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Peroxy Acid Oxidation of Cyclopropenes. Evidence for a Dual Pathway[1]

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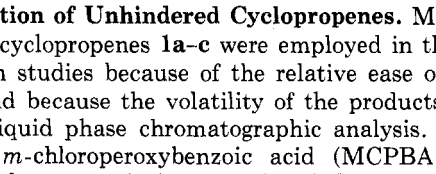
Unhindered alkyl cyclopropenes **1** ($R_1 \neq R_2$; $R_3 = R_4$) unsymmetrically substituted at the carbon–carbon double bond undergo oxidation with *m*-chloroperoxybenzoic acid (MCPBA) in methylene chloride to afford two α,β-unsaturated carbonyl compounds, **3** and **4**, probably *via* unstable 2-oxabicyclo[1.1.0]butane intermediates **2**. Hindered cyclopropenes bearing a hydrogen at the 3 position undergo a novel oxidative fragmentation reaction under similar conditions to give acetylenes and anhydrides as primary products. The mechanism of this transformation has been shown to involve cyclopropenyl cations as intermediates which react with a second mole of MCPBA, generating unstable peroxy esters. The latter intermediates suffer facile fragmentation to acetylenes and anhydrides. Cyclopropenyl cations also react with hydrogen peroxide and base, affording acetylenes and carboxylic acids.

The peracid oxidation of cyclopropenes **1** has been proposed to proceed *via* oxabicyclobutane intermediates **2**.[1,3] Table I summarizes the number of possible α,β-unsaturated carbonyl compounds which could arise from the simple isomerization of various substituted oxabicyclobutanes by cleavage of two peripheral σ bonds. Cyclopropenes of type **1** ($R_1 = R_2$; $R_3 \neq R_4$) have been shown to afford one α,β-unsaturated ketone as a mixture of cis and trans isomers.[3]

In order to obtain evidence for the postulated oxabicyclobutanes it was of interest to us to investigate the oxidation of cyclopropenes of type **1** where $R_1 \neq R_2$ and $R_3 = R_4$, since isomerization in these cases could produce two structurally different α,β-unsaturated carbonyl compounds. Indeed Moore[4a] and Skattebøl[4b] have found that the thermal isomerization of a similarly substituted bicyclobutane bearing two different groups at ring fusion atoms 1 and 3 but identical groups at positions 2 and 4 gives both possible butadienes (eq 1).[5]

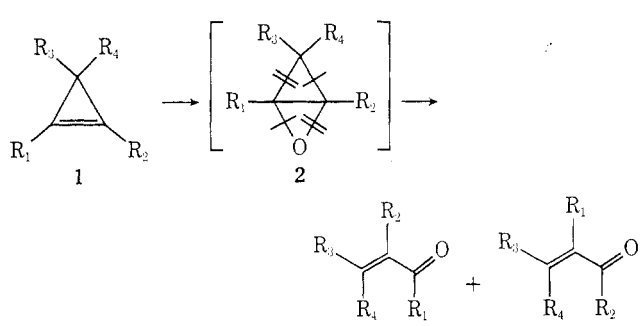


(1)

Results and Discussion

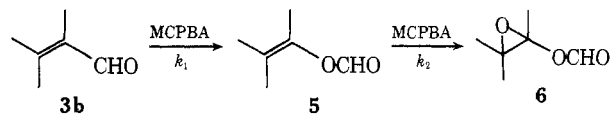
Oxidation of Unhindered Cyclopropenes. Methyl-substituted cyclopropenes **1a–c** were employed in the peracid oxidation studies because of the relative ease of preparation,[6] and because the volatility of the products facilitated gas–liquid phase chromatographic analysis. The reaction of *m*-chloroperoxybenzoic acid (MCPBA) with 1-methycyclopropene (**1a**), 1,3,3-trimethylcyclopropene (**1b**), and tetramethylcyclopropene (**1c**) was investigated in methylene chloride at 0°. In each case the reaction was exothermic and accompanied by the precipitation of *m*-chlorobenzoic acid (MCBA). For **1b** and **1c** aqueous basic work-up provided a colorless oil which was analyzed by glpc and spectral methods. For **1a** the solubility and polymerization tendency of the oxidation products precluded aqueous basic work-up. The work-up conditions involved filtration and careful solvent removal followed by direct glpc analysis. The results are summarized in Table II.

Table I



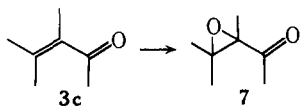
Cyclopropene	Products	Cis–trans pairs
$R_1 \neq R_2$; $R_3 \neq R_4$	4	2
$R_1 \neq R_2$; $R_3 = R_4$	2	0
$R_1 = R_2$; $R_3 \neq R_4$	2	1
$R_1 = R_2$; $R_3 = R_4$	1	0

An excess of cyclopropene is desirable to minimize the formation of secondary oxidation products arising from Baeyer–Villiger and/or epoxidation reactions. For example, when 1,3,3-trimethylcyclopropene (**1b**) was oxidized with 1 equiv of MCPBA in methylene chloride at 0°, a mixture of three components was obtained, namely, mesityl oxide (**4b**, ~31%), α,β-dimethylcrotonaldehyde (**3b**, ~54%), and the epoxyformate ester **6** (~15%) in addition to unreacted **1b**. The structures of **3b**, **4b**, and **6** were assigned on the basis of ir, nmr, and mass spectral data accrued on samples isolated by preparative glpc. In an independent experiment the oxidation of **3b** under the conditions of its formation afforded only **6** and unreacted **3b**. Thus **6** is a secondary oxidation product arising presum-



ably from Baeyer–Villiger oxidation of **3b** followed by epoxidation of the vinyl formate ester **5**.[7] The absence of **5**

indicates that epoxidation of **5** is faster than Baeyer-Villiger oxidation of **3b** (*i.e.*, $k_2 > k_1$). Similarly, treatment of tetramethylcyclopropene (**1c**) with 1 equiv of MCPBA afforded α-methylmesityl oxide (**3c**, ~65%) and its corresponding epoxide **7** (~35%) in addition to unreacted **1c**.

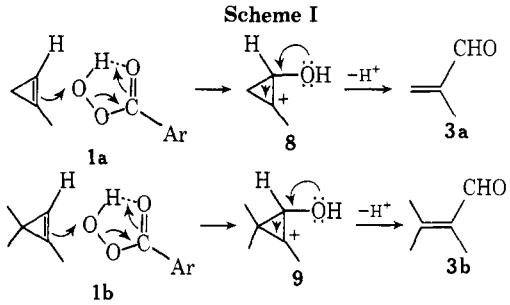


3c **7**

The formation of **7** by the epoxidation of **3c** was demonstrated in a separate control experiment. Only when the ratio of cyclopropene to oxidant was 3:1 or greater was it possible to obtain **3c** exclusively. The structures of **3c** and **7** were assigned on the basis of ir, nmr, and mass spectral data obtained from samples isolated by preparative glpc.

In principle, the reaction of a peracid with a cyclopropene could proceed *via* a polar carbonium ion mechanism. For example, the reaction of unsymmetrical cyclopropenes **1a** and **1b** may be envisioned as proceeding by way of the more stable cyclopropyl carbonium ions **8** and **9**, respectively, as a result of electrophilic attack of the peracid on the less substituted olefinic carbon atom. Disrotatory electrocyclic ring opening followed by deprotonation would afford the observed aldehydes **3a** and **4b**, respectively (Scheme I). Indeed, the reaction of **1a** and **1b** with chlorosulfonyl isocyanate has been reported to give products derived from electrophilic attack on the double bond to generate the more stable cyclopropyl carbonium ion which subsequently undergoes rearrangement to the observed products. Of particular importance here is the regioselectivity of the reaction (*i.e.*, no products resulting from attack at the more substituted position were observed) and the facile tendency of the cyclopropyl ion to rearrange in preference to internal capture to give an azabicyclopentane derivative.[8]

Scheme I



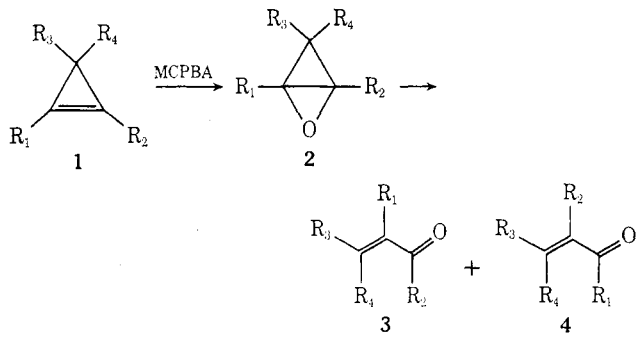
The arguments against a polar mechanism for the peracid oxidation of cyclopropenes are summarized below.

(1) If a polar mechanism were operative, α,β-unsaturated aldehydes **3a** and **3b** should be the predominant if not exclusive products from the oxidation of cyclopropenes **1a** and **1b**, respectively. However, both an α,β-unsaturated aldehyde and an α,β-unsaturated ketone were observed in the oxidation of each cyclopropene, and, furthermore, there was little preference for one product over the other.

(2) If a polar mechanism were operative, the rate of oxidation of tetramethylcyclopropene (**1c**) should not be greater than about twice that of 1,3,3-trimethylcyclopropene (**1b**) since a tertiary cyclopropyl carbonium ion can be generated in each case, but statistically there are two possible equivalent tertiary ions that can be generated from **1c** *vs.* only one from **1b**.

In a direct competition experiment a mixture of 1 equiv of each of the cyclopropenes **1b** and **1c** was treated with 0.8 equiv of MCPBA in carbon tetrachloride at 0°. After 15 min a starch-iodide test revealed complete consumption of oxidant. Glpc analysis of the ratio of starting cyclopropenes and oxidation products in the crude reaction mixture indicated that tetramethylcyclopropene (**1c**) is more reactive than 1,3,3-trimethycyclopropene (**1b**) by a factor of about 6. This result is consistent with a mechanism involving symmetrical electrophilic attack of the peracid on the π bond of the cyclopropene to afford an oxabicyclobutane intermediate in analogy with simple olefin epoxidation.

Table II
Products of the Peracid Oxidation of Cyclopropenes

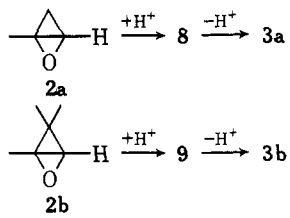


	Yield,[a] %	Yield,[a] %
1a, R_1 = Me; R_2 = R_3 = R_4 = H	42[b]	58[b]
1b, R_1 = R_3 = R_4 = Me; R_2 = H	69[b]	31[b]
1c, R_1 = R_2 = R_3 = R_4 = Me	100	

[a] Represent glpc yields. [b] Average of four runs.

The product ratios obtained in our studies do not reflect any appreciable specificity in the direction of the ring opening of the oxabicyclobutane intermediates **2a** and **2b** and are inconsistent with a stepwise protolytic pathway for reasons which have already been discussed above (Scheme II).

Scheme II

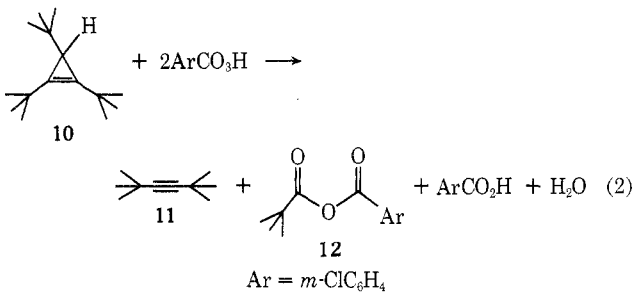


On the basis of these results, it appears that, if oxabicyclobutanes are intermediates, their rearrangement is proceeding *via* a concerted process. Furthermore, since oxabicyclobutanes (**2**) cannot even be detected by nmr spectroscopic analysis of the reaction mixtures at 0°,[3b] the activation energy for the isomerization of **2** must be considerably lower than that for the analogous isomerization of bicyclobutanes.[5,9]

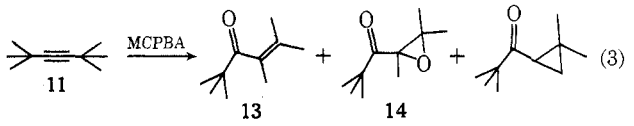
Oxidation of Hindered Cyclopropenes. Since our initial studies provided evidence for the intervention of oxabicyclobutanes as unstable intermediates in the peracid oxidation of unhindered cyclopropenes, it was of interest to us to investigate the oxidation of hindered *tert*-butyl-substituted cyclopropenes. Although the rate of oxidation of the more hindered double bond should be slower, it was anticipated that the resulting oxabicyclobutanes might be capable of isolation or at least detection. As a result of *tert*-butyl substitution, such elusive systems as aziridinones, diaziridinones, cyclopropanones, allene oxides, and

oxadiaziridines have been successfully prepared, isolated, and characterized.

Treatment of a solution of 1,2,3-tri-*tert*-butylcyclopropene (**10**)[10] in methylene chloride with 1 equiv of MCPBA at room temperature resulted in an immediate exothermic reaction and the precipitation of MCBA. Examination of the reaction mixture with starch–iodide indicated the complete consumption of oxidant. Analysis of the reaction mixture after extraction with aqueous sodium bicarbonate by infrared and nmr spectroscopy as well as glpc revealed the presence of two components in addition to unreacted **10.** The infrared spectrum exhibited two strong bands at 1815 and 1745 cm^{-1} with the former being the more intense, characteristic of acyclic anhydrides.[11] The nmr spectrum in the upfield region showed the presence of unreacted **10** along with two other singlets at δ 1.16 and 1.37. The aromatic region exhibited two multiplets of equal area at δ 7.45–7.75 and 7.90–8.10 which were identical with the absorption exhibited by the *m*-chlorobenzoyl moiety. By glpc two volatile components were detected and separated on a preparative scale and shown to be cyclopropene **10** and di-*tert*-butylacetylene (**11**) by comparison of spectra and glpc retention times with those of authentic samples. Brief shaking of an ether solution of the crude reaction mixture with aqueous sodium carbonate led to a disappearance of the 1815- and 1745-cm^{-1} bands in the infrared and the nmr absorption at δ 1.37 as well as the complex aromatic region (4 H) between δ 7.45 and 8.10. On the basis of these experimental observations, the structure of this nonvolatile (glpc), base-sensitive component was deduced to be the mixed anhydride **12** of pivalic and *m*-chlorobenzoic acids. The structure of **12** was verified by comparison of the infrared and nmr spectra with those of an authentic sample prepared by the reaction of pivaloyl chloride with MCBA in ether–pyridine. Since nmr integration indicated that unreacted cyclopropene **10,** di-*tert*-butylacetylene (**11**), and anhydride **12** were present in equimolar quantities, the stoichiometry of this novel oxidative fragmentation reaction requires 2 mol of MCPBA/mol of **10** (eq 2).

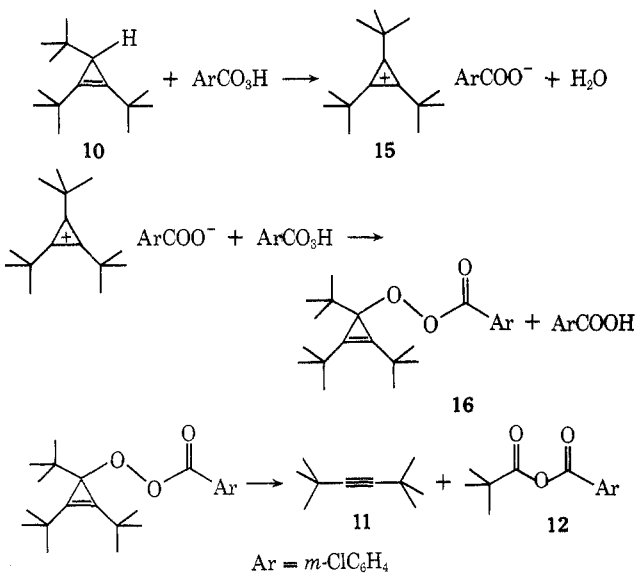


However, when the molar ratio of MCPBA to **10** was 2:1, secondary products arising from the competing MCPBA oxidation of di-*tert*-butylacetylene (**11**) were observed (eq 3).[12] No oxabicyclobutane or α,β-unsaturated



ketone products derived from the epoxidation of **10** were detected. The formation of an acetylene and a mixed anhydride from the peracid oxidation of a hindered cyclopropene represents a novel departure from the normal behavior of unhindered cyclopropenes toward peracids. Since this transformation cannot be readily interpreted in terms of an oxabicyclobutane intermediate, the reaction was subjected to further mechanistic scrutiny. Neither 1,2,3-tri-*tert*-butyl-3-methylcyclopropene[10] nor 1,2-di-*tert*-butyl-3-methyl-3-phenylcyclopropene reacted with MCPBA under similar conditions, suggesting that the hydrogen at the 3 position was abstracted in the reaction. Conclusive evidence was provided by the reaction of **10** with MCPBA in methylene chloride in the presence of perchloric acid. An nmr spectrum of the reaction mixture revealed a singlet at δ 1.58 corresponding to tri-*tert*-butylcyclopropenyl perchlorate (**17**).[10] Furthermore, the addition of ether to the reaction mixture resulted in the precipitation of **17** as a white, crystalline solid. The intermediacy of the tri-*tert*-butylcyclopropenyl cation was established by subjection of **17** to similar reaction conditions (*i.e.*, MCPBA, sodium *m*-chlorobenzoate, CH_2Cl_2) which resulted in the formation of **11** and **12.** The mechanism for the oxidative fragmentation of **10** is outlined in Scheme III. The reaction of **10** with MCPBA was unaffected by the presence of the radical scavengers bromotrichloromethane or β,β-dichlorostyrene, precluding a mechanism involving radical abstraction of hydrogen as the first step in the formation of cyclopropenyl cation **15.** Thus, the process appears to involve a direct formal hydride transfer from the 3 position of cyclopropene **10** to the terminal electrophilic oxygen of MCPBA to generate tri-*tert*-butylcyclopropenyl *m*-chlorobenzoate (**15**).[13] Subsequent reaction of cation **15** with a second mole of MCPBA would be expected to afford peroxy ester **16,** the probable precursor of **11** and **12.** Peroxy ester **16** could neither be isolated nor detected by nmr spectroscopy under the reaction conditions. The instability of **16** is not surprising in view of the fact that the peroxide intermediates proposed in the oxidative decarbonylation of cyclopropenones[14] and cyclopropanones[15] with MCPBA and hydrogen peroxide, respectively, were not isolated under the reaction conditions. DePuy has observed that the related nitrite esters of cyclopropanols are extremely unstable, even at −50°.[16] The low activation energy for the decomposition of these three-membered ring nitrites and peroxides probably reflects (at least in part) a relief of ring strain in the transition state by partial ring opening.

Scheme III
MCPBA oxidation of 10

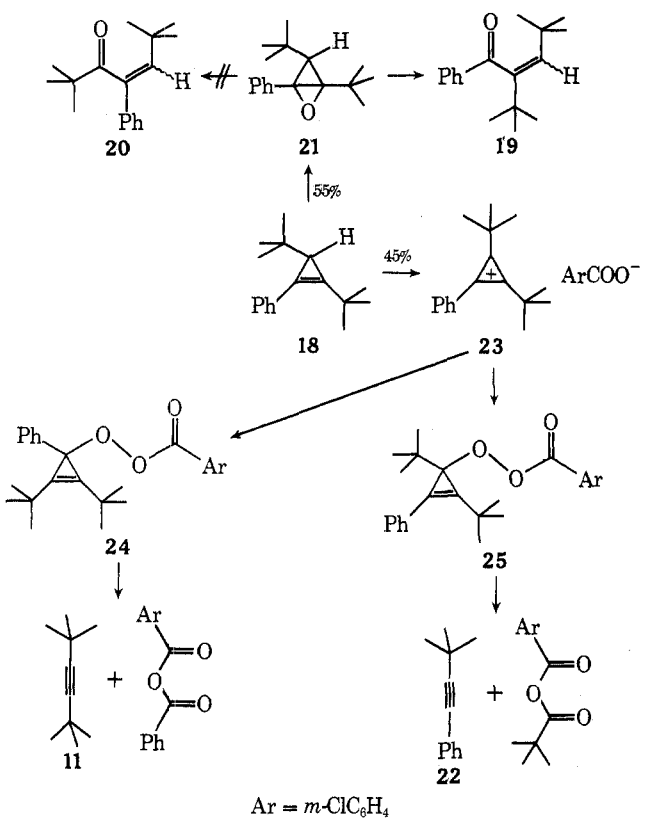


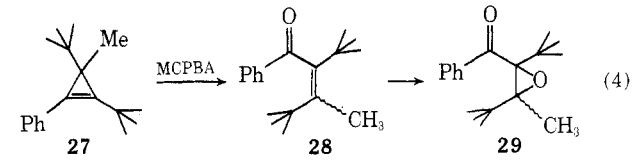
In theory, the decomposition of peroxy ester **16** may proceed *via* a concerted, radical, or ionic process.[17] However, if a radical or ionic mechanism is operative, it must be intramolecular (*i.e.*, radical or ion pair), since radical scavengers had no significant effect on the reaction of **10**

with MCPBA and, furthermore, the reaction of tri-*tert*-butylcyclopropenyl perchlorate (17) with MCPBA in the presence of sodium acetate resulted in no incorporation of acetate into the anhydride product. ^{18}O-labeling studies are necessary to elucidate the mechanistic details of this reaction.

The reaction of 1-phenyl-2,3-di-*tert*-butylcyclopropene (18) with MCPBA in methylene chloride afforded α,β-unsaturated ketone 19 (55%) as well as di-*tert*-butylacetylene (11) and phenyl-*tert*-butylacetylene (22) (combined yield 45%) in the ratio of 1:3.5. The products derived from 18 are indicative of a competitive dual oxidative pathway as illustrated in Scheme IV. The proposed mechanism involves epoxidation of 18 to generate the intermediate oxabicyclobutane 21, which subsequently undergoes isomerization to α,β-unsaturated ketone 19 (stereochemistry uncertain). The other possible isomeric α,β-unsaturated ketone 20 could not be detected. Alternatively, hydride abstraction from 18 by MCPBA generates phenyldi-*tert*-butylcyclopropenyl *m*-chlorobenzoate (23), which can be detected by nmr as the perchlorate salt 26 (δ 1.67, s) when the reaction is conducted in the presence of perchloric acid. Subsequent reaction of cation 23 with MCPBA generates peroxy esters 24 and 25 (not isolated but presumably in the ratio of 1:3.5) which decompose to afford the acetylene and anhydride products. In an independent experiment, the reaction of phenyldi-*tert*-butylcyclopropenyl perchlorate (26)[10] with MCPBA and sodium *m*-chlorobenzoate in methylene chloride gave acetylenes 11 and 22 in the expected ratio of 1:3.5 but not α,β-unsaturated ketone 19. These results support the intermediacy of peroxy esters 24 and 25 in the formation of acetylenes 11 and 22, respectively, and exclude 24 as a possible precursor to 19 in the peroxy acid oxidation of 18. In accordance with the proposed mechanism, oxidation of cyclopropene 27 afforded only epoxy ketone 29 (stereochemistry uncertain), which undoubtedly arises from epoxidation of α,β-unsaturated ketone 28 (eq 4).

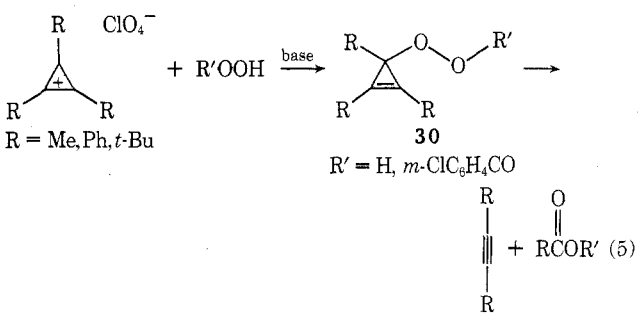
Scheme IV
MCPBA Oxidation of 18





(4)

We have also found that cyclopropenyl cations undergo facile oxidative fragmentation by treatment with hydrogen peroxide (as well as MCPBA) and base to afford acetylenes and carboxylic acids as primary products, presumably *via* hydroperoxycyclopropene intermediates 30 (R′ = H).[18]



(5)

Experimental Section

General. Melting points were taken on a Kofler micro heating stage. All melting points and boiling points are uncorrected. Infrared spectra were obtained on a Perkin-Elmer Model 337 grating spectrophotometer and were calibrated with polystyrene. Ultraviolet and nmr spectra were recorded on a Cary Model 14 recording spectrophotometer and a Varian A-60A spectrometer, respectively. Chemical shifts are reported in parts per million (ppm) relative to tetramethylsilane with the letter in parentheses indicating multiplicity: s, singlet; d, doublet; t, triplet; q, quartet; m, multiplet. All analytical and preparative glpc was conducted on an Aerograph A-90P gas chromatograph fitted with a thermal conductivity detector, recorder, and Disc chart integrator. Mass spectra were obtained on a Hitachi RMU-6D mass spectrometer and only *m/e* values which are ≥5% of the base peak are reported.

Materials. Unless otherwise indicated, all commercial reagent solvents were used without further purification. The *m*-chloroperoxybenzoic acid (MCPBA) obtained from the Aldrich Chemical Co. contained about 15% of *m*-chlorobenzoic acid, which was removed by extraction with a phosphate buffer of pH 7.5. The purified MCPBA was then recrystallized twice from benzene and dried in a vacuum desiccator. The 90% hydrogen peroxide was obtained from the FMC Corp. *p*-Toluenesulfonhydrazine (Aldrich) was purified by recrystallization from hot methanol. Sodium *m*-chlorobenzoate was prepared by titrating a methanolic solution of *m*-chlorobenzoic acid to a phenolphthalein end point followed by thorough drying at 1 mm for 48 hr.

Preparation of Unhindered Cyclopropenes 1a–c. 1-Methylcyclopropene (1a), 1,3,3-trimethylcyclopropene (1b), and tetramethylcyclopropene (1c) were prepared by reported procedures.[19]

MCPBA Oxidation of 1a. The peroxy acid oxidation of 1-methylcyclopropene (1a) was conducted in duplicate by two different procedures, both of which gave nearly identical results. In both cases, a large excess of cyclopropene was employed to avoid secondary oxidation reactions.

Procedure A. Approximately 5 ml of 1a was distilled through a gas sparger into a stirred solution of 2.0 g of MCPBA in 25 ml of dichloromethane at −10° (ice–salt bath). Within minutes a copious white precipitate of *m*-chlorobenzoic acid formed and within 15 min a starch–iodide test revealed the complete consumption of oxidant. The precipitate was filtered and the filtrate was examined directly by glpc (0.25 in. × 20 ft aluminum column packed with 20% Carbowax 20M on Chromosorb W, AW-DMCS, 80/100 mesh; column temperature 30°). Methacrolein (3a) and methyl vinyl ketone (4a) were identified by comparison of glpc retention

times with those of authentic samples (Aldrich Chemical Co.). Ir and nmr analysis of the crude reaction mixture likewise affirmed the presence of **3a** and **4a** in the ratio indicated in Table II.

Procedure B. Alternatively, approximately 5 ml of cyclopropene **1a** was diluted with 30 ml of dichloromethane at −78°. After the addition of 2.5 g of MCPBA the mixture was stirred and slowly warmed to 0° over 30 min, after which time a starch–iodide test revealed the complete consumption of peroxy acid. The precipitate of *m*-chlorobenzoic acid was filtered and the filtrate was examined directly by glpc as in procedure A. Procedure B was found to be superior in that the lower reaction temperature permitted much more effective control of the highly exothermic oxidation.

MCPBA Oxidation of 1b. To a stirred solution of 0.370 g (4.5 mmol) of 1,3,3-trimethylcyclopropene (**1b**) in 10 ml of dichloromethane at 0° was added in one portion 0.775 g (4.5 mmol) of MCPBA. Within 5 min a copious white precipitate formed. After stirring for 30 min at 0° a starch–iodide test revealed the absence of oxidant. The *m*-chlorobenzoic acid was removed by filtration and glpc analysis (0.25 in. × 10 ft aluminum column packed with 15% SE-30 on Chromosorb W, AW-DMCS, 80/100 mesh; column temperature 125°) of the clear, colorless filtrate revealed the presence of three components in the ratio of 31:15:54. The dichloromethane solution was extracted with two 10-ml portions of 5% $NaHCO_3$ and dried over anhydrous $MgSO_4$, the solvent was removed *in vacuo*, and the residue was subjected to preparative glpc under the same conditions described above. The separated components were identified on the basis of the following data. Mesityl oxide (**4b**, 31%) was identified by comparison of ir, nmr, and glpc retention time with those of an authentic sample (Aldrich). α,β-Dimethylcrotonaldehyde (**3b**, 54%) was identified on the basis of the following spectral properties: nmr ($CDCl_3$) δ 10.1 (s, 1 H), 2.20 (q, 3 H, J = 1.5 Hz), 1.97 (s, 3 H), 1.74 (q, 3 H, J = 1.5 Hz); ir (CCl_4) 3020 (m), 1670 (s), 1640 (s), 1380 (m), 1300 cm^{-1} (s); mass spectrum m/e (rel intensity) 39 (90), 40 (70), 41 (57), 42 (33), 43 (69), 44 (100), 45 (30), 51 (13), 53 (27), 55 (67), 57 (44), 59 (42), 69 (60), 70 (12), 71 (40), 85 (12), 87 (22), 97 (18), 98 (73), 99 (25).

Epoxyformate ester **6** (15%) was identified on the basis of the following spectral properties: nmr ($CDCl_3$) δ 8.0 (s, 1 H), 2.2 (s, 3 H), 1.5 (s, 6 H); ir (CCl_4) 1715 (s), 1185 cm^{-1} (s); mass spectrum m/e (rel intensity) 39 (38), 40 (41), 41 (36), 42 (39), 43 (96), 57 (60), 58 (10), 59 (100), 60 (20), 61 (14), 69 (37), 70 (64), 85 (20), 87 (50), 102 (27).

The mass spectrum of **6** did not reveal a parent ion at m/e 130 but exhibited a major peak at M − 28 (m/e 102), characteristic of formate esters.[20] Under the oxidation conditions **3b** afforded only **6** and unreacted **3b**.

MCPBA Oxidation of 1c. To a stirred solution of 0.530 g (5.52 mmol) of tetramethylcyclopropene (**1c**) in 6 ml of dichloromethane at 0° was added in one portion 0.950 g (5.52 mmol) of MCPBA. A starch–iodide test 15 min after initiation of the reaction revealed complete consumption of oxidant. The white precipitate of *m*-chlorobenzoic acid was filtered and the clear, colorless filtrate was analyzed by glpc (same column as above for **1b**; column temperature 130°), which revealed the presence of two components in the ratio of 65:35. The dichloromethane solution was extracted twice with 5 ml of 5% $NaHCO_3$ solution and dried over anhydrous $MgSO_4$. After removal of the solvent *in vacuo* the resultant oil was subject to preparative glpc under the same conditions as described above. The structures of the isolated components were assigned on the basis of the following spectral characteristics.

α-Methylmesityl oxide (**3c**, 65%) exhibited nmr ($CDCl_3$) δ 2.23 (s, 3 H), 1.87 (s, 6 H), 1.78 (s, 3 H); ir ($CHCl_3$) 2910 (m), 1685 (s), 1625 (m), 1450 (m), 1380 (m), 1355 (m), 1280 (m), 1200 (m), 1130 (m), 1083 cm^{-1} (m); mass spectrum m/e (rel intensity) 39 (38), 41 (100), 43 (90), 53 (16), 55 (11), 67 (10), 69 (100), 97 (52), 112 (78).

3,4-Dimethyl-3,4-epoxypentan-2-one (**7**, 35%) had nmr ($CDCl_3$) δ 2.22 (s, 3 H), 1.45 (s, 3 H), 1.37 (s, 3 H), 1.23 (s, 3 H); ir ($CHCl_3$) 1705 (s), 1380 (m), 1100 cm^{-1} (m); mass spectrum m/e (rel intensity) 39 (32), 40 (10), 41 (77), 42 (23), 43 (97), 44 (13), 45 (10), 53 (17), 55 (26), 57 (50), 58 (10), 59 (12), 71 (100), 85 (18), 86 (93), 88 (15), 113 (73), 128 (7).

The reaction of **3c** with MCPBA under the oxidation conditions afforded **7**.

Competitive MCPBA Oxidation of 1b and 1c. A solution of 0.044 g (0.46 mmol) of tetramethylcyclopropene (**11c**) and 0.038 g (0.046 mmol) of 1,3,3-trimethylcyclopropene (**1b**) in 0.5 ml of dichloromethane contained in a 5-ml round-bottomed flask was cooled to 0° in an ice bath. MCPBA (0.067 g, 0.39 mmol) was then added in one portion with stirring. A strarch–iodide test indicated that all of the oxidant was consumed after 30 min. The crude reaction mixture was analyzed directly for products and remaining reactants by glpc on a 0.25 in. × 15 ft aluminum column packed with 15% SE-30 on Chromosorb W, AW-DMCS, 80/100 mesh (column temperature 20° for reactants and 70° for products). Disc integration of the product and reactant peaks indicated a sixfold preference in the rate of oxidation of **1c** relative to **1b**.

MCPBA Oxidation of 1,2,3-Tri-*tert*-butylcyclopropene (10). To a stirred solution of 0.208 g (1.00 mmol) of **10** in 10 ml of dichloromethane was added 0.618 g (4.00 mmol) of MCPBA at room temperature. After the initial exothermic reaction subsided, the mixture was stirred at room temperature for 2 hr. The crude reaction mixture was then transferred to a separatory funnel and extracted with two 15-ml portions of ice-cold 5% aqueous $NaHCO_3$. The organic layer was dried over anhydrous magnesium sulfate and the solvent was removed *in vacuo* to give a pleasant-smelling oil which revealed ir absorption bands at 1815, 1745, and 1700 cm^{-1} (CCl_4). The nmr spectrum in CCl_4 revealed the presence of two components: mixed anhydride **12** of pivalic and *m*-chlorobenzoic acids and epoxy ketone **14**, derived from enone **13**, the major primary oxidation product of di-*tert*-butylacetylene (**11**). The ir and nmr absorptions of the anhydride were identified by comparison with spectra obtained from an authentic sample prepared by the reaction of *m*-chlorobenzoic acid with pivaloyl chloride in ether–pyridine. Since the mixed anhydride failed to elute from glpc columns, it was removed from the crude reaction mixture by extraction with aqueous sodium carbonate. The remaining epoxy ketone **14** was purified by preparative glpc on a 0.25 in. × 10 ft aluminum column packed with 15% SE-30 on Chromosorb W, AW-DMCS, 80/100 mesh (column temperature 130°) to afford a white, crystalline solid: mp 40°; nmr (CCl_4) δ 1.48 (s, 3 H), 1.35 (s, 3 H), 1.25 (s, 9 H), 1.20 (s, 3 H); ir (CCl_4) 2960 (s), 2870 (m), 1700 (vs), 1490 (s), 1380 (s), 1130 (s), 1110 (m), 1040 (m), 1000 (m), 800 (m), 835 cm^{-1} (m); uv (EtOH) 292 mμ (ε 40), 285 (39); mass spectrum m/e (rel intensity) 41 (40), 43 (55), 44 (11), 57 (100), 69 (10), 71 (19), 85 (20), 86 (21), 95 (7), 97 (6), 103 (7), 155 (10), 170 (1.5).

Anal. Calcd for $C_{10}H_{18}O_2$: C, 70.55; H, 10.66. Found: C, 70.90; H, 10.57.

Epoxy ketone **14**, isolated from the MCPBA oxidation of cyclopropene **10**, proved to be identical in every respect with the product derived from the MCPBA oxidation of di-*tert*-butylacetylene (**11**). When **10** was oxidized with only 1 equiv of MCPBA, **11** was detected by nmr [δ 1.18 (s)] and glpc comparison with an authentic sample. By increasing the quantity of peroxy acid used, secondary oxidation of **11** to enone **13** and epoxy ketone **14** was observed.

MCPBA Oxidation of 10 in the Presence of Perchloric Acid. To a stirred solution of 0.083 g (0.48 mmol) of MCPBA in 3 ml of dichloromethane at 0° was added 0.072 g (0.50 mmol) of 70% perchloric acid. Then, with continued stirring at 0°, 0.091 g (0.43 mmol) of **10** in 0.2 ml of dichloromethane was added dropwise. After stirring at 0° for 30 min the dichloromethane was removed *in vacuo* and 10 ml of ether was added to the residue. The resultant white solid was filtered and recrystallized from acetone to afford tri-*tert*-butylcyclopropenyl perchlorate (**17**, 0.095 g, 72%). The structure of **17** was established by comparison of its nmr spectrum [$CDCl_3$, δ 1.58 (s)] and melting point (248–250° dec) with those of an authentic sample.

The reaction of MCPBA–$HClO_4$ with cyclopropenes **10** and **18** was conducted in nmr tubes at normal probe temperature (~40°). The cyclopropene was added *via* syringe to a solution of excess MCPBA and HIO_4 in dichloromethane and the progress of the reaction was followed by nmr spectroscopy. The cyclopropenyl perchlorate salts **17** and **26** were detected by their characteristic absorption at δ 1.58 and 1.67, respectively.

MCPBA Oxidation of Tri-*tert*-butylcyclopropenyl Perchlorate (17).[21] A 5-ml round-bottomed flask was charged with 1 ml of dichloromethane, 0.026 g (0.14 mmol) of sodium *m*-chlorobenzoate, and 0.025 g (0.14 mmol) of MCPBA. To this mixture was added in one portion 0.044 g (0.14 mmol) of cation **17**. An exothermic reaction ensued which was complete within 5 min. After stirring for 15 min at room temperature the precipitate was removed by filtration and the clear, colorless filtrate was examined by nmr. The alkyl region revealed two singlets at δ 1.37 (9 H) due to the *tert*-butyl group of mixed anhydride **12** and a singlet at δ 1.18 (18 H) due to di-*tert*-butylacetylene (**11**). The presence of **11**

was further established by glpc. Extraction of the crude reaction mixture with cold, aqueous $NaHCO_3$ left only the mixed anhydride **12** and acetylene **11**. Removal of the solvent and the highly volatile **11** left the anhydride, whose ir spectrum was superimposable on that of an authentic sample. Triphenyl-[22] and trimethylcyclopropenyl perchlorate[23] reacted similarly under essentially identical conditions.

MCPBA Oxidation of 1-Phenyl-2,3-di-*tert*-butylcyclopropene (18). To a stirred solution of 0.77 g (3.4 mmol) of **18** in 10 ml of dichloromethane at room temperature was added 0.96 g (5.6 mmol) of MCPBA. The mixture was stirred for 4 hr at room temperature, by which time a starch–iodide test revealed the complete consumption of oxidant. The reaction mixture was transferred to a separatory funnel, extracted with three 5-ml portions of 5% aqueous $NaHCO_3$, and dried over anhydrous $MgSO_4$. Solvent removal afforded a colorless oil which was shown to consist of three components by glpc on a 0.25 in. × 5 ft aluminum column packed with 20% Carbowax 20M on Chromosorb W, AW-DMCS, 80–100 mesh (column temperature 160°). The components were isolated by preparative glpc and identified as epoxy ketone **14** (10%) by its retention time and comparison of spectra, phenyl *tert*-butylacetylene (**22**, 35%) by its retention time and comparison of spectra with those of an authentic sample, and finally enone **19** (55%), mp 74–76° (pentane), on the basis of the following data: nmr (CCl_4) δ 0.92 (s, 9 H), 1.07 (s, 9 H), 5.54 (s, 1 H), 7.20–7.60 (m, 3 H), 7.80–8.05 (m, 2 H); ir (CCl_4) 2950 (s), 2900 (m), 2865 (m), 1665 (s), 1475 (m), 1450 (m), 1220 (s), 810 (s), 596 cm^{-1} (s); mass spectrum *m/e* (rel intensity) 41 (22), 43 (10), 57 (32), 77 (34), 83 (10), 105 (100), 173 (14), 187 (6), 229 (43), 244 (13); uv (EtOH) 249 mμ (ϵ 12,100).

MCPBA Oxidation of Phenyl-di-*tert*-butylcyclopropenyl Perchlorate (26).[10] The procedure for the reaction of **26** with MCPBA and sodium *m*-chlorobenzoate in methylene chloride was similar to that described for **17**. Glpc and spectral analysis demonstrated that acetylenes **11** and **22** were produced in the expected ratio of 1:3.5. α,β-Unsaturated ketone **19** was not detected in the reaction mixture.

MCPBA Oxidation of 1-Phenyl-2,3-di-*tert*-butyl-3-methylcyclopropene (27). To a solution of 0.068 g (0.28 mmol) of **27** in 2.5 ml of dichloromethane was added 0.098 g (0.57 mmol) of MCPBA and the mixture was stirred at room temperature for 2 weeks. Intermittent glpc analysis of the reaction mixture indicated the slow disappearance of **27** with the concomitant appearance of product. At the end of the 2-week period, the crude reaction mixture was diluted with 5 ml of dichloromethane and extracted with three 3-ml portions of 5% aqueous $NaHCO_3$. After the organic layer was dried over anhydrous $MgSO_4$, the solvent was removed under reduced pressure and the resultant residue was dissolved in 1 ml of hexane. The white crystals which separated out were collected by suction filtration and recrystallized twice from hexane to affort 20 mg of a compound, mp 123–124°, which was identified as epoxy ketone **29** on the basis of the following data: nmr (CCl_4) δ 0.83 (s, 9 H), 1.01 (s, 9 H), 1.57 (s, 3 H), 7.20–7.45 (m, 3 H), 7.70–7.95 (m, 2 H); ir (CCl_4) 3065 (w), 2980 (s), 2920 (m), 2880 (m), 1690 (s), 1595 (m), 1480 (m), 1445 (m), 1395 (m), 1375 (m), 1370 (m), 1240 (s), 1232 (s), 860 (s), 697 cm^{-1} (s); mass spectrum *m/e* (rel intensity) 41 (78), 43 (68), 44 (11), 55 (13), 57 (100), 69 (25), 77 (73), 85 (27), 105 (100), 106 (37), 134 (16), 157 (14), 173 (31), 203 (13), 217 (100), 218 (206), 258 (2), 274 (0.25); uv (EtOH) 249 mμ (ϵ 11,600).

Hydrogen Peroxide Oxidation of Cyclopropenyl Cations. The reaction of cyclopropenyl cations with hydrogen peroxide and base was conducted under a variety of conditions. Under one set of conditions, 1 equiv of cation was added to 1 equiv of 90% hydrogen peroxide in the presence of 1 equiv of a base such as sodium *m*-chlorobenzoate in dichloromethane at room temperature. The reactions were exothermic and complete within 5 min and gave only the corresponding acetylene and carboxylic acid in quantitative yield. Other bases such as sodium carbonate and sodium acetate were also employed. More polar solvents such as nitromethane and methanol were used in some instances where greater solubility was desired.

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