurry of 1 g of LAH in 100 mL of ether in an ice bath was added 1 g of **1a** in ether at a rate to maintain the temperature below 5 °C. Immediately after the addition of **1a**, 2 mL of saturated Na_2SO_4 solution was added slowly. Filtration and removal of solvent gave 0.5 g (66%) of **1b** which was 96% pure by GLPC: IR 3.05, 5.40, 6.9, and 9.9 μm; NMR δ 1.14 (t, 6, J = 7 Hz), 1.15 (t, 1, J = 7 Hz), 2.43 (q, 4, J = 7 Hz), 3.41 (d, 2, J = 7 Hz), and 4.20 (s, 1).

Anal. Calcd for $C_8H_{14}O$: C, 76.14; H, 11.18. Found: C, 76.0; H, 11.2.

Peracid Oxidation of 1b. A mixture of 1 g of **1b** and 2 g of MCPBA (1.5 equiv) in 20 mL of CH_2Cl_2 was stirred for 6 h in an ice bath. After workup the solvent was removed under vacuum at 0 °C to give 1.1 g (96%) of a mixture of two compounds in a 65:35 ratio. The major component was (*E*)-4-ethyl-6-hydroxy-4-hexen-3-one (**2b**): IR 2.98, 5.88, 6.10, and 8.05 μm; NMR δ 1.08 (t, 3, J = 7 Hz), 1.18 (t, 3, J = 7 Hz), 2.18 (q, 2, J = 7 Hz), 2.68 (q, 2, J = 7 Hz), 3.51 (d, 2, J = 6 Hz), 4.50 (s, 1), and 6.72 (t, 1, J = 6 Hz).

Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.3; H, 10.0.

The minor component was (*Z*)-4-ethyl-6-hydroxy-4-hexen-3-one (**3b**): IR 2.98, 5.89, 6.11, and 8.15 μm; NMR δ 1.03 (t, 3, J = 7 Hz), 1.20 (t, 3, J = 7 Hz), 2.20 (q, 2, J = 7 Hz), 2.70 (q, 2, J = 7 Hz), 4.31 (d, 2, J = 6 Hz), 4.73 (s, 1), and 5.65 (t, 1, J = 6 Hz).

Anal. Calcd for $C_8H_{14}O_2$: C, 67.57; H, 9.92. Found: C, 67.6; H, 9.8.

Oxidation using peracetic acid in an ice bath for 24 h resulted in recovery of starting material, as did oxidation with peroxybenzimidic acid.

Peracid Oxidation of 1b in Methanol. A mixture of 0.5 g of **1b** and 1 g of MCPBA (1.5 equiv) in 25 mL of methanol was stirred in an ice bath for 6 h. Addition of 25 mL of CH_2Cl_2 and processing as described above gave a **2b**–**3b** mixture in a 70:30 ratio (93%).

Peracid Oxidation of 1b in Cyclohexane. A mixture of 0.5 g of **1b** and 1 g (1.5 equiv) of MCPBA in 25 mL of cyclohexane was stirred at 0 °C for 6 h. After workup as described above the solvent was removed under vacuum to give a 60:40 ratio of **2b**/**3b**.

Photoequilibration of 2b and 3b. Pure samples of **2b** and **3b** were independently irradiated in a Rayonet reactor with 3100-Å bulbs until an identical cis–trans ratio of 27:73 was observed (3 h).

Acid Stability of 2b and 3b. Samples of pure **2b** and **3b** were stirred with 0.5 g of *m*-chlorobenzoic acid and 0.5 g of MCPBA in 25 mL of CH_2Cl_2 for 24 h in an ice bath. Workup and analysis as described above indicated no interconversion of isomers under these reaction conditions.

1,2-Di-*tert*-butyl-3,3-dimethylcyclopropene (1c). To 1 g of di-*tert*-butylcyclopropenone[25] in 50 mL of ether was added 10.4 mL of a 1.15 M MeLi solution. After stirring 2 h, 1 mL of water was added and stirring was continued for an additional 2 h. The solution was dried and 1 mL of 10% $HClO_4$ in acetic anhydride was added dropwise at 0°C. The solid thus formed was removed by filtration and washed with ether. To this material suspended in 100 mL of ether was added 10.4 mL of 1.15 M MeLi solution. After stirring 3 h, 1 mL of water was added, the ether solution was dried, and the solvent was removed to give 1,2-di-*tert*-butyl-3,3-dimethylcyclopropene (**1c**): IR 5.50, 7.19, 9.58, and 10.0 μm; NMR δ 0.98 (s, 6) and 1.21 (s, 18).

Anal. Calcd for $C_{13}H_{24}$: C, 86.59; H, 13.41. Found: C, 86.3; H, 13.7.

Peracid Oxidation of 1c. A mixture of 300 mg of **1c** and 600 mg (2 equiv) of MCPBA in 10 mL of CH_2Cl_2 was stirred at 0 °C for 2 h. The mixture was worked up in the usual fashion and the solvent was removed under vacuum at 0 °C to give 295 mg (90%) of 2,5,5-trimethyl-3-*tert*-butyl-2-hexen-4-one (**2c**), pure by GLPC: IR 5.91, 6.13, 7.18, 7.32, 9.56, and 10.0 μm; NMR δ 1.15 (s, 9), 1.21 (s, 9), 1.96 (s, 3), and 2.16 (s, 3).

Anal. Calcd for $C_{13}H_{24}O$: C, 79.53; H, 12.32. Found: C, 79.4; H, 12.4.

Reaction of 1,2,3-Tri-*tert*-butylcyclopropene[25] (1d) with Ozone. Into a solution of 172 mg of **1d** in 10 mL of CH_2Cl_2 at −78 °C was bubbled 1 equiv of ozone from a Welsbach ozone generator. After bubbling nitrogen through the solution for 30 min, it was allowed to warm to room temperature. Removal of the solvent under vacuum gave a mixture of two compounds in a 90:10 ratio. The major compound isolated by GLPC (160 mg, 80%) was assigned as 2,2,6,6-tetramethyl-4-*tert*-butyl-3,5-heptadione, (**4**): IR 5.80, 10.0 μm; NMR δ 0.97 (s, 9), 1.14 (s, 18), and 4.55 (s, 1); mass spectrum *m/e* 57 (100), 85 (60), 128 (18), 141 (7), 156 (2), 169 (3), 183 (7), 184 (7), and 240 (2).

Anal. Calcd for $C_{15}H_{28}O_2$: C, 74.95; H, 11.74. Found: C, 74.6; H, 11.7.

Inspection of the reaction mixture by NMR at −78 °C indicated that **4** was already formed and no change was observed upon warming. A reaction under identical conditions in methanol solvent gave similar results.

4-*tert*-Butyl-2,2-dimethyl-4-penten-3-one (9). A 3-g sample of 2,2,5,5-tetramethyl-3,4-hexadione was treated with 12 mL of a 1.7 M methyllithium solution in 300 mL of ether at room temperature and stirred for 2 h. A 5-mL sample of acetyl chloride was added and stirring was continued for an additional 3 h. The reaction was quenched by the addition of 10 mL of water. The mixture was washed with water and a solution of $NaHCO_3$, and dried. The ether was removed by vacuum and the crude material passed through a flow system pyrolysis tube at 450 °C. The collected 4-*tert*-butyl-2,2-dimethyl-4-penten-3-one (**9**) was purified by GLPC and gave: IR 5.95, 6.17, 7.22, 7.38, 7.80, 8.31, 9.61, 10.0, 11.0, and 11.4 μm; NMR δ 1.13 (s, 9), 1.19 (s, 9), 5.02 (s, 1), and 5.25 (s, 1).

Photolysis of 9. A 50-mg sample of **9** was dissolved in 125 mL of pentane and irradiated through Pyrex at −78 °C with a Hanovia medium-pressure Hg arc. After 12 h the pentane was removed. The NMR of the residue indicated only starting material. Irradiation *through quartz* under the same conditions for 30 min gave three products by GLPC in a 96:2:2 ratio. Collection of the major product by GLPC and spectral analysis indicated 1-*tert*-butyl-3,3-dimethyl-2-methylenecyclobutanol (**10**): IR 2.80, 2.93, 6.05, 7.24, 7.32, 8.87, 10.4, 11.2, and 11.6 μm; NMR δ 0.92 (s, 9), 1.07 (s, 3), 1.24 (s, 3), 1.88 (AB, 2, $\Delta\nu$ = 0.4 ppm, J = 13 Hz), 1.75 (s, 1), 4.91 (s, 1), and 5.05 (s, 1).

Anal. Calcd for $C_{11}H_{20}O$: C, 78.51; H, 11.98. Found: C, 78.6; H, 12.0.

Peracid Oxidation of 11. A mixture of 1 g of **11** and 5.2 g of MCPBA (4.5 equiv) in 25 mL of CH_2Cl_2 was refluxed for 8 h. The usual workup gave 1.3 g of a mixture of 5 products in a 1:2:5:90:2 ratio by GLPC. The first product was identified as di-*tert*-butylacetylene by spectral comparison with an authentic sample.[26] The second product was identified as 2,3,5,5-tetramethyl-2-hexen-4-one (**12**) by GLPC retention time and mass spectral comparison with an authentic sample:[19] mass spectrum *m/e* 154 (9), 139 (8), 97 (87), 83 (45), 69 (22), and 57 (100). The third product was identified as 1,2,2-trimethylcyclopropyl *tert*-butyl ketone (**13**) by spectral comparison with an authentic sample.[27] The fourth product was identified as 2,3,5,5-tetramethyl-2,3-epoxy-4-hexanone (**14**) by spectral comparison with an authentic sample:[19] IR 5.91, 7.25, 7.31, 8.0, 11.4, and 12.0 μm; NMR δ 1.36 (s, 3), 1.29 (s, 3), 1.16 (s, 9), and 1.14 (s, 3); mass spectrum *m/e* 170 (19), 155 (40), 138 (1.5), 113 (15), 86 (62), 85 (46), 71 (57), and 57 (100). The fifth product was identified as 2,2,5,5-tetramethyl-3,4-hexadione (**15**) by spectral comparison with an authentic sample.

An identical experiment was conducted in which a slow stream of nitrogen was passed through the reaction mixture. The exiting gases were passed through $CaSO_4$ and a weighed drying tube containing Ascarite. The Ascarite gained 28.0 mg in weight which corresponds to a 97% yield of CO_2.

Peracid Oxidation of Di-*tert*-butylacetylene. A solution of 1 g of di-*tert*-butylacetylene was oxidized under the conditions described for di-*tert*-butylcyclopropenone to give **12**, **13**, **14**, and **15** in a 3:5:90:2 ratio by GLPC (94% total yield).

Reaction of 11 with Ozone. A solution of 1 g of **11** in 50 mL of CH_2Cl_2 at −78 °C was saturated with ozone from a generator until a blue color persisted. The color remained for 24 h, after which excess ozone was removed by passing through a nitrogen stream. Warming the reaction mixture to room temperature and removal of the solvent gave only recovered **11**.

Peracid Oxidation of Diphenylcyclopropenone (21). A mixture of 1 g of **21**[23] and 4.2 g (5 equiv) of MCPBA in 50 mL of CH_2Cl_2 was refluxed for 8 h. Usual workup gave 1.3 g of 40:10:50 mixture of diphenylacetylene, benzophenone, and benzil.

Hydrogen Peroxide Oxidation of 21. A mixture of 1 g of **21**, 0.5 g of NaOH, 2 mL of water, and 5 mL of 40% H_2O_2 in 25 mL of dioxane was stirred at room temperature for 24 h. The mixture was poured into 200 mL of water, acidified with 10% HCl, and extracted with ether. Drying and removal of the solvent gave a 30:10:40:20 mixture of diphenylacetylene, benzophenone, benzil, and benzyl phenyl ketone: mass spectrum *m/e* 196 (15), 178 (5), 165 (4), 105 (100), 92 (36), 78 (60), 51 (48), and 45 (42).

Reaction of 21 with Base. A mixture of 1 g of **21**, 0.5 g of NaOH, and 2 mL of water in 25 mL of dioxane was stirred for 24 h at room temperature. The mixture was poured into water, acidified with 10% HCl, and extracted with ether. Solvent removal gave crystalline *cis*-1,2-diphenylacrylic acid (**22**).[23]

Hydrogen Peroxide Oxidation of 22. A mixture of 0.5 g of **22**, 0.5 g of NaOH, 2 mL of water, and 5 mL of 40% H_2O_2 in 25 mL of dioxane was stirred at room temperature for 24 h. The mixture was poured into water, acidified with 10% HCl, and extracted with ether. Drying and removal of the solvent gave only benzyl phenyl ketone in 93% yield.

Peracid Oxidation of Cycloheptenocyclopropenone (24). A mixture of 1 g of **24**[28] and 5 g (3 equiv) of MCPBA in 50 mL of methylene chloride was stirred at reflux for 8 h. The usual workup gave a mixture of six products by GLPC in a 85:10:1:1:2:1 ratio. The major component was chlorobenzene (51% yield); the 10% product was cycloheptanone (6% yield based on starting cyclopropenone).

Registry No.—**1a**, 35920-11-7; **1b**, 65016-07-1; **1c**, 65016-08-2; **1d**, 23438-08-6; **2a**, 65016-09-3; **2b**, 65016-10-6; **2c**, 65016-11-7; **3a**, 65016-12-8; **3b**, 65016-13-9; **4**, 65016-14-0; **9**, 35373-26-3; **10**, 65016-15-1; **11**, 19985-79-6; **12**, 17325-92-7; **14**, 42915-86-6; **21**, 886-38-4; **24**, 696-47-9; ethyl diazoacetate, 623-73-4; methyllithium, 917-54-4; 2,2,5,5-tetramethyl-3,4 hexadione, 4388-88-9; di-*tert*-butylacetylene, 17530-24-4.

References and Notes

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