CH_3), 4.13 (s, 2 H of CH_2), 6.80 (s, 2 H of mesitylene moiety), 6.67 ("d," H_e, J_{ef} = 7.5 Hz), 6.93 ("d," H_g, $J \cong 7$ Hz), 7.32 (m, H_f, $J \cong 7.5$ and 2 Hz), 8.42 ("d," H_h) (H_e, H_f, H_g, and H_h are presumed to be at positions 6′, 5′, 4′, and 3′ of the pyridine ring, respectively); ir (neat) 3080–2850, 1610, 1580, 1565, 1465, 1430, 1370, 1200, 1145, 1090, 1048, 1030, 990, 850, 750 cm^{-1}; mass spectrum m/e (rel intensity) 212 (6), 211 (32), 196 (100), 181 (34), 119 (25), 91 (25), 77 (21), 51 (32), 39 (37), m* 182 (211 → 196), 167.2 (196 → 181), doubly charged 105.5, 104.5, 97.5, 96.5, 90.5, 89.5.

Anal. Calcd for $C_{15}H_{17}N$: C, 85.26; H, 8.11; N, 6.63. Found:[16] C, 85.13; H, 8.27; N, 6.71.

4-Mesitylmethylpyridine (2), alternatively named as 2,4,6-trimethyl-4′-azadiphenylmethane, had bp 138–139° (0.75 Torr); mp 40–41° (from ether); nmr (CCl_4) δ 2.10 (s, 6 H of *o*-CH_3's), 2.22 (s, 3 H of *p*-CH_3), 3.88 (s, 2 H of CH_2), *ca.* 6.8 (s, 2 H of mesitylene moiety), *ca.* 6.82 (d, 2 H), 8.28 (d, 2 H, J = 6 Hz); ir (neat) 3080–2860, 1601, 1480, 1440, 1410, 1370, 1215, 1068, 1028, 993, 882, 853, 780, 722, 603 cm^{-1}; mass spectrum m/e (rel intensity) 212 (16), 211 (100), 196 (78), 181 (27), 133 (67), 119 (37), 91 (16), 77 (14), m* 182 (211 → 196), 167.2 (196 → 181), doubly charged 105.5, 104.5, 103.5, 97.5, 96.5, 90.5, 89.5, 83.5, 82.5.

Anal. Calcd for $C_{15}H_{17}N$: C, 85.26; H, 8.11; N, 6.63. Found:[16] C, 85.23; H, 8.19; N, 6.80.

Registry No. 2, 43136-90-9; 2-picolyl anion, 18860-16-7; 4-picolyl anion, 18860-18-9; 2-benzylpyridine, 101-82-6; 4-benzylpyridine, 2116-65-6; 4-benzhydrylpyridine, 3678-72-6; 2-mesitylmethylpyridine, 43136-96-5.

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(2) Grateful recipient of a fellowship, 1971–1972, from the Schweizerische Stiftung fur Stipendien auf dem Gebiete der Chemie.

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Thermolysis of Peresters. The Relative Stability of Allylic and Propargylic Radicals

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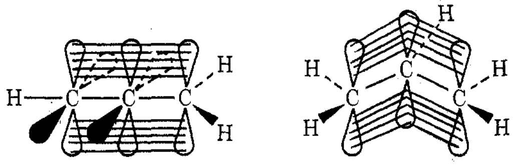
tert-Butyl peroxy-2,2-dimethylbutenoate (7) undergoes thermolysis in cumene with $\Delta H^* = 24.0 \pm 0.3$ kcal mol^{-1} and $\Delta S^* = -1.0 \pm 1.0$ eu while *tert*-butyl peroxy-2,2-dimethylbutynoate (8) shows activation parameters of $\Delta H^* = 27.1 \pm 0.6$ kcal mol^{-1} and $\Delta S^* = 4.7 \pm 1.8$ eu. The difference in activation enthalpies is interpreted in terms of polar effects and not on the basis of radical stabilities. Other evidence suggests that propargylic radicals are slightly less stable than allylic radicals, but the difference is too small to measure accurately by present techniques.

A propargyl radical (1) can be regarded as an allyl radical (2) with an additional π bond perpendicular to the plane of the orbital bearing the odd electron. In view of the geometric change imposed by this extra bond, one might ask whether the two species differ in stability. A more stable radical will have a greater resonance energy (RE), which is defined for our purposes as the difference between the bond dissociation energy (BDE) of an appropriate saturated compound and that of the unsaturated one.



1 2

$$\text{RE(allyl)} = \text{BDE(propyl H)} - \text{BDE(allyl H)}$$

$$\text{RE(propargyl)} = \text{BDE(propyl H)} - \text{BDE(propargyl H)}$$

Bond dissociation energies and hence radical stabilities have been determined by such "physical" methods as mass spectroscopic appearance potentials,[2,3,13] iodine-catalyzed equilibration,[4,11,12] pyrolytic techniques,[7,14] and shock-tube studies.[9] In surveying some of the results for allylic and propargylic radicals (*cf.* Figure 1) two general trends can be observed: a lower resonance energy in the more recent measurements and slightly less stabilization for propargylic than for allylic radicals. However, the latter observation is tenuous in view of the experimental uncertainties involved.

Another general approach to the question of radical stabilities assumes that the activation energy for thermolysis of a radical precursor reflects the stability of the radical.[15] Two classes of organic molecules which exhibit such a trend are azo compounds and peresters; in fact, some information regarding the stability of allylic and propargylic radicals is available from studies of their thermolysis. In 1967, Martin and Sanders[16] reported that perester 3 decomposed with an activation enthalpy 4.0 kcal mol^{-1} less than that of the analagous propargylic perester 4 and concluded that "the 2-butenyl radical is about 4 kcal mol^{-1} more stable than the 2-butynyl radical." More recently, one of us[17] found that azo compounds 5 and 6 decomposed with nearly the same activation enthalpy and suggested that the resonance energy of the dimethylallyl radicals differed little from that of dimethyl-

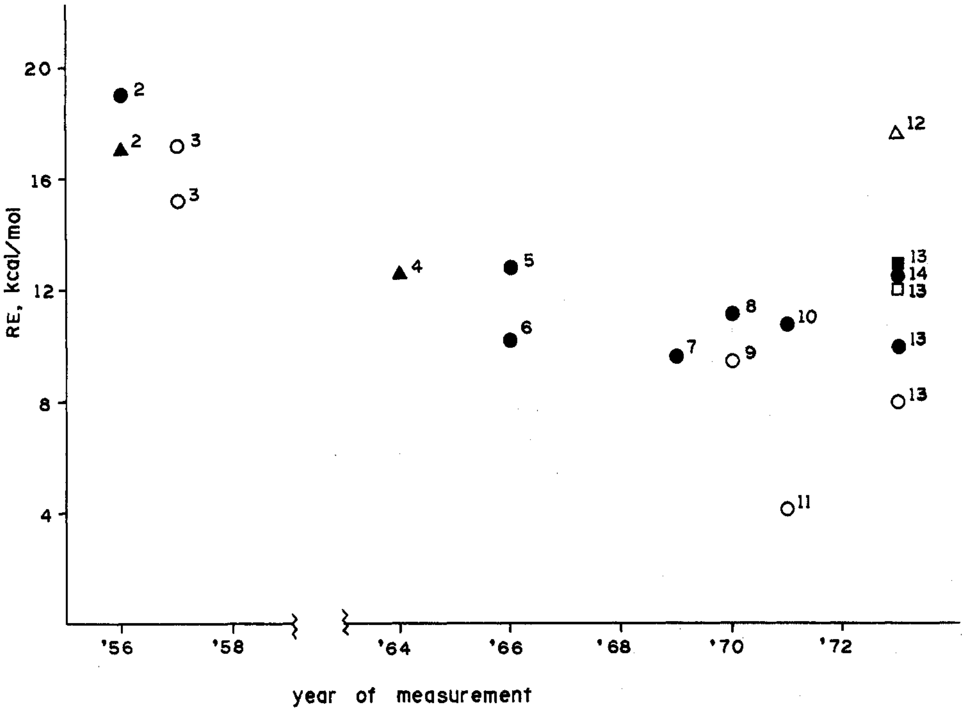


Figure 1. Resonance energy (RE) of allylic and propargylic radicals: ●, allyl; ○, propargyl; ■, 1,1-dimethylallyl; □, 1,1-dimethylpropargyl; ▲, 1-butenyl; △, 2,3-dimethylbutenyl. References are given to the right of each point.

Table I
Kinetic Data for Thermolysis of Peresters in Cumene

Compd	Temp, °C	Concn, M	k, sec^{-1} × 10^4
7	42.42	0.085	0.904
	44.88	0.090	1.232
	50.25	0.120	2.296
	50.30	0.030	2.349
	54.75	0.090	4.033
	57.95	0.085	5.660
8	44.85	0.096	0.1874
	50.10	0.092	0.3609
	54.79	0.092	0.6777
	60.20	0.090	1.306
	63.81	0.090	2.124
$PhCH_2CO_3Bu$-*t*	79.61	0.11	0.690[a]
	79.6	0.1	0.677[b]
	79.6	0.06	0.721[c]
	79.7		0.868[d]

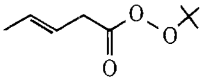
[a] This work. [b] Reference 20. [c] Reference 21. [d] Reference 22.

Table II
Activation Parameters for Perester Thermolysis

Compd	ΔH^*, kcal mol^{-1}	ΔS^*, eu	Ref
7	24.03 ± 0.3	−1.0 ± 1.0	This work
8	27.10 ± 0.6	4.7 ± 1.8	This work
3	25.8	−2.5	16
4	29.8	5.9	16

propargyl radicals. This discrepancy seemed too large to explain on the basis of the number of methyl groups.

On the assumption that the perester experiments could be complicated by induced decomposition or double-bond migration,[18] we prepared two new peresters 7 and 8, which are exactly analogous to the azo compounds 5 and 6. The propargylic perester again showed a greater activation enthalpy, in support of the earlier experimental work.[16] However, we propose that this trend is related less to radical stability than it is to polar effects in perester thermolysis. If allylic radicals are more stable than propargylic, the difference is too small to measure by present techniques.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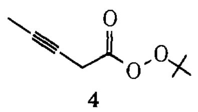
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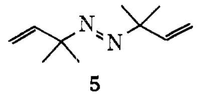
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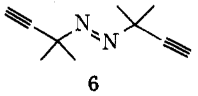
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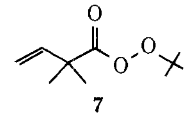
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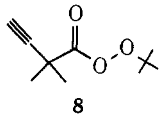
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Results

Peresters 7 and 8 were synthesized by treating the appropriate acid chlorides with the sodium salt of *tert*-butyl hydroperoxide in methylene chloride and were purified by column chromatography. Their spectral properties, given in the Experimental Section, were consistent with the assigned structure and indicated high purity. Despite the ominous combination of an acetylene with a peroxide linkage in 8, no difficulty was encountered in handling this material. The carboxylic acid which led to 7 was prepared by carbonation of the Grignard reagent from 3-chloro-3-methyl-1-butene. At the outset of this work, 2,2-dimethylbutynoic acid was an unknown compound. It was prepared for other work in this laboratory, in which connection its synthesis will be published.[19]

Decomposition of 7 and 8 in degassed cumene was followed by carbon dioxide evolution on an automated constant-volume kinetic apparatus. To ensure the reliability of our technique, the rate constant for decomposition of *tert*-butyl phenylperacetate was determined in the same manner as those of 7 and 8 and the value obtained was in excellent agreement with previously reported work.[20-22] The results are shown in Tables I and II.

Induced decomposition is a potential problem in many perester thermolyses and may lead to incorrect activation parameters.[23,24] Unlike the peresters studied by Martin and Sanders,[16] compounds 7 and 8 possess no hydrogens α to the carbonyl group, thereby precluding a known mechanism for induced decomposition which begins with abstraction of these hydrogens. It should be noted that the *gem*-dimethyl group in 7 and 8 also prevents double-bond migration, a problem encountered in another β,γ-unsaturated perester.[18] Relatively low concentrations of the peresters were decomposed in cumene as solvent to decrease the probability of radical attack on the starting material. No dependence of rate on initial concentration was observed and the first-order plots were linear to at least 75% reaction. The activation plot for 7 was nicely linear but, in the case of 8, either the fastest or the slowest point was slightly off the line. Even if induced decomposition were the cause of this possible curvature, it would not account for the higher activation enthalpy of 8 than 7; in fact, it is more important to look for this complication in 7. If induced decomposition were to occur by attack of radicals at the peroxide linkage,[25] formation of carbonyl-containing products would be expected. This possibility was ruled out by removing most of the cumene *in vacuo* from completely decomposed samples of 7 and taking an ir spectrum of the residue. The absence of carbonyl bands also argues against lactone formation by direct reaction of the vinyl group with the peroxide linkage or by cyclization of the intermediate acyloxy radical.

Discussion

A Polanyi plot[26] provides a convenient way of determining the degree to which the activation energy for thermolysis of a radical precursor reflects the stability of the radical. This treatment is based upon the premise that the activation energy for production of R· is proportional to the R–H bond dissociation energy. Plots for azo compounds and peresters are shown in Figures 2 and 3, respectively. The large amount of scatter in Figure 2 may be attributed to (a) induced decomposition in some of the gas-phase studies on the lower azoalkanes;[27-40] (b) inclusion of values obtained in different laboratories over a span of 40 years; (c) possible steric effects; and (d) uncertainty in bond dissociation energies. Despite these problems, the slope of the graph appears to be approximately unity, showing that azo compound activation energies are very sensitive to stability of the incipient radical.

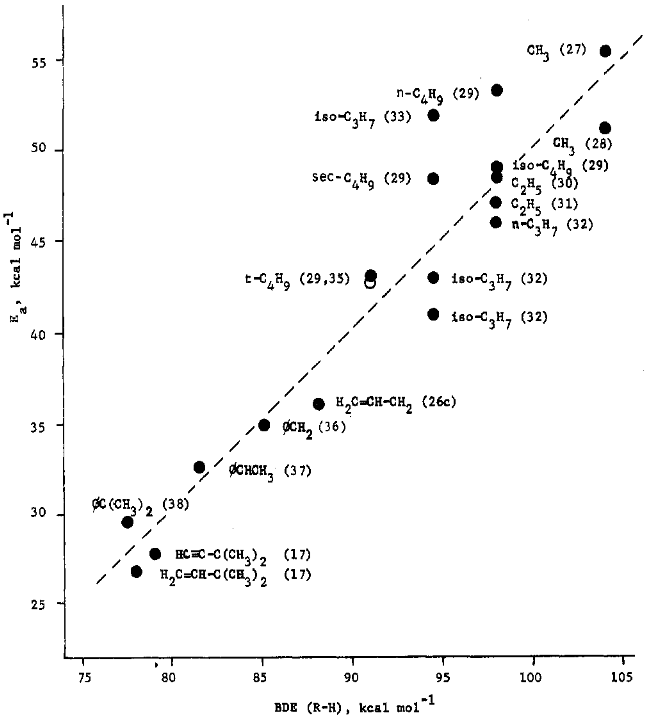


Figure 2. Polanyi plot for azoalkanes. Bond energies are from ref 13 and 26b and from data in ref 8. Activation energies are from the references in parentheses.

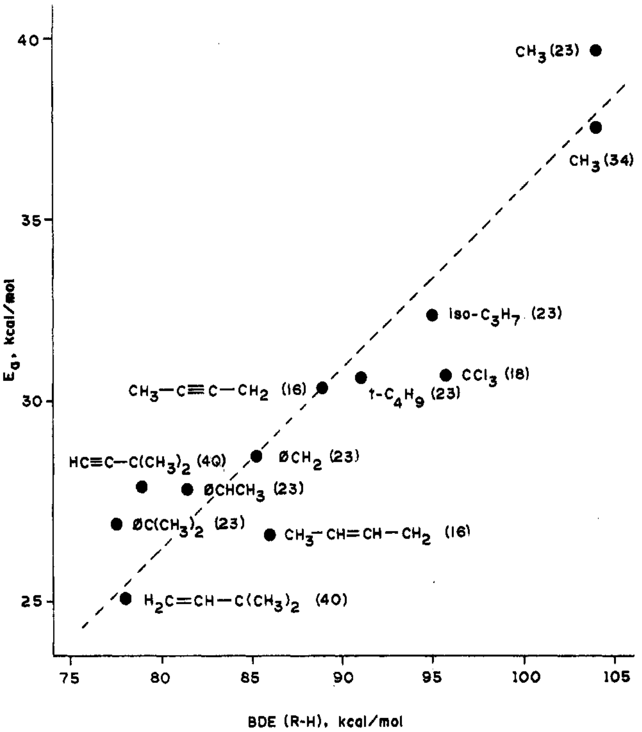
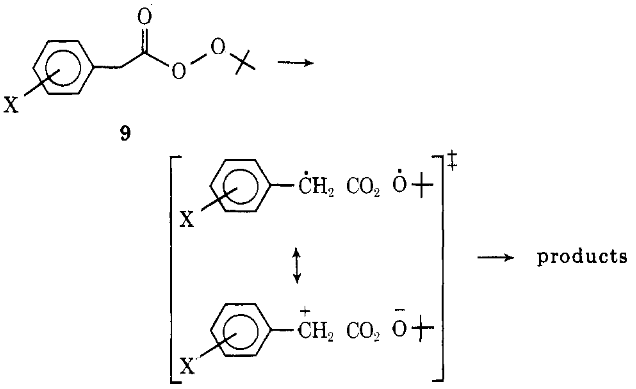


Figure 3. Polanyi plot for *tert*-butyl peresters. See caption for Figure 2.

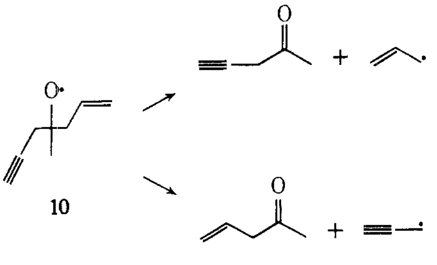
The perester plot also shows considerable scatter but the slope is about half that of the azoalkanes. Thus, although there must be some C–CO$_2$ bond breaking in the transition state for perester thermolysis, the difference in activation energy for two given peresters is considerably less than the difference in alkyl radical stability. The mechanism of perester thermolysis has been investigated by a variety of other techniques and the consensus is that the transition state for decomposition is characterized by only minimal stretching of the C–CO$_2$ bond.[15,20,41,42]

If one accepts the conclusion from Figure 1 that allylic radicals are of similar stability to propargylic radicals and the argument that peresters are not very sensitive to radical stability, how can the higher activation enthalpy for the propargylic peresters be explained? A possible answer is based upon the known effect of substituent polarity on their thermolysis rates;[23,39] for example, the series of substituted *tert*-butyl phenylperacetates 9 exhibits ρ = −1.20.[43] An acetylenic group is far more effective at in-



ductive electron withdrawal than a vinyl group, as shown by their σ_I values of 0.35 and 0.09, respectively.[44] This inductive effect is consistent with the considerably slower solvolysis rate of propargylic halides compared to analogous allylic halides.[45] Thus in the transition state for perester thermolysis, development of positive charge at the carbon α to the carbonyl group is inhibited by the electron-withdrawing nature of the triple bond. We suggest that this effect, and not that of radical stability, is responsible for the higher activation enthalpy of the propargylic compared to the allylic peresters. Operation of a polar effect is not inconsistent with the idea of minimal C-CO_2 bond breaking in the transition state because (a) there must be *some* C-CO_2 bond breaking or Figure 3 would show zero slope and (b) the degree of such bond breaking should depend upon the stability of the incipient carbon radical,[18] which, in the present case, is high. In contrast to peresters, azo compounds show virtually no effect of substituent polarity,[46] so that the data of Figure 2 may be taken as an indication of similar stability for allylic and propargylic radicals.

Since neither physical methods nor azo compound activation energies are sufficiently accurate to detect bond energy differences on the order of 1 kcal mol^{-1}, some other approach must be devised. Competition methods immediately come to mind; for example, the products of β scission of radical **10** might tell which radical is more stable. Unfortunately, this process is again influenced more by polar effects than by radical stability.[42] It has been recently reported[47] that allyl and propargyl radicals are formed with about the same ease when triethylsilyl radicals were allowed to compete for their halides. This process exhibits a polar effect opposite to that of peresters and more quantitative studies may prove interesting.[48]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Experimental Section

tert-**Butyl Peroxy-2,2-dimethylbutenoate (7).** A 5.6-g (50 mmol) portion of anhydrous sodium *tert*-butylperoxide[49] prepared from sodium hydride and 95% *tert*-butyl hydroperoxide was suspended in 210 ml of methylene chloride at −5 to −10°. A solution of 4.8 g (36 mmol) of 2,2-dimethylbutenoyl chloride in 70 ml of methylene chloride was added over a 15-min period. The solution was stirred at −5° for 1 hr, overnight at 5°, and finally at room temperature for 1 hr. The solid was filtered off and the filtrate was evaporated. The residue was taken up in ether, shaken with 15 ml of cold 10% aqueous sodium hydroxide followed by three washings with water, and dried ($MgSO_4$), and solvent was evaporated to give 4.1 g of clear oil. The product was purified by chromatography with pentane on 40 g of 100-200 mesh Florisil maintained at 10° by a refrigerated jacket: ir (CCl_4) 3110 (w), 1770 (s), 1638 (m) and 1088 cm^{-1} (s); nmr (CCl_4) δ 1.27 (s, *tert*-butyl), 1.32 (s, *gem*-dimethyl), 5.0 (m, terminal CH_2), and 5.9 (q, vinyl).

tert-**Butyl Peroxy-2,2-dimethylbutynoate (8).** A 3.1-g portion of the sodium salt of *tert*-butyl hydroperoxide was treated with 2.7 g of 2,2-dimethylbutynoyl chloride as above. When the reaction was complete, 50 ml of water was added to dissolve the solids and the aqueous layer was discarded. The remainder of the work-up was as described above and yielded 2.32 g of clear oil: ir (CCl_4) 3330 (s), 1778 (s), and 1100 cm^{-1} (s); nmr (CCl_4) sharp singlets at δ 1.30 (*tert*-butyl), 1.48 (*gem*-dimethyl), and 2.20 (acetylenic hydrogen).

Kinetics. The CO_2 yield from 0.027 M **7** in toluene was determined early in the course of this work as 80.2%. Kinetics were carried out by dissolving the peresters in cumene at a concentration of 0.08-0.12 M. For each run, about 1 ml of the solution was degassed by three freeze-thaw cycles and about 12 cm pressure of nitrogen was admitted. The automated kinetic apparatus employed operated at constant volume and provided a plot of pressure *vs.* time. Evolution of CO_2 broke an electrical contact on one side of a manometer and a motor-driven mercury syringe restored contact. A linear potentiometer sensed the position of the syringe and provided a signal to a chart recorder. Points were read off the resulting plot and evaluated by a weighted least-squares computer program.

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Registry No. 7, 49586-04-1; **8,** 49586-05-2.

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

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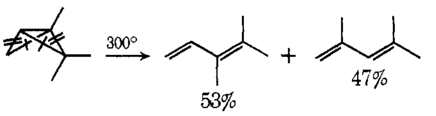
Unhindered alkyl cyclopropenes **1** ($R_1 \neq R_2$; $R_3 = R_4$) unsymmetrically substituted at the carbon–carbon double bond undergo oxidation with *m*-chloroperoxybenzoic acid (MCPBA) in methylene chloride to afford two α,β-unsaturated carbonyl compounds, **3** and **4**, probably *via* unstable 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]

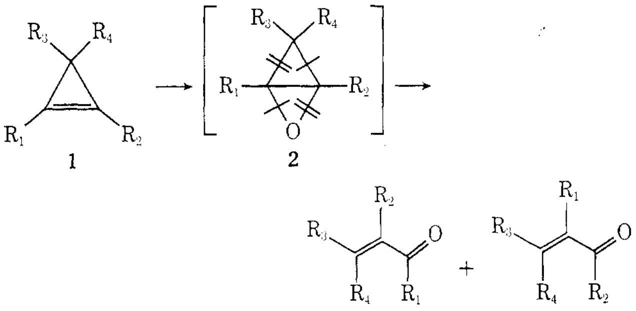


(1)

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