The following 1-methylcyclobutanols were prepared by exchange with D_2O in the mass spectrometer inlet system: **1-methylcyclobutanol-*O-d* (5g)** (75% d_1, 25% d_0); **1-methylcyclobutanol-*2,2,4,4-d$_4$-O-d*** **(5i)** (41% d_5, 55% d_4, 3.6% d_3); **1-methyl-*d$_3$*-cyclobutanol-*O-d*** **(5b)** (73% d_4, 22% d_3, 5% d_2).

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Vinyl Radicals. V. The Relative Reactivity of the 2-Methylpropenyl Radical

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Abstract: The thermal decompositions of 3-ethyl-2-pentenoyl and 3-methyl-2-butenoyl peroxides and *tert*-butyl peresters have been studied as possible sources of 2-ethyl-1-butenyl and 2-methylpropenyl radicals. Intermediate acyloxy radicals are formed which partition between intramolecular H abstraction and decarboxylation. 2-Methyl-2-butenoyl peroxide is shown to be a useful source of 2-methylpropenyl radicals for experiments competing benzylic hydrogen donors (k_H) *vs.* carbon tetrachloride (k_{Cl}) at 78°. The relative reactivity of the 2-methylpropenyl radical toward benzylic hydrogens is primary : secondary : tertiary 1.0 : 3.9 : 8.6, with a marked preference for chlorine abstraction, k_H/k_{Cl} for toluene = 0.048. The effects of para substituents on the reactivities of substituted toluenes toward 2-methylpropenyl radicals are small.

Vinyl radicals are readily available from the thermal and photochemical decompositions of the corresponding α,β-unsaturated peresters and diacyl peroxides[1-3] and as intermediates in free radical additions to alkynes.[4-8] The details of these reactions and the behavior of the vinyl radicals have been studied in some detail. The vinyl systems show typical radical reactions such as displacement on hydrogen,[1-2] halogen,[3] and sulfur,[9] and addition to aromatic rings.[10] Because vinyl radicals represent a fundamental structural type of carbon radical, it seemed worthwhile to seek quantitative data on their chemical behavior. This paper reports a study of the relative reactivity of the 2-methylpropenyl radical toward a series of benzylic hydrogen donors and carbon tetrachloride. Similar reactivity studies are already available for a large number of other types of free radicals.[11-20] The experimental technique involves a competition between H donor (reaction 1) and Cl donor (reaction 2) for the vinyl radical (V·). Under favorable circumstances,[14] the ratio of the yields of products is related to the ratio of rate constants of the competing reactions (3). The assumptions involved in the use of eq 3 will be examined in connection with the pertinent experimental data.

$$V\cdot + RH \xrightarrow{k_H} VH \qquad (1)$$

$$V\cdot + CCl_4 \xrightarrow{k_{Cl}} VCl \qquad (2)$$

$$\frac{k_H}{k_{Cl}} = \frac{[VH][CCl_4]}{[VCl][RH]} \qquad (3)$$

The Decomposition of 3-Methyl-2-butenoyl Peroxide (I). Product Studies. The peroxide is readily obtained by the reaction of 3-methyl-2-butenoyl chloride with urea peroxide.[21] The purified material is a crystalline solid and the nmr spectrum reveals no trace of the β,γ isomer. The peroxide in cumene at 110° gives CO_2 (45%),[22] dicumyl, and an acidic fraction whose weight accounts for 59% of the weight of the starting peroxide. Decomposition in carbon tetrachloride at 110° also gives an acidic fraction as the major reaction product (67% of the weight of the starting peroxide). The yields of vinyl radical products from the peroxide at 78 and 110° in cumene and carbon tetrachloride are given in Tables I and II, respectively.

It is clear from the data that the decomposition of peroxide I involves more than simple oxygen–oxygen homolysis and subsequent decarboxylation of the acyloxy radicals to give vinyl radicals. Most striking are the low yields of carbon dioxide and vinyl radical prod-

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[22] Yields of products from peroxides are based on a stoichiometry of 2 mol of product/mol of peroxide.

Table I. Decomposition of I in Cumene

[I], *M*	*T*, °C	*t*, hr	% yield of isobutene
0.107	110	4	23
0.021	110	4	27
0.107	78	12	15
0.021	78	12	19

Table II. Decomposition of I in Carbon Tetrachloride[a]

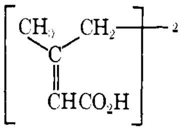
			% yield	
[I], *M*	*T*, °C	*t*, hr	$CHCl_3$	1-Chloro-2-methyl-propene-1
0.019	110	4	7.8	42
0.019[b]	110	4	8.5	42
0.097	110	4	7.7	36
0.097[b]	110	4	7.0	36
0.019	78	12	7.0	31
0.097	78	12	6.5	24
0.097[b]	78	12	6.7	25
0.050[c]	78	12	7.0	25

[a] Isobutene was not detected in any of these decompositions. The limit of detectability corresponded to 0.25% yield. [b] 0.25 *M* water added before decomposition. [c] 0.033 *M* 3-methyl-2-butenoic acid added before decomposition.

ucts and the high yields of acidic products. The acidic fractions from decompositions of I in cumene and carbon tetrachloride are viscous oils. The spectral characteristics of the oils are similar, giving evidence for carboxylic acid, olefinic, and allylic structural units. In addition, the acidic fraction from cumene gives ir and nmr evidence for the incorporation of cumyl fragments and the ir spectrum of the acidic fraction from carbon tetrachloride shows incorporation of trichloromethyl units. Small amounts of the same crystalline solid were isolated from both acidic fractions. This material gives nmr and mass spectra in accord with structure II. The mass spectrum shows the highest peak at *m*/*e* 180 (II − H_2O), a major peak at 152 (−CO), and the base peak at 107 (−HC_2O_3), in accord with initial formation of the anhydride of II.[23] Further insight into the nature and source of the acidic products comes from abortive experiments involving other potential vinyl radical sources.

$[(CH_3)_2C{=}CHCO_2]_2$

I



$$\left[\begin{array}{c}CH_3\ \ CH_2-\\ \diagdown\!\diagup\\ C\\ \|\\ CHCO_2H\end{array}\right]_2$$

II

tert-Butyl 3-methylper-2-butenoate is obtained as a colorless liquid which is isomerically homogeneous by nmr. Decomposition of the perester in cumene at 110° gives carbon dioxide (43%) and a significant acidic fraction (37% of the weight of the starting perester). This acidic fraction is spectroscopically comparable to that obtained from the corresponding peroxide. Analytical scale decomposition in cumene (0.11 *M*) at 110° gives acetone (9%), *tert*-butyl alcohol (78%), and isobutene (30%). Decomposition in carbon tetrachloride (0.1 *M*) at 110° gives acetone (60%), methyl chloride (36%), 1-chloro-2-methylpropene-1 (9%), isobutene (~1%), chloroform (10%), and hexachloroethane (9%) (see Experimental Section, Table IX). The radical nature of the decomposition is clear from the nature of the products, but the yields of vinyl radical products, isobutene, and 1-chloro-2-methylpropene-1 are surprisingly low. The yields of the vinyl products are notably concentration and temperature dependent, increasing with increasing temperature and with decreasing perester concentration.

Attempts to use 3-ethyl-2-pentenoyl peroxide and the related *tert*-butyl perester as sources of the 2,2-diethylvinyl radical were particularly revealing. Decomposition of the perester (0.12 *M*) in cumene at 110° gives acetone (7%), *tert*-butyl alcohol (72%), carbon dioxide (10%), 2-ethyl-1-butene (3%), and dicumyl (Experimental Section, Table VIII). The bulk of the starting perester is recovered as a acidic fraction (65% of the weight of the initial perester). This acidic fraction contains only trace amounts (2–3%) of the monomeric acids, 3-ethyl-2-pentenoic acid or the isomeric 3-ethyl-3-pentenoic acids. The nmr spectrum reveals acidic, aromatic, vinyl, allylic, and aliphatic protons and the ir suggests unsaturated carboxylic acids. Titration gives an apparent molecular weight of 231, suggesting the incorporation of cumyl fragments. The mass spectrum of the acidic fraction showed peaks at *m*/*e* 254, 246, 236, 228, and a base peak at 119 (cumyl cation). The decomposition of the corresponding peroxide, 3-ethyl-2-pentenoyl peroxide, was studied briefly in cumene at 110° and gives comparable results. Yields of carbon dioxide and 2-ethyl-1-butene (<0.6%) are low. The acidic fraction weighs 75–81% as much as the starting peroxide and does not contain detectable amounts of 3-ethyl-2-pentenoic acid or the isomeric 3-ethyl-3-pentenoic acids.

Intramolecular H Abstraction by the Acyloxy Radical. The results of these product studies on several related peroxides and peresters are most economically explained in terms of competitive reactions of the intermediate acyloxy radicals of the general structural type III. The low yields of carbon dioxide and vinyl radical products and high yields of acidic products are observed for both peroxides and peresters, indicating a common explanation. The perester decompositions are normal with respect to the *tert*-butoxy fragment, in accord with one-bond oxygen–oxygen homolysis.[1,2] Acyloxy radicals are thus implicated as the intermediates common to both peroxide and perester decompositions; competitive rates of decarboxylation and intramolecular hydrogen abstraction lead to vinyl radicals and allylic radicals, respectively (Scheme I). The reactive vinyl radicals pursue normal reactions with solvent, generating olefin (VH), and vinyl chlorides (VCl), and cumyl and trichloromethyl radicals. The less reactive allylic radicals disappear by self-dimerization or cross-dimerization with cumyl or trichloromethyl radicals. The acidic fraction is, in principle, a complicated mixture of structurally similar carboxylic acids. In the simplest case involving the decomposition of 3-methyl-2-butenoyl peroxide in cumene, there are ten different carboxylic acids (excluding enantiomers) derivable from head to head, tail to tail, head to tail, head to cumyl, and tail to cumyl coupling.

The intramolecular H abstraction pathway is totally consistent with the characteristics of the acidic products.

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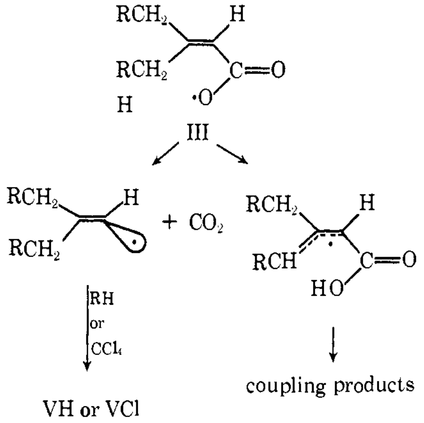
[23] S. J. Weininger, V. T. Mai, and E. R. Thornton, *J. Amer. Chem. Soc.*, **86**, 3632 (1964).

Scheme I

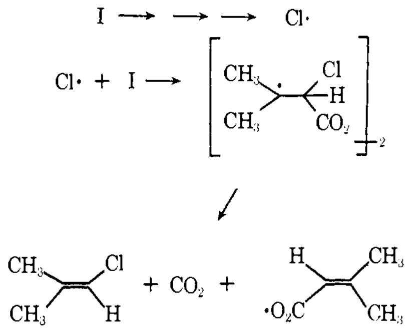


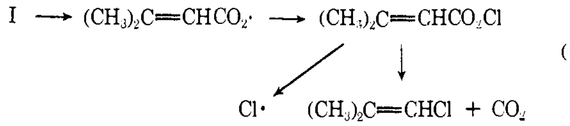
A wide variety of other conceivable schemes are eliminated by the observations that monomeric ethylpentenoic acids are not important reaction products. In addition, the yields of carbon dioxide and vinyl radical products are temperature dependent, as anticipated for competitive reactions of the acyloxy radical III. The yields of vinyl radical products are greater from 3-methyl-2-butenoyloxy systems than from 3-ethyl-2-pentenoyloxy radicals, in accord with a scheme in which decarboxylation competes with abstraction from primary and secondary positions, respectively. A similar decarboxylation/abstraction competition was observed for the acyloxy radicals from *o*-benzylbenzoyl peroxide and *o*-methylbenzoyl peroxide.[24] On the other hand, the competition was not apparent in our study[1] of the decomposition of *tert*-butyl *trans*-α,β-dimethylpercinnamate, suggesting that decarboxylation of the α,β-unsaturated acyloxy radical is facilitated by an α-methyl substituent. Similar competitions are not observed in the decomposition of aliphatic peroxides and peresters,[14,25–27] implying an increased activation energy for the decarboxylation of the α,β-unsaturated acyloxy radicals.

In summary, the decomposition of 3-methyl-2-butenoyl peroxide (I) in cumene or carbon tetrachloride gives low, but useful, yields of the appropriate vinyl radical products. The major cause of the low efficiency in the production of vinyl radical products is traceable to competitive reactions of the vinyl radical precursor, the 3-methyl-2-butenoyloxy radical. In particular, there is no evidence from the gross chemistry of the decomposition that the peroxide cannot be used as a source of 2-methylpropenyl radicals for the competitions described by eq 3.

Applicability of Equation 3. The derivation of eq 3 assumes that there are no extraneous sources of olefin and vinyl chloride and that these products are stable to the reaction conditions. Specific information on these points is available from the decomposition of peroxide I in carbon tetrachloride (Table II). Isobutene was not detectable in any of these decompositions, thereby ruling out trivial sources of H-abstraction product. 3-Methyl-2-butenoic acid was deliberately added in one experiment; the lack of formation of isobutene eliminates decarboxylation of the acid as a route to olefin. We were particularly concerned about the possibility of induced formation of vinyl chloride. Decomposition of the peroxide in carbon tetrachloride might generate chlorine atoms. These chlorine atoms might add to peroxide and ultimately produce vinyl chloride by a route not involving vinyl radicals (Scheme II). Similar induced reactions of α,β-unsaturated systems are known.[28] An induced formation of products is ruled out by the inverse variations in product yields with peroxide and perester concentration (Tables I, II, IX). Induced reactions, in general, show a direct correlation with initiator concentration, leading to the prediction that olefin and/or vinyl chlorine yields should increase with increasing concentration of peroxide or perester. The inverse relationship, in fact, suggests a side reaction which serves to divert peroxide or perester from the normal pathway which gives vinyl radicals. Allylic abstraction or addition to the double bond by trichloromethyl radical would provide reasonable routes for destruction of starting material. Finally, the most reasonable source of the chlorine atoms in Scheme II involves formation of an acyl hypochlorite intermediate (reaction 4). This hypochlorite might decompose to chlorine atoms or decompose directly to vinyl chloride. In any case, both pathways are eliminated by the observation (Table II) that the yields of vinyl chloride are not decreased by the presence of water. In conclusion, both the gross and detailed characteristics of the peroxide decompositions confirm that olefin and vinyl chloride are formed only *via* the appropriate abstraction reactions.

Scheme II





$$\begin{tikzcd} I \arrow[r] & (CH_3)_2C{=}CHCO_2\cdot \arrow[r] & (CH_3)_2C{=}CHCO_2Cl \arrow[dl] \arrow[d] \\ & Cl\cdot & (CH_3)_2C{=}CHCl + CO_2 \end{tikzcd} \qquad (4)$$

The stability of the products to the reaction conditions was tested by doping decomposition mixtures with isobutene and vinyl chloride. The vinyl chloride is recovered unchanged, but isobutene is consumed. The free radical addition product of isobutene and carbon tetrachloride is readily detectable at the end of the decomposition. This secondary reaction was minimized by studying product yields at low conversions of peroxide to isobutene. Since independent experiments showed that solutions containing unreacted peroxide form vinyl radical products in the course of vpc anal-

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Table III. k_H/k_{Cl} Ratios Derived from the Decomposition of I in Cumene at 78°

[I], *M*	[Cumene]/[CCl_4]	% conversion	k_H/k_{Cl}
0.026	6.18	32	0.136
		55	0.141
		100	0.136
0.050	2.73	15	0.148
		50	0.142
		100	0.107
0.052	6.14	20	0.142
		53	0.144
		72	0.155
		84	0.132
		100	0.118
0.054	12.98	15	0.144
		37	0.143
		60	0.129
		100	0.132
0.100	6.14	6.1	0.144
		6.7	0.143
		12	0.142
		100	0.105
0.110	6.18	15	0.144
		37	0.139
		100	0.100
0.254	6.18	23	0.143
		29	0.140
		100	0.075

Table IV. k_H/k_{Cl} Ratios for the 2-Methylpropenyl Radical at 78°

SH	[I], *M*	[SH]/[CCl_4]	% conversion	k_H/k_{Cl}
Toluene	0.023	8.29	24	0.049
	0.238	8.29	19	0.048
	0.049	3.62	15	0.048
	0.052	17.07	24	0.049
	0.107	8.07	9	0.048
Ethylbenzene	0.022	7.18	20	0.127
	0.223	7.18	19	0.127
	0.051	3.14	22	0.129
	0.056	14.94	19	0.125
	0.049	7.18	16	0.127
Cumene	0.026	6.18	16	0.136
	0.254	6.18	23	0.143
	0.050	2.73	15	0.148
	0.054	12.98	15	0.144
	0.100	6.14	6	0.144
tert-Butylbenzene	0.021	5.66	21	0.012
	0.204	5.66	21	0.010
	0.054	5.66	20	0.010
	0.054	11.92	20	0.008
	0.112	5.66	12	0.010
p-Xylene	0.110	6.81	7	0.114
	0.110	6.81	17	0.112
	0.100	9.39	6	0.110
	0.100	9.39	18	0.112
p-Chlorotoluene	0.099	7.27	7	0.057
	0.099	7.27	20	0.057
	0.103	10.14	8	0.056
	0.103	10.14	17	0.057
p-Methylanisole	0.104	6.77	7	0.064
	0.104	6.77	14	0.069
	0.102	9.43	16	0.066
Anisole	0.099	7.93	18	0.012
	0.102	10.85	14	0.013
p-Nitrotoluene	0.103	0.687	12	0.122
	0.103	0.687	13	0.121

ysis, triphenylphosphine was used[29] to quench undecomposed peroxide. Control experiments established the applicability of the quenching system. The validity of the low conversion yields is established by the fact that the carbon tetrachloride–isobutene adduct was not detectable. In addition, the k_H/k_{Cl} values (Tables III and IV) are independent of per cent conversion in the low conversion region. These ratios fall off at high conversion in the direction required by isobutene consumption. The variation in k_H/k_{Cl} with per cent conversion is also most dramatic at high initial peroxide concentrations (Table III).

Equation 3 further assumes that the reactions leading to olefin and vinyl chloride are the same order in vinyl radical, are first order in radical scavenger, and that the ratio of scavenger concentrations remains constant. Identical order with respect to radical concentration is related to the induced schemes discussed earlier. In addition, the k_H/k_{Cl} ratios are independent of initial peroxide concentration (Tables III and IV). The k_H/k_{Cl} values are also independent of the ratio of scavenger concentrations (Table III and IV). The variation in the ratio of scavenger concentrations in any given run can be approximated from the initial peroxide concentration or measured before and after reaction. These tests showed $<2\%$ variation in the scavenger ratio. A halogenation chain involving the solvents[30] is ruled out by the low yields of chloroform.

Relative Reactivity Data. k_H/k_{Cl} Values. As described in the previous section, the k_H/k_{Cl} data in Table IV are consistent with the derivation of eq 3. The individual results were averaged to give the rate constant ratios summarized in Table V. *tert*-Butylbenzene was used as a model for the reactivity of the β-methyl hydrogens of ethylbenzene and cumene. Anisole served as a model for the reactivity of the methoxy hydrogens of *p*-methoxytoluene. Corrected k_H/k_{Cl} ratios per α-hydrogen are also shown in Table V. The reactivity pattern of the 2-methylpropenyl radical is compared to those of other common atoms and radicals in Table VI.

The 2-methylpropenyl radical occupies an intermediate position on the overall scale of available radical reactivities. It is similar to other localized carbon radicals, but is more discriminating than chlorine atoms and *tert*-butoxy radicals, and less selective than stabilized carbon radicals such as polystyryl and trichloromethyl. The close parallel in selectivity between the structurally related phenyl and vinyl radicals is noteworthy. The reactivity data for the 2-methylpropenyl radical provide a reference point for evaluation of the effects of α-substitution, hybridization, and transition state geometry on the rates of H abstraction by vinyl radicals. The latter question has been considered by Heiba and Dessau, who observed relative reactivities of 1:22:650 for cyclic, intramolecular 1,5 abstraction of primary, secondary, and tertiary aliphatic hydrogens by an α-alkylvinyl radical. These authors noted that such high selectivity would not be expected in intermolecular reactions involving a linear transition state geometry for H transfer.[7]

The k_H/k_{Cl} data for the 2-methylpropenyl radical reacting with para-substituted toluenes are not correlated by the Hammett equation. With the exception of *p*-nitro, the effects of the substituent are small, as observed for the reactions of phenyl radical.[15,19] Anom-

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Table V. Summary of k_H/k_{Cl} Ratios for the 2-Methylpropenyl Radical at 78°

H donor	k_H/k_{Cl} (uncor)	k_H/k_{Cl} per α-hydrogen	Relative reactivity per α-hydrogen[a]
Toluene	0.048 ± 0.0009[b] (11)[c]	0.016	1.0
Ethylbenzene	0.127 ± 0.0013 (5)	0.062	3.9
Cumene	0.143 ± 0.0028 (10)	0.137	8.6
tert-Butylbenzene	0.010 ± 0.0015 (5)		
p-Xylene	0.112 ± 0.0012 (7)	0.019	1.2
p-Chlorotoluene	0.057 ± 0.0006 (6)	0.019	1.2
p-Nitrotoluene	0.121 ± 0.0007 (2)	0.040	2.5
p-Methoxytoluene	0.066 ± 0.0022 (6)	0.018	1.1
Anisole	0.012 ± 0.0003 (3)		

[a] Toluene as reference. [b] Standard deviation. [c] The number in parentheses is the degrees of freedom.

Table VI. Reactivities of Benzylic Hydrogen Donors (per α-Hydrogen) toward Free Radicals

R·	*T*, °C	Toluene	Ethylbenzene	Cumene	Ref
$Cl\cdot$	40	(1)	2.5	5.5	*a*
$(CH_3)_3CO\cdot$	40	(1)	3.2	6.9	*b*
$(CH_3)_2C{=}CH\cdot$	78	(1)	3.9	8.6	*c*
$C_6H_5\cdot$	60	(1)	4.6	9.7	15
$CH_3\cdot$	65	(1)	4.1	12.9	*d*
p-$BrC_6H_4\cdot$	60	(1)	4.7	13.8	19
$ROO\cdot$	90	(1)	7.9	12.5	*e*
$C_6H_5\dot{C}HCH_2\sim$	60	(1)	8	20	*f*
p-$O_2NC_6H_4\cdot$	60	(1)	6.2	26.0	19
$Br\cdot$	40	(1)	17.2	37.0	*g*
$Cl_3C\cdot$	40	(1)	50	260	*g*

[a] G. A. Russell, *J. Amer. Chem. Soc.*, **80**, 4987, 4997, 5002 (1958). [b] C. Walling and B. B. Jacknow, *ibid.*, **82**, 6108 (1960). [c] This work. [d] J. A. Myer, V. Stannett, and M. Szwarc, *J. Amer. Chem. Soc.*, **83**, 25 (1961). [e] G. A. Russell, *ibid.*, **78**, 1047 (1956). [f] R. A. Gregg and F. R. Mayo, *Discuss. Faraday Soc.*, **2**, 328 (1947). [g] G. A. Russell and C. DeBoer, *J. Amer. Chem. Soc.*, **85**, 3136 (1963).

alously high reactivity for *p*-nitrotoluene in reaction with the *p*-bromophenyl radical has been previously noted.[19]

The ratio of the rate constants for H abstraction from toluene and chlorine abstraction from carbon tetrachloride for a series of radicals varies by almost a factor of 10^3, as shown in Table VII. The data are undoubtedly the result of a subtle interplay of several factors. The gross aspects of the series, however, show an interesting example of polar effects on radical reactions. Thus, radicals which readily bear a positive charge in the transition state show small k_H/k_{Cl} values, while larger k_H/k_{Cl} values are characteristic of systems which reluctantly bear positive charge. Heiba and Dessau have reported competitive intramolecular H abstraction and intermolecular reaction with carbon tetrachloride by a secondary vinyl radical,[7] while only the reaction with carbon tetrachloride is observed for the corresponding secondary alkyl radical. They have rationalized these observations in terms of reactivity (selectivity) differences between the two radicals. Thus, the less reactive (more selective) alkyl radical reacts almost exclusively by the lower activation energy pathway involving carbon tetrachloride. Another factor of importance may involve the different sensitivities of alkyl and vinyl radicals to polar effects. The data in Table VII suggest that radicals of comparable reactivity, as judged by the profile for a series of benzylic H donors, may still show different behavior in a k_H/k_{Cl} competition.

Table VII. Values of k_H/k_{Cl} for Various Radicals. Toluene as the H Donor

Radical	*T*, °C	k_H/k_{Cl}	Ref
$C_6H_5\dot{C}HCH_2\sim$	60	0.0014	*b*
n-$C_6H_{13}\cdot$	74	0.006	14
$(CH_3)_2C{=}CH\cdot$	78	0.048	*a*
2-C_6H_5-*c*-$C_3H_4\cdot$	110	0.104	20
$C_6H_5\cdot$	60	0.27, 0.36	15, 19
$CH_3\cdot$	100	0.75	13
p-$BrC_6H_4\cdot$	60	0.79	19
p-$NO_2C_6H_4\cdot$	60	1.67	19

[a] This work. [b] See Table VI, footnote *f*.

Experimental Section

Melting points and boiling points are uncorrected. Ir spectra were recorded on a Perkin-Elmer Model 421 infrared spectrophotometer as neat films. Nmr spectra of neat liquids were recorded on a Varian A-60 (60 MHz) spectrometer, or on a Jeolco C-60HL (60 MHz) spectrometer. Mass spectra were recorded on an Atlas CH-4 mass spectrometer by Mrs. Judy Lewis or on an Hitachi-Perkin-Elmer RMU-6E mass spectrometer by Mrs. Eloise Rohner. Vapor phase chromatographic (vpc) analyses were performed on F & M Models 700 and 720 dual column instruments equipped with thermal conductivity detectors and a Perkin-Elmer Model 900 dual column instrument equipped with a flame ionization detector. All analyses were carried out on aluminum or stainless steel 0.25-in. diameter columns using helium as the carrier gas. Elemental analyses were performed by Spang Microanalytical Laboratory, Ann Arbor, Mich., or by Micro-Tech Laboratories, Skokie, Ill.

Chemicals. All reagents and solvents used were reagent grade. Commercially available toluene, ethylbenzene, cumene, *tert*-butylbenzene, and *p*-xylene, used as solvents in peroxide and perester decompositions, were purified by shaking with small portions of concentrated sulfuric acid, washing with saturated sodium carbonate solution and water, drying, and distillation through a 12-in. Vigreux column. Center cuts (bp range <1°) were stored over 4A molecular sieves and under nitrogen.

p-Chlorotoluene (Eastman) was purified by distillation. A center cut, bp 158.5-159.5° (750 mm), $n^{27}D$ 1.5177 (lit.[31] $n^{19}D$

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(31) R. C. Weast, Ed., "Handbook of Chemistry and Physics," 48th ed, Chemical Rubber Co., Cleveland, Ohio, 1967, pp C168-C579.

1.5199), was stored over 4A molecular sieves. *p*-Nitrotoluene (Eastman), practical grade, mp 51.5–53.2°, was purified by recrystallization of 100 g from 300 ml of 95% ethyl alcohol to yield pale yellow needles, mp 53.0–53.8° (lit.[31] mp 51.7°). *p*-Methylanisole (Eastman) was used as obtained, $n^{18}\mathrm{D}$ 1.5132 (lit.[31] $n^{19}\mathrm{D}$ 1.5124). Anisole (Eastman) was purified by distillation through a 12-in. Vigreux column. A center cut, bp 151.5–152.0° (752 mm), $n^{27}\mathrm{D}$ 1.5139 (lit.[31] $n^{26}\mathrm{D}$ 1.5179), was stored over 4A molecular sieves. Carbon tetrachloride (Baker), spectral grade, was used as received.

All these solvents were tested for the presence of peroxides by combining a few drops of hydrocarbon in acetone with a few milliliters of acetone containing sodium iodide. The solution was allowed to stand at room temperature for 1 hr, and the failure of a yellow or brown color to develop was interpreted as indicating the absence of peroxide. All the solvents appeared at least 99.5% pure when examined by gas chromatography on two separate columns.

3-Ethyl-2-pentenoyl Peroxide. 3-Ethyl-2-pentenoic acid is obtained as a mixture with *cis*- and *trans*-3-ethyl-3-pentenoic acid by the reaction of ethyl bromoacetate with diethyl ketone in the presence of magnesium. Hydrolysis and dehydration of the intermediate hydroxy ester give a mixture of acids in which the α,β-unsaturated 3-ethyl-2-pentenoic acids predominate.[32] The β,γ-unsaturated acids are removed by preferential formation and extraction of their iodolactones.[33] Isolation and distillation of the unreacted, α,β-unsaturated isomer give 3-ethyl-2-pentenoic acid: bp 123–125° (28 mm); $n^{13.6}\mathrm{D}$ 1.4672; nmr δ 12.48 (s, 1 H), 5.61 (s, 1 H), 2.65 (q, 2 H), 2.22 (q, 2 H) 1.07 (t, 6 H). The β,γ isomers could not be detected by nmr; 1.0% contamination was observable. 3-Ethyl-2-pentenoyl chloride is obtained by reaction of the acid with thionyl chloride;[32] the nmr spectrum failed to reveal contamination by the β,γ isomers. The acid chloride was also converted to the ethyl ester and the ester examined by vpc; only the α,β-unsaturated ester was observed under conditions (10% diisodecyl phthalate on 60–80 Chromosorb W, 6 ft, flow 100 cc/min, programmed at 3°/min from 80°, injector 280°) which clearly separated authentic samples of ethyl 3-ethyl-2-penteneoate and ethyl *cis*- and *trans*-3-ethyl-2-pentenoate.

3-Ethyl-2-pentenoyl peroxide is synthesized from 3-ethyl-2-pentenoyl chloride by reaction with urea peroxide. An 8-g (0.085 mol) sample of the urea–peroxide complex, hexane (100 ml), and pyridine (12.0 ml, 0.15 mol) are mixed and stirred at 0°. 3-Ethyl-2-pentenoyl chloride (13.1 g, 0.089 mol) is added dropwise and the mixture stirred for 11 hr at 0°. The mixture is then added to 150 ml of ice and stirred for 1 hr. The hexane layer is separated and washed with four 25-ml portions of 10% hydrochloric acid at 0°, one 25-ml portion of distilled water, four 25-ml portions of saturated sodium carbonate solution, and finally with 25 ml of distilled water. The hexane layer is dried over magnesium sulfate and filtered, and the hexane removed by rotary evaporation at room temperature. The resultant yellow-green oil is taken up in hexane and the solution cooled in a Dry Ice–acetone bath to give crystals which are collected and redissolved in fresh hexane. Removal of the solvent at 0° with an aspirator yields 11.2 g (52.0%) of a slightly yellow-green oil. Titration for peroxide[34] content showed 79.8% peroxide. The oil is evacuated at 0.2 mm for 4 hr, 75 ml of anhydrous ether is added, and the solution placed in a Dry Ice–acetone bath for 4 hr.[35] Cubic colorless crystals form, and the majority of the ether is decanted. This procedure is repeated and a final evacuation for 2 hr gives a colorless oil at room temperature which can be maintained as a solid at 5°. Titration for peroxide showed 97.4% peroxide: nmr δ 5.61 (s, 1 H), 2.62 (q, 2 H), 2.27 (2, 2H), 1.07 ppm (t, 6 H); ir 1785, 1755, and 1630 cm^{-1}.

Anal. Calcd for $C_{14}H_{22}O_4$: C, 66.11; H, 8.72. Found: C, 65.99; H, 8.67.

tert-**Butyl 3-Ethylper-2-pentenoate.** The perester is prepared by the reaction of sodium *tert*-butyl hydroperoxide[36] with 3-ethyl-2-pentenoyl chloride. To 11.7 g (0.104 mol) of sodium *tert*-butyl hydroperoxide suspended in 500 ml of dichloromethane at 0° is slowly added 11.3 g (0.077 mol) of 3-ethyl-2-pentenoyl chloride in 250 ml of dichloromethane. The reaction mixture is stirred at 0° for 1 hr and allowed to stand overnight at 5°. The mixture is filtered and the solvent removed *in vacuo* at 0°. Diethyl ether (50 ml) is added and the solution extracted twice with saturated sodium carbonate solution and once with distilled water. The aqueous extracts are combined and back-extracted twice with ether. All the ether layers are combined and dried over magnesium sulfate. After filtration, the solvent is removed at 0° (0.3 mm) to yield 11.20 g (71.7%) of a very pale yellow liquid. Titration for peroxide content showed 100.1% perester: nmr δ 5.55 (s, 1 H), 2.62 (q, 2 H), 2.23 (q, 2 H), 1.27 (s, 9 H), and 1.07 ppm (t, 6 H); ir 1755 and 1640 cm^{-1}.

Anal. Calcd for $C_{11}H_{20}O_3$: C, 65.97; H, 10.06. Found: C, 65.86; H, 10.02.

The perester could be repurified as needed by column chromatography on silica gel (60–200 mesh) using 50:50 hexane–dichloromethane as eluent. The nmr spectrum and peroxide titration were used to determine purity of the perester.

3-Methyl-2-butenoyl Peroxide (I). 3-Methyl-2-butenoic acid is recrystallized from water, mp 67.8–68.8°. Reaction with thionyl chloride at 0° gives, after distillation, 3-methyl-2-butenoyl chloride: bp 55–57° (28 mm); $n^{20}\mathrm{D}$ 1.4776 (lit.[37] bp 71–72° (50 mm), $n^{20}\mathrm{D}$ 1.4675).

The corresponding peroxide is synthesized from the acid chloride using urea peroxide. The urea–peroxide complex (28.2 g, 0.300 mol), hexane (250 ml), and pyridine (30 ml, 0.375 mol) are mixed and stirred at 0°. To this mixture, 34.1 g (0.290 mol) of 3-methyl-2-butenoyl chloride is added dropwise, and the mixture stirred for 5 hr at 0°. The mixture is then stirred for an additional 16 hr while the temperature is allowed to increase to room temperature. The mixture is then added to 300 ml of ice and stirred for 1 hr. The hexane layer is separated and washed with four 25-ml portions of 10% hydrochloric acid at 0°, one 25-ml portion of distilled water, four 25-ml portions of saturated sodium carbonate solution, and finally with 25 ml of distilled water. The hexane layer is dried over magnesium sulfate and filtered, and the hexane removed *in vacuo* at room temperature. The slightly yellow solid is taken up in anhydrous diethyl ether, and the solution cooled in a Dry Ice–acetone bath to give white crystals. The majority of the ether is decanted. This procedure is repeated twice and the remaining ether removed at 0.2 mm for 4 hr to yield 12.0 g (41.7%) of white crystalline solid, mp 68.0–69.0°. Titration for peroxide showed 95.1% peroxide: nmr δ 5.78 (m, 1 H), 2.25 (d, 3 H), and 2.00 (d, 3 H); ir 1760 and 1641 cm^{-1}; mass spectrum (20 eV) *m/e* (relative intensity) 198 (13.5) (parent), 154 (5.1), 101 (10.2), 100 (100.0), 85 (29.8), 84 (33.3), 83 (100.0), 82 (41.1), 58 (12.6), 55 (100.0), 54 (20.6), 53 (14.2), 44 (23.4), 43 (12.3), 41 (29.1), 39 (29.8), 29 (41.1), 28 (66.0), 18 (24.1).

Anal. Calcd for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 60.67; H, 7.14.

tert-**Butyl 3-Methylper-2-butenoate.** The perester is prepared by the reaction of sodium *tert*-butyl hydroperoxide[36] with 3-methyl-2-butenoyl chloride. To 22.40 g (0.200 mol) of sodium *tert*-butyl hydroperoxide suspended in 500 ml of dichloromethane at 0° is slowly added 18.8 g (0.159 mol) of 3-methyl-2-butenoyl chloride in 250 ml of dichloromethane. The reaction mixture is stirred for 15 hr while the temperature is allowed to increase to room temperature. The mixture is filtered and the solvent removed at 0°. Diethyl ether (50 ml) is added to the residue, and the solution extracted twice with saturated sodium carbonate solution and once with distilled water. The aqueous extracts are combined and back-extracted twice with ether. All the ether layers are combined, dried over magnesium sulfate and filtered, and the solvent is removed at 0°. The residue, 23.50 g (86.7%) of colorless oil, is chromatographed on silica gel using petroleum ether (bp 30–60°) as eluent. Solvent is removed, and the residue evacuated at 0.2 mm for 3 hr to yield a colorless oil. Titration for peroxide content showed 94.8% perester: $n^{20.5}\mathrm{D}$ 1.4485; nmr δ 5.58 (m, 1 H), 2.12 (d, 3 H), 1.86 (d, 3 H), and 1.25 (s, 9 H); ir 1755 and 1640 cm^{-1}; mass spectrum (20 eV) *m/e* (relative intensity) 172 (0.3) (parent), 154 (1.1), 114 (2.9), 100 (18.1), 97 (11.9), 84 (20.0), 83 (100.0), 59 (73.8), 58 (50.0), 57 (33.8), 56 (15.0), 55 (74.4), 44 (18.8), 43 (100.0), 41 (43.8), 39 (15.0), 31 (16.3), 29 (37.5), 28 (32.5), 18 (27.5), 15 (30.0).

Anal. Calcd for $C_9H_{16}O_3$: C, 62.76; H, 9.37. Found: C, 62.97; H, 9.32.

Large Scale Decompositions. Characterization of Products. *tert*-**Butyl 3-Ethylper-2-pentenoate in Cumene.** A solution of 3.3396 g (16.67 mmol) of *tert*-butyl 3-ethylper-2-pentenoate in 50 ml of cumene (perester concentration = 0.3335 *M*) was placed in a 100-ml flask arranged for nitrogen sweep. The solution was

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(32) G. A. R. Kon and R. P. Linstead, *J. Chem. Soc.*, 616 (1925).
(33) R. P. Linstead and C. J. May, *ibid.*, 2565 (1927).
(34) L. S. Silbert and D. Swern, *Anal. Chem.*, **30**, 385 (1958).
(35) C. C. Price and H. Morita, *J. Amer. Chem. Soc.*, **75**, 3686 (1953).
(36) J. P. Lorand and P. D. Bartlett, *ibid.*, **88**, 3294 (1966).

(37) G. B. Payne, *J. Org. Chem.*, **31**, 718 (1966).

degassed by three freeze–pump–thaw cycles and placed in an oil bath at 110.3° ± 0.2°. Nitrogen was purified through ascarite and calcium chloride and passed through the solution at a rate of 25–28 ml/min for the course of the decomposition (24 hr).

A. Volatile Materials. The exit gases were conducted through two Dry Ice–acetone traps and two ascarite/$Mg(ClO_4)_2$ absorption tubes. The tubes absorbed 0.0665 g (9.1%) of carbon dioxide. The material that collected in the Dry Ice trap was transferred to a 10-ml volumetric flask which was fitted with a serum cap, and 0.2137 g of ethyl alcohol was added as an internal standard. The material was shown to be 2-ethyl-1-butene (3.8% yield), acetone (9.6%), *tert*-butyl alcohol (77.1%), and cumene by vpc retention time and coinjection with authentic samples. The material which coinjected with 2-ethyl-1-butene was collected from the vpc and gave an ir spectrum (CCl_4) identical with that of authentic 2-ethyl-1-butene. A 50-μl sample of the mixture remaining in the decomposition flask was analyzed by vpc. An equivolume sample of a standard solution of 3-ethyl-2-pentenoic acid in cumene was also analyzed, and the areas of the acid peaks were compared, demonstrating a 1.7% yield of 3-ethyl-2-pentenoic acid and/or 3-ethyl-3-pentenoic acids. The α,β and β,γ isomers are not separated by these conditions (25% Carbowax 20M on 60–80 Chromosorb W, 10 ft, flow 100 cc/min, injector 260°, column 225°).

B. Acidic Material. The cumene solution was extracted with saturated sodium carbonate solution, and the aqueous layer backwashed with diethyl ether. Isolation of the acidic products by neutralization and extraction yielded 2.1692 g of titration of highly viscous, slightly yellow oil. Titration of a sample of this acidic material in a mixture of water and ethyl alcohol (not quite all would dissolve) indicated a neutralization equivalent of 231.1 g/equiv. The acidic material showed the following spectral data: nmr (CCl_4) δ 12.05 (s, relative area = 1.00), 7.21 (s, 2.3), 5.60 (m, 1.1), and 0.70–3.00 ppm (m, 14.5); ir (CCl_4) 3100 (broad), 3050, 3010 and 2950, 1690, 1635, 1230, 930, 870, and 690 cm^{-1}; mass spectra (15, 70 eV) *m/e* (relative intensity) 254 (0.1, 0.1), 246 (0.2, 0.2), 236 (0.8, 0.3), 228 (0.7, 0.4), 144 (6.1, 3.6), 128 (21.2, 13.8), 121 (8.9, 9.9), 119 (100, 100), 117 (20.0, 28.2), 99 (8.3, 11.4), 91 (1.1, 19.3), 57 (4.5, 13.1), 44 (0.7, 5.1), 43 (2.5, 16.5), and 18 (2.3. 11.9).

Anal. Found: C, 72.21; H, 9.28; O, 18.24.

C. Nonvolatile, Neutral Material. The cumene was then removed from the reaction mixture by distillation under reduced pressure, yielding a crystalline residue. Recrystallization from ethyl alcohol gave dicumyl, mp and mmp 116–117°; the infrared spectrum was identical with that of an authentic sample. A second decomposition of the perester in cumene (0.1230 *M*) at 110° gave results comparable to those detailed above.

tert-**Butyl 3-Methylper-2-butenoate in Cumene.** A solution of 0.9261 g (5.375 mmol) of *tert*-butyl 3-methylper-2-pentenoate in 50 ml of cumene (perester concentration = 0.1075 *M*) was treated as described above at 110.0 ± 0.5° for 26 hr. The ascarite/magnesium perchlorate tubes absorbed 0.1023 g (43.2%) of carbon dioxide. The cumene solution was extracted with saturated sodium carbonate solution and distilled water, and the extracts were worked up to give 0.3433 g of viscous, slightly yellow oil. The nmr spectrum of this material showed the following absorptions: nmr (CCl_4) δ 11.62 (s), 7.23 (m), 5.65 (m), 5.47 (m), 4.95 (s), 3.32, 3.08, 2.45, 1.72 (s), and 1.62 (m).

The cumene was removed from the reaction mixture by distillation under reduced pressure, yielding a crystalline residue. Recrystallization from ethyl alcohol gave dicumyl, mp and mmp 116–117°; the infrared spectrum was identical with that of an authentic sample.

3-Methyl-2-butenoyl Peroxide (I) in Carbon Tetrachloride. A solution of 4.952 g (24.98 mmol) of I in 50 ml of carbon tetrachloride (peroxide concentration = 0.4996 *M*) was placed in a 150-ml Carius tube. The solution was degassed by three freeze–thaw cycles, evacuated, and sealed. The sealed tube was placed in an oil bath maintained at 110 ± 0.5° for 4 hr. The tube was cooled to room temperature and opened, and the contents were transferred to a separatory funnel. The solution was extracted with saturated sodium carbonate solution and then with 25 ml of distilled water. The aqueous layers were combined, back-washed with 25 ml of carbon tetrachloride, and worked up to give 3.300 g of viscous, slightly yellow oil. This acidic material showed the following spectral data: nmr (CCl_4) 11.80 (s), 6.01 (s), 5.83 (m), 4.38 (s), 3.60 (s), 2.47 (s), 2.30 (s), and 2.05 (s); ir (CCl_4) 3000 (broad), 1700, 1648, and 710 cm^{-1}; ir (Nujol) 2900, 1700, 1650, 795 and 714 cm^{-1}; mass spectrum (70 eV) *m/e* (relative intensity) 201 (6.8), 199 (8.4), 163 (10.0), 147 (11.6), 145 (29.5), 100 (18.4), 99 (17.0) 91 (30.5), 83 (100.0), 82 (41.1). 77 (32.6), 65 (26.8), 55 (41.1). 44, 43, 41. 39. 38, 36, 35, 28, and 27 (all >100.0).

Anal. Found: C, 40.51; H, 4.51; Cl, 35.87.

Upon attempting to redissolve this acidic material in carbon tetrachloride, a white powder remained insoluble. The solid was collected, washed with carbon tetrachloride, and air dried. This solid, mp 196.0–198.0°, gave an undepressed mixture melting point with similar material (II) isolated from the acidic fraction formed in the large-scale decomposition of 3-methyl-2-butenoyl peroxide in cumene. The ir spectrum (KBr) was identical with that of material obtained in a similar manner from the decomposition of 3-methyl-2-butenoyl peroxide in cumene.

Anal. Calcd for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 57.14; H, 6.36, ash.

Methyl chloride, chloroform, hexachloroethane, and 1-chloro-2-methyl-1-propene were identified as reaction products by vpc retention times and coinjections with authentic samples. In addition, the vpc peak which coinjected with 1-chloro-2-methylpropene-1 was introduced into the RMU-6E mass spectrometer. The mass spectrum coincided with respect to *m/e* values and relative intensities with that of an authentic sample obtained by vpc–mass spectrometry on a standard solution of the vinyl chloride.

3-Methyl-2-butenoyl Peroxide (I) in Cumene. A solution of 1.0195 g (5.143 mmol) of I in 50.0 ml of cumene (peroxide concentration = 0.1029 *M*) was decomposed at 110.0 ± 0.5° for 24 hr as described above for the peresters in cumene. The ascarite/magnesium perchlorate tubes absorbed 0.200 g (45.1%) of carbon dioxide. The cumene solution was cooled to room temperature and extracted with saturated sodium carbonate solution and distilled water. The aqueous extracts were combined and back-washed with diethyl ether and worked up to give 0.5972 g (58.6% of starting material by weight) of white, viscous oil. The residue showed the following spectral absorptions: nmr (CCl_4), δ 11.32 (s), 7.07 (s), 5.37 (s), 4.87 (s), 3.23 (s), 2.40 (s), 2.17 (s), 1.92 (s), 1.50 (s), and 1.33 (s); ir (CCl_4) 3000 (broad) 1695, 1645, 1260 and 700 cm^{-1}. Upon attempting to dissolve the acidic material in carbon tetrachloride for the above spectra, a white powder remained insoluble. This solid, mp 194.0–196.5°, showed the following spectral absorption: nmr (CD_3SOCD_3) δ 5.50 (s, relative area = 16), 3.28 (s), 2.23 (s, 29 units), and 2.05 (s, 56 units); ir (KBr) 2980 (broad), 1695, 1630, 1255, 870, and 720 cm^{-1}. This spectrum was identical with that obtained for material from the decomposition of 3-methyl-2-butenoyl peroxide in carbon tetrachloride. The mass spectrum (70 eV) *m/e* (relative intensity) at an inlet temperature of 180° showed 180 (14.8, anhydride formation), 165 (22.8), 162 (38.4), 152 (50), 137 (12.8), 135 (29.6), 134 (60), 119 (14.4), 111 (15.2), 108 (11.2), 107 (100), 106 (14.4), 100 (12), 95 (11.2), 92 (11.2), 92 (31.2), 92 (10.8), 91 (44), 83 (16.4), 82 (32.2), 81 (11.6), 79 (18.0), 77 (16.8), 71 (10.4), 67 (16.8), 65 (10.4), 55 (20.4), 54 (14.4), 53 (48.0), 51 (12.8).

Anal. Calcd for $C_{10}H_{14}O_4$: C, 60.59; H, 7.12. Found: C, 59.51; H, 6.86, ash.

Isobutene was identified by vpc retention time and coinjection with authentic material. The vpc peak in question was diverted into the RMU-6E mass spectrometer. The mass spectrum was identical with respect to *m/e* and relative intensities with that for an authentic sample obtained by vpc–mass spectrometry of a standard solution of isobutene in carbon tetrachloride.

Small-Scale Decompositions. The procedures described below apply to all decompositions (0.75–1.50 ml of solution) in which product analyses were made by vpc. The desired amount of perester or peroxide was weighed into a 10-ml volumetric flask, and solvent added to the mark. Peroxide or perester solution (0.75–1.50 ml) was measured *via* a syringe into reaction tubes constructed from Pyrex tubing. The tube was degassed by three freeze–pump–thaw cycles at 0.02 mm and sealed. A silicone oil bath maintained at 200 ± 1°, an oil bath maintained at 110.0 ± 0.5°, and a refluxing 95% ethyl alcohol bath maintained at 78.2 ± 0.5° were used in the thermal decompositions. Tubes were removed from these baths at measured intervals and stored in Dry Ice–acetone; the tubes were cracked and fitted with serum caps shortly before analysis. Carefully measured amounts of internal standard solution were then added to the capped reaction tubes by a 100-μl Hamilton syringe fitted with a "Chaney adapter." Ethyl alcohol was used as the internal standard in the quantitative determination of products from the decomposition of *tert*-butyl 3-ethylper-2-pentenoic and *tert*-butyl 3-methylper-2-butenoate. A 100-μl sample of the reaction tube containing internal standard was analyzed on a Carbowax 20M column (10 ft × 0.25 in., 25% on 60–80 Chromosorb W) at 70° with an injector temperature of

Table VIII. Decomposition of *tert*-Butyl 3-Ethylper-2-pentenoate in Cumene

			% yield		
[P], *M*	*T*, °C	*t*, hr	2-Ethyl-1-butene	Acetone	*tert*-Butyl alcohol
0.004	200	1	11	26	57
0.078	200	1	9.2	28	56
0.004	110	6	3.9	12.2	62
0.100	110	6	3.1	8.0	59
0.122	110	24	3.5	7.2	72
0.334	110	20	3.8[a]	9.6	77

[a] *cis*- and *trans*-2-ethyl-2-butene were not observed. The limit of detectability corresponded to 0.1% yield.

Table IX. Decomposition of *tert*-Butyl 3-Methyl-per-2-butenoate

				% yield						
Solvent	[P], *M*	*T*, °C	*t*, hr	VH[a]	VCl[b]	$CHCl_3$	Acetone	*tert*-Butyl alcohol	CH_3Cl	C_2Cl_6
Cumene	0.004	200	2	53						
	0.105	200	2	48			31	57		
	0.004	110	24	37						
	0.113	110	24	31			9.1	78		
CCl_4	0.004	200	2	0	43	Trace			85	
	0.110	200	2	0	21	7.7	82		54	40
	0.004	110	24	1.6	18	Trace			84	
	0.100	110	24	1.2	8.7	10	60		36	8.9

[a] VH = isobutene. [b] VCl = 1-chloro-2-methylpropene-1.

260°, a detector temperature of 280°, and a helium flow of 100 cc/min: 2-ethyl-1-butene, 2.8 min; acetone, 6.3 min; *tert*-butyl alcohol, 9.6 min; and ethyl alcohol, 12.3 min. *n*-Pentane was used as an internal standard in the quantitative determination of products from the decomposition of *tert*-butyl 3-methylper-2-butenoate. A 25-μl sample of the reaction tube containing internal standard was analyzed on an SF-96 column (15 ft × 0.25 in, 25% on 60–80 Chromosorb A) at 80° with an injector temperature of 240°, a detector temperature of 280°, and a helium flow of 50 cc/min: methyl chloride, 4.5 min; isobutene, 5.9 min; *n*-pentane, 9.1 min; chloroform, 19.6 min; 1-chloro-2-methyl-1-propene, 21.2 min.

Quantitative determinations of isobutene, 1-chloro-2-methyl-1-propene, and chloroform in the decomposition of 3-methyl-2-butenoyl peroxide were made by vpc analysis of equivolume injections of reaction and standard solutions. A 50-μl Hamilton syringe fitted with a "Chaney adapter" was used to make repetitive 25- or 50-μl injections on the SF-96 column under the conditions described above. Quantitative determinations of hexachloroethane and 3-methyl-2-butenoic acid were made using equivolume injections of reaction and standard solutions. Analyses were performed on an SE-30 methyl column (10 ft × 0.25 in., 10% on 45–60 Chromosorb W (acid washed) at 100° with an injector temperature of 275°, a detector temperature of 320°, and a helium flow of 50 ml/min: 3-methyl-2-butenoic acid, 10.4 min; hexachloroethane, 15.9 min.

Standard solutions were used to establish vpc response factors. To minimize evaporation of the solutes, a volumetric was partially filled with solvent, fitted with a serum cap, and weighed. Standards were then added through the serum cap with a syringe and the flask was weighed again. Dilution to the mark with solvent gave the standard solution. Volumes of methyl chloride and isobutene were measured in a gas buret and transferred quantitatively to an evacuated flask containing a measured volume of solvent to give standard solutions. The total estimated error for the volume measurement was ±2%. The flask was closed with a stopcock and samples were removed through the stopcock with a syringe; the concentrations of the standards decreased only slightly (2–3%) over an 8-month period.

All vpc peak areas were determined by repeated scans with a Gelman planimeter; reproducibility was within 1–2%. The data were recorded in Tables I, II, VIII, and IX.

Small-Scale Decompositions to Determine k_H/k_{Cl}. The procedures described below apply to all small-scale decompositions (1.00 ml of solution) in which the relative yields of isobutene and 1-chloro-2-methyl-1-propene were determined by vpc. The desired amount of perester or peroxide was weighed into a 10-ml volumetric flask. Carbon tetrachloride was added to the flask by tuberculin syringe and weighed; the hydrocarbon solvent was then added to 10 ml and weighed. Into the reaction tubes, 1.00 ml of peroxide or perester solution was carefully measured by a 1.00-ml tuberculin syringe. The reaction tubes were degassed by three freeze–pump–thaw cycles, sealed, and heated as previously described. Tubes were removed at appropriate times and stored in Dry Ice–acetone; the tubes were then cracked and fitted with a serum cap shortly before analysis. Unreacted diacyl peroxide in low conversion runs was destroyed by the addition of an appropriate volume of a standard solution of triphenylphosphine (Eastman Kodak Co.) in carbon tetrachloride (1.0–1.1 *M*) to the capped reaction tubes.[29] Volumes of quench sufficient to produce a phosphine concentration equal to five times the initial peroxide concentrations were used. The peroxide–phosphine mixtures were allowed to stand for 3 hr at room temperature before vpc analysis. Quantitative determination of the relative amounts of isobutene and 1-chloro-2-methylpropene-1 was made by vpc analysis of equivolume injections of reaction and standard solutions. A 50-μl Hamilton syringe fitted with a "Chaney adapter" was used to make repetitive 25- or 50-μl injections. Analyses were performed on an SF-96 column (15 ft × 0.25 in., 25% on 60–80 Chromosorb A, 70°) on the F & M 700 instrument with an injector temperature of 175°, a detector temperature of 280°, and a helium flow of 40 cc/min; isobutene, 7.0 min; 1-chloro-2-methyl-1-propene, 33.4 min. The column temperature was then raised to 300° to improve solvents and higher boiling products.

The relative molar response factor for isobutene and 1-chloro-2-methylpropene-1 was determined by the analysis of five standard solutions of varying concentrations to be 1.14 ± 0.05. Subsequent measurements were used to confirm the validity of the correction factor for each particular analytical run.

Peak areas of reaction products and standard reactions, as measured by five tracings with a Gelman planimeter, were generally reproducible to within 1–2%, although slightly larger variations were evident on some of the smaller peaks. The measurement of peak areas is, in general, more precise under the conditions employed in this study than the reproducibility of absolute or relative peak areas from injection to injection. The standard deviation in the determination of the relative molar response factor of ±4% represents a good measure of the precision of the determination of this study. The molar ratio of carbon tetrachloride to hydrogen donor solvent was calculated from the weights of each.

Each entry in Tables III and IV represents the results of a single reaction tube. Triplicate injections were made of some reaction tubes heated for the shortest times to determine the reproducibility of peak area and area ratios under these limiting conditions. A precision of ±4% or better in absolute and relative peak areas was obtained in all cases.

Decomposition of 3-Methyl-2-butenoyl Peroxide in the Presence of 1-Chloro-2-methyl-1-propene. 3-Methyl-2-butenoyl peroxide was decomposed in 6.22:1.00 cumene:carbon tetrachloride at 110.0 ± 0.5° for 4 hr in the presence of deliberately added 1-chloro-2-methylpropene-1. The peak areas for chloroolefin were determined in the usual way for (A) 0.0618 *M* 3-methyl-2-butenoyl peroxide, (B) 0.0309 *M* peroxide and 0.0183 *M* chloroolefin, and (C) 0.0366 *M* chloroolefin. Results are shown in Table X. The ratio of chloride peak area/peroxide concentration due to peroxide decomposition was determined from A and assumed to apply to chloroolefin formed from peroxide in B. The ratio of peak area/

Table X

Tube	[I], *M*	Added [VCl], *M*	Peak area VCl(obsd)
A-1	0.0618	0	175
A-2	0.0618	0	171
B-1	0.0309	0.0183	254[a]
B-2	0.0309	0.0183	251[a]
C-1	0	0.0366	328
C-2	0	0.0366	338
C-3	0	0.0366	324

[a] Predicted peak area VCl = 252.

chloroolefin concentration due to added chloroolefin was determined from C and assumed to apply to chloroolefin added to B. The sum of these predicted chloroolefin peak areas for B gives a calculated peak area for B, which is compared to the observed chloroolefin peak area for B. The agreement between calculated and observed values demonstrates the stability of chloroolefin to the reaction conditions.

Decomposition of 3-Methyl-2-butenoyl Peroxide in the Presence of 3-Methyl-2-butenoic Acid. A degassed carbon tetrachloride solution, 0.500 *M* in 3-methyl-2-butenoyl peroxide and 0.033 *M* in 3-methyl-2-butenoic acid, was heated at 78.0 ± 0.2° for 12 hr. The solution was then analyzed for 3-methyl-2-butenoic acid by vpc. Equivolume (50 μl) injections of reaction solution and a standard solution of 0.0331 *M* in 3-methyl-2-butenoic acid were injected on an SE-30 methyl column (10 ft × 0.25 in., 10% on 45-60 acid-washed Chromosorb W, F & M 720 instrument) at 100° with an injector temperature of 240°, a detector temperature of 310°, and a helium flow of 50 cc/min: 3-methyl-2-butenoic acid, 10.4 min. The average peak area for the solution containing acid was 280.8. Since the yield of acid produced in the thermal decomposition of 3-methyl-2-butenoyl peroxide is immeasurably small at this peroxide concentration, the added acid was therefore recovered unreacted. 2-Methylpropene was not detected; analysis of standard solutions showed that 0.25% yield was readily observable.

3-Methyl-1,1,1,3-tetrachlorobutane. Authentic material was prepared by the benzoyl peroxide catalyzed addition of carbon tetrachloride to 2-methylpropene: bp 79–83° (21 mm); $n^{17.5}$D 1.4855 (lit.[38] bp 64–75° (7 mm); n^{20}D 1.4850); nmr 3.408 (s, 1 H), 1.85 (s, 3 H); ir 3040, 2990, 765, 705 cm^{-1}. 3-Methyl-1,1,1,3-tetrachlorobutane was identified as a reaction product in k_H/k_{Cl} runs by vpc retention time. Approximately 0.05 *M* 3-methyl-2-butenoyl peroxide in 17:1 toluene:carbon tetrachloride solvent mixtures was decomposed at both 110.0 ± 0.5° for 4 hr and 78.0 ± 0.2° for 12 hr. Analysis on an SE-30 methyl column (10 ft × 0.25 in., 10%, temperature programmed at 2°/min from 70 to 90° and held at 90°, He flow 100 cc/min, F & M 720 instrument, injector 250°, detector 310°) gave a peak which was enhanced in size, but not altered in shape, by the coinjection of authentic 3-methyl-1,1,1,3-tetrachlorobutane. Decomposition of 0.1034 *M* 3-methyl-2-butenoyl peroxide in a 10.14:1.00 *p*-chlorotoluene–carbon tetrachloride solvent mixture at 78.0 ± 0.2° for 24 hr (100% conversion) also gave a peak which was enhanced in size, but not altered in shape, by the coinjection of authentic adduct. Decomposition for 10 min (17% conversion) produced no detectable peak in this region, and the presence of a peak in this region was questionable for decomposition for 30 min (37% conversion). Analyses of standard solutions showed that reaction of ~5% of the isobutene to form adduct would have been detected in the lowest conversion run (17%).

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Polyene Antibiotics. II. The Structure of Tetrin A[1,2]

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Abstract: Structure **1** ($C_{34}H_{51}NO_{13}$) has been assigned to tetrin A, from consideration of the structures of certain degradation products, including 3,15-dimethylhexacosane (**7**) and 12-methyl-13-hydroxy-2,4,6,8,10-tetradecapentaenal (**15**), and from nmr and mass spectral properties of a number of derivatives, especially *N*-acetyltetrin A and decahydrotetrin A.

The antibiotic tetrin, which inhibits the growth of yeasts and fungi, was first reported in 1960[4] and immediately recognized as a member of the family of antibiotics containing an isolated tetraene chromophore.[5] Somewhat later we reported our initial chemical studies on tetrin,[1] which revealed that the antibiotic consists of two closely related components, tetrins A and B. Tetrin A is about three times as active against *Penicillium oxalicum* and the separated components were also characterized by their chemical and physical properties. From microanalyses of the antibiotics and derivatives, tetrins A and B were assigned the tentative formulas $C_{35}H_{53-55}NO_{13}$ and $C_{34-35}H_{53-55}NO_{14}$, respectively. Both compounds contain the tetraene chromophore; both gave mycosamine on acidic hydrolysis. Since tetrins A and B represent the only reported isolation of two tetraene antibiotics from the same microorganism, their structures, and especially the differences between them, are of special interest. In the present report we assign structure **1** (Figure 1) to tetrin A. Our studies with tetrin B are described separately.[6]

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