Organic Peroxides. IX.[1] Kinetics of the Thermal Decomposition of Bis(5-hexenoyl) Peroxide in Toluene. General Solution of the First-plus-*x*-Order Rate Expression[2]

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Results of iodometric kinetics experiments are reported for decompositions of 5-hexenoyl peroxide in toluene and benzene at temperatures between 60 and 85°. The kinetic behavior in 0.03 *M* toluene solutions is such as to suggest that the peroxide undergoes a relatively simple homolytic decomposition at low concentrations. Kinetics data on a 0.2 *M* solution in toluene are used to estimate the importance of radical induced decomposition in that solvent, using the general solution for the first-plus-*x*-order rate expression, $\ln([P]^{1-x} + \alpha) = (x - 1)k_dt + \ln([P]_0^{1-x} + \alpha)$, in which $\alpha = k_i/k_d$. Data for the 0.2 *M* toluene solution fit this equation with any number of x,α combinations, when $1 < x < 2$. Products of the decomposition in toluene are those which are typical of diacyl peroxide decompositions. There is a more pronounced decrease in the yields of C-5 olefins in the presence of DPPH than there is in the yields of other products, which indicates that the main product derived from free 4-pentenyl radicals in toluene is 1-pentene. The failure of the 4-pentenyl radical to cyclize in solution is in agreement with some observations published by others.

This paper is a continuation of a series of papers dealing with unsaturated diacyl peroxides.[5]

Results

The results of some iodometric kinetics experiments on 5-hexenoyl peroxide in dilute toluene solutions at several temperatures between 60 and 85°, and one experiment on the decomposition of *n*-hexanoyl peroxide in toluene at 77°, are reported in Table I.

For the most part, the kinetics data were obtained on 0.03 *M* toluene solutions. These data were found to fit the first-order rate law to a high degree of precision throughout a substantial per cent decomposition. Therefore, the rate constants for the kinetics experiments at 0.03 and 0.036 *M* are apparent k_d values derived from the first-order rate law.

However, a plot of ln [P] *vs.* time for the kinetics experiment at 0.22 *M* 5-hexenoyl peroxide concentration in toluene showed definite curvature,[6–8] such as to suggest that the correct form of the rate law is

$$-d[P]/dt = k_d[P] + k_i[P]^x \qquad (1)$$

in which the exponent $x > 1$. The integral of eq 1, when $x \neq 1$, is eq 2, in which $\alpha = k_i/k_d$.

$$\ln([P]^{1-x} + \alpha) = (x - 1)k_dt + \ln([P]_0^{1-x} + \alpha) \qquad (2)$$

Equation 2 correctly reduces to the first-order rate law at $\alpha = 0$. It shows no dependence upon peroxide concentration at $x = 1$, under which condition the first-order rate law with slope equal to the sum of rate constants $(k_d + k_i)$ applies. Equation 2 behaves most poorly when x is near unity and α is large with respect to $[P]^{1-x}$.

When the $[P],t$ data for the 0.22 *M* run are plotted according to the first-order law, a decrease in rate at long times is observed. Therefore, the correct value of x in eq 2 lies in the range 1–2.

Computer programs were devised for the determination of the optimum values of x, α, k_d, and the intercept. If the residual is defined as the difference between the two sides of eq 2, the least-squares values of x and α are 1.91 and 1.85, respectively. The corresponding least-squares value for k_d is presented in Table I, and plotted in Figure 1. While the least-squares value of x is in fair agreement with the mechanism we subsequently propose, one must be most circumspect in deciding upon the correct values of x and α from $[P],t$ data in which [P] is determined by iodometric titration.

The equation is quite insensitive, and when x is assigned any fractional value between 1.1 and 2.0, a corresponding α can be computed which will accommodate $[P],t$ data for the 0.22 *M* run quite well. Thus, the average per cent error in peroxide concentration, *i.e.*, $100[\Sigma([P]_{\text{obsd}} - [P]_{\text{calcd}})^2/n]^{1/2}/[\bar{P}]$, lies between 0.51 and 0.61% for $x = 1.91$, $\alpha = 1.85$ (the least-square values); for $x = 2.0$, $\alpha = 2.1$; for $x = 1.5$, $\alpha = 1.8$;[9] and even for $x = 1.3$, $\alpha = 2.7$.[9] Likewise, values for the per cent error in k_d, *i.e.*, 100σ (in k_d)$/k_d$, lie in the range 0.45–0.50% for all the x,α pairs mentioned, and for many additional x,α pairs.

Ideally, the value of k_d deduced from eq 2 using data from the 0.22 *M* run should be *lower* than the apparent value of k_d deduced from the first-order law using the data from the 0.036 *M* run. While the least-squares values of x and α do not yield an equation which meets this condition, Figure 1 shows that the k_d obtained from eq 2 (with $x = 1.91$, $\alpha = 1.85$) lies very near the value predicted by the $1/T$ line defined by the k_d's determined

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(1) A complete list of previous papers is given in paper VIII in this series: R. C. Lamb and J. R. Sanderson, *J. Amer. Chem. Soc.*, **91**, 5034 (1969).

(2) Presented at the 158th National Meeting of the American Chemical Society, New York, N. Y., Sept 7–12, 1969. Supported, at East Carolina University, by a grant from the National Science Foundation (NSF-GP-7393). Preliminary work at the University of Georgia was supported by a grant from the Air Force Office of Scientific Research (AF-AFOSR-543-64). *Cf.* "12th Annual Chemistry Program Review," AFOSR-66-1854, Fiscal Year 1966, pp 134–138.

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(4) This paper was taken in part from the thesis of W. E. McNew, Jr., presented in partial fulfillment of the requirements for the M.S. degree, University of Georgia, June 1965.

(5) (a) R. C. Lamb, F. F. Rogers, Jr., G. C. Dean, Jr., and F. W. Voigt, Jr., *J. Amer. Chem. Soc.*, **84**, 2635 (1962); (b) R. C. Lamb, P. W. Ayers, and M. K. Toney, *ibid.*, **85**, 3483 (1963); (c) R. C. Lamb, J. G. Pacifici, and P. W. Ayers, *J. Org. Chem.*, **30**, 3099 (1965); (d) R. C. Lamb, J. G. Pacifici, and L. P. Spadafino, *ibid.*, **30**, 3102 (1965); (e) R. C. Lamb, L. P. Spadafino, R. G. Webb, E. B. Smith, W. E. McNew, and J. G. Pacifici, *ibid.*, **31**, 147 (1966). References 5a–e constitute a partial list of previous papers.

(6) C. G. Swain, W. H. Stockmayer, and J. T. Clarke, *J. Amer. Chem. Soc.*, **72**, 5426 (1950).

(7) P. D. Bartlett and K. Nozaki, *ibid.*, **69**, 2299 (1947); *ibid.*, **68**, 1686 (1946); *ibid.*, **68**, 1495 (1946).

(8) W. E. Cass, *ibid.*, **68**, 1976 (1946).

(9) The last two x,α pairs give $k_d = 7.31 \times 10^{-5}$ and 4.90×10^{-5} sec^{-1}, respectively, which are considerably lower than the value of k_d observed for 0.036 *M* run.

TABLE I

DECOMPOSITION RATES OF 5-HEXENOYL AND HEXANOYL PEROXIDE

Medium	$[P]_0$[a]	No. of samples	Temp, °C	$10^5(k_d \pm \sigma)$, sec^{-1}	Half-life, min	Per cent reaction
			5-Hexenoyl Peroxide			
Toluene	0.030	6	60.1	1.06 ± 0.02	1089	44
Toluene	0.030	7	70.4	4.15 ± 0.03	278.3	77
Toluene	0.036	7	76.4	8.59 ± 0.05	134.5	72
Toluene	0.218	9	76.4	9.30 ± 0.04[b]	124.2[d]	81
Toluene	0.218	9	76.4	9.43 ± 0.04[c]	122.5[d]	81
Toluene	0.030	7	77.0	10.08 ± 0.08	144.7	76
Toluene	0.030	5	85.0	26.68 ± 0.17	43.3	57
			Hexanoyl Peroxide			
Toluene	0.030	7	77.0	11.86 ± 0.08	97.4	78

[a] Initial molar peroxide concentration. [b] Calculated by adjustment of data to eq 2, with $x = 1.91$ and $\alpha = 1.85$. [c] Same data as used in previous entry, adjusted to eq 2, with $x = 2$ and $\alpha = 2.1$. [d] These values were calculated from $(\ln 2)/k_d$, in which k_d was obtained from eq 2. The measured half-life was actually near 90 min.

at other temperatures. (Obviously, the apparent k_d value obtained with the 0.036 M solution at 76.4° is low.)

It is instructive to consider the average fraction of the peroxide which undergoes induced decomposition within a given run. The *instantaneous* fraction (f) of the peroxide which undergoes induced decomposition is given by eq 3.

$$f = \frac{k_i[P]^x}{k_d[P] + k_i[P]^x} = 1 - [1/(1 + \alpha[P]^{x-1})] \qquad (3)$$

The *average* fraction ($\bar{f}$) may then be defined by eq 4.

$$\bar{f} = \frac{\int_0^{P_0} [1 - (1/1 + \alpha[P]^{x-1})]d[P]}{\int_0^{P_0} d[P]} = 1 - (1/[P]_0)\int_0^{P_0} \frac{d[P]}{1 + \alpha[P]^{x-1}} \qquad (4)$$

The necessary integral cannot be obtained in closed form except for $x = 1.5$ or 2. Since the latter value is very near our least-squares value of x, *we* may approximate $\bar{f}$ using eq 5.

$$\bar{f} = 1 - (1/\alpha[P]_0) \ln (1 + \alpha[P]_0) \qquad (5)$$

With the x,α pair 2, 2.1, the following values of $\bar{f}$ may be calculated: 0.18 at $[P]_0 = 0.22$ M; 0.10 at 0.11 M; 0.037 at 0.036 M; and 0.031 at 0.030 M. Inasmuch as the latter calculation shows that only 3% of the peroxide decomposes by induced decomposition at $[P]_0 = 0.03$ M (at 76.4°), we have not attempted to adjust data from the 0.030 M runs to eq 2.

If the small amount of induced decomposition in the 0.030 M runs is ignored, and all the "k_d" values for 0.03 M toluene solutions listed in Table I are treated as first-order rate constants, and adjusted by least-squares to a log (k_d/T) *vs.* $(1/T)$ function, one obtains the following parameters: $\Delta H^* = 30.2 \pm 0.4$ kcal and $\Delta S^* = +9.2$ eu.

The products of the decomposition were determined by glpc and are presented in Table II. For the decompositions in toluene solutions, the product analysis accounts for 87% of the C-5 hydrocarbon groups which were present in the original peroxide samples. Yields of the same products were also measured for decompositions in toluene containing excess DPPH.

Discussion

The weight of evidence indicates that, in 0.03 M solution in toluene, 5-hexenoyl peroxide decomposes predominantly by a relatively simple homolytic process. These points of evidence are as follows. (a) The kinetics data for 0.03 M toluene solutions follow the first-order law through two or more half-lives to a high degree of precision. (b) Careful analysis of kinetics of a 0.22 M solution indicates that approximately 3% of the peroxide decomposes by radical induced decomposition at 0.03 M concentration. (c) The value obtained

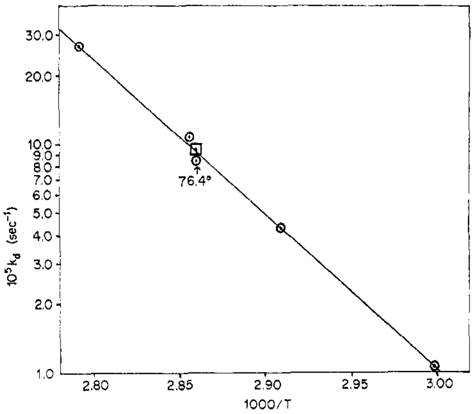


Figure 1.—Plot of log (10^5k_d) *vs.* $1000/T$ for decompositions of bis(5-hexenoyl) peroxide in toluene. ⊙, observed first-order rate constants obtained on 0.030 or 0.036 M solutions. ⊡, k_d's obtained by adjustment of data from 0.22 M run to eq 2.

TABLE II

DECOMPOSITION PRODUCTS OF 5-HEXENOYL PEROXIDE[a]

	Peroxide, M		
Products	0.11–0.22 (toluene)[b,c]	0.11 (toluene, 0.1 M DPPH)	0.22 (toluene, 0.22 M DPPH)
1-Pentene and 1,4-pentadiene	0.80	0.11	0.02
1,9-Decadiene	0.16	0.15	0.10
4-Pentenyl 5-hexenoate	0.16	0.08	0.06
5-Hexenoic acid	0.11	n.d.	n.d.
6-Phenyl-1-hexene[d]	0.22	0	0
Bibenzyl	0.16–0.11	0	0

[a] Yields are based on glpc data, and are given in mole per mole of peroxide; n.d. = not determined. [b] Data in this column are averaged for four decompositions at $[P]_0 = 0.11$, 0.13, 0.15, and 0.22 M. Only bibenzyl yield showed $[P]_0$ dependence. The yields obtained were 0.16, 0.15, 0.12, and 0.11 mol/mol peroxide, respectively. [c] The C-5 alkenes were not separated. In addition to the products listed, a trace of benzyl 5-hexenoate was observed. [d] The isomeric ring-substitution product, 5-(p-tolyl)-1-pentene, could not be detected in the reaction mixtures.

for E_a (30.9 kcal) is not significantly lower than those for propionyl (31.1 kcal) and *n*-butyryl (31.2 kcal)[10] peroxides in toluene. (d) The observed rate of decomposition of 5-hexenoyl peroxide is 20% less than that of its saturated analog, hexanoyl peroxide, at 77°. (e) The activation entropy, ΔS^*, is significantly positive, which is to be expected for homolysis, but not for rearrangement reactions in which cyclic or highly polar transition states are involved.

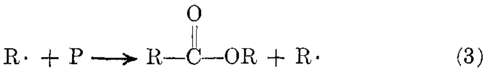
The kinetics data will not support a postulate of neighboring group effect of the double bond, such as has been postulated for decompositions of some 5-phenyl-4-pentenoyl peroxides,[5a,e] and for other peroxides of similar structure.[11] This observation is in keeping with previous evidence which we have reported for decompositions of 6-heptenoyl[5b] and 4-pentenoyl[5e] peroxides.

Therefore, the mechanism of decomposition of bis(5-hexenoyl) peroxide in toluene at 0.03 *M* is, predominantly, a first-order homolysis of the type that is usual for saturated aliphatic diacyl peroxides.

Inasmuch as induced decomposition constitutes no more than 20% of the reaction even at $[P]_0 = 0.22$ *M*, the delineation of the exact mechanism of induced decomposition is more difficult. Nevertheless, we do feel that the information which has been collected on the decompositions of bis(5-hexenoyl) peroxide suggests the following tentative mechanism, in which the terminology used is that of Swain, Stockmayer, and Clark.

$$\mathrm{P} \longrightarrow 2e\mathrm{R}\cdot \quad (e = \text{free radical efficiency}) \qquad (1)$$

$$\mathrm{R}\cdot + \mathrm{SH} \longrightarrow \mathrm{RH} + \mathrm{S}\cdot \qquad (2)$$



$$\mathrm{R}\cdot + \mathrm{P} \longrightarrow \mathrm{R}{-}\overset{\overset{\mathrm{O}}{\|}}{\mathrm{C}}{-}\mathrm{OR} + \mathrm{R}\cdot \qquad (3)$$

$$\mathrm{R}\cdot + \mathrm{R}\cdot \longrightarrow \mathrm{RR}\ (\text{or disproportionation products}) \qquad (5)$$

$$\mathrm{R}\cdot + \mathrm{S}\cdot \longrightarrow \mathrm{RS}\ (\text{or disproportionation products}) \qquad (6)$$

$$\mathrm{S}\cdot + \mathrm{S}\cdot \longrightarrow \mathrm{SS} \qquad (7)$$

R— or R· = 4-pentenyl group or free radical

S— or S· = benzyl group or free radical

None of the three possible termination steps can be rigorously denied by our product studies, for the products contain 1,9-decadiene (RR), 6-phenyl-1-hexene (RS), and bibenzyl (SS). To be sure, the latter two compounds are not formed in the presence of DPPH, while the yield of 1,9-decadiene is only slightly affected by DPPH. While this is good evidence that 1,9-decadiene is, for the most part, a cage recombination product, there is no way of determining from our data that the C-5 olefins are not formed in part from disproportionation of the 4-pentenyl radical.

In this regard, we undertook some experiments on the decompositions of bis(5-hexenoyl) peroxide in toluene containing BDPA[1,12] with the view of determining the efficiency (e) of radical production by the peroxide. Although BDPA undergoes considerable spontaneous fading in toluene at 76.4°,[5e] the efficiency appears to be in the range 0.45–0.53. The point to be made here is that, although the two termination products, 6-phenyl-1-hexene and bibenzyl, constitute the major portion of termination, these products apparently cannot account for all of the termination required by the efficiency experiments. Therefore, we cannot totally exclude R· + R· (reaction 5) as a termination reaction.

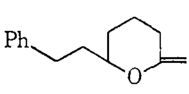
The yield of ester, 4-pentenyl 5-hexenoate, is decreased significantly in the presence of 0.1 *M* DPPH, and, although a substantial portion of the ester must be formed in cage reactions or as a rearrangement product of the peroxide, the evidence seems to indicate that a free radical is involved in the formation of a portion of it. It is for this reason that we have suggested that 4-pentenyl 5-hexenoate is a possible product of induced decomposition.

Given R· + P as the induced decomposition step, and all three termination steps, and making the assumption that $k_6 = 2(k_5k_7)^{1/2}$, one can deduce the following steady-state solution for R·.

$$(\mathrm{R}\cdot)_{\mathrm{ss}} = \frac{[2k_1f\mathrm{P}]}{k_2[\mathrm{SH}] + 2(k_1k_5f[\mathrm{P}])^{1/2}} \approx (2k_1f/k_2[\mathrm{SH}])[\mathrm{P}]$$

The approximation results from the fact that $k_2[\mathrm{SH}]$ is very likely at least an order of magnitude greater than $2(k_1k_5f[\mathrm{P}])^{1/2}$. The approximate solution for $(\mathrm{R}\cdot)_{\mathrm{SS}}$ leads to a rate expression of the form of eq 1 in which $x = 2$, which is very near our least-squares value of 1.93.

Early in this work, it was anticipated that the double bond would be involved in the induced decomposition, *via* a mechanism similar to that described by Hart and Cloupek.[13] This line of reasoning led us to synthesize 7-phenyl-5-heptanolactone (**1**) which could conceivably have been formed by the reaction of benzyl radicals with bis(5-hexenoyl) peroxide. However, we were unable to detect this lactone in the decomposition products of the peroxide in 0.22 *M* toluene solution.



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The product studies indicate that the 4-pentenyl radical is a major initial product of the homolysis of 5-hexenoyl peroxide in toluene, inasmuch as the presence of excess DPPH reduces the yield of C-5 olefins (1-pentene and 1,4-pentadiene) by a factor of eight. Neither cyclopentane, cyclopentene, nor methylcyclobutane was observed in the products; therefore, the 4-pentenyl radical does not cyclize in toluene. This result is in agreement with observations of Walling and Pearson,[14] who generated the 4-pentenyl radical by reacting 4-pentene-1-thiol with triethyl phosphite; by Walling, Cooley, Ponaras, and Racah,[15] who generated the radical by the reaction of tri-*n*-butyltin hydride with 5-bromo-1-pentene; and by Kaplan,[16] who reported a "trace" of cyclopentyl benzoate in the decomposition of benzoyl peroxide in the presence of 5-iodo-1-pentene at 115°.

Finally, we wish to reemphasize the fact that the same set of [P],*t* data can be described accurately by eq 2

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[10] J. Smid, A. Rembaum, and M. Szwarc, *J. Amer. Chem. Soc.*, **78**, 3315 (1956).

[11] T. W. Koenig and J. C. Martin, *J. Org. Chem.*, **29**, 1520 (1964).

[12] (a) C. F. Koelsch, *J. Amer. Chem. Soc.*, **79**, 4439 (1957); (b) S. L. Solar and R. M. Lindquist, *ibid.*, **82**, 4285 (1960); (c) R. Kuhn and F. A. Neugebauer, *Monatsh. Chem.*, **95**, 3 (1964).

[13] H. Hart and F. J. Cloupek, *J. Amer. Chem. Soc.*, **85**, 1155 (1963). See also ref 5b.

[14] C. Walling and M. A. Pearson, *ibid.*, **86**, 2262 (1964).

[15] C. Walling, J. H. Cooley, A. A. Ponaras, and E. J. Racah, *ibid.*, **88**, 5361 (1966).

[16] L. Kaplan, *J. Org. Chem.*, **32**, 4059 (1967).

with a variety of x,α pairs, particularly when the fraction of peroxide which undergoes induced decomposition ($\bar{f}$) is small.

Experimental Section[17]

5-Hexenoic Acid.—The procedure described by De La Mare, Kochi, and Rust[18] was used, except that the quantities of reagents were tripled, and the procedure for the isolation of the product was altered.

The chloroform layer was extracted with saturated sodium bicarbonate solution which was subsequently acidified and extracted with ether. The ether extract was dried and the ether was removed. The crude acid remaining was distilled at reduced pressure three or four times in order to render the acid colorless and of high purity.

A typical synthesis produced about a 25% yield of the acid, bp 55.5–58° (0.4 mm) and $n^{25}\mathrm{D}$ 1.43244 (lit.[19] $n^{20}\mathrm{D}$ 1.4343). The ir spectrum showed the C=O band at 1715, the C=C band at 1645, and $\mathrm{RCH{=}CH_2}$ bands at 990 and 913 $\mathrm{cm^{-1}}$. The acid chloride was prepared by treatment of the acid with phosphorus trichloride. The infrared spectrum showed the C=O band at 1832, the C=C band at 1645, and $\mathrm{RCH{=}CH_2}$ bands at 990 and 917 $\mathrm{cm^{-1}}$.

5-Hexenoyl peroxide was prepared by treatment of the acid chloride with an excess of sodium peroxide in ether at 0°, following the procedure described by Hart and Wyman[20] for the preparation of cyclopropaneformyl peroxide.

The peroxide could not be made to crystallize. The purity of the liquids was determined by iodometric titration with standardized 0.01 *N* sodium thiosulfate. The peroxide was discarded if the purity was less than about 95%. Infrared spectra showed the carbonyl doublet at 1923 and 1783 $\mathrm{cm^{-1}}$, and $\mathrm{RCH{=}CH_2}$ bands at 991 and 917 $\mathrm{cm^{-1}}$. Hexanoyl peroxide was prepared by a similar procedure.

4-Pentenyl 5-Hexenoate.—This ester was prepared by the reaction of 4-penten-1-ol with an equivalent quantity of acid chloride.

After washing the organic layer with sodium bicarbonate solution and drying, distillation was performed on an 18-in. spinning-band column at a constant pressure of 1 mm. A small fraction having a characteristic ester odor was collected, bp 69.0–70.0° and $n^{25}\mathrm{D}$ 1.44072, and used in preparing a standard solution for use in gas–liquid chromatography analyses. The ir spectrum showed a C=O band at 1724, a CO band at 1157, a C=C band at 1631, and $\mathrm{RCH{=}CH_2}$ bands at 990 and 906 $\mathrm{cm^{-1}}$. *Anal.* Calcd for $\mathrm{C_{11}H_{18}O_2}$: C, 72.45; H, 9.96. Found:[21] C, 72.56; H, 9.85.

1,9-Decadiene was prepared by a Grignard coupling method described by von Braun, *et al.*[22] 6-Phenyl-1-hexene was similarly prepared by coupling 3-phenylpropylmagnesium chloride with allyl bromide.[23]

7-Phenyl-5-heptanolactone (**1**).—This lactone was prepared by subjecting 2-(2-phenylethyl)cyclopentanone to the Baeyer–Villiger reaction, using the peroxytrifluoroacetic acid method according to a procedure described by Smissman, Muren, and Dahle.[24] The starting ketone was synthesized by a method described by Adkins and Hager,[25] mp (of its 2,4-dinitrophenylhydrazone) 90–92°. The ir spectrum of the lactone showed strong peaks at 1757, 1250, 1053, and 704 $\mathrm{cm^{-1}}$. Its nmr spectrum showed aliphatic and aromatic absorptions in a 11:5 ratio required of the expected lactone. The aliphatic protons appeared as a group of overlapping multiplets at 1.3–3.05 and as a multiplet centered at δ 4.15 in a 10:1 ratio. The latter absorption may be ascribed to the methine proton deshielded by the ether oxygen. The presence of a second multiplet centered at δ 3.6 could be ascribed to the corresponding methylene proton absorption of the possible isomeric lactone. The relative intensity of the multiplet at δ 3.6 and 4.15 suggested the presence of less than 15% of the isomeric lactone.

Kinetics Runs.—The solvents used were of reagent grade, and were redistilled before use. Approximately 4-ml portions of a peroxide solution were transferred into previously weighed kinetic vials using a 5-ml syringe equipped with a long, slim hypodermic needle. The vials were then stoppered, weighed, and placed in a Dry Ice–acetone bath. The vials were degassed and sealed under vacuum. The bath used was thermostated to ±0.02°. After its heating period, the contents of each vial were analyzed by iodometric titration, using isopropyl alcohol as the assay solvent.

Product Studies.—The product-study runs were carried out with vials similar to those used for kinetics runs. The product yields were obtained by comparing glpc peak areas with those of authentic standards.

Registry No.—5-Hexenoyl peroxide, 26384-97-4; hexanoyl peroxide, 2400-59-1; 4-pentenyl 5-hexenoate, 26384-99-6.

Acknowledgment.—We are indebted to the grant agencies which made this work possible,[1] and to Mr. Floyd E. Woodard for the synthesis of **1** and for his considerable help with the computer work.

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(17) Perkin-Elmer Models 421, 137, and Beckman IR-12 infrared spectrophotometers were used in this work. Beckman GC-2 and Perkin-Elmer Mod 1 900 gas chromatographs were used in the products study. A Hitachi PE Model R-20 nmr spectrometer was used to record the nmr spectra; tetramethylsilane was the internal standard. Boiling points are uncorrected.

(18) H. E. De La Mare, J. A. Kochi, and F. F. Rust, *J. Amer. Chem. Soc.*, **85**, 1437 (1963); See also F. B. LaForge, N. Green, and W. A. Gersdorff, *ibid.*, **70**, 3707 (1948).

(19) A. Michael and H. S. Mason, *ibid.*, **65**, 683 (1943).

(20) H. Hart and D. R. Wyman, *ibid.*, **81**, 4895 (1959).

(21) Analysis performed by Midwest Microlab, Inc., Indianapolis, Ind.

(22) J. von Braun, H. Deutsch, and A. Schmatlock, *Ber.*, **45**, 1246 (1912).

(23) H. Pines, N. C. Sih, and E. Lewicki, *J. Org. Chem.*, **30**, 1457 (1965).

(24) E. E. Smissman, J. F. Muren, and N. A. Dahle, *ibid.*, **29**, 3517 (1964). *Cf.* L. F. Fieser and Mary Fieser, "Reagents for Organic Synthesis," Wiley, New York, N. Y., 1967, pp 821–827.

(25) H. Adkins and G. F. Hager, *J. Amer. Chem. Soc.*, **71**, 2965 (1949).