Intramolecular Hydrogen Atom Transfer Reactions of ω-Formylalkyl Radicals in Vapor and Liquid Phases

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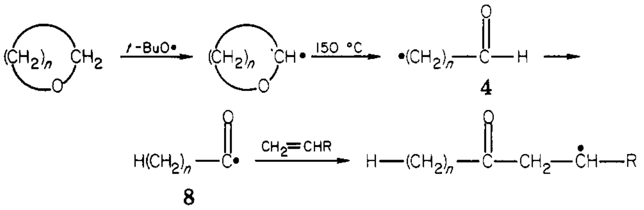
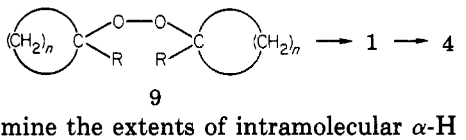
A series of ω-formyl- (–CHO and –CDO) -*n*-butyl, -*n*-pentyl, and -*n*-hexyl radicals (4) has been generated in vapor and solution phases. In the vapor phase, intramolecular aldehyde H- (or D-) atom transfer is a facile process proceeding through 6- or 7-membered transition states. In solution phase, intramolecular aldehydic H-atom transfer occurs to an extent of 74% via a 6-membered transition state but to only 29% or 38% via 7- or 8-membered transition states, respectively. Indirect evidence from both vapor- and solution-phase experiments indicates that intramolecular α-H atom abstraction in ω-formyl radicals (4) occurs to about 10% in competition with aldehydic H-atom abstraction via 6- and 7-membered transition states but not at all via a 5-membered transition state.

There have been numerous studies of the chemistry of alkyloxyl and cycloalkyloxyl radicals.[1-5] At temperatures above about 150 °C, β-scission becomes competitive with intermolecular disproportionation and H-atom transfer processes, giving rise to ω-formyl- or ω-ketoalkyl radicals (4) (Scheme I). Intramolecular α-H-atom abstraction in the case of ω-keto radical 4 ($n = 5$, R = CH_3) has been shown to give dimer 6 ($n = 5$, R = CH_3) in 30% yield.[6] The extent to which analogous ω-formyl radicals also undergo α-H-atom abstraction has not been established. α-H-atom abstraction in ω-formyl radical 4 ($n = 5$, R = H) was found not to occur in studies of Pd(II) catalyzed decomposition of a tetradeuterated cyclohexyl hydroperoxide.[7] However, whether or not ω-H (or D) atom transfer occurred in the absence of Pd(II) was not discussed. Abstraction of aldehyde H atoms in ω-formyl radicals 4 ($n = 3, 4, 5$), to give acyl radicals 8 ($n = 3, 4, 5$), was reported in solution phase studies of the attack of *t*-BuO· radicals on cyclic ethers.[8] A 41% yield of 4-dodecanone was isolated from the reaction of tetrahydrofuran with 1-octene. Yields of ketone products from the corresponding 4- and 6-membered ethers were not reported.



We now report results of thermolysis studies of recently prepared dicycloalkyl peroxides[9] 9 ($n = 4, 5, 6$; R = H or D) which were decomposed in vapor and solution phases to generate corresponding cycloalkyloxyl radicals 1 and ω-formylalkyl radicals 4. The purpose of the studies was to determine the extents of intramolecular α-H and aldehydric H abstraction processes and the relative dependence of each on carbon atom chain length.



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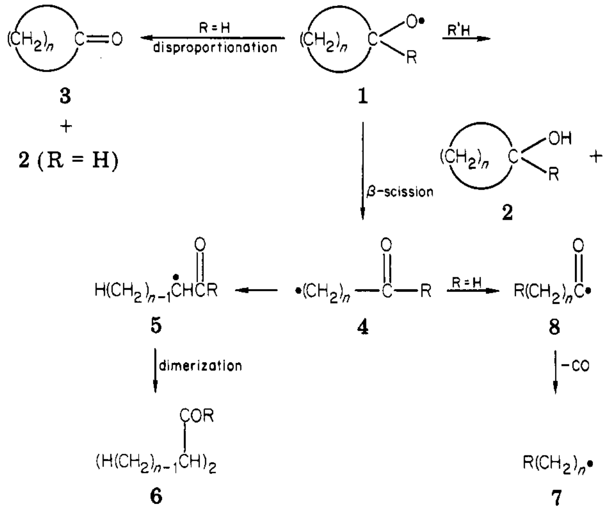
Scheme I[a]



[a] R = H or alkyl.

Results and Discussion

Thermal decompositions of solutions of 1–12 weight % dicycloalkyl peroxides 9 were done in Freon 113 (Du Pont) fluorocarbon, dodecane, or methylcyclohexane-d_{14} solvents in sealed glass or stainless steel tubes at 160 °C. Product identification was made by GC/MS. Initial experiments were done with undeuterated peroxides to determine the distribution of products obtained under various conditions. The perdominant reaction products were ketone 3 and alcohols 2, accounting for >90% of the starting dialkyl peroxides 9. The ratios of 3/2 depend on O_2 pressure. For example, 9 ($n = 5$) was thermolyzed in Freon 113 at 160 °C under N_2 and under 500 psi O_2. The resulting 3/2 ratios were 1/4 (N_2) and 17/1 (O_2), providing support for direct oxidation of cycloalkyloxyl radicals to ketones. Related examples of vapor–phase oxidations of *n*-butyloxy radicals by O_2 to give *n*-butyraldehyde are known.[10] High O_2 pressures (500 psi) also resulted in efficient O_2 trapping of radicals to give mainly hydroxy acids and dibasic acids, with only minor amounts of monobasic acids. The presence of even atmospheric air pressure in place of nitrogen

$$1 \xrightarrow{O_2} 3 + HO_2\cdot$$

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[1] Gray, P.; Williams, A. *J. Chem. Soc.* **1961**, 2620.
[2] Takagi, H.; Washida, N.; Bandow, H.; Okuda, M. *J. Phys. Chem.* **1981**, *85*, 2701.
[3] Gray, P.; Williams, A. *Trans. Faraday Soc.* **1959**, *55*, 760.
[4] Howard, J. A., Williams, G. H., Ed. "Advances in Free-Radical Chemistry"; Academic Press: New York, 1972; Vol. IV, pp 49–173.
[5] Kochi, Jay K., Ed. "Free Radicals"; Wiley: New York, 1973; Vol. II, pp 665–710.
[6] Milas, N. A.; Perry, L. H. *J. Am. Chem. Soc.* **1946**, *68*, 1938.
[7] Formanels, K.; Aune, J. P.; Jouffret, M.; Metzger, J. *Nouv. J. Chim.* **1979**, *3*, 311.
[8] Wallace, T. J.; Gritter, R. J. *J. Org. Chem.* **1961**, *26*, 5256.
[9] Druliner, J. D. *Synth. Commun.* **1983**, *13*(2), 115.
[10] (a) Niki, H.; Maker, P. D.; Savage, C. M.; Breitenbach, L. P. *J. Phys. Chem.* **1981**, *85*, 2698. (b) Carter, W. P. L.; Darnall, K. R.; Lloyd, A. C.; Winer, A. M.; Pitts, J. N., Jr. *Chem. Phys. Lett.* **1976**, *42*, 22.

0022-3263/83/1948-4951$01.50/0

Table I. Amounts of Different Hydrocarbon Products Obtained from Thermolysis of Dicycloalkyl Peroxides at 160 °C in Solution

			hydrocarbon product ratios, %[a]				
compd	solvent	atm	*n*-propane	*n*-butane	*n*-pentane	*n*-hexane	total yield[b]
9 ($n = 4$)	$CD_3C_6D_{11}$	air	0	100			2
9 ($n = 4$)	$CD_3C_6D_{11}$	air	0	100			
9-d_2 ($n = 4$)	$C_{12}H_{26}$	N_2	0	100			
9 ($n = 5$)	$CD_3C_6D_{11}$	air		2	98		
9 ($n = 5$)	$CD_3C_6D_{11}$	N_2		13	87		22
9 ($n = 5$)	$C_{12}H_{26}$	air		11	89		
9-d_2 ($n = 5$)	$C_{12}H_{26}$	N_2		trace	100		
9 ($n = 6$)	$CD_3C_6D_{11}$	air			8	92	7
9-d_2 ($n = 6$)	$C_{12}H_{26}$	N_2			6	94	27

[a] Product ratios determined by comparison of capillary column GC peak area percentage ratios. [b] Approximate yields of butane, pentane, and hexane were determined in those experiments in which area percentages of solvent peaks were determined.

Table II. Percentages of Deuterium Enrichment in $H(CH_2)_nH$ Products from Thermolysis of d_0 and d_2 Dicycloalkyl Peroxides at 160 °C in Solution

		$H(CH_2)_nD/H(CH_2)_nH$ ratio	
compd	solvent	air	N_2
9-d_0 ($n = 4$)	$CD_3C_6D_{11}$	15/85	12/88
9-d_0 ($n = 5$)	$CD_3C_6D_{11}$	29/71	19/81
9-d_0 ($n = 6$)	$CD_3C_6D_{11}$	7/93	8/92
9-d_2 ($n = 4$)	$C_{12}H_{26}$		74/26
9-d_2 ($n = 5$)	$C_{12}H_{26}$		29/71
9-d_2 ($n = 6$)	$C_{12}H_{26}$		38/62

Table III. Extents of Different H Atom Reaction Pathways for ω-Formyl Radicals in Solution at 160 °C under N_2

	H atom abstraction reaction pathway, %		
$\cdot(CH_2)_nCHO$	intramolecular aldehydic[a]	from solvent[a]	from other C-H sources[b]
$n = 4$	74	12	14
$n = 5$	29	19	52
$n = 6$	38	8	54

[a] Data from Table II. [b] Calculated as 100% - [% intramolecular aldehydic H atom abstraction + % H atom abstraction from solvent.

significantly reduced the yields of hydrocarbons obtained (Table I). Thus, all thermolyses of deuterated peroxides were done under an atmosphere of N_2 or atmospheric air pressure to minimize O_2 trapping of alkyl radicals in competition with intramolecular H-atom transfer processes. Because the *n*-alkanes were much better resolved by capillary GC than were the aldehydes or acids, they were chosen for quantification of deuterium isotopic enrichment. The combined amounts of $H-(CH_2)_n-H$ plus $H-(CH_2)_n-D$ and $H(CH_2)_{n-1}-H$ plus $H-(CH_2)_{n-1}-D$ products from **9** ($n = 4, 5, 6$; R = H or D) are listed in Table I and show that alkanes resulting from loss of one carbon (–CO) predominate over alkanes formed from loss of two carbons by about a factor of 10. With **9** ($n = 4$) only butane is formed. The absence of any detectable propane suggests that the lower alkanes are not formed by oxidation of $H-(CH_2)_n\cdot$ radicals but may be derived primarily from intramolecular α-H atom abstraction processes. Rearrangement of **4** ($n = 4$) to **5**, proceeding through a 5-membered transition state, would be energetically less favorable than analogous rearrangements with $n = 5$ or 6 which involve 6- and 7-membered transition states, respectively.[11]

Percentages of deuterium enrichment in $H(CH_2)_nH$ products were determined, both for decomposition of **9** ($n = 4, 5, 6$) in $CD_3C_6D_{11}$ and for **9**-d_2 ($n = 4, 5, 6$) in $C_{12}H_{26}$ (Table II). The results for the d_0 compounds show no major differences in the amounts of deuterium enrichment under N_2 or air. These data also provide a measure of the reproducibility of the measurements (±10%). The extent of deuterium atom abstraction from $CD_3C_6D_{11}$ solvent was not strongly dependent on chain length of the ω-formylalkyl radicals **4**. The upper limit on the amount of aldehydic D-atom transfer which occurred via an intramolecular process in **4**-*d* ($n = 4$) was moderately large (74%), corresponding to a favorable 6-membered transition state. The corresponding amounts of intramolecular aldehydic D-atom transfer for **4**-*d* ($n = 5$ and 6) were about half of that. Only upper limits can be set since small amounts of intermolecular H-atom abstraction could also have occurred in solution. Studies on the effect of chain length on intramolecular H-atom abstraction have been reported in solution phase studies of *n*-alkyloxyl radicals generated by alkyl hypochlorite decomposition at 0 °C.[12] A 6-membered transition state was favored over a 7-membered one by a factor of about 16. However, no rearrangements of the alkyloxyl radicals via 8-membered transition states were observed. The rearrangement of ω-formyl radical **4**-*d* ($n = 6$) involving an 8-membered transition state for intramolecular abstraction could be facilitated by the lower aldehydic C–H bond energy of 88 kcal/mol compared with a secondary C–H bond energy of 94 kcal/mol.[13] The percentages of various pathways for H atom abstraction by radicals **4** ($n = 4, 5, 6$) which occurred in solution phase reactions at 160 °C, are shown in Table III. About half of the H-atom abstraction with $n = 5$ and 6 occurred via intermolecular processes compared with only about 14% in the case of $n = 4$, which gives the most favorable transition state for intramolecular H-atom transfer.

Vapor-Phase Thermolyses. Vapor phase thermolyses were done by injecting micro liter amounts of neat dialkyl peroxides **9** ($n = 4$ and 5) into a glass reservoir heated at 80–110 °C from which the compounds could vaporize through a glass capillary into the ion source of a mass spectrometer. The ion source was heated to 200 °C to decompose the dialkyl peroxides to form radicals. The ion source also contained about 0.3 torr of N_2 pressure and a small amount of tetracyanoquinodimethane (TCNQ) for trapping and analyzing carbon-centered radicals.[14] The same techniques were not successful in the case of di-

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(11) Kochi, Jay K., Ed. "Free Radicals"; Wiley: New York, 1973; Vol. I, pp 378–382.

(12) Walling, C. *J. Am. Chem. Soc.* **1963**, *85*, 1597.

(13) Kerr, J. A. *Chem. Rev.* **1966**, *66*, 465.

(14) (a) McEwen, C. N.; Rudat, M. A. *J. Am. Chem. Soc.* **1979**, *101*, 6470. (b) *Ibid.* **1981**, *103*, 4343. (c) *Ibid.* **1981**, *103*, 4349. (d) *Ibid.* **1981**, *103*, 4355.

cycloheptyl peroxide because of insufficient volatility to give the required radical flux. Both d_0 and d_2 dicyclopentyl and dicyclohexyl peroxides were analyzed. In the case of **9** (n = 4), the major radicals trapped by TCNQ were $nC_4H_9\cdot$ and H· with virtually no C_1, C_2, C_3, or C_5 alkyl radicals.[15] Radical **9** (n = 5) likewise gave mostly n-$C_5H_{11}\cdot$ and H· radicals with only minor amounts of C_1, C_2, C_3, C_4, or C_6 radicals. When the starting material was **9** (n = 5), an oxygen-containing carbon-centered radical, isomeric with the ω-formylpentyl radical **4** (n = 5), was observed with an intensity equal to about 10% that of n-$C_5H_{11}\cdot$. No significant amount of the corresponding radical was observed starting with **9** (n = 4). A possible explanation is that the trapped oxygen-containing radical when n = 5 was the stabilized α-formyl radical **5** (n = 5) formed by intramolecular H-atom transfer of radical **4** (n = 5). Formation of **5** (n = 5) proceeds via a favorable 6-membered transition state. Formation of homologous **5** from **4** with n = 4 would require a much less favorable 5-membered transition state and was not observed. The energetics of gas phase intramolecular H atom transfer processes requiring 5- and 6-membered transition states have recently been discussed.[14c] Significantly faster rearrangements involving 6-membered transition states have been noted for both thermally and chemically activated radicals.

With **9**-d_2 as starting material, (n = 4), n-butyl radicals were trapped by TCNQ and contained at least 86% monodeuteration.[16] Collision Induced Decomposition (CID) analysis of the trapped n-butyl radicals showed loss of $C_3H_6D\cdot$ fragments consistent with a location of D in the methyl group of **8** (n = 4, R = D). Likewise, **9**-d_2 (n = 5) gave rise to n-pentyl radicals containing at least 95% monodeuteration. CID analysis of the TCNQ-trapped n-pentyl radicals showed the presence of both 2-pentyl and 1-pentyl radicals, in agreement with results obtained previously for pentyl radicals generated from n-hexylamine.[14b] The isomeric pentyl-d radicals contained D enrichment in the propyl and butyl portions. Precise analysis of the positions of D in the 1- and 2-pentyl radicals was not possible because of the degree of peak overlap of peaks differing by only one mass unit. The high level of deuterium enrichment found in n-butyl and isomeric pentyl radicals, generated from **4**-d with n = 4 and 5, indicates that gas phase intramolecular H-atom transfer of ω-formyl radicals proceeding through both 6- and 7-member transition states is quite favorable.

Experimental Section

Undeuterated and α,α'-dideuterated dicycloalkyl peroxides were prepared by reaction of KO_2 and the appropriate cycloalkyl methanesulfonate esters as recently reported.[9] Characterization of each of the dicycloalkyl peroxides was based on attainment of correct m/e values by GC/MS analysis and by analysis of the major ketone (**3**) and alcohol (**2**) thermolysis products by LC, GC, and GC/MS.[9]

The percentages of deuterium enrichment in the peroxide-d_2 were established by GC/MS analyses. The complete regiospecificity of α,α' deuterium incorporation was based on GC/MS analyses of starting cycloalkyl-α-d methanesulfonate esters and precursor cycloalkanols-α-d used for syntheses.

Gas chromatography was carried out using a Varian Model 3700 instrument equipped with a flame ionization detector and a 25-M Carbowax 20M glass capillary column. GC/MS analyses were performed using a Varian Model 3700 gas chromatograph coupled to a VG Micromass Model 16F mass spectrometer. Vapor phase MS analyses were done using a VG ZAB-2F mass spectrometer.

Solution-Phase Thermolysis of α,α'-Dideuteriodicyclohexyl Peroxide [9-d_2 (n = 5)] in Dodecane. A solution containing **9**-d_2 (0.058 g, 0.29 mmol) dissolved in 1.87 mL of dodecane was placed into a 10-mL glass tube equipped with a Teflon (Du Pont) fluorocarbon resin stopcock and was purged of air by bubbling with N_2 for 15 min. Analysis of the solution by GC/MS gave a parent peak of m/e 200 (calcd m/e for $C_{12}H_{10}D_2$ 200). The N_2-purged tube was sealed and was heated at 160 °C for 1 h. A GC/MS analysis of the product solution for low-boiling hydrocarbons revealed a major peak for pentane and a trace peak for butane. Comparison of peak intensities for $C_5H_{11}D$ (m/e 73) and C_5H_{12} (m/e 72) showed a ratio of 40/100, corresponding to 29% $C_5H_{11}D$/71% C_5H_{12} after correction of the $C_5H_{11}D$ peak intensity for 1.1% natural abundance ^{13}C.

Vapor-Phase Thermolysis of α,α'-Dideuteriodicyclohexyl Peroxide 9-d_2. A 10-μL sample of neat **9**-d_2 (n = 5) was injected into a 15-mL glass reservoir held at 110 °C from which it could escape through a glass capillary into the ion source of the mass spectrometer, which was maintained at 200 °C. A pressure of about 10^{-4} torr of TCNQ and about 0.3 torr of N_2 were also present in the ion source. The mass spectrum showed major ions corresponding to trapped $C_3H_7\cdot$, $C_5H_{10}D\cdot$, $C_5H_{11}\cdot$, and $C_6H_{10}DO\cdot$ with relative intensities of 24:100:10:14. The calculated ratio of $C_5H_{10}D\cdot/C_5H_{11}\cdot$ was 10:1.

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Registry No. 1 (n = 4; R = H), 53578-06-6; 1 (n = 5; R = H), 3384-35-8; 1 (n = 6; R = H), 78939-49-8; 9 (n = 4; R = H), 55999-66-1; 9 (n = 5; R = H), 1758-61-8; 9 (n = 6; R = H), 86148-71-2; $\cdot(CH_2)_4CHO$, 78939-50-1; $\cdot(CH_2)_5CHO$, 59282-49-4; $\cdot(CH_2)_6CHO$, 78939-51-2; H, 1333-74-0.

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[15] Carbon-centered radicals were trapped with TCNQ and were characterized, free of neutral organic byproducts.

[16] Some loss of deuterium enrichment in ω-formyl radicals from H–D exchange with H_2O on heated glass and metal surfaces is expected.

Aerosol Direct Fluorination Syntheses: Alkyl Halides, Neopentyl Chloride and Bromide, Free Radicals vs. Carbocations

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Aerosol direct fluorination of neopentyl chloride produces perfluoroneopentyl chloride in 74% yields. Analogous fluorination of neopentyl bromide produces perfluoroisopentane in 63% yield. Data are presented that support a carbocation rearrangement in the fluorination of neopentyl bromide. The carbocations are presumed to arise from disproportionation of neopentylbromine fluorides.

The direct fluorination of alkyl halides to perfluoroalkyl halides would provide a method of obtaining specific fluorocarbons in which the site for further reaction has been preselected prior to fluorination. the fluorination of chloroalkanes by metathesis using HF, F^-, or SbF_3 does not provide for prior selection of residual halogens although