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High-Pressure Studies. VIII. Thermal Decomposition
of Isomeric *tert*-Butyl Vinyl Peresters in Solution

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High-Pressure Studies. VIII. Thermal Decomposition of Isomeric *tert*-Butyl Vinyl Peresters in Solution¹

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Abstract: The effects of pressure on the rates and decomposition products of the *cis* and *trans* isomers of *tert*-butyl 2-propyl-2-peroxypentanoate were determined using the solvent cumene. The data indicate that both isomers decompose by one-bond O–O scission to yield geminate vinylcarboxy and *tert*-butoxy radicals. The isomeric vinylcarboxy radicals appear to have different reactivities. The data indicate that the initially formed geminate pairs recombine to regenerate starting material in competition with disproportionation and separative diffusion. The apparent activation volumes for the two isomers are different (*cis*, $+6.8 \pm 0.4$ cm³/mol; *trans*, $+9.0 \pm 1.0$ cm³/mol) and this suggests that recombination of the radical pair derived from the *trans*-perester is more competitive with disproportionation and separative diffusion than that for the other isomer. Disproportionation to form 3-heptyne and 3,4-heptadiene is more favorable from the *cis*-vinylcarboxy radical and it also appears that this radical undergoes unimolecular decarboxylation more rapidly than the corresponding isomer. The isomeric vinyl radicals ultimately formed from these peresters equilibrate rapidly at atmospheric pressure, but the data suggest that application of pressure permits preequilibrium trapping.

Effects of pressure on decomposition rates and products of free-radical initiators have been used to probe their decomposition mechanisms.^{1a,3} Observed activation volumes for one-bond scission initiators are substantially larger than those for two-bond initiators (Table I)^{1a,3,4} and this has been rationalized as the kinetic result of cage return of the primary radical products in the former systems.^{1a,3,5} We have

(1) (a) Parts VI and VII: R. C. Neuman, Jr., and J. V. Behar, *J. Org. Chem.*, **36**, 654, 657 (1971). (b) Support by the National Science Foundation (GP-8670) is gratefully acknowledged. (c) Presented at the ACS-CIC Joint Meeting, Toronto, Canada, May 24–29, 1970, Abstracts, Phys 056.

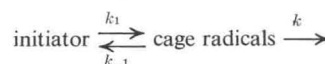
(2) Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research through a graduate student fellowship to G. D. H. (1969–1970).

(3) (a) R. C. Neuman, Jr., and R. J. Bussey, *J. Amer. Chem. Soc.*, **92**, 2440 (1970); (b) R. C. Neuman, Jr., *Intra-Sci. Chem. Rep.*, **3**, 269 (1969); (c) R. C. Neuman, Jr., and J. V. Behar, *J. Amer. Chem. Soc.*, **91**, 6024 (1969); (d) R. C. Neuman, Jr., and R. J. Bussey, *Tetrahedron Lett.*, 5859 (1968); (e) R. C. Neuman, Jr., and J. V. Behar, *ibid.*, 3281 (1968); (f) R. C. Neuman, Jr., and J. V. Behar, *J. Amer. Chem. Soc.*, **89**, 4549 (1967).

(4) (a) A. E. Nicholson and R. G. W. Norrish, *Discuss. Faraday Soc.*, **22**, 97 (1956); (b) A. E. Nicholson and R. G. W. Norrish, *ibid.*, **22**, 104 (1956); (c) C. Walling and J. Pellon, *J. Amer. Chem. Soc.*, **79**, 4786 (1957); (d) C. Walling, H. N. Moulden, J. H. Waters, and R. C. Neuman, Jr., *ibid.*, **87**, 518 (1965); (e) C. Walling and G. Metzger, *ibid.*, **81**, 5365 (1959); (f) C. Walling and H. P. Waits, *J. Phys. Chem.*, **71**, 2361 (1967); (g) A. H. Ewald, *Discuss. Faraday Soc.*, **22**, 138 (1965).

obtained the majority of the pressure data for two-bond initiators, but our results for one-bond systems were limited to a cursory study of *tert*-butyl perbenzoate.^{3c} We report here a more detailed pressure study of two isomeric *tert*-butyl vinyl peresters which we presumed would fall within this latter class of initiators.⁶ The kinetic and product data for *cis*- and *trans-tert*-butyl 2-propyl-2-peroxypentanoate (**1** and **2**)⁷ in cumene: (1) support the one-bond scission decomposition

(5) For the general homolytic scission mechanism below, ΔV_{obsd}^*



equals $\Delta V_1^* + RT \partial \ln(1 + k_{-1}/k)/\partial P$. The latter term should be positive since k includes k_d which is greatly pressure retarded. For two-bond scission, $k_{-1} = 0$; hence if values of ΔV_1^* are similar for one- and two-bond scission, ΔV_{obsd}^* for the former would be greater than for the latter.^{1a,3}

(6) See (a) L. A. Singer and J. Chen, *Tetrahedron Lett.*, 4849 (1969); (b) L. A. Singer and N. P. Kong, *J. Amer. Chem. Soc.*, **89**, 5251 (1967); (c) R. M. Fantazier and J. A. Kampmeier, *ibid.*, **88**, 5219 (1966); (d) L. A. Singer and N. P. Kong, *ibid.*, **88**, 5213 (1966); (e) J. A. Kampmeier and R. M. Fantazier, *ibid.*, **88**, 1959 (1966).

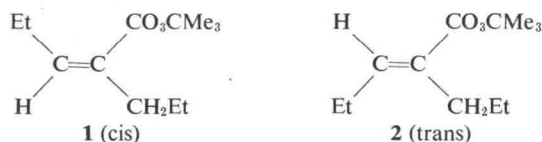
(7) (a) Structural assignments are consistent with nmr positions of vinyl proton signals^{6b,d} and independent syntheses of the carboxylic acid precursors from the corresponding vinyl iodides;^{7b} complete details are outlined in G. D. H.'s Ph.D. Dissertation, University of California, Riverside, Calif., 1970; (b) R. C. Neuman, Jr., and G. D. Holmes, *J. Org. Chem.*, **33**, 4317 (1968).

Table I. Observed Decomposition Activation Volumes for Free-Radical Initiators

Compd	Solvent	T, °C	ΔV_{obsd}^*
One-bond scission initiators			
Benzoyl peroxide	CCl ₄	60	+10 ^a
	Styrene	30	10 ^b
	Acetophenone	80	5 ^c
<i>tert</i> -Butyl peroxide	Benzene	120	13 ^d
	CCl ₄		13 ^d
	Cyclohexene		7 ^d
	Toluene		5 ^d
<i>tert</i> -Butyl perbenzoate	Cumene	80	11 ^e
Pentaphenylethane	Chlorobenzene		13 ^e
	Toluene	70	13 ^f
Two-bond scission initiators			
AIBN	Toluene	70	+4 ^f
Azocumene	Cumene	55	5.0 ^g
	Chlorobenzene		4.3 ^g
<i>p,p'</i> -Dimethylazocumene	Cumene		4.6 ^g
Di- <i>tert</i> -butyl hyponitrite	<i>n</i> -Octane		4.3 ^h
Carbo- <i>tert</i> -butylperoxy-cyclohexane	Cumene	80	3.9 ^e
<i>tert</i> -Butyl phenylperacetate			0.4 ^{e,i}
<i>m</i> -Cl isomer			1.6 ⁱ
<i>p</i> -Cl isomer			1.2 ⁱ
<i>p</i> -CH ₃ isomer			0.2 ⁱ
<i>p</i> -CH ₃ O isomer		60	0.2 ⁱ

^a Reference 4a. ^b Reference 4b. ^c References 4c and 4d; this value may be low due to induced decomposition. ^d References 4e and 4f. ^e Reference 3c. ^f Reference 4g. ^g M. Amrich, unpublished work. ^h Reference 3a. ⁱ Reference 1a; these values are pressure dependent and approach +3 to +4 cm³/mol at high pressure; they include contributions from solvation effects.

mechanism and our proposals about homolytic scission activation volumes; (2) indicate that the primary geminate vinylcarboxy and *tert*-butoxy radicals re-



combine to regenerate starting material; (3) suggest that the isomeric vinylcarboxy radicals have different reactivities; and (4) indicate that pressure may facilitate preequilibrium trapping of the isomeric vinyl radicals formed by decarboxylation of the vinylcarboxy radicals.

Results and Discussion

Activation parameters calculated from the atmospheric pressure rate data (Table II) for **1** and **2** are similar to those for other structurally dissimilar vinyl peresters^{6d} (Table III), indicating that all decompose by one-bond O–O scission.⁸ In agreement with our expectations, the observed decomposition activation volumes (**1**, +6.8 ± 0.4 cm³/mol; **2**, +9.0 ± 1.0 cm³/mol) calculated from the variable-pressure rate data (Table IV; Figure 1) are positive and larger than those found for two-bond scission systems (see Table I).⁵ This indicates that the primary radicals return to starting perester (k_{-1} ; eq 1) in competition with separative diffusion (k_d) and other cage reactions (k). Such cage return has not been previously proposed for

(8) Induced decomposition does not appear to be important in these systems. No curvature was observed in any of the first-order rate plots; at 100.15° (Table II) decomposition of **1** and **2** was followed through four half-lives. There was no consistent variation in the rate constants with concentration at 100.1° (Table II).

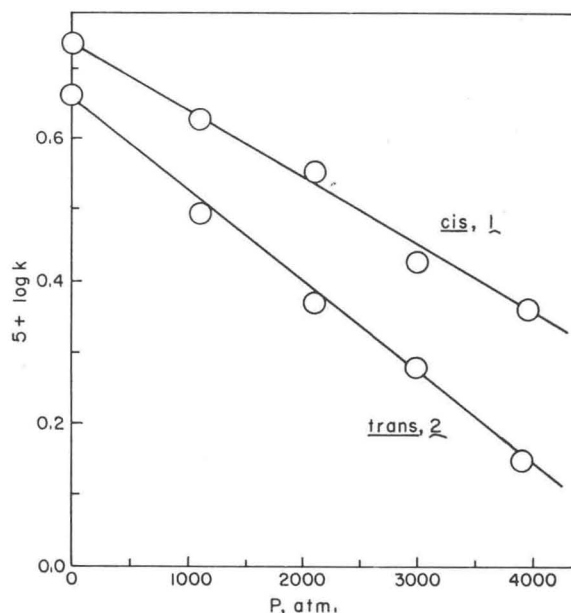
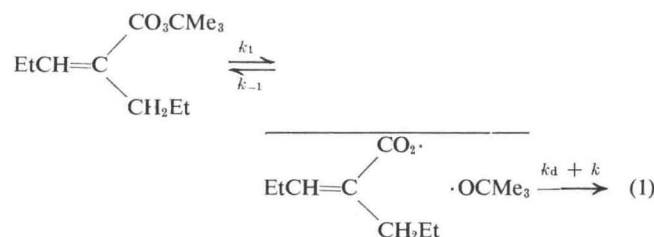


Figure 1. Pressure dependence of the apparent decomposition rate constants of **1** and **2** in cumene (100.1°).



vinyl peresters, but seems reasonable in view of other examples of such processes involving acyloxy and/or *tert*-butoxy radicals.^{4f,9}

Table II. Rate Constants for Thermal Decomposition of **1** and **2** in Cumene at Atmospheric Pressure^{a,b}

Perester	$T, ^\circ\text{C}$	Concn, M	$10^5k, \text{sec}^{-1}$
1 (cis)	94.94 ± 0.06	0.142	2.78 ± 0.03
			2.77 ± 0.02
	100.10 ± 0.08	0.130	5.30 ± 0.14
		0.052	5.51 ± 0.11
			5.30 ± 0.16
	100.15 ± 0.05	0.142	5.58 ± 0.09
			5.55 ± 0.09
	110.08 ± 0.10		17.3 ± 0.30
		17.1 ± 0.20	
2 (trans)	94.94 ± 0.06	0.121	2.47 ± 0.08
			2.47 ± 0.03
	100.10 ± 0.08	0.130	4.61 ± 0.11
		0.052	4.66 ± 0.16
			4.89 ± 0.15
	100.15 ± 0.05	0.121	4.42 ± 0.02
			4.51 ± 0.02
	110.08 ± 0.10	0.121	16.4 ± 0.50
16.3 ± 0.60			
16.5 ± 0.60^c			

^a Degassed solutions in sealed ampoules. ^b Errors are standard deviations from least-squares analysis of the data for each run. ^c Not degassed.

(9) (a) J. W. Taylor and J. C. Martin, *J. Amer. Chem. Soc.*, **89**, 6904 (1967); (b) T. Koenig and M. Deinzer, *ibid.*, **88**, 4518 (1966); (c) W. A. Pryor and K. Smith, *ibid.*, **89**, 1741 (1967); (d) H. Kiefer and T. G. Traylor, *ibid.*, **89**, 6667 (1967); (e) T. Koenig and M. Deinzer, *ibid.*, **90**, 7014 (1968); (f) T. Koenig, *ibid.*, **91**, 2558 (1969); (g) T. Koenig and R. Cruthoff, *ibid.*, **91**, 2562 (1969); (h) J. C. Martin and J. H. Hargis,

Table III. Comparison of Activation Parameters for Decomposition of Various *tert*-Butyl Vinyl Peresters

R ₁	R ₂	Isomer	ΔH^* , kcal/mol	ΔS^* , eu	ΔF^* , kcal/mol ^b
C ₆ H ₅	C ₆ H ₅	Cis ^a	32.7 ± 0.2	13.3 ± 0.6	27.7
		Trans ^a	32.0 ± 0.3	8.0 ± 0.8	29.0
C ₆ H ₅	CH ₃	Cis ^a	30.6 ± 0.3	5.1 ± 0.7	28.7
		Trans ^a	30.0 ± 0.6	1.0 ± 1.4	29.6
CH ₃ CH ₂	CH ₃ CH ₂ CH ₂	Cis (1)	32.8 ± 0.5	9.4 ± 1.2	29.2
		Trans (2)	34.4 ± 0.7	13.5 ± 1.9	29.4

^a Reference 6d. ^b Calculated at 373°K.Table IV. Rate Constants for Thermal Decomposition of 1 and 2 in Cumene at Various Pressures (100.1°)^a

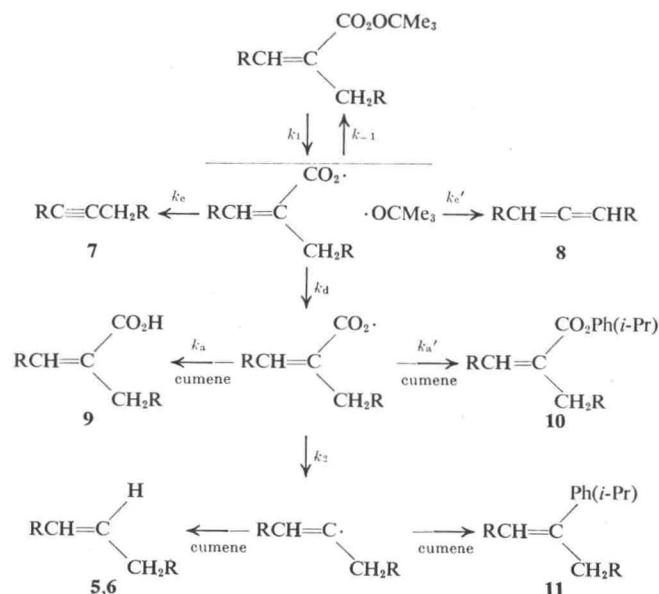
Perester	P, atm	10 ⁵ k, sec ⁻¹	ΔV_P^* , cm ³ /mol ^c
1 (cis)	1	5.45 ± 0.12 ^b	(6.8 ± 0.4)
	1090	4.26 ± 0.12	6.9
	2100	3.59 ± 0.12	6.1
	2990	2.68 ± 0.15	7.3
	3950	2.31 ± 0.08	6.7
2 (trans)	1	4.62 ± 0.11 ^b	(9.0 ± 1.0)
	1090	3.13 ± 0.05	10.9
	2100	2.35 ± 0.05	9.9
	2990	1.91 ± 0.06	9.1
	3910	1.42 ± 0.09	9.2

^a Solutions degassed and reaction ampoules prepared under inert atmosphere. Errors in rate constants are standard deviations arising from least-squares analysis of the kinetic data. ^b Rate constants at atmospheric pressure are averages of all data at 100.1° from Table II for each perester. ^c Values given in brackets arise from a least-squares treatment of all of the data for each perester. Values at pressure *P* were calculated from the equation $\Delta V_P^* = (RT/P) \ln (k_0/k_P)$.

The larger value of ΔV_{obsd}^* for the *trans*-perester 2 suggests that differences in k_{-1} and/or k (eq 1) exist between 1 and 2 such that cage return is relatively more important in the latter case. This would indicate that the isomeric vinylcarboxy radicals have differing reactivities. The data do not permit an analysis of k_{-1} , but the product distributions and their pressure dependences (*vide infra*) indicate that k is greater for 1 than for 2, the correct relationship to correspond with the differences in ΔV_{obsd}^* .

It has been noted^{6d} (Table II) that *cis*-vinyl peresters decompose more rapidly than their *trans* isomers, and explanations have been proposed which do not consider the possibility of cage return (k_{-1}) or an isomer dependence of the ratio $k_{-1}/(k + k_d)$. Since both may be generally important in these systems it is probable that the previous explanations are inadequate.

The products and their pressure dependences (Tables V and VI) are best accounted for by Scheme I.^{10,11} Allenes (e.g., 8) have not previously been reported in studies of vinyl peresters, nor have products such as 10 and 11 derived from attack of vinylcarboxy and vinyl radicals, respectively, on the solvent. Quantitative data for 10 and 11 are not available, but both appear to have



been formed.^{12,13} They may account for the low-product balances which have traditionally characterized studies of vinyl peresters.⁶

The acetylene and allene (7 and 8) are proposed to arise from the initial cage in competition with return and separative diffusion. While their absolute yields vary with pressure (Table V) their ratios (Table VI) are relatively constant for each perester, supporting their origins from common precursors by similar mechanisms. The larger values of 7/8 from 1 suggest that *trans* elimination of CO₂ to form 3-heptyne (7) is preferable to *cis* elimination.

The ratio $(k_e + k_e')/k_d$, formally equal to the product ratio $(7 + 8)/(5 + 6 + 9 + 10 + 11)$, should increase with pressure since diffusion rate constants (k_d) are markedly decreased by pressure.^{3a} While quantitative data for 10 and 11 are not available, $(7 + 8)/(5 + 6 + 9)$ does increase. If it is assumed that 10 and 11 account for the balance of the reaction products, the calculated ratios $(7 + 8)/(5 + 6 + 9 + 10 + 11)$ also increase with pressure. Additionally, they are about twice as large for 1 as for 2 just as observed for $(7 + 8)/(5 + 6 + 9)$.

(12) We have synthesized the *cis* and *trans* para-substituted isomers of 11 and determined that both are reaction products by glpc comparisons; the traces of the reaction mixtures suggest that the meta isomers may also be present; their yields decrease with increasing pressure. We have synthesized a para isomer of 10; there is indication by glpc that it is present in low yield in a high-pressure reaction mixture of the corresponding perester; it is not present in atmospheric pressure reaction mixtures.

(13) Precedents for reactions like those giving 10 and 11 include: (a) P. Spagnolo and M. Tiecco, *Tetrahedron Lett.*, 2313 (1968); (b) J. Saltiel and H. C. Curtis, *Mol. Photochem.*, 1, 239 (1969); (c) J. R. Shelton and C. W. Uzelmeier, *J. Amer. Chem. Soc.*, 88, 5222 (1966); (d) see also ref 6c, p 1961, line 9.

J. Amer. Chem. Soc., 91, 5399 (1969); (i) W. A. Pryor and K. Smith, *ibid.*, 92, 5403 (1970).

(10) We estimate that 5–10% decomposition of the peresters could have occurred during higher temperature and low-pressure conditions prevailing during the initial stages of each pressure run.^{1a} This leads to no problem in the kinetic studies,^{3c} but the product yields reflect this nonequilibrium decomposition. However, the ratios (Table VI) are relatively temperature insensitive and corrections for the nonequilibrium pressures would tend to enhance the observed trends.

(11) Based on our data (*vide infra*) and those of others, cage decarboxylation of the initially formed vinylcarboxy radicals appears to be unimportant.^{6c,d}

Table V. Products from Decomposition of 1 and 2 in Cumene^a

<i>P</i> , atm	<i>T</i> , °C	Concn, <i>M</i>	—3-Heptene—		3-Heptyne (7)	3,4-Hepta- diene (8)	Acid (9) ^b	<i>tert</i> - Butyl alcohol	Acetone	Total acyl- oxy ^c	Total <i>tert</i> - butyl ^d
			Cis (5)	Trans (6)							
1. <i>tert</i> -Butyl <i>cis</i> -2-Propyl-2-peroxypentenoate											
1	94.9	0.14	23.7	25.7	6.6	4.3	5.3	85.2	4.2	65.6	89.4
	100.2		22.6	23.6	6.3	3.9	5.0	71.8	5.7	61.4	77.5
	110.1		25.7	26.8	6.3	4.0	5.7	65.8	5.2	68.5	71.0
	110.1 ^e		23.0	28.5	5.9	3.6	<i>f</i>	71.4	5.5	<i>f</i>	76.9
1050	100.1	0.13	18.4	20.9	10.2	7.2	7.7	74.5	2.8	64.4	77.3
2100	14.0		16.7	11.7	8.4	10.0	70.3	1.9	60.8	72.2	
2990	12.7		15.7	16.5	9.4	8.6	70.4	1.8	62.9	72.2	
3950	10.8		13.3	13.0	9.7	9.2	72.7	1.7	56.0	74.4	
2. <i>tert</i> -Butyl <i>trans</i> -2-Propyl-2-peroxypentenoate											
1	94.9	0.12	26.1	28.0	3.1	2.8	8.2	69.5	6.4	68.2	75.9
	100.2		26.8	27.3	3.1	2.7	8.2	75.4	8.5	68.1	83.9
	100.0	0.15 ^a	12.4	18.7	3.6	3.8	33.7	86.5	9.1	72.2	95.6
	110.1		26.1	28.1	3.0	2.8	8.8	69.4	6.4	68.8	75.8
1050	110.1 ^e	0.06	20.8	27.1	2.7	2.5	<i>f</i>	77.5	5.5	<i>f</i>	83.0
	110.1		25.6	28.4	2.8	2.8	<i>f</i>	70.4	7.1	<i>f</i>	77.5
	100.1		21.8	24.0	6.0	5.7	10.0	78.1	3.8	67.5	81.9
	2100		17.5	19.1	7.1	6.9	13.8	83.0	2.8	64.4	85.8
2990	3910	0.13	13.6	15.7	7.5	7.1	21.6	75.1	2.5	65.5	77.6
10.4			12.2	6.9	7.0	23.2	73.9	3.1	59.7	77.0	

^a Analyzed by glpc; absolute percentage yields based on starting perester; values are averages of duplicate or triplicate runs; errors in quoted yields of products are about 2% for 5–8 and tert-butyl alcohol, about 5% for acetone, and perhaps as high as 10% for 9; solutions degassed, see footnotes Tables II and IV. ^b Determined by infrared analyses. ^c Sum of 5 through 9. ^d Sum of tert-butyl alcohol and acetone. ^e Not degassed. ^f Not determined. ^g Solvent tetralin.

Table VI. Product Ratios from Decomposition of 1 and 2 in Cumene^a

P , atm	T , °C	Concn, M	(7 + 8)/(5 + 6 + 9)	7/8	9/(5 + 6)	5/6
1. <i>tert</i> -Butyl <i>cis</i> -2-Propyl-2-peroxypentenoate						
1	94.9	0.14	0.2	1.5	0.1	0.93 ± 0.01
	100.2		0.2	1.6	0.1	0.96 ± 0.02
	110.1		0.2	1.6	0.1	0.96 ± 0.02
	110.1 ^b		<i>c</i>	1.6	<i>c</i>	0.81 ± 0.00
1050	100.1	0.13	0.4	1.4	0.2	0.87 ± 0.03
2100	0.5		1.4	0.3	0.84 ± 0.02	
2990	0.7		1.8	0.3	0.81 ± 0.02	
3950	0.7		1.3	0.4	0.80 ± 0.01	
2. <i>tert</i> -Butyl <i>trans</i> -2-Propyl-2-peroxypentenoate						
1	94.9	0.12	0.1	1.1	0.2	0.93
	100.2		0.1	1.2	0.2	0.98 ± 0.02
	100.0	0.15 ^d	0.1	1.0	1.1	0.66
	110.1		0.1	1.1	0.2	0.93 ± 0.02
	110.1 ^b	0.06	<i>c</i>	1.1	<i>c</i>	0.79 ± 0.04
	110.1		<i>c</i>	1.0	<i>c</i>	0.90 ± 0.03
1050	100.1		0.13	0.2	1.1	0.2
2100	0.3	1.0		0.4	0.91 ± 0.01	
2990	0.3	1.1		0.7	0.87 ± 0.01	
3910	0.3	1.0		1.0	0.85 ± 0.01	

^a See footnotes, Table V; product ratios calculated using data from Table V. ^b Not degassed. ^c Data for 9 not available. ^d Solvent tetralin.

9) (Table VI). This suggests that $(k_e + k_e')_1 > (k_e + k_e')_2$ in agreement with the conclusions derived from the comparative values of ΔV_{obsd}^* for 1 and 2.¹⁴

The ratio k_a/k_2 would be expected to increase with pressure since hydrogen abstraction and decarboxylation should be, respectively, accelerated and retarded. This is indicated by the increase in 9/(5 + 6) for each perester (Table VI). Since these ratios are larger from 2 than from 1, decarboxylation of vinylcarboxy radicals from 1 appears to be better than decarboxylation of those from 2.

At atmospheric pressure, the cis/trans 3-heptene ratios (5/6) are essentially the same indicating rapid

equilibration of vinyl radicals.^{6,15} In the absence of such equilibration, 1 and 2 would be expected to yield exclusively 6 and 5, respectively. It is interesting to note that the ratios 5/6 for the two isomers seem to diverge with increasing pressure, and the direction of this divergence could be accounted for by trapping of the isomeric vinyl radicals prior to complete equilibration.¹⁶

(15) G. D. Sargent and M. W. Browne, *J. Amer. Chem. Soc.*, **89**, 2788 (1967).

(16) (a) In the solvent tetralin, a better hydrogen donor,^{16b} the yields of 7 and 8 remained essentially the same as in cumene, while that of the acid 9 increased markedly at the expense of 5 and 6 (see Tables V and VI). This supports Scheme I. (b) See C. Walling, "Free Radicals in Solution," Wiley, New York, N. Y., 1957, p 422.

(14) The sum $k_e + k_e'$ (Scheme I) is identical with the rate constant k (eq 1). The values of k_a should be isomer independent.

Experimental Section

General. Cumene (MCB) was purified by shaking with concentrated sulfuric acid and distillation at atmospheric pressure under an atmosphere of nitrogen. *tert*-Butyl hydroperoxide (Wallace and Tiernan) was purified by vacuum distillation at room temperature. Reagent grade *cis*- and *trans*-3-heptene,^{7b} 3-heptyne, *tert*-butyl alcohol, and acetone were used as glpc standards without further purification.

2-Hydroxy-2-propylpentanoic Acid. The compound 2-hydroxy-2-propylpentanoic acid was synthesized by the procedure of Lucas and Prates,^{17,18} using 556 g (5 mol) of 4-heptanone, 270 g (5.5 mol) of sodium cyanide, and 450 g (5 mol) of concentrated nitric acid. Vacuum distillation of the reaction mixture yielded 392 g (3.4 mol) of unreacted 4-heptanone and 84.8 g of acid, which was then recrystallized from diethyl ether (33.5% yield): bp 100–115° (1 mm); mp 77–79°; ν 3510 (OH), 3300–2600 cm^{-1} (acid OH); nmr singlet (broad and concentration dependent), τ –2.9, complex multiplet, 8–9.5.

***cis*- and *trans*-2-Propyl-2-pentenoic Acid.** Decomposition of neat 2-hydroxy-2-propylpentanoic acid at 250°^{17,18} for 0.5 hr yielded *cis*- and *trans*-2-propyl-2-pentenoic acid in a ratio of 2:1 as shown by nmr (longer times yielded more *trans* acid). The isomeric acids were separated by distillation using a Teflon spinning band column. The overall yield of 2-propyl-2-pentenoic acid was 92 g (0.647 mol; 84%); *cis* acid bp 87° (1.2 mm); ν 3500 (OH), 1630 cm^{-1} (C=O); nmr, triplet centered at τ 3.99 (1 H), complex multiplet between 7.0 and 9.5 (12 H), singlet at –2.8 (1 H); *trans* acid, bp 103° (1.0 mm); ν 3500 (OH), 1640 cm^{-1} (C=O); nmr triplet centered at τ 3.09 (1 H), complex multiplets between 7.0 and 9.5 (12 H), singlet at –2.3 (1 H). *Anal.* Calcd for $\text{C}_8\text{H}_{14}\text{O}_2$: C, 67.57; H, 9.92; O, 22.50. Found (mixture of *cis* and *trans*): C, 68.12; H, 9.96; O, 22.59.

***cis*-2-Propyl-2-pentenoyl Chloride.** The *cis* acid chloride was prepared using the sodium salt of the *cis* acid and oxalyl chloride.^{6e,19,20} A solution of 3.32 g (0.023 mol) of *cis*-2-propyl-2-pentenoic acid in 25 ml of pentane was added dropwise at room temperature to a slurry of 0.72 g (0.03 mol) of sodium hydride (Alpha) in 100 ml of pentane and the solution was stirred for 0.5 hr. A 1-ml aliquot of pyridine was added and the solution was cooled to –25°. A solution of 5.01 g (0.04 mol) of oxalyl chloride (MCB) in 50 ml of pentane was then added dropwise to the solution held at –25° over a period of 1 hr. The mixture was subsequently stirred for 10 hr at 0° and filtered under vacuum, and the pentane and excess oxalyl chloride were removed using a rotary evaporator. *cis*-2-Propyl-2-pentenoyl chloride was obtained as a slightly yellow liquid: 3.5 g (95%); ν 1760 (C=O), 1625 cm^{-1} (C=C); nmr triplet at τ 4.10 (1 H), complex multiplets at 7.62 and in the region 8.5–9.1 (12 H).

***trans*-2-Propyl-2-pentenoyl Chloride.** The *trans* acid chloride was prepared from the *trans* acid and thionyl chloride by conventional methods. The product was vacuum distilled: bp 82–84° (10 mm); yields were 95–100%. ν 1760 (C=O), 1643 cm^{-1} (C=C); nmr triplet centered at τ 2.89 (1 H), complex multiplets between 7.4 and 9.3 (12 H).

***tert*-Butyl *cis*-2-Propyl-2-peroxy-pentenoate.** To a slurry of 0.96 g (0.04 mol) of NaH (Alpha) in 300 ml of pentane was added dropwise 3.6 g (0.04 mol) of *tert*-butyl hydroperoxide (Wallace and Tiernan) in 50 ml of pentane. The slurry was stirred at room temperature for 4.5 hr and cooled to –25°, and 3.5 g (0.022 mol) of *cis*-2-propyl-2-pentenoyl chloride in 50 ml of pentane was added dropwise. After the addition of the acid chloride was completed, a solution of 3.2 g (0.04 mol) of pyridine in 25 ml of pentane was added dropwise and the solution was stirred for 3 hr as it warmed to room temperature. The solution was then washed successively with cold water, cold 10% sulfuric acid, cold 10% sodium bicarbonate, and cold water, and then dried over Drierite. The pentane was removed using a rotary evaporator. The perester was obtained as a clear liquid: 3.71 g (79%); ν 1740 (C=O), 1632 cm^{-1} (C=C); nmr triplet at τ 4.23 (1 H), complex multiplets at 7.79 and between 8.30 and 9.15, and a singlet at 8.70

(combined 21 H). An analytical sample was chromatographed on Florisil and purity checked by infrared. *Anal.* Calcd for $\text{C}_{12}\text{H}_{22}\text{O}_5$: C, 67.26; H, 10.35. Found: C, 66.78; H, 10.16.

***tert*-Butyl *trans*-2-Propyl-2-peroxy-pentenoate.** **Method A.** To a solution containing 4 g (0.025 mol) of acid chloride and 2.7 g (0.03 mol) of *tert*-butyl hydroperoxide in 50 ml of pentane at –10° was added dropwise 2.0 g (0.025 mol) of pyridine. After addition was complete the solution was stirred for 1 hr and then washed successively with cold 10% sulfuric acid, cold 10% sodium bicarbonate, and water. The pentane solution was then dried and the pentane removed *in vacuo* yielding 5.1 g (0.023 mol) of perester (93.5% yield): ν 1734 (C=O), 1636 cm^{-1} (C=C); nmr triplet at τ 3.41 (1 H), complex multiplets at 7.80 and 8.92, and a singlet at 8.71 (combined 21 H). An analytical sample was chromatographed on Florisil and purity checked by ir. *Anal.* Calcd for $\text{C}_{12}\text{H}_{22}\text{O}_5$: C, 67.26; H, 10.35. Found: C, 66.03; H, 9.98.

Method B. See procedure for the *cis* perester.

1,1-Dibromo-*trans*-2,3-diethylcyclopropane. This compound was synthesized using the procedure of Doering.²¹ Vacuum distillation yielded 2.5 g of product (19%, probable cause of low yield was the use of commercial potassium *tert*-butoxide): bp 79–82° (11 mm); nmr multiplet centered at τ 8.5 (4 H), and a multiplet of triplets centered at 8.91 (8 H).

3,4-Heptadiene. This allene was prepared from the dibromocyclopropane compound above by reaction with methyllithium.²² Distillation yielded 1.1 g of product: bp 101–103° (micro); ν 1970 cm^{-1} ; nmr pentet τ 4.95 (2 H), multiplet at 8.1 (4 H), and a triplet at 9.05 (6 H).

***cis*- and *trans*-4-(*p*-Isopropylphenyl)-3-heptene.** Equimolar amounts of *p*-bromocumene (K and K) and magnesium metal were allowed to react to form the Grignard reagent. This was treated with 4-heptanone and the alcohol resulting from hydrolysis was isolated from aqueous solution and dehydrated with iodine in acetic acid. The product was isolated, vacuum distilled (bp 90–95° (0.6 mm)), and chromatographed on Florisil: nmr multiplet at τ 2.9 (4 H), triplet at 4.4 and triplet at 4.6 (combined 1 H), multiplets at 7.2 and at 7.8 (combined 7 H), doublet at 8.8, and multiplet of overlapping triplets at 9.1 (combined 12 H). Glpc analysis indicated the presence of two components in roughly equal amounts. These were presumed to be the *cis* and *trans* isomers and this is supported by the two triplets in the region τ 4.4–4.6. The isomers were separately collected. *Anal.* Calcd for $\text{C}_{16}\text{H}_{24}$: C, 88.82; H, 11.18. Found: isomer A (lesser component), C, 88.97, 88.94; H, 11.03, 11.06; isomer B (greater component), C, 89.05, 89.04; H, 10.95, 10.96.

***p*-Isopropylphenyl *trans*-2-Propyl-2-pentenoate.** A solution of 10 g (0.074 mol) of *p*-isopropylphenol (K and K) in 25 ml of anhydrous ether was added to a pentane slurry of 3.25 g of a 57% dispersion of sodium hydride (0.077 mol). After reaction was complete an 11.8-g sample (0.074 mol) of the acid chloride of *trans*-2-propyl-2-pentenoic acid in pentane was added. The resulting solution was stirred for 3.5 hr at room temperature, washed successively with water, 10% sodium bicarbonate solution, and water, and dried. After removal of the solvent, the crude product was chromatographed on Florisil and a sample collected by glpc for microanalysis: nmr complex multiplet at τ 3.0 (5 H), septet at 7.2 and multiplet at 7.7 (combined 5 H), doublet at 8.8 and complex multiplet at 9.0 (combined *ca.* 15 H). The nmr spectral data indicate that the vinyl proton falls in the aromatic multiplet. The integration indicates the presence of impurities. Infrared: 1755 cm^{-1} (C=O). *Anal.* Calcd for $\text{C}_{17}\text{H}_{24}\text{O}_2$: C, 78.42; H, 9.29; O, 12.29. Found: C, 76.45, 76.52; H, 9.20, 9.30; O, 14.16, 14.06.

Product Analysis. Gas-liquid partition chromatographic analyses of the thermal decomposition products were performed using a 30 ft \times 1/8 in. copper column packed with 20% 3 M AgNO₃-Carbowax 20M on firebrick connected to a 6 ft \times 1/8 in. 10% SE-30 (F and M) stainless steel column in conjunction with an Aerograph Hi-Fi Model 600 flame ionization gas chromatograph (oven 95°; 20 ml/min N₂ flow) equipped with a Disc Integrator. Identities of all products were based on retention times compared to those of authentic samples; yields were determined using standard solutions.

Kinetics. A detailed description of the infrared analysis methods and high-pressure procedures have been presented.³⁰

(17) H. J. Lucas and A. N. Prates, *J. Amer. Chem. Soc.*, **59**, 2168 (1937).

(18) K. C. Chan, R. A. Jewell, W. H. Nutting, and H. Rappoport, *J. Org. Chem.*, **33**, 3382 (1968).

(19) A. L. Wilds and C. H. Shunk, *J. Amer. Chem. Soc.*, **70**, 2427 (1948).

(20) A. R. Adams and L. H. Ulich, *ibid.*, **42**, 599 (1920).

(21) W. von E. Doering and A. K. Hoffmann, *ibid.*, **75**, 6162 (1954).

(22) L. Skattebøl, *Acta Chem. Scand.*, **17**, 1683 (1963).

(23) J. M. Walbrick, J. W. Wilson, Jr., and W. M. Jones, *J. Amer. Chem. Soc.*, **90**, 2895 (1968).