Radical Nature of Pathways to Alkene and Ester from Thermal Decomposition of Primary Alkyl Diacyl Peroxide

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Thermal decomposition of a primary alkyl diacyl peroxide **2** is investigated. Dependence of product yields on temperature, viscosity, and solvent polarity is examined in a variety of media. The excess of the alkene disproportionation product **4** and the presence of ester **3** and acid **5** is argued to demonstrate the existence of a discrete acyloxy−alkyl geminate radical pair. Stereoselective deuterium labeling of **2** and subsequent ^{1}H-NMR analysis of the resulting isotopomers of **4** confirm the radical nature of detected decomposition products.

Introduction

Acyloxy radicals, **1**, are reactive intermediates in organic reactions ranging from the Barton[1] and related reactions, Hundsdiecker[2] reactions to Kolbe electrolysis and thermal or photodecomposition of diacyl peroxides and other acyloxy derivatives.[3] They also serve as intermediates in generation and calibration of many of the "radical clocks".[4]

$$\underset{\mathbf{1}}{RCO_2^{\bullet}} \longrightarrow R^{\bullet} + CO_2$$

The most obvious chemical property of these radicals is the relative ease with which they undergo decarboxylation to produce the corresponding R· radical. Knowledge of the rate of this reaction is not only of intrinsic interest because of the simplicity of the process, but is also essential if one is to understand fully the distribution of radical-derived products formed from acyloxy radical precursors. Determination of the electronic structures of these species has also proven to present interesting theoretical[5] and experimental challenges.

Decarboxylation rates of aroyloxy radicals (R = substituted phenyl) have been measured, or estimated, by a variety of methods including indirect comparison with trapping rates[6,7] direct detection optically,[8] or by EPR[9] and by comparison with nuclear hyperfine frequencies via measurement of CIDNP enhancement factors.[10] These studies indicate decarboxylation rate constants at 80 °C of the order of 10^7 s^{-1}, and an activation energy of 8−9 kcal/mol.

Much less certain is the decarboxylation rate of $RCO_2^{\bullet}$, when R is primary, secondary, or tertiary alkyl or benzyl. The acetoxy radical (R = CH_3) decarboxylation rate has been estimated from product yields[11] and CIDNP enhancement factors[12] to be 10^9 s^{-1} at 80 °C with an activation energy of approximately 7 kcal/mol. Estimates for the decarboxylation rate of $RCO_2^{\bullet}$ with R = CH_3, CH_3CH_2, $(CH_3)_2CH$, $(CH_3)_3C$, $PhCH_2$, and $PhCH_2CH_2$ were recently obtained by comparison with electron-transfer rates within the naphthylmethyl−acyloxy radical pairs,[13] assumed independent of the nature of R, and calibrated by the known decarboxylation rate of 9-methylfluorenoyloxy radical.[14] However, the former investigation suggests that the decarboxylation rate for the propanoyloxy radical is 2×10^9 s^{-1}. This implies that it should be possible to observe net CIDNP polarization in photolysis or thermolysis of dipropanoyl or other primary peroxides which is contrary to the results reported previously.[12]

Without exception primary, secondary, or tertiary alkyl or benzyl acyloxy radicals decarboxylate too rapidly to maintain concentrations sufficient for direct detection using currently available techniques. For example, only alkyl radical pairs and radicals formed by H abstraction from the alkyl chains or reactant molecules are seen[15] by EPR during photolysis of single crystals of bis-decanoyl peroxide at 10−20 K. Furthermore, in many cases products containing the acyloxy group have not been detected during the thermal decomposition of diacyl peroxides, as would be expected for recombination of intermediate acyloxy−alkyl radical pair (Scheme 1). This has given rise to an assumption that acyloxy radicals which produce R· more stable then $CH_3^{\bullet}$ do not exist as discrete chemical intermediates but undergo C−C bond

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(2) For reviews see Wilson, J. *Org. React.* **1957**, *9*, 332. See also Skell, P. S.; May, D. D. *J. Am. Chem. Soc.* **1981**, *103*, 967.

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(5) (a) Feller, D.; Huyser, E. S.; Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1983**, *105*, 1459. (b) Feller, D.; Borden, W. T.; Davidson, E. R. *J. Am. Chem. Soc.* **1983**, *105*, 3347. (c) Rauk, A.; Yu, D.; Armstrong, D. A. *J. Am. Chem. Soc.* **1994**, *116*, 8222.

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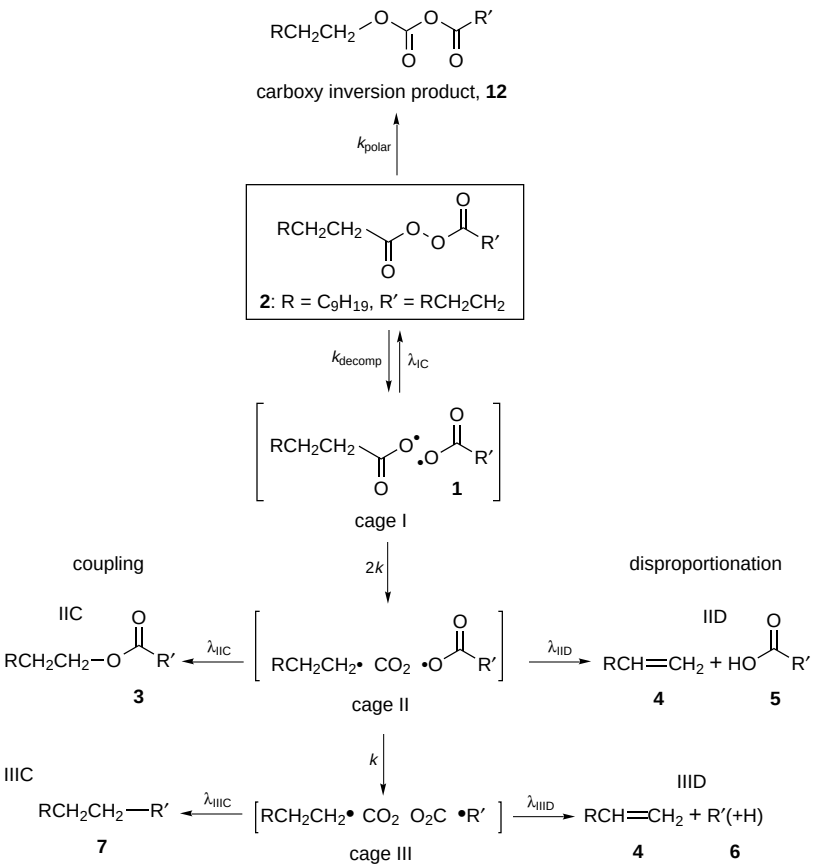
Scheme 1



scission in synchrony with reaction of the precursor molecule.[16] Early evidence for such a conclusion came from observation of declining activation energies for thermolysis of diacyl peroxides[15a] and peresters[15b] with increasing R· stability. Perhaps the strongest evidence against a discrete acyloxy intermediate is failure to detect CIDNP in products of acyloxy−alkyl cage II coupling and disproportionation.[17] In those cases where products containing the acyloxy groups, such as esters or carboxylic acids, have been isolated, it has been assumed that they arise from ionic side reactions related to the formation of the carboxy inversion product[18] or else has been reported without comment.[19]

We report here the results of a detailed study of the products formed when lauroyl peroxide (**2**) is decomposed thermally in a variety of solvents at temperatures ranging from 80−140 °C. This investigation was prompted both by the isolation of appreciable quantities of the corresponding ester **3** and carboxylic acid **5**, and by the discovery of an excess of 1-undecene (**4**), above what is expected from the yield of *n*-undecane (**6**), by simple disproportionation of two undecyl radicals in cage III. Both observations could be explained by the presence of the acyloxy radical **1** as a discrete intermediate in cage II recombination. We have also used stereospecific deuterium labeling to further explore the origin of the products listed above.

Results

Decomposition Rates. First-order rate constants for thermolysis of **2** in four solvents representing the range of polarity and radical reactivity used in this study were determined from semilog plots of the ^{1}H-NMR signal of **2** vs time.[20] In all cases, decomposition of **2** at 89 °C showed clean first-order behavior over at least 4 half-lives. First-order rate constants, k_{decomp}, were $(3.1 \pm 0.5) \times 10^{-4}$ s^{-1} in $C_6D_5CD_3$ (toluene-d_8) and $(1.9 \pm 0.2) \times 10^{-4}$ s^{-1} in PFMCH (perfluoromethylcyclohexane). In both cases the initial concentration of **2** was 0.01 M. At higher initial concentration of **2**, 0.1M, k_{decomp} were $(2.0 \pm 0.2) \times 10^{-4}$ s^{-1} in HCA (hexachloroacetone) and $(2.6 \pm 0.1) \times 10^{-4}$ s^{-1} in C_6D_6 (benzene-d_6). The values of these rate constants are consistent with the reported[21] value of 3.4×10^{-4} s^{-1} for the rate constant for decomposition of 10% w/v **2** in Primol C mineral oil at 89 °C. The lack of dependence of k_{decomp} on solvent polarity supports the predominantly nonionic nature of the reaction. The insensitivity of k_{decomp} to changes in peroxide concentration rules out a substantial contribution from induced peroxide decomposition.[18] Measurements of k_{decomp}, however, cannot detect minor reaction pathways of either type.

Product Yields. The yields of hydrocarbon products of decomposition of **2,** 1-undecene (**4**), *n*-undecane (**6**), and

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(17) (a) Cooper, R. A.; Lawler, R. G.; Ward, H. R. *J. Am. Chem. Soc.* **1972**, *94*, 545. (b) Kaptein, R. *Adv. Free-Radical Chem*. **1975**, *4*, 319.

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(20) Two different samples were thermolyzed and at least 10−18 points were used for a semilog first-order plot for each sample. The quoted error of the slope (k_{decomp}) represents two standard deviations.

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Table 1. Relative Excess of 1-Undecene (4) Observed in Various Media

solvent and conditions	E_T[a]	85 °C	105 °C	relative excess at 85 °C	relative excess at 105 °C
n-C_8H_{18}	30.9	6.8 ± 0.2[b] 2.9 ± 0.1[c]		1.4 ± 0.1	1.3 ± 0.4[d]
$C_6H_5CH_3$	33.9	6.2 ± 0.2 2.9 ± 0.1	5.7 ± 0.2 2.5 ± 0.1	1.1 ± 0.1	1.2 ± 0.1
e		6.1 ± 0.2 2.8 ± 0.1		1.1 ± 0.1	
f			5.6 ± 0.2 2.8 ± 0.1		1.0 ± 0.1
$ClCH_2CH_2Cl$	41.9	6.2 ± 0.1 3.2 ± 0.1		0.9 ± 0.1	
CH_3CN	46.9	4.4 ± 0.1 2.2 ± 0.1		1.0 ± 0.1	

[a] Dimroth solvent polarity parameter, reference 22. [b] % yield of **4** (an average of at least three separate samples, the yield for each sample is an average of at least four separate injections).[c] % yield of **6** (an average of at least three separate samples, the yield for each sample is an average of at least four separate injections). [d] Determined from molar ratio, [**4**]/[**6**]. [e] $C_6H_5CH_3$ with 0.01 M $BrCCl_3$. [f] $C_6H_5CH_3$ mixed with crushed glass ampule.

n-docosane (**7**), were determined from thermolysis of dilute (10^{-3} to 10^{-4} M) solutions and analyzed using capillary gas chromatography. In the dilute solutions O_2 serves as the radical scavenger, whereas at higher peroxide concentrations the solvent itself, or an added scavenger such as $BrCCl_3$, plays that role. The yields of lauroyl lauroate (**3**), undecyl chloride or bromide (**13a** or **13b**, products of undecyl radical scavenging in chlorine or bromine donating solvents), lauric acid (**5**), and carbonic anhydride (**12**) were obtained by ^{1}H-NMR on partially reacted 0.1 M solutions. Under the conditions employed for product analysis radical−radical products derived from **2** arise exclusively from geminate recombination, i.e., terminal encounters of escaped radicals have been eliminated. Overall, **7** accounted for 24−28% of alkyl radicals produced by each mole of **1**, cage escape products (either **13a** or **6** in chlorine- or hydrogen-donating solvents, respectively) for 25−37%, **4** for 6−7%, **6** for 3%, carbonic anhydride (**12**) for 3−12%, **5** for 3%, and **3** for 10−13%. Identified products yielded material balance of 74−92% in the solvents studied. The existence of the acyloxy−alkyl radical pair (cage II) for a sufficient time to permit formation of recombination products is consistent with the following observations: (1) products **3** and **5** contain intact acyloxy groups, (2) yields of **4** are consistently higher than those of **6**, and (3) the yields of **5** and excess **4** are nearly the same.

Constancy of Excess Of Alkene. The yields of **4** and **6** were determined under a variety of conditions in order to explore possible sources of excess **4.** Table 1 summarizes the relative excess of **4** obtained in various media. It is apparent that the relative excess of **4** is nearly independent of temperature and insensitive to solvent polarity. The excess cannot be attributed to the reaction of **2** at a glass surface, since the yields are unchanged in samples decomposed in the presence of finely powdered Pyrex glass of the type used in ampoules employed for decomposition (row 4 in Table 1). Samples decomposed with addition of 0.01 M $BrCCl_3$ as an extra scavenger (row 3 in Table 1) do not differ from those samples which rely on oxygen scavenging only, thus precluding the formation of excess **4** from reaction of the radicals with oxygen. An interesting feature of Table 1 is the invariance of relative excess of **4** with change in solvent polarity as measured by the Dimroth E_T scale.[22] As will be discussed further below, this is evidence against excess **4** arising from the rearrangement product, **12**, which is known in other cases to be formed by a polar mechanism.[17] Indeed, in CH_3CN, the most polar solvent used, the reduction in yields of both **4** and **6** (row 6, Table 1) would be expected, with a corresponding increase in the yield of "polar" product.[18]

Table 2. Yields of 3, 5, and Excess 4 from Thermolysis of 1 in Various Solvents[a]

solvent	4	6	yield (%) of **4** (excess)	5	3[b]
HCA[b]	5.6 ± 0.4	2.8 ± 0.1[d]	2.8 ± 0.4	2.6 ± 0.3	11.3 ± 1.2
$Cl(CH_2)_2Cl$	6.2 ± 0.1	3.2 ± 0.1	3.0 ± 0.2	4.2 ± 0.2	10.3 ± 1.1
$C_6D_5CD_3$	6.5 ± 0.3[c]	2.9 ± 0.1	3.6 ± 0.3	3.4 ± 0.2	11.9 ± 1.0
C_6D_6	6.1 ± 0.2	2.8 ± 0.2	3.3 ± 0.3	2.9 ± 0.2	10.6 ± 1.0
n-C_8H_{18}	6.8 ± 0.2	2.9 ± 0.1	3.9 ± 0.2	3.3 ± 0.3	12.3 ± 1.3

[a] T = 83 °C. [**2**]$_o$ is 10^{-4} M unless noted otherwise. [b] 0.1 M **2**, T = 83 °C, reaction time 5 min. [c] 0.1 M **2**, plus 0.2 M cyclohexene. [d] 0.1/M **2**, plus 0.1 M $BrCCl_3$.

In order to confirm that **4** and **6** arise from geminate radical coupling, experiments were carried out using several scavengers and solvents in addition to those shown in Table 1. The results are summarized in Table 2. Decomposition of 0.1 M **2** in HCA (hexachloroacetone) at 140 °C was examined because this is the concentration, solvent, and temperature often chosen for CIDNP studies.[10,12] Furthermore, HCA is usually considered to be capable of efficient scavenging of radicals escaping recombination, thereby assuring that alkane **6** arises solely from geminate pairs. It was determined, however, that HCA is not as efficient a scavenger as $BrCCl_3$. The average yield of **6** drops from 3.6 ± 0.3% to 2.8 ± 0.1% when $BrCCl_3$ is added to the HCA solution, suggesting that in the pure solvent some of the alkane product arises from random encounters of nonscavenged radicals or, more likely, by abstraction of hydrogen from the relative high concentration of unreacted **2** or reaction products. Although the yields of **4** and **6** in 0.1 M HCA solution at 140 °C are very similar to those obtained from 10^{-4} M solutions of **2** in toluene at 105 °C when efficient oxygen scavenging is employed (see Table 1, rows 2,4), it must be cautioned that in the presence of peroxide, HCA removes some of the alkene, presumably by radical chain addition. This was confirmed by observing that the recovery of alkene from solutions of **4** in HCA heated at 140 °C for 12 min was lessened when **2** was present whereas **4** itself does not react under these conditions. This result is not unexpected, since alkenes tend to undergo efficient radical-initiated chlorination by halogenated solvents.[23] Indeed, < 0.1% yield of **4** is detected when **2** is thermalized in the presence of $BrCCl_3$. It is therefore likely that the actual yield of **4** in HCA is somewhat higher than 5.6%.

When 0.1 M **2** is decomposed in $C_6D_5CD_3$, the yield of **4** is 8.4 ± 0.5%, higher than observed when oxygen scavenging is employed with 10^{-4} M **2** in this solvent (Table 1, entries 2, 3). This suggests a contribution from random radical encounters. Addition of 0.2 M cyclohexene as a radical scavenger reduced the yield of **4** to 6.5 ± 0.3%, but as expected the yield of **6** remained high at 26.3 ± 1.7%. With 0.1 M added $BrCCl_3$, however, the yield of **6** from 0.1 M solution of **2** in $C_6D_5CD_3$ was

(22) Dimroth, K.; Reichardt, C. *Ann. Chem.* **1963**, *1*, 661.
(23) De Tar, D.; Wells, D. *J. Am. Chem. Soc.* **1960**, *82*, 5839.

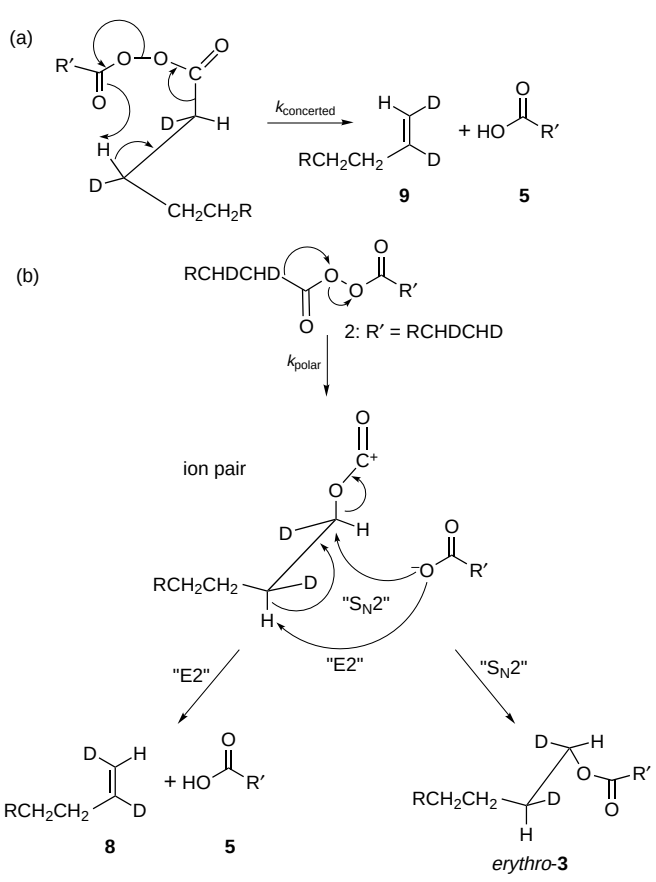
reduced to 2.9 ± 0.1%, in good agreement with the yields obtained with efficient oxygen scavenging of the dilute solution (Table 1, entries 2, 3). Since it was important for ^{2}H-labeling experiments using NMR (see below) that all of **4** come from geminate radical sources, 0.2 M cyclohexene was employed as a scavenger when ^{2}H-labeled **2** was thermalized in $C_6D_5CD_3$.

Table 2 also lists the yields of ester **3** and acid **5** in the solvents discussed above, along with the corresponding yields of excess **4**. It is apparent that the observed yield of **5** correlates well with the excess of **4**. Also notable is the insensitivity of the yield of ester **3** to the type of solvent or the temperature employed. This supports the assumption that **3**, **5**, and excess **4** are produced from reactions within the geminate alkyl acyloxy radical pair (cage II). It should be noted, however, that variable amounts of undecyl alcohol were detected in some samples. One possible source of alcohol is the hydrolysis of carboxy inversion product **12**.[18] Since the other product of the hydrolysis would be acid **5**, it is possible that unless care is taken to exclude moisture the yield of **5** might be higher than expected from the radical pathway alone.

The yields of the various products from thermolysis of **2** reported here compare favorably with previously observed yields of similar products from thermolysis of **2**[21] and the related symmetric dipropanoyl[19] and diheptanoyl[23] peroxides containing primary alkyl groups. In these reports the yields of alkane disproportionation product, when determined under efficient scavenging conditions, range from 2.8% to 3.8%. Significantly, a two-to-three-fold excess of alkene disproportionation products is also observed.[23] Yields of ester, ranging from 11% to 13%, are similar to those seen here. Yields of heptanoic acid, estimated from the titration of scaled up thermolysis samples of heptanoyl peroxide, ranged from 1% to 16% but were generally not considered reliable indicators of a free-radical process.[23] A reliable acid yield of 3%, however, reported by Pryor et al.[24] from 0.6 M **2** in C_6D_6 at 80 °C, is similar to our findings.

Thermal Stability of Products. It has been suggested that carboxy inversion products analogous to **12** may decompose by either concerted or ionic mechanisms to form ester[25] and alkene.[26] Previous investigations of the thermal stability of carboxy inversion products from primary alkyl-aroyl peroxides, however, suggest that the rate of thermal decomposition of **12** should be ca. 20-fold slower than that of the precursor peroxide.[27] Measurement of the stability of **12** confirmed this prediction. Liu and co-workers[18b] determined that **12** decomposes with first-order rate constant of 7×10^{-6} s^{-1} at 80 °C in C_6H_6, compared to $2-3 \times 10^{-4}$ s^{-1} for decomposition of **2** at the same temperature. We conducted a more detailed analysis of the kinetics of decomposition of **2** in C_6D_6 in order to eliminate the possibility that **3** and excess **4** are derived from **12**. A solution of **2** (0.1 M) was decomposed at 83 °C in C_6D_6 and the time evolution of ^{1}H-NMR

Scheme 2



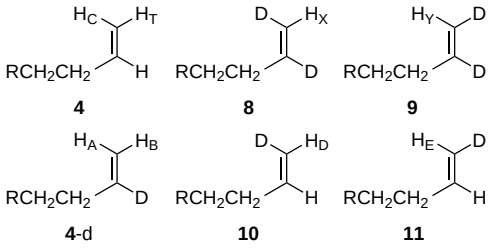
signals of **12**, **3**, and **4** was monitored over a period of 18 h. It was found that **12** is formed in 6% yield at the rate of peroxide decomposition and then decomposes slowly over a period of 12 h to produce an equivalent amount of ester **3**. The first-order rate constants $(2.6 \pm 0.1) \times 10^{-4}$ s^{-1} for decomposition of **2** and $(1.0 \pm 0.1) \times 10^{-5}$ s^{-1} for **12** are in good agreement with previous reports,[18b] indicating that a negligible amount of **3** over the time required for decomposition of **2** is the result of thermolysis of **12**. It is also found that the yield of **4** remains constant after all of **2** is decomposed. Concentration of **4** in another sample was followed by GC over a total of 12 half-lives of peroxide decomposition, and its yield remained constant at 6.5 ± 0.2%.

Stereochemistry of Formation of Excess Alkene. Scheme 2 illustrates two other possible sources of excess **4** in thermolysis of **2**. Process a is a concerted pathway, previously suggested by Szwarc,[19] not unlike the well documented pyrolysis of esters.[28] The latter reaction proceeds through a six-membered transition state, follows the Ei mechanism and gives the syn-elimination alkene product exclusively.[29] Although the temperature required for ester pyrolysis is relatively high (300-550 °C), the greater overall reactivity of peroxides might be expected to lower the activation energy for the analogous process. If **2** is to produce **4** by the Ei mechanism, it is likely that the eight-membered transition state shown in Scheme 2 would be involved and *cis*-1-undecene-1,2-d_2 (**9**) obtained from the stereospecifically deuterated peroxide shown. Although the literature pertaining to the chemistry of the carbonyl group does not seem to

(24) Pryor, W. A.; Davis, W. H. *J. Am. Chem. Soc.* **1974**, *96*, 7557.
(25) Oae, S.; Kashiwari, T.; Kozuka, S. *Chem. Ind. (London)* **1965**, 1694.
(26) (a) Lamb, R.; Sanderson, J. *J. Am. Chem. Soc.* **1969**, *91*, 4034. (b) Lamb, R.; Pacifici, J.; Ayers, P. *Ibid* **1965**, *87*, 3928. (c) Hart, H.; Cipriany, R. *Ibid* **1962**, *84*, 3697. (d) Bartlett, P.; Leffler, J. *Ibid* **1950**, *72*, 3030. (e) Kharasch, M.; Kuderna, J.; Nudenberg, W. *J. Org. Chem.* **1955**, *19*, 1283. (f) Green, F. *J. Am. Chem. Soc.* **1955**, *77*, 4869. (g) de Tar, D.; Weiss, C. *Ibid* **1957**, *79*, 3045. (h) Green, F.; Stein, H.; Chu, C.; Vane, M. *Ibid* **1964**, *86*, 2080.
(27) Kline, M., Ph. D. Dissertation, Brown Univ., 1982.
(28) DePuy, R, King, J. *Chem. Rev.* **1960**, *60*, 431.
(29) March, J. *Advanced Organic Chemistry;* Wiley-Interscience; New York, 1985, Chap. 17, pp 896−905.

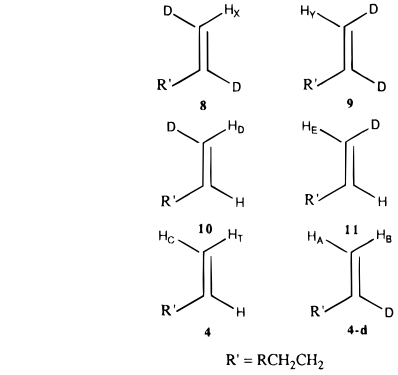
contain an example of a reaction proceeding through an eight-membered transition state, nevertheless, we felt that this possibility should be explored.

Also shown in Scheme 2 is a possible mechanism (b) for formation of **5** and excess **4** via a rearranged ion pair. This pair is well-known to give rise to carboxy inversion product **12**, which however, we have shown cannot itself produce a significant amount of **4**. If the ion pair were to give rise to **3** the process would be likely to proceed with inversion of stereochemistry. Similarily, alkene **4** would be formed by an antiperiplanar stereoelectronic pathway. These pathways are labeled in Scheme 2b as "S_N2" and "E2", respectively. In an attempt to determine the stereochemistry of formation of **3** and **4** from **2** we prepared ^{2}H-labeled **2** as the *threo*-2,3-d_2 stereoisomer and examined the stereochemistry of the resulting alkene isotopomers by ^{1}H-NMR. Since the sample of *threo*-2,3-d_2 **2** also contained monodeuterated **2** and a small amount of *erythro* **2** (see Experimental Section), a total of 6 isotopomers of **4** were observed.



As is apparent from Scheme 2, the ratio of **8**/**9** (or **10**/**11**) may be used to differentiate the concerted or ion-pair pathways to **4** from the radical route. The latter would be accompanied by rapid rotation along the C_1-C_2 bond and should give equal amounts of C_1 alkene stereoisomers. Pathways **a** and **b**, however, would yield unequal amounts of these isomers. The ^{1}H-NMR spectrum of the alkene region of 0.1 M *threo*-2,3-d_2 **2** thermalized in HCA at 140 °C is shown in Figure 1. The spectra of the same region both from HCA and 89 °C thermolysis of *threo*-2,3-d_2 **2** in $C_6D_5CD_3$ together with the simulation of these spectra using the program PANIC are shown in Figure 2. The spectra were obtained with simultaneous decoupling of the allyl CH_2 protons. The relative amounts of the isotopomers determined from these spectra are listed in column 5 of Table 3. The observed ratios of deuterated isotopomers of **4** are compared with ratios predicted for pure radical and mixed radical/nonradical pathways. When allowance is made for the fact that isotope effects on hydrogen removal are not included in the predicted ratios, the results support a radical route to excess **4**.

The attempt to analyze the stereochemistry of the alkyl group in the ester **3** unfortunately gave ambiguous results. Although the ^{2}H-decoupled ^{1}H-NMR of the undecyl-1,2-d_2 group of chloroalkane **13** shows both *erythro*- ($J_{1,2}$ of 8.3 Hz) and *threo*- ($J_{1,2}$ of 6.2 Hz) isomers, only one doublet ($J_{1,2}$ of 5.7 Hz) is seen for the alcohol undecyl-1,2-d_2 groups of ester **3**, acid **5**, and undecyl alcohol. Previously reported[30] values of $J_{1,2}$ in the esters *threo*- and *erythro*-1-acetoxy-3,3-dimethylbutane-1,2-d_2 are 6.1 and 8.8 Hz, respectively. This appears to be consistent with a *threo* assignment for the coupling constant observed from the alcohol group of the undecyl-1,2-d_2 **3**, i.e., with retention of configuration in the



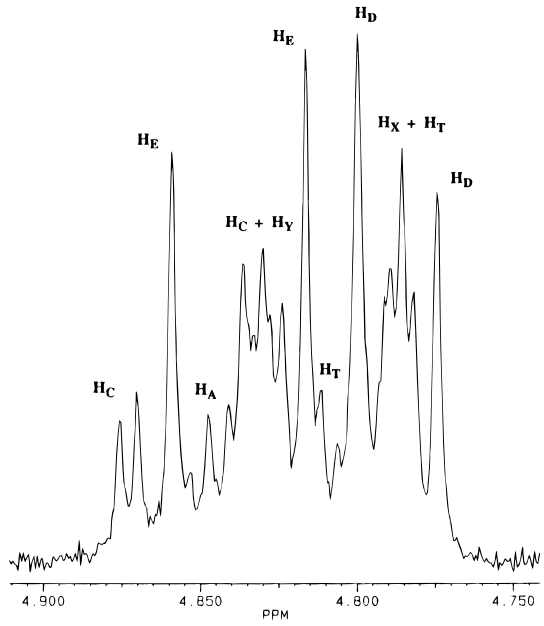


Figure 1. Allyl CH_2-decoupled ^{1}H-NMR spectrum of the terminal CH_2 alkene region of **4** from 0.1 M *threo*-2,3-d_2-**2** thermalized in $C_6D_5CD_3$ at 80 °C. The labels of various protons of isotopomers correspond to the structures shown to the right of the spectrum.

formation of **3** from *threo*-2,3-d_2 **2.** However, the *tert*-butyl group (in the model compound) is much bulkier than the *n*-nonyl group in undecyl-1,2-d_2 **3**, making the equilibrium populations of rotational conformers very different and a direct comparison impossible. Similarly, equating the populations of rotational conformers in **13** and **3** is unrealistic because of the differences in steric bulk between the chlorine and lauroyloxy groups.

In an attempt to determine whether the stereoisomeric deuterated esters could be distinguished by NMR, a known mixture of esters with *threo* and *erythro* configurations was prepared by thermolysis of a mixture of *threo*- and *erythro*-1,2-d_2 **2** (see Experimental Section). The mixture contained *threo*-2,3-d_2 **2** and *erythro*-2,3-d_2 **2** (in 1:1 ratio), as well as 2-*d* and 3-*d* **2**. The impurity of 2-*d* **2**, however, was higher in this mixture than in the sample of pure *threo* peroxide. Figure 3 shows the superimposed signals of the alcohol α-protons of **3** from *threo*-2,3-d_2 **2** and from the 1:1 mixture of *threo*-2,3-d_2 and *erythro*-2,3-d_2 **2** obtained ^{2}H-decoupling. Both peaks of the doublets of undecyl-1,2-d_2 group have nearly identical line widths (ca. 2 Hz), suggesting that regardless of whether **3** retains or scrambles the original stereochemistry, the difference in $J_{1,2}$ between the *threo* -and *erythro*-1,2-d_2 **3** is too small to be detected by ^{1}H-

(30) (a) Whitesides, G. *J. Am. Chem. Soc.* **1967**, *89*, 1135. (b) Whitesides, G. *Ibid* **1974**, *96*, 2814.

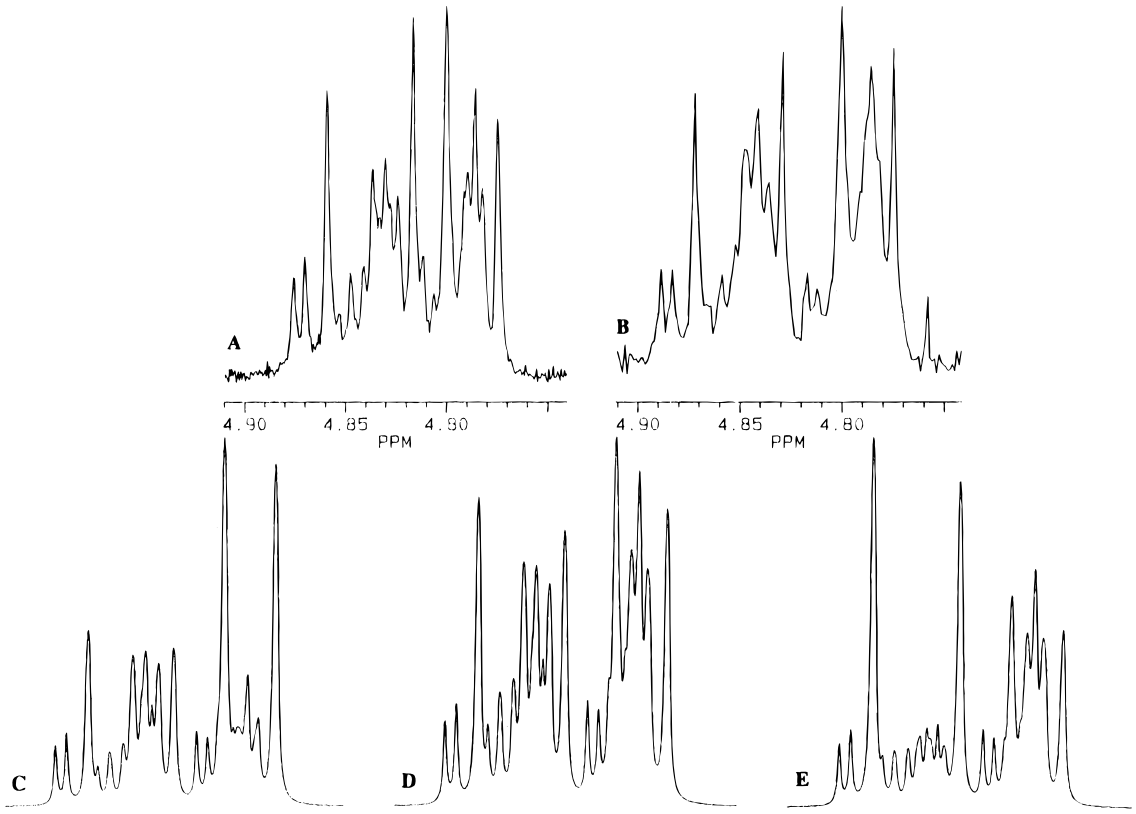


Figure 2. Experimental (top) and simulated (bottom) allyl CH_2-decoupled ^{1}H-NMR spectra of the terminal CH_2 alkene region of **4** from 0.1 M *threo*-2,3-d_2-**2**. (A) Spectrum obtained after thermolysis of **2** in $C_6D_5CD_3$ at 80 °C, (B) in HCA at 140 °C, (C) simulated with the relative amounts of alkenes corresponding to 50%:50% polar/radical pathway (see Table 3), (D) 100% radical, and (E) 50%:50% concerted/radical pathway.

Table 3. Expected and Observed Relative Yield of Isotopomers of 4 from Thermolysis of *threo*-1,2-d_2-2[a]

alkene	50% radical and 50% polar	radical pathway only	50% radical and 50% concerted	observed[b]
9	1.85	1.29	0.73	1.7 ± 0.1
8	0.73	1.29	1.85	1.4 ± 0.1
11	2.44	1.87	1.31	1.4 ± 0.1
10	1.31	1.87	2.44	1.5 ± 0.1
4-*d*	**1**	**1**	**1**	**1**
4	1	1	1	1.0 ± 0.1
[**11**]/[**10**]	2.05	1	0.48	1.1 ± 0.1 1.0 ± 0.1[c]
[**9**]/[**8**]	0.34	1	2.98	1.1 ± 0.1 1.0 ± 0.1[c]

[a] HCA at 140 °C unless indicated otherwise. [b] Relative yields are calculated for an initial mixture of **2** consisting of 58% *threo*-2,3-d_2, 4% *erythro*-2,3-d_2, 24% 3-*d* and 14% 2-*d*. Possible kinetic isotope effects have been ignored. All yields are relative to 1-undecene-2-*d*, the alkene expected to show least isotope effect on it's yield. Errors are from replicate integrations of single spectra obtained from HCA or $C_6D_5CD_3$ solutions. [c] $C_6D_5CD_3$, 80 °C, ratios only determined.

NMR. Attempts to convert (in situ) the small yield of **3** to alkyl chloride, for which the signals of *erythro* and *threo* isomers were resolvable, were not successful.

Conclusions

The results presented in this paper suggest that excess alkene **4**, ester **3**, and acid **5** seen in thermal decomposition of lauroyl peroxide are the products of a radical process and not a result of a random artifact or intervention of the ionic intermediates as was proposed previously. The evidence for this conclusion includes (1) the presence of the appropriate amount of **5** in the product mixture, as expected from 1:1 stoichiometry of the disproportionation reaction within the undecyl−lauroyloxy radical pair, (2) absence of correlation between the amount of excess **4** and the polarity of the medium, and (3) the complete scrambling of the ^{2}H label in the alkene products from stereospecificaly deuterated **2**. At an initial peroxide concentration of 10^{-4} M, and under conditions of efficient scavenging by dissolved oxygen, the excess of **4** was observed to be nearly constant in all solvents studied, despite significant variations in the individual yields of **4** and **6**. The literature contains two examples of detection of excess alkene from thermolysis of symmetrical diacyl peroxides. The alkene excess in thermolysis of propionyl peroxide[19] was determined to be 2.6-fold (at 65 °C), and a 2-fold excess of hexene over the yield of hexane was observed in thermolysis of heptanoyl peroxide.[23] It therefore may be confidently stated that the alkene excess is not an isolated phenomenon, but is apparently characteristic of the thermal decomposition of straight chain symmetrical primary diacyl peroxides. Ester **3**, the coupling product of the recombination reaction within the undecyl−lauroyloxy radical pair, also does not appear to be a consequence of the polar rearrangement. Its yield is insensitive to solvent polarity and is nearly constant in the temperature range of 60−120 °C, precluding its formation from carboxy inversion product **12**, which is stable at the temperatures employed. Evaluation of the rate of decomposition of lauroyloxy radical **1** (R = $C_{11}H_{23}$) from the temperature and viscosity dependence of cage product yields will appear in future publications.

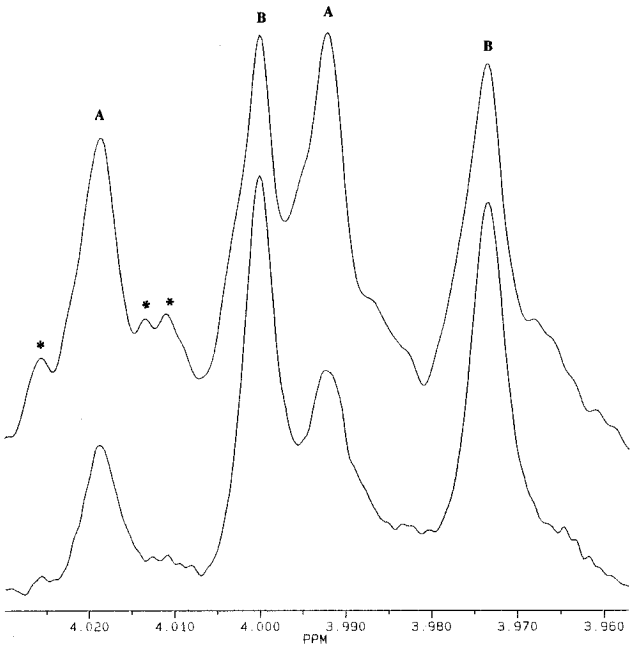


Figure 3. Superimposed ^{1}H-NMR signals of the alcohol α-protons of **3** from 1:1 mixture of *threo*-2,3-d_2- and *erythro*-2,3-d_2- (top trace) and *threo*-2,3-d_2-**2** (bottom trace) obtained with ^{2}H-decoupling. Peaks labeled B in the top trace arise from overlap of the signals from *threo*- and *erythro*-**3**-d_2. Peaks labeled A correspond to the residual monodeuterated **3**, those marked with * are from unidentified impurities. Details of spectrum acquisition are given in the Experimental Section.

Experimental Section

General Methods. Peroxide samples were heated in sealed glass ampules (4 mm i.d., ca. 5 cm in length) in an oil bath equipped with proportional temperature controller and the mercury thermometer readable to ±0.05 °C. For the determination of the yields of **3**, **2** was decomposed in 1.7 mL V-vials equipped with the screw-caps and Teflon septa. Since oxygen scavenging was desired, the samples were not degassed. The total decomposition time at each temperature was adjusted to ensure greater than 98% decomposition of the peroxides. Peroxide samples in HCA were immediately cooled in an ice−water bath and stored at −20 °C to prevent further reaction between the alkene product and solvent. For the kinetic runs the samples were decomposed in 5 mm sealed NMR tubes for periods of time varying between 5 and 60 min and were rapidly cooled in an ice-water bath prior to NMR analysis at room temperature. A single sample was used for each series of decomposition times, being alternately cooled and heated.

Materials. Toluene and benzene were obtained from Aldrich and distilled from CaH_2. Hexachloroacetone (HCA) was obtained from Aldrich and vacuum distilled (80 °C). *n*-Octane contained an appreciable amount of *n*-dodecane as determined by GC, and was slowly redistilled through a Vigreaux fractionating column. $ClCH_2CH_2Cl_2$ was obtained from Fischer Chemical Co. and purified by repeated washing with concentrated H_2SO_4 followed by distillation from molecular sieves.[31] Crown ether (18-crown-6, Aldrich, 95%) was recrystallized from acetonitrile. Hydrogen peroxide (90%) was obtained from FMC corporation.

Lauroyl Chloride. A 12 g amount of lauric acid was refluxed in approximately 50 mL of thionyl chloride. The product was vacuum distilled (60 °C, 1.0 torr) to give faintly yellow liquid. IR (neat) 1800 cm^{-1}. 400 MHz ^{1}H-NMR ($CDCl_3$): δ 2.78 (t, 2H), other signals same as for **2** below.

Lauroyl Peroxide (2). The commercially available compound (Alperox 95% or Aldrich, 98%) was purified by repeated crystallization from $CHCl_3/CH_3OH$ (1:1). Purified **2** contained less than ca. 0.2% lauric acid as evidenced by the 400 MHz ^{1}H-NMR of a 0.6 M sample in $CDCl_3$. Lauroyl peroxide was also prepared by the procedure due to Swern.[32] Lauroyl chloride (3.68 g, 0.017 mol) was added to diethyl ether (30 mL) in a 50 mL round bottom flask and cooled to 0−2 °C with an ice−water bath. Hydrogen peroxide (3 mL, 90% in H_2O, 0.013 mol) was added with vigorous magnetic stirring. Pyridine (1.67 mL, .0204 moles) was added dropwise in 100 μL portions over 1 min time intervals. Following the complete addition of pyridine, the ice bath was removed, and the reaction mixture was stirred for an additional 1 h. The pyridinium hydrochloride precipitate was filtered, and the remaining ether layer was washed twice with 20 mL portions of 5% HCl, twice with 25 mL portions of 5% $NaHCO_3$ and twice with 25 mL portions of distilled water. The product was recrystallized from cold diethyl ether. IR (Nujol mull): 1812, 1780 cm^{-1} [lit.[27] 1813, 1778 cm^{-1}]. 400 MHz ^{1}H-NMR ($CDCl_3$): δ 2.4 (t, 2H), δ 1.7 (quintiplet, 2H), δ 1.3 (broad, 16H), δ 0.9 (t,3H).

Methyl (triphenylphosphoranylidene)acetate. This compound was prepared by dissolving commercially available (carbomethoxymethyl)triphenylphosphonium bromide (Aldrich) (12 g, 0.029 moles) in 180 mL distilled water and titrating with 1.0 M NaOH (phenolphthalein indicator). The resulting fine white precipitate of the ylide was vacuum filtered and redissolved in 100 mL of CH_2Cl_2 to be used in the step below.

***Trans*-2-Dodecenoic Acid.** The acid was prepared by adding the ylide prepared above to 4.2 mL (0.022 mol) of decanal in 100 mL of CH_2Cl_2 in a 500 mL roundbottom flask. The solution was refluxed for 5 h, and the CH_2Cl_2 was removed by distillation. The resulting methyl *trans*-2-dodecenoate was saponified by addition of 170 mL of 0.3 M KOH in EtOH/water (9/8 v/v) and refluxing for 3 h. Ethanol was removed by distillation, and the aqueous layer was washed with a total of 500 mL of diethyl ether and acidified with concentrated HCl. The acid was extracted into a total of 200 mL of CH_2Cl_2, and the solvent was removed by rotary evaporation yielding 3.58 g (81%) of a mixture of *trans*- and *cis*-2-dodecenoic acids: 400 MHz ^{1}H-NMR ($CDCl_3$): δ 6.92 (dt, 1H, α alkene proton, J = 15.7 Hz (*trans* acid)], 6.2 (dt, 1H, α alkene proton, J = 11.6 Hz (*cis* acid)], 5.78 (dt, 1H, β alkene proton, J = 15.7 Hz (*trans* acid)], 5.73 (dt, 1H, β alkene proton, J = 11.6 Hz (*cis* acid)], δ 2.62 (qd, 2H, γ-CH_2 of *cis* acid), 2.2 (qd, 2H, γ-CH_2 of *trans* acid), 1.2−1.5 (broad, 18H), 0.9 (t, 3H). Ratio of *trans*/*cis* acid: 14/1. The product contained 7% *cis* acid and was used without further purification.

***threo*-2,3-Dideuteriolauric Acid.** This acid was prepared from the *trans*-2-dodecenoic acid by the procedure of Simon.[33] *trans*-2-Dodecenoic acid (0.93 g, 0.0047 mol, containing 7% *cis* acid) was added to 20 mL of dry benzene. Wilkinson's catalyst, $ClRh(PPh_3)_3$ (0.08 g, 0.000086 mol), was placed into a movable side-arm of a 50 mL roundbottom flask attached to the vacuum line and evacuated. Oxygen was removed from the sample by three freeze-pump-thaw cycles (pump cycle, 3 min), 99.9% $^2H_2$ (ca. 150 mL, 0.006 mol) was admitted into the flask, and the side-arm was rotated to deliver the open glass ampule containing the catalyst into the solution. Vigorous magnetic stirring with a Teflon-coated stirring bar was commenced at room temperature. The progress of the reaction was monitored by following the consumption of $^2H_2$ via a mercury manometer attached to the vacuum line. After uptake of $^2H_2$ ceased (ca. 3 days), the line was opened to air and the solvent was removed by rotary evaporation. The resulting solid residue was stirred with 0.5 M NaOH. The resulting solid soap was washed with ether, suspended in distilled water, acidified with concentrated HCl, and extracted with CH_2Cl_2. After drying the solution over anhydrous $MgSO_4$, removal of solvent yielded 0.6 g (62% yield) of a pure compound. ^{1}H- and ^{13}C-NMR spectra of the product were identical to those of undeuterated lauric acid, except for small isotope effects on chemical shifts and line broadening due to interactions with ^{2}H.

(31) Perrin, D.; Armargero, W. *Purification of Organic Chemicals;* Pergamon Press: New York, **1988**.

(32) Silbert, L.; Swern, D. *J. Am. Chem. Soc.* **1958**, *81*, 2364.

(33) (a) Simon, H.; Berngruber, O. *Tetrahedron* **1970**, *26*, 1401. (b) Simon, H. *Z. Naturforsch.* **1969**, *24b*, 1195.

Bis(*threo*-2,3-dideuteriolauroyl) Peroxide. This compound was prepared according to the procedure given for the lauroyl peroxide above. ^{1}H- and ^{13}C-NMR spectra of the product were essentially identical to those of **2**, except for small isotope effects on chemical shifts and line broadening due to interactions with ^{2}H. 250 MHz ^{1}H-NMR (^{2}H decoupling) showed the product to contain 58% of *threo*-2,3-dideuterio-**2** ($J_{H,H}$ 6.49 Hz), 4% of *erythro*-2,3-dideuterio **2**, 24% of 3-*d*-**2**, and 14% 2-d-**2**. It was not possible to obtain a precise estimate of the amount of fully protonated **2** in the mixture of deuterated isomers by either ^{1}H- or ^{13}C-NMR. We are confident that the maximum amount of **2**-*d* present is about the same as that of *erythro*-2,3-dideuterio **2**. In any event, excess of **2** will only effect the **4**/**4**-*d* ratio (see Table 3) which is not used as the primary indicator for the radical nature of the **3**, **5**, and excess **4**.

Mixture of *trans*- and *cis*-2-Dodecenoic Acids. The mixture was prepared from *trans*-2-dodecenoic acid methyl ester by the procedure of Lewis.[34] The methyl ester of *trans*-2-dodecenoic acid was obtained by stirring 1.5 g. (0.0074 mol) of the acid in 40 mL of 14% BF_3/CH_3OH complex (Aldrich) for 7 h. The resulting solution was mixed with 50 mL of distilled water and extracted twice with 20 mL of CH_2Cl_2. Removal of CH_2Cl_2 yielded 1.38 g (87%) of ester. The resulting ester was combined with 0.419 g (0.0031 mol) of $AlCl_3$ in 40 mL of CH_2Cl_2 in a Vycor irradiation vessel, degassed by bubbling N_2 through the solution for ca. 3 min and irradiated at 254 nm for 4 h at room temperature in a Rayonet reactor. Upon completion of the photolysis, the solution was washed twice with 40 mL portions of water and the organic phase was dried over anhydrous $MgSO_4$. After the removal of solvent, the yield of mixed methyl *cis*- and *trans*-2-dodecenoates was 0.99 g (63%). The mixture was found to contain 55% *trans* and 45% *cis* esters by ^{1}H-NMR. This mixture was saponified by the method given for the *trans*-2-dodecenoate to yield 0.76 g of the mixture of *cis*- and *trans*-2-dodecenoic acids. The resulting material was converted to a mixture of bis(*threo*-2,3-dideuterio)lauroyl and bis(*erythro*-2,3-dideuteriolauroyl) peroxides according to the procedure given for preparation of bis(*threo*-2,3-dideuteriolauroyl) peroxide above.

Analysis of Decomposition Products of Peroxides. Gas Chromatographic Analysis. GC analysis was performed using a chromatograph equipped with FID detector and a wall-coated open tubular column (12 m length × 0.2 mm i.d.) coated with 0.33 μm thick cross-linked dimethylpolysiloxane liquid stationary phase. Injector and detector temperatures were 200 °C for the analysis of **4** and **6** and 340 °C for the analysis of **7**. Column temperature was held constant at 180 °C for docosane runs and was ramped from 80 °C to 120 °C at 10 °C/min for undecene and undecane runs. Flow rates were the following: air (to FID detector) 450 mL/min, hydrogen (to FID detector) 30 mL/min, nitrogen (make-up gas) 30 mL/min. Split vent flow was 8.5 mL/min, septum purge 2.9 mL/min. Linear velocity of the carrier gas (He) was optimized at 33 cm/s by maximizing the column efficiency as judged by the ratio of peak retention time to the peak width at half-height. Since the amount of analyte was very small (ca. <1 nM for **4** and **6**) the splitless injection technique was used. Injection volumes varied from 0.6 μL (for concentrated samples) to 1.2 μL for more dilute samples. Retention times and response factors for all components were determined by using authentic samples and were checked occasionally and found not to vary appreciably with time or solvent. When acetonitrile solutions were analyzed, all of the GC peaks were small and broad. The cut-and-weigh procedure had to be used for integration of these peaks since electronic integration did not yield reproducible data. Time delay for the solvent purge was optimized by determining the areas of the analyte peaks while varying the purge vent time. It was found that the optimal purge time for analysis of **4** and **6** was 0.5 min and for **7** was 0.3 min. To ensure the precision of analyses, calibration plots of relative areas of FID signals to the molar ratios of analytes were prepared using *n*-dodecane as the standard for the signals of **4** and **6** and *n*-eicosane for the **7**. These calibration plots showed that the intercepts were insignificantly different from 0. Peak areas were determined using electronic integration and checked by the cut-and-weigh method.

^{1}H-NMR Analysis of Peroxide Decomposition Products. The initial concentration of the peroxide was either 0.01 M or 0.1 M as noted in the text. The chemical shifts of the signals for the peroxide decomposition products were confirmed in all solvents using authentic materials. All of the NMR product yield determinations were performed using the 400 MHz spectra. Spectral size was 64 K in all such samples, and an acquisition time of 4.6 s was sufficient to eliminate all relaxation distortions between pulses for all products of interest. Spectra were recorded using a ca. 15° pulse angle. To enhance the precision of the determinations the integration was performed after the FID was exponentially broadened (line broadening constant varied from 0.3 to not more than 0.5 Hz) and zero-filled to 128 K. All peaks were baseline corrected prior to integration. For all of the 0.01 M or 0.1 M samples, the yield of **4** (determined by GC) was used to convert the integrals of the other signals to actual yields. For example, the yields of **3** were obtained by comparing the integral of the α protons of the ester to the terminal protons of the alkene. For partially decomposed samples the yield of **4** was determined by GC of completely reacted samples.

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JO9512766

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