(2) (a) R. V. Hoffman and H. Shechter, *J. Am. Chem. Soc.*, **93**, 5940 (1971); (b) R. V. Hoffman and H. Shechter, *ibid.*, preceding paper in this issue.

(3) (a) Hydrolysis of furoyl cyanide, as prepared from furoyl chloride and hydrogen cyanide,[16] with concentrated hydrochloric acid yields (2-furyl)glyoxylic acid. Esterification of (2-furyl)glyoxylic acid with ethanol as catalyzed by hydrogen chloride gives ethyl (2-furyl)glyoxylate. (b) E. Fischer and H. Brauns, *Ber.*, **46**, 892 (1913). (c) N. Saldabols and A. Hillers, *Latv. PSR Zinat. Akad. Vestis, Kim. Ser.*, 704 (1964); *Chem. Abstr.*, **62**, 16246a (1968).

(4) (a) An extension of the method of A. Koch, M.S. Thesis, The Ohio State University, 1969; (b) A. Koch, private communication.

(5) (a) The vinyl coupling constant of **6**, $J_{vinyl} = 11$ Hz, is identical with those of **3** as previously determined.[2] (b) The trans isomer of **6** could not be detected in the crude reaction product by NMR methods.

(6) R. Silverstein and G. Bassler, "Spectrometric Identification of Organic Compounds", Wiley, New York, N.Y., 1967.

(7) The conversion of **4** in acetic acid/ethyl ether and in acetic acid/dichloromethane to **6** indicates that carbenic decomposition is a significant process even though the reaction environments are highly acidic (equivalent quantities of acetic acid to **4** were used in these experiments).

(8) The rate of decomposition of **4** is not greatly affected by addition of acetic acid, benzoic acid in ethyl ether, or various alcohols. Acid-catalyzed decomposition does not appear to be a major response of **4** under these conditions.

(9) M. I. Ushakov and V. F. Kucherov, *J. Gen. Chem. USSR* (*Engl. Transl.*), **14**, 1073 (1944); *Chem. Abstr.*, **40**, 7185 (1945); (b) V. F. Kucherov, *J. Gen. Chem. USSR* (*Engl. Transl.*), **20**, 1885 (1950); *Chem. Abstr.*, **45**, 2928 (1951); (c) V. F. Kucherov, *Sb. Statei Obshch. Khim.*, **1**, 681 (1953); *Chem. Abstr.*, **49**, 999 (1955).

(10) (a) Hydrolyses of furfuryl derivatives to derivatives of levulinic acid are presumed to involve 2-alkylidene-5-hydroxy-2,5-dihydrofurans as reaction intermediates. (b) A. P. Dunlap and F. N. Peters, "The Furans", ACS Monograph 119, Reinhold, New York, N.Y., 1953, pp 642–652. (c) E. J. Stamhuis, W. Dreuth, and H. Van Den Berg, *Recl. Trav. Chim. Pays-Bas*, **83**, 167 (1964). (d) A. Kankaanpera and P. Salomaa, *Acta. Chem. Scand.*, **21**, 575 (1967). (e) D. S. Noyce and G. V. Kaiser, *J. Org. Chem.*, **34**, 1008 (1969), and references cited therein.

(11) (a) T. Reichstein, *Ber.*, **63**, 749 (1930); (b) T. Reichstein and R. Zschokke, *Helv. Chim. Acta*, **15**, 1124 (1932); (c) E. W. Scott and J. R. Johnson, *J. Am. Chem. Soc.*, **54**, 2549 (1932); (d) ref 10b, p 551; (e) K. Y. Novitskii, K. Gresl, and Y. K. Yurev, *Zh. Org. Khim.*, **1**, 539 (1965).

(12) A. I. Scott, "Interpretation of the Ultraviolet Spectra of Natural Products", Macmillan, New York, N.Y., 1964.

(13) (a) The deshielding of H_5 in **20a** may be related to (1) the diminished electron density at the δ position because of the conjugated ester function, (2) the electron-withdrawing effect of the acetal moiety adjacent, and (3) the rigid geometry of the ring system which holds H_5 in the deshielding region of the exocyclic α,β double bond.[13b] (b) J. R. Dyer, "Applications of Absorption Spectroscopy of Organic Compounds", Prentice-Hall, Englewood Cliffs, N.J., 1965.

(14) J. B. Jones, *J. Chem. Soc.*, 5729 (1963).

(15) When a dichloromethane solution of **24a** is irradiated for 1 h with a Hanovia medium-pressure lamp (450-W), a 79:21 mixture of **24a**:**20a** results.

(16) (a) Diphenyldiazomethanes decompose in alcoholic and in aqueous solvents via diphenylcarbene intermediates to yield benzhydryl alkyl ethers and benzhydrols. These processes do *not* involve nucleophilic attack of the diazo compounds on the hydroxylic solvents to form diazonium or carbenium ion intermediates. Phenyldiazomethanes, however, are decomposed by hydroxylic solvents via diazonium ion mechanisms. (b) D. Bethell, D. Whittaker, and J. B. Callister, *J. Chem. Soc.*, 2466 (1965). (c) D. Bethell and R. D. Howard, *J. Chem. Soc. B*, 745 (1969). (d) D. Bethell, A. R. Newall, and D. Whittaker, *ibid.*, 23 (1971). (e) R. J. Miller, Ph.D. Dissertation, The Ohio State University, 1975. (f) D. Bethell and D. Whittaker, *J. Chem. Soc. B*, 778 (1966).

(17) M. Hine and J. Hine, *J. Am. Chem. Soc.*, **74**, 5266 (1952).

(18) E. Wenkert, B. L. Mylari, and L. L. Davis, *J. Am. Chem. Soc.*, **90**, 3871 (1968), have suggested that reactions of diazomethyl ketones with silver ion involve metalized intermediates such as $RCOCHAgN_2^+$, $RCOCAgN_2$, or/and $RCOC^+HAg$.

(19) R. G.Salomon and J. K. Kochi, *J. Am. Chem. Soc.*, **95**, 3300 (1973), and references cited therein have observed that the active catalyst in copper ion catalyzed cyclopropanations by diazo compounds is Cu^I and that various coordinating ligands markedly affect the electronic structure and stereoselectivity of the metal–carbene complexes.

(20) (a) J. L. Erickson, J. M. Dechary, and M. R. Kesling, *J. Am. Chem. Soc.*, **73**, 5301 (1951); (b) P. Yates, *ibid.*, **74**, 5376 (1952).

(21) The UV spectrum of **4** has λ_{max} 220 nm (ϵ 5000), 240 (5900), and 300 (4100). The long wavelength trails into the red region and at 366 nm has an extinction coefficient of <200. Use of a 2 M excess of Michler's ketone assures that the photosensitizer absorbs >98% of the incident light at 366 nm. The light was filtered (Corning no. 3718, λ >330 nm) to prevent primary excitation of **4** at lower wavelengths.

(22) (a) The intra- and the intermolecular products of photolysis and photosensitization of (2-*n*-butylphenyl)diazomethane in cyclohexane are identical.[22b] Similarly, there is no difference in the respective intramolecular products of photolytic and photosensitized decompositions of methyl α-diazo-2,3-dimethylcyclopropane ($1\alpha,2\alpha,3\beta$)acetate,[22c] methyl α-diazo-2,3-dimethylcyclopropane ($1\alpha,2\beta,3\beta$)acetate,[22c] and ethyl α-diazophenylthiolacetate.[22d] On the other hand, the respective carbenic products of photolysis and photosensitization of 2-methyl-2-phenyldiazopropane,[22e] the sodium salt of brexan-4-one tosylhydrazone,[22f] and alcoholic solutions of diazoacetophenone[22g] vary greatly. (b) T. A. Baer and C. D. Gutsche, *J. Am. Chem. Soc.*, **93**, 5180 (1971). (c) R. R. Gallucci and M. Jones, Jr., *ibid.*, **98**, 7704 (1976). (d) G. G. Orphanides, Ph.D. Dissertation, The Ohio State University, 1972. (e) J. J. Havel, *J. Org. Chem.*, **41**, 1464 (1976). (f) A. Nickon, F. Huang, R. Weglein, K. Matsuo, and H. Yagi, *J. Am. Chem. Soc.*, **96**, 5264 (1974). (g) A. Padwa and R. Layton, *Tetrahedron Lett.*, 2167 (1965).

Photolysis of *tert*-Butyl Hydroperoxide in Alcohols. A Carbon-13 CIDNP Study[1]

W. B. Moniz,[2] S. A. Sojka,[3] C. F. Poranski, Jr.,* and D. L. Birkle[4]

Contribution from the Chemistry Division, Naval Research Laboratory, Washington, D.C. 20375.

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Abstract: We have observed carbon-13 CIDNP during photolysis of *tert*-butyl hydroperoxide (*t*-BuOOH) in a variety of alcohols. Interpretation of this CIDNP provides mechanistic insight into the photodecomposition. Most notable was the detection of simple enols **5** and *tert*-butylperoxy compounds **3** as transient intermediates. A major polarization pathway was the free-radical encounter of *tert*-butylperoxy and ketyl radicals. Production of β-hydroxy radicals was a preferential polarization route for 2-methylpropanol (**1E**) and 3-methyl-2-butanol (**1L**).

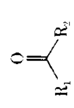
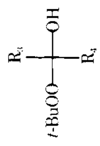
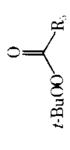
Introduction

Our interest in the mechanism of hydrocarbon autoxidation led us to use carbon-13 CIDNP to study the photochemical decomposition of *tert*-butyl hydroperoxide in a variety of alcohols. We anticipated obtaining intimate mechanistic details about the autoxidation process through understanding more fully the radical chemistry of hydroperoxides. Carbon-13 CIDNP has been a powerful tool for elucidating the elementary processes of radical decompositions.[5] Hydroperoxides and alcohols are formed during the autoxidation process.[6] Although their thermal reactions have been characterized, the photochemical reactions of hydroperoxides have not been extensively studied.[6,7] Photochemical initiation of hydroperoxide decomposition allows independent control of reaction conditions, a distinct advantage for carbon-13 CIDNP using Fourier transform NMR.[8-10]

Experimental Section

NMR Measurements. The spectrometer system was a modified Varian HA-100 operating at 25.15 MHz with an external fluorine-19 field-frequency lock. A NIC-80 data system was used for signal accumulating and processing. A 90° pulse took 105 μs. The spectral

Table I. Reaction Products Identified from Carbon-13 CIDNP Signals Observed during Photolysis of *t*-BuOOH in Alcohols

	parent alcohol ROH	 2		 3		 4	$R_7R_8C{=}C(OH)R_6$ 5		
	R	R_1	R_2	R_3	R_4	R_5	R_6	R_7	R_8
A	CH_3			H	H				
B	CH_3CH_2	CH_3	H	CH_3	H	CH_3	H	H	H
C	$CH_3CH_2CH_2$	CH_3CH_2	H	CH_3CH_2	H	CH_3CH_2	H	CH_3	H
D	$CH_3(CH_2)_3$					$CH_3CH_2CH_2$			
E	$(CH_3)_2CHCH_2$					$(CH_3)_2CH$			
F	$CH_3CH_2(CH_3)CHCH_2$					$CH_3CH_2(CH_3)CH$			
G	$(CH_3)_2CH$	CH_3	CH_3	CH_3	CH_3		CH_3	H	H
H	$CH_3CH_2(CH_3)CH$	CH_3CH_2	CH_3	CH_3CH_2	CH_3	CH_3	(a) CH_3	CH_3	H
							(b) CH_3CH_2	H	H
I	$CH_3CH_2CH_2(CH_3)CH$	$CH_3CH_2CH_2$	CH_3			CH_3	(a) CH_3	CH_3CH_2	H
							(b) $CH_3CH_2CH_2$	H	H
J	$CH_3(CH_2)_3CHCH_3$	$CH_3(CH_2)_3$	CH_3				$CH_3(CH_2)_3$	H	H
K	$(CH_3CH_2)_2CH$	CH_3CH_2	CH_3CH_2	CH_3CH_2	CH_3CH_2	CH_3CH_2			
L	$(CH_3)_2CH(CH_3)CH$	$(CH_3)_2CH$	CH_3	$(CH_3)_2CH$	CH_3	CH_3			
M	$(CH_3)_3C(CH_3)CH$	$(CH_3)_3C$	CH_3			CH_3			
N	$PhCHCH_3$	phenyl	CH_3						
O	C_6H_{11}						$(CH_2)_2$	$(CH_2)_2$	H

width was 6275 Hz, and a matched 4-pole Butterworth filter was used for signal filtering. The number of data points Fourier transformed was 4K. The pulse repetition time was 10 s, and 100 scans were accumulated before, during, and after irradiations. The beam of the mercury-xenon arc source was passed through Corning glass filters CS-954 and CS-054, resulting in a combined transmittance of greater than 50% at wavelengths longer than 315 nm, and less than 1% at wavelengths shorter than 305 nm. Sample temperature during photolysis was 44 ± 2 °C. The optical arrangement for in-probe irradiation has been previously described.[8,10]

Carbon-13 chemical shifts were measured relative to the methyl carbons of the appropriate alcohols and converted to the Me_4Si parts per million scale using the relationship $\delta_{Me_4Si} = \delta_{ROH} + X$. The values used for X for the corresponding alcohol are taken from the literature[11] and are given below as the ordered pairs (ROH, X): (**1A**, 49.3); (**1B**, 17.9); (**1C**, 10.3); (**1D**, 13.9); (**1E**, 19.2); (**1F**, 11.4); (**1G**, 25.4); (**1H**, 10.2); (**1I**, 14.3); (**1J**, 14.2); (**1K**, 10.1); (**1L**, 18.3); (**1M**, 18.2); (**1N**, 25.1); and (**1O**, 26.2). Assignments of CIDNP signals to particular carbon atoms were based on chemical shift similarity with authentic or closely related compounds. Chemical shift agreement within ±0.5 ppm was taken as positive identification. In some cases, proton coupled carbon-13 CIDNP spectra were obtained in order that signal multiplets and C-H coupling constants could be used as additional assignment aids.

A Varian HA-100 spectrometer operating at 100 MHz in the CW mode was used to obtain the proton spectra of reaction mixtures. Proton chemical shifts were measured relative to an internal Me_4Si reference. The Me_4Si also provided a homonuclear locking signal. In some cases, spiking experiments were conducted to confirm the presence of a reaction product.

Material Preparation. The alcohols and *t*-BuOOH, commercially obtained, were dried over molecular sieves, carefully distilled, and stored in a refrigerator. Distillation removed water from the alcohols, and water and *t*-BuOH from *t*-BuOOH. The purity was determined by ^{1}H NMR spectroscopy. The concentration of *t*-BuOOH in the alcohols varied from 5 to 50% by volume. The samples, in 7.5 mm o.d. Pyrex NMR tubes, were deoxygenated with a stream of high-purity nitrogen before photolysis.

Preparation of *tert*-Butylperoxyhemiacetals 3A-C.[12] To a stirred solution of formaldehyde, acetaldehyde, or propionaldehyde in diethyl ether at 0 °C was dropwise added an equimolar solution of *t*-BuOOH in diethyl ether. After 1 h at 0 °C, the ice bath was removed and the reaction mixture was allowed to warm to room temperature. The solvent was carefully flash evaporated at room temperature and the residue examined by ^{1}H and ^{13}C NMR. *tert*-Butylperoxymethanol (**3A**): ^{1}H NMR (CCl_4): δ 5.49 (s, broad, 1 H, -OH), 5.02 (s, 2 H, $-CH_2$), 1.24 (s, 9 H, $-CH_3$); ^{13}C NMR (methanol) δ 91.9 ($-OCH_2OH$), 80.2 (-COO-), 26.2 ($-CH_3$). 1-*tert*-Butylperoxyethanol (**3B**): ^{1}H NMR (CCl_4) δ 5.13 (q, 1 H, -CH), 4.50 (s, broad, 1 H, -OH), 1.22 (s, broad, 12 H, $-CH_3$); ^{13}C NMR (ethanol) δ 96.8 (-OCHOH), 79.5 (-COO-), 26.3 ($-CH_3$, butyl), 25.8 ($-CH_3$, ethyl). 1-*tert*-Butylperoxypropanol (**3C**): ^{1}H NMR (CCl_4) δ 5.04 (t, 1 H, CH), 1.23 (s, 9 H, $-CH_3$), 1.6 (m, 2 H, $-CH_2$), 0.92 (t, 3 H, $-CH_3$); ^{13}C NMR (propanol) δ 101.1 (-OCHOH), 80.0 (-COO-), 37.1 ($-CH_2$), 26.5 ($-CH_3$, butyl), 23.2 ($-CH_3$, propyl).

Results

Carbon-13 CIDNP signals from the starred carbons of one or more of reaction products **2**-**5** (Scheme I) were observed during the photolysis of *t*-BuOOH in alcohols **1**. The structures of the alcohols and products are given in Table I. Table II lists

Scheme I

ROH + *t*-BuOOH
1

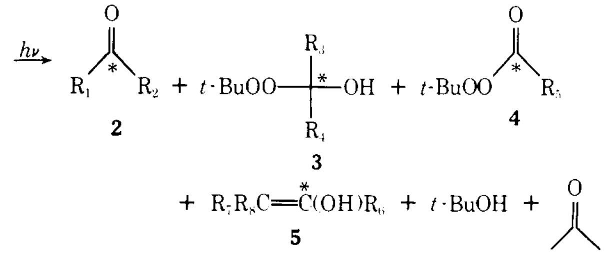


Table II. Carbon-13 Chemical Shifts of Carbons Exhibiting the CIDNP Effect for the Indicated Structures (ppm Relative to Me$_4$Si)[a]

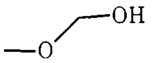
derivative	2		3		4		5
A			92.0[b]	(91.9)[c]			
B	200.4	(200.2)	96.9[d]	(96.8)	169.0	(169.1)	148.1[e]
C	202.8	(202.8)	101.3	(101.1)	172.3	(171.8)[f]	142.4[g]
D					171.3		
E					174.7[h]	(174.2)	
F					174.0[i]		
G	207.6	(207.2)	101.2				156.8[j]
H	209.8	(209.3)	102.8		168.7	(169.1)	(a) 148.9[g] (b) 161.9
I	207.6	(207.6)			168.2	(169.1)	(a) 150.1[g] (b) 160.1
J	208.9	(208.5)					160.2
K	212.2	(212.4)	104.3		171.9	(171.8)[k]	
L	212.7	(212.8)	104.3		168.4	(169.1)[l]	
M	213.5	(213.2)			168.4	(169.1)[m]	
N	198.3	(198.4)					
O							150.5

[a] Carbon-13 chemical shifts in parentheses are from measurements on authentic products. All CIDNP signals were in emission unless otherwise noted and are assigned to the starred carbons in Scheme I. [b] This signal was observed in normal absorption after photolysis. Triplet ($^1J_{CH}$ = 163 Hz). Signals at 26.2, 90.5, and 54.4 ppm were present in the spectrum obtained after photolysis. These were assigned to the methyl carbons of **3A**, the methylene carbon of **6A**, and the methyl carbon **6A**, respectively. The chemical shifts from authentic products were 26.2, 90.7, and 54.4 ppm. [c] Triplet ($^1J_{CH}$ = 162 Hz). [d] Doublet ($^1J_{CH}$ = 175 Hz). [e] Doublet ($^1J_{CH}$ = 169 Hz). Signals at 94.2 and 62.0 ppm were present in the spectrum obtained after photolysis. These were assigned to the methine and methylene carbons of **6B**, respectively. The chemical shifts from authentic **6B** were 94.2 and 61.9 ppm. [f] Additional CIDNP emission signal detected at 83.5 ppm and assigned to the quaternary *tert*-butyl carbon of perester **4C**. Authentic product gave a chemical shift of 83.0 ppm for this carbon. [g] The cis/trans relationship in this enol is not known. [h] Singlet. Additional CIDNP emission signals were observed at 144.7 and 81.0 ppm. The signal at 144.7 ppm was assigned to the quaternary carbon of allylic alcohol **7E**, and the signal at 81.0 ppm remains unassigned. The chemical shift of the quaternary carbon from authentic **7E** was 144.7 ppm. [i] Additional CIDNP emission at 82.8 ppm tentatively assigned to quaternary *tert*-butyl carbon of perester **4F**. [j] A CIDNP absorption signal was detected at 95.3 ppm and assigned to the methylene carbon of enol **5G**. [k] A CIDNP absorption signal was observed at 176.6 ppm and assigned to the carbonyl carbon of propionic acid (**8K**). Authentic **8K** gave a carbonyl chemical shift of 177.0 ppm. An additional emission signal at 141.6 ppm was assigned to the quaternary carbon of olefin **9**. Authentic **9** gave a chemical shift of 141.5 ppm. [l] A CIDNP absorption signal appearing at 173.4 ppm was assigned to the carbonyl carbon of acetic acid (**8L,M**). A CIDNP emission at 148.8 ppm was assigned to the substituted sp^2 carbon of allylic alcohol **7L**. The chemical shift measured for this peak in authentic **7L** was 148.9 ppm. Additional emission signals at 83.1 and 75.2 ppm were tentatively assigned to *tert*-butylperoxy-containing products, and the one at 83.1 ppm was assigned to the quaternary *tert*-butyl carbon of perester **4K**. [m] A CIDNP absorption signal appearing at 173.5 ppm was assigned to the carbonyl carbon of acetic acid (**8L,M**). A CIDNP emission at 141.4 ppm was assigned to the quaternary carbon of olefin **9**. An additional emission at 78.0 ppm remains unassigned.

the ^{13}C chemical shifts of the CIDNP lines and the shifts we measured for available authentic products. The CIDNP signals were mostly in emission. The ^{13}C NMR signals from the alcohols *t*-BuOOH and *t*-BuOH did not appear to be polarized.

In general, the alcohol was oxidized to the corresponding carbonyl-containing compound (**2**). In some cases, *tert*-butylperoxy compounds (**3**) were observed. A perester (**4**) was often produced. Surprisingly, simple enols (**5**) were frequently detected as transient intermediates. The reaction always produced *t*-BuOH and acetone. The *t*-BuOH could be detected in the ^{13}C spectra obtained after photolysis, while acetone was identified by ^{1}H NMR analysis of the crude reaction mixtures.

Primary Alcohols. Figure 1 shows the ^{13}C spectra recorded during and after the photolytic decomposition of *t*-BuOOH in methanol (**1A**). The spectrum obtained during irradiation displayed one distinct emissive signal assigned to the methylene carbon of hemiperacetal **3A**. The spectrum recorded after irradiation showed this signal in normal absorption, as well as additional product peaks due to hemiacetal **6A** and *tert*-butyl alcohol.


6A

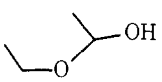
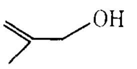
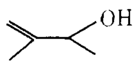

6B

Figure 2 shows the carbon-13 CIDNP spectra obtained during photolysis of *t*-BuOOH in ethanol (**1B**). Four distinct emission signals were observed and assigned to the indicated carbon of acetaldehyde (**2B**), hemiperacetal **3B**, *tert*-butyl peracetate (**4B**), and transient enol **5B**. After photolysis, additional signals due to hemiacetal **6B** were detected. The emission signal from enol **5B** was assigned on the basis of the observed doublet in the proton-coupled carbon-13 CIDNP spectrum and the chemical shift similarities to vinyl ethers and vinyl acetates.[13]

Similar ^{13}C signals were observed in the photolysis of *t*-BuOOH in 1-propanol (**1C**). Four weak emission signals were assigned to propionaldehyde (**2C**), hemiperacetal **3C**, perester **4C**, and transient enol **5C**. An additional emission signal was assigned to the quaternary *tert*-butyl carbon of **4C**.

The photolysis of *t*-BuOOH in 2-methylpropanol (**1E**) apparently takes a slightly different course. Surprisingly, allylic alcohol **7E** was detected by virtue of the CIDNP emission from the quaternary carbon. A CIDNP emission at 81.0 ppm was assigned to the quaternary *tert*-butyl carbon of perester **4E**.


7E


7L

The photolysis of *t*-BuOOH in alcohols **1D** and **1F** led to the detection of peresters **4D** and **4F**, respectively. In the case of alcohol **1D**, an additional CIDNP emission was tentatively assigned to the quaternary *tert*-butyl carbon of perester **4D**.

Secondary Alcohols. The photolysis of secondary alcohols **1G–N** gave rise to emissive CIDNP signals from the carbonyl carbons of ketones **2G–N**. These signals, in general, were augmented at the expense of other CIDNP signals when the photolyses were run with a trace (10^{-4} M) of *p*-toluenesulfonic

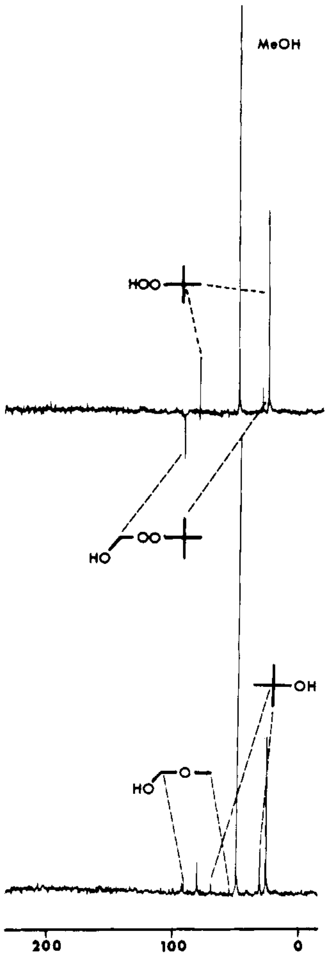
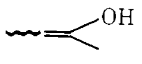
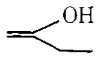


Figure 1. Carbon-13 spectra recorded during (top) and after (bottom) photolysis of *t*-BuOOH in methanol (**1A**). Starting concentration of the *t*-BuOOH was 10% (v/v).

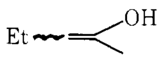
acid. Hemiketals **3G, 3H, 3K,** and **3L** were detected, as well as peresters **4H, 4I, 4K, 4L,** and **4M.** Interestingly, two different intermediate enols were detected in the case of alcohols **1H** and **1I.** 2-Butanol (**1H**) gave rise to enols **5Ha** and **5Hb.**



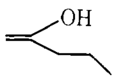
5Ha



5Hb



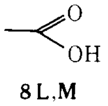
5Ia



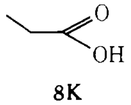
5Ib

Similarly, 2-pentanol (**1I**) gave enols **5Ia** and **5Ib.** Figure 3 shows the photolysis of *t*-BuOOH in 2-butanol (**1H**) with and without a trace of *p*-toluenesulfonic acid. This figure clearly shows the two enolic species **5Ha** and **5Hb** and the dramatic effect of trace acid.

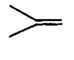
The photolysis of *t*-BuOOH in alochols **1K, 1L,** and **1M** produced CIDNP absorption from the carbonyl carbon of a carboxylic acid (propionic acid **8K** from alcohol **1K** and acetic acid **8L,M** from alcohols **1L** and **1M**). Additionally, 2-methylpropene (**9**) was detected during the photolysis in alcohols **1K** and **1M,** while allylic alcohol **7L** was observed in the reaction with alcohol **1L.**



8L,M



8K



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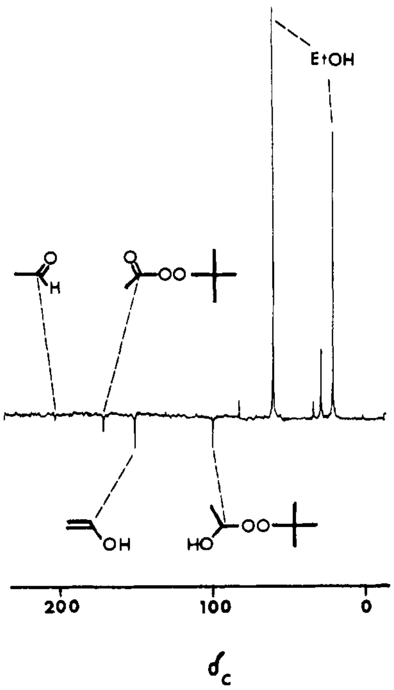


Figure 2. Carbon-13 spectrum recorded during photolysis of *t*-BuOOH in ethanol (**1B**). Starting concentration of *t*-BuOOH was 10% (v/v).

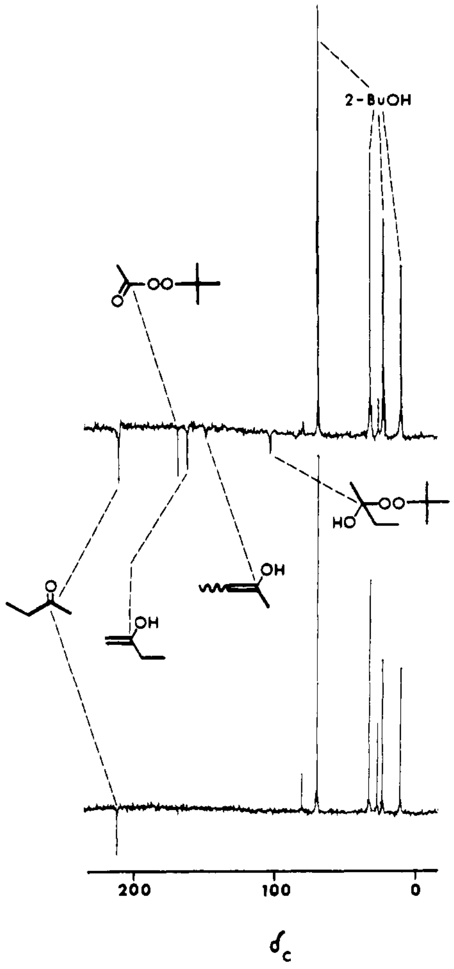


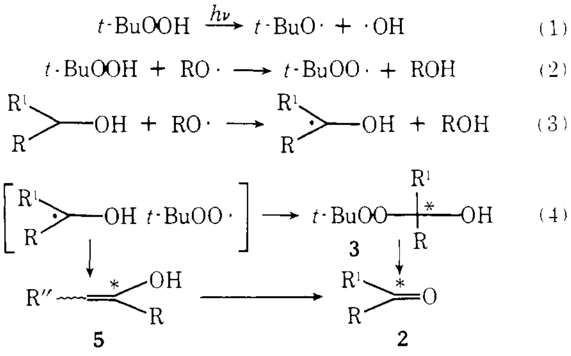
Figure 3. Carbon-13 spectra recorded during photolysis of *t*-BuOOH in 2-butanol (**1H**). The top spectrum clearly shows two enolic signals. The bottom spectrum was of the same reaction but with 10^{-4} M *p*-toluenesulfonic acid added. Starting *t*-BuOOH concentration was 5% (v/v).

Table III. Photolysis Product Yields as % of *t*-BuOOH Reacted, Measured by ^{1}H NMR Spectroscopy

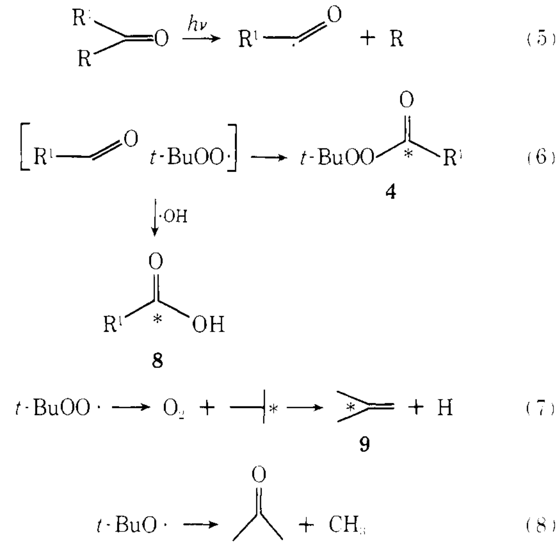
product	mol % product yield				
	1A	**1B**	**1G**	**1H**	**1L**
t-BuOH	66	30	63	10	63
acetone	1	5	{38}[a]	3	3
2		26		81	20
3	12	10			
4		7		3	7
6	20	23			
8				3	7
% unreacted *t*-BuOOH	17	39	36	36	70

[a] It is not possible to determine the relative production of acetone by the two possible routes, although the amount produced by β-scission of *t*-BuO· is probably on the order of 1–2%.

Scheme II



Scheme III



^{1}H NMR Analysis. The crude reaction mixtures for several alcohol photolyses were analyzed by ^{1}H NMR spectroscopy. Table III shows the relative mol % of the indicated product for 1000 s of photolysis time. Integrated peak ratios were used. The *tert*-butyl methyl proton areas were used to analyze for *t*-BuOOH, *t*-BuOH, **3**, and **4** while the methyl proton areas were used for acetone, **2**, **6**, and **8**.

Discussion

From the observed polarizations and reaction products, we postulate the general mechanisms given in Schemes II and III. Scheme II portrays the production of pertinent radicals and the formation of enols, hemiacetals, or hemiketals and aldehydes or ketones. Scheme III illustrates other reactions which may occur.

Photolysis of *t*-BuOOH gives *tert*-butoxy and hydroxy radicals (eq 1).[14] Any oxy radical in solution can remove the hydrogen from *t*-BuOOH to produce the *tert*-butylperoxy radical and an alcohol (eq 2). This latter process is especially important at high hydroperoxide concentrations.[15] The alcohol is subsequently attacked by any oxy radical to yield a ketyl radical and an alcohol (eq 3). The rate constants for hydrogen atom abstraction by peroxy radicals are small, especially for tertiary peroxy radicals, and typically one to two orders of magnitude smaller than those for hydrogen atom abstraction by oxy radicals.[16] Consequently, the peroxy radical population is expected to dominate by virtue of the rapid destruction of oxy radicals via the reactions of eq 2 and 3.

As a general rule, if a radical can be observed by ESR, it can be a radical pair partner for CIDNP. The *tert*-butylperoxy radical has been observed by ESR,[16] as have ketyl radicals during irradiation of peroxides in alcohols.[17] Oxy radicals in the liquid phase have not been detected by ESR,[18] nor is there a documented example of CIDNP generated from a radical pair containing an oxy radical as a partner. Radicals which have degenerate π orbitals (e.g., hydroxyl, chloro) have large spin-orbit interactions which tend to short circuit nuclear polarizations.[19]

Thus, we conclude that polarization is produced in the *tert*-butylperoxy-ketyl radical cage (eq 4). Collapse gives polarized *tert*-butylperoxy compounds (**3**). Disproportionation gives polarized enols (**5**). Both radicals may escape this cage to suffer other fates. The enols (**5**) are transient intermediates and tautomerize to the corresponding carbonyl-containing compounds (**2**); the polarization is remembered during tautomerization. Unstable *tert*-butylperoxy compounds (**3**) may also decompose to carbonyl-containing compounds (**2**). Both tautomerization of **5** and decomposition of **3** are greatly enhanced by trace acid catalysis.[20]

Secondary reaction of **2** may occur as illustrated in Scheme III. Aldehydes may lose an aldehydic proton and ketones may α-cleave to provide a source of radicals (eq 5). These radicals may encounter free *tert*-butylperoxy radicals (eq 6). Collapse of this polarizing cage produces polarized peresters (**4**). Escape of radicals may yield polarized acids (**8**) after combination with free hydroxy radicals. Polarized *tert*-butylperoxy radicals may fragment to form oxygen and *tert*-butyl radicals which produce polarized olefin (**9**) upon disproportionation (eq 7).

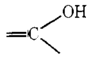
The ^{1}H NMR spectra revealed that a small amount of acetone was always produced. This product may be formed by β-scission of *tert*-butoxy radicals (eq 8). This process does not lead to polarized acetone.

These mechanistic schemes are subject to validation by application of the CKO theory[21] of CIDNP using Kaptein's equation.[22] Table IV evaluates eq 9, where Γ, the net polarization, is positive for enhanced absorption and negative for emission. The multiplicity of the polarizing radical pair is given by μ. The type of product-forming step (in-cage or out of cage processes) is given by ϵ. The spectroscopic splitting factor difference is Δg, and A is the electron-carbon hyperfine interaction constant.

$$\Gamma = \mu\epsilon\Delta g A \qquad (9)$$

In order that Schemes II and III be supported, there must be agreement between the observed polarization sign, Γ, and the theoretical predicted sign. The spectroscopic splitting factors are known for the radicals under consideration; that for *tert*-butylperoxy radical (2.0137)[18b] is greater than that for ketyl radicals (2.0030–2.0033).[17b] The hyperfine interaction constants for all carbon-centered radicals have positive signs.[23] The multiplicity of the radical pairs must be triplet as they are formed by free-radical encounters. The type of product-forming step is, of course, dictated by the mechanistic scheme. As Table IV shows, there is agreement between the

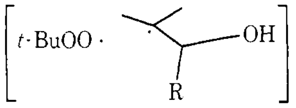
Table IV. Evaluation of Kaptein's Expression for Products Formed during Photolysis of *t*-BuOOH in Alcohols

product	carbon	μ	ϵ	Δg	A	Γ exptl	Γ calcd
2	C=O	+	+	−	+	E	E
3	O-C-O	+	+	−	+	E	E
4	C=O	+	+	−	+	E	E
	O—C<	+	+	+	$-^{b}$	E	E
5		+	+	−	+	E	E
7	=C<	+	+	−	+	E	E
8	C=O	+	−	−	+	A	A
9	=C<	+	−	+	+	E	E

[a] μ is + for triplet pairs and pairs formed from free-radical encounters, − for singlet pairs; ϵ is + for cage products, − for escape products; Δg is + for the radical with the larger g factor, − for the radical with the smaller g factor; Γ is + for enhanced absorption (A) and − for emission (E). [b] The sign of the constant for this oxyradical is not known but is taken to be −, in order that the experimental and calculated polarization signs agree.

predicted and observed polarization signs, thus supporting the mechanistic details of Schemes II and III.

Additional polarization pathways exist during photolysis of *t*-BuOOH in alcohols **1E** and **1L.** In this case, radical pair **10** is produced. Evidently, production of β-hydroxyalkyl radical is more favorable for these alcohols. Upon disproportionation, radical pair **10** yields allylic alcohols **1E,L.** Alcohol



10

1F is structurally similar to **1E** and **1L** and might also form allylic alcohol. We detected no CIDNP attributable to allylic alcohol during photolysis of *t*-BuOOH in **1F.** However, the CIDNP which we did observe in this system was very weak.

It is noteworthy that secondary alcohols possessing two or more γ carbons give rise to polarized acids **8** and olefin **9.** We attribute this to the increased importance of reactions in Scheme III. The ketones resulting from secondary alcohol oxidation are susceptible to α-cleavage[24] and lead to increased production of the alkanoyl-*tert*-butylperoxy polarizing cage (Scheme III).

Transient Enols 5. One of the benefits of CIDNP is that it may reveal the presence of transient intermediates which have not been previously suspected or detected as being on a reaction pathway. The observation of these intermediates may profoundly influence the mechanistic interpretation of a particular reaction. Such is the present case where transient enolic species (**5**) were observed as direct precursors to the oxidized products (**2**). The pathway is firmly established solely on the basis of the carbon-13 CIDNP results. Simple enols have been observed by proton CIDNP in other types of reactions.[25-28]

Carbon-13 CIDNP provides an additional tool to study these unstable enols. The carbon-13 chemical shifts of these unique species have been previously discussed and have revealed the electronic nature of this unusual class of compounds.[29] Their sensitivity to acid catalysis has been demonstrated above. Kinetic studies are possible and may provide insight into the nature of the enol-keto tautomerism and the lifetime of the enols.

Most interesting are the cases where two enolic species are observed, as for alcohols **1H** and **1I.** The ketyl radicals produced from these alcohols evidently disproportionate in two different ways because of the availability of two different β hydrogens. The reason this occurs must include structural and thermodynamic factors. Further studies of these particular systems may shed light on the contributions of such factors. In the same vein, the detection of β-hydroxy radicals in the case of alcohols **1E** and **1L** is of interest. Apparently, formation of β-hydroxy radicals is favored in these cases.

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(2) Author to whom reprint requests should be addressed.

(3) Hooker Chemical and Plastics Corp., Research Center, Grand Island Complex, Niagara Falls, N.Y. 14302.

(4) NRL Summer Program Participant.

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