85 (4), 84 (9), 83 (6), 57 (100), 41 (24).

Fluorination of 1-(4-Methoxyphenyl)-4-*tert*-butylcyclohexene (1b). To a solution of 1 mmol of alkene in methylene chloride (2 mL) in a Kel-F vessel was added 1 mmol of xenon difluoride at room temperature, and under stirring, trace amounts of hydrogen fluoride were introduced into the reaction mixture. The reaction was complete in 1 h, the reaction mixture was diluted with methylene chloride, and after the usual workup procedure, the crude reaction mixture was analyzed by NMR spectroscopy (product distribution is presented in Table I). Products were isolated by preparative TLC (SiO_2; chloroform–cyclohexane, 4:6).

***r*-1-(4-Methoxyphenyl)-1,*c*-2-difluoro-*t*-4-*tert*-butylcyclohexane (2b):** yield 53 mg (19%); white crystalline compound: mp 138–140 °C; NMR $\delta(F_1)$ −159.1 (dm, $^3J_{F_1H_6}$ = 42 Hz), $\delta(F_2)$ −190.5 (ddm, $^2J_{F_2H_2}$ = 48 Hz, $^3J_{F_2H_3}$ = 48 Hz), $\delta((CH_3)_3)$ 1.0 (s, 9 H), δ(H) 1.6–2.1 (m, 7 H), $\delta(OCH_3)$ 3.9 (s, 3 H), $\delta(H_2)$ 4.7 (d, 1 H, $^2J_{F_2H_2}$ = 48 Hz), $\delta(C_6H_4)$ 7.2 (m, 4 H); mass spectrum (relative intensity) (mol wt calcd for $C_{17}H_{24}OF_2$ 282.1795, found 282.1790), *m/e* (relative intensity) 283 (M^+ + 1, 4), 282 (M^+, 14), 262 (6), 246 (19), 225 (15), 185 (15), 184 (100), 169 (31), 165 (33), 152 (11), 147 (20), 141 (29), 139 (14), 121 (15), 115 (24), 57 (49).

***r*-1-(4-Methoxyphenyl)-1,*t*-2-difluoro-*t*-4-*tert*-butylcyclohexane (4b):** yield 73 mg (26%); white crystalline compound; mp 87–89 °C; NMR $\delta(F_1)$ −178.7 (m), $\delta(F_2)$ −186.8 (dm $^2J_{F_2H_2}$ = 48 Hz), $\delta((CH_3)_3)$ 1.0 (s, 9 H), δ(H) 1.6–2.1 (m, 7 H), $\delta(OCH_3)$ 3.9 (s, 3 H), $\delta(H_2)$ 4.7 (dddd, 1 H, $^2J_{F_2H_2}$ = 48 Hz, $^3J_{F_1H_2}$ = 24 Hz, $^3J_{H_2H_{3a}}$ = 10 Hz, $^3J_{H_2H_{3e}}$ = 4.5 Hz), $\delta(C_6H_4)$ 7.3 (m, 4 H); mass spectrum (mol wt calcd for $C_{17}H_{24}OF_2$ 282.1795, found 282.1800), *m/e* (relative intensity) 283 (M^+ + 1, 10), 282 (M^+, 70), 262 (22), 225 (17), 185 (20), 184 (50), 169 (14), 165 (100), 152 (20), 147 (10), 141 (11), 139 (11), 121 (15), 115 (13), 57 (80).

Halofluorination of 1-Phenyl-4-*tert*-butylcyclohexene (1a). A 0.6-mmol sample of *N*-chlorosuccinimide or *N*-bromosuccinimide, 1 mL of diethyl ether, and 1 mL of a 70% mixture of HF–pyridine were stirred at 0 °C until the *N*-halosuccinimide was dissolved, and then at room temperature 0.5 mmol of 1-phenyl-4-*tert*-butylcyclohexene was added. After being stirred 2 h at room temperature, the reaction mixture was poured onto ice, and the products were extracted with diethyl ether. The diethyl ether extract was washed with water, aqueous KOH (10%), and water and dried over Na_2SO_4, and the solvent was evaporated in vacuo. The crude reaction mixture was analyzed by NMR, and the product distribution is presented in Table I. Products were isolated by preparative TLC with cyclohexane.

***r*-1-Phenyl-1-fluoro-*c*-2-bromo-*t*-4-*tert*-butylcyclohexane (2c):** yiLd 41 mg (26%); white crystalline compound; mp 84–86 °C; NMR $\delta(F_1)$ −143.0 (dm, $^3J_{F_1H_6}$ = 45 Hz), $\delta((CH_3)_3)$ = 1.0 (s, 9 H), δ(H) 1.6–2.3 (m, 7 H), $\delta(H_2)$ 4.5 (br s, 1 H), $\delta(C_6H_5)$ 7.3 (m, 5 H); mass spectrum (mol wt calcd for $C_{16}H_{22}BrF$ 312.0889, found 312.0880), *m/e* (relative intensity) 314 (M^+ + 2, 2) 312 (M^+, 2), 258 (2), 256 (2), 212 (12), 156 (30), 155 (100), 154 (44), 153 (10), 91 (10), 77 (16), 57 (33), 41 (14).

***r*-1-Phenyl-1-fluoro-*c*-2-bromo-*c*-4-*tert*-butylcyclohexane (3c):** yield 42 mg (27%); oily compound; NMR $\delta(F_1)$ −126.5 (ddm, $^3J_{F_1H_6}$ = 14 Hz $^3J_{F_1H_2}$ = 14 Hz), $\delta((CH_3)_3)$ 1.0 (s, 9 H), δ(H) 1.3–2.6 (m, 7 H), $\delta(H_2)$ 4.5 (ddd, 1 H, $^3J_{H_2H_{3e}}$ = 5 Hz, $^3J_{H_2H_{3a}}$ = 14 Hz, $^3J_{F_1H_2}$ = 14 Hz), $\delta(C_6H_5)$ 7.3 (m, 5 H); mass spectrum (mol wt calcd for $C_{16}H_{22}BrF$ 312.0889, found 312.0900), *m/e* (relative intensity) 314 (M^+ + 2, 2), 312 (M^+, 2), 258 (2), 256 (2), 212 (11), 156 (31), 155 (100), 154 (35), 91 (12), 83 (10), 77 (18), 57 (70), 41 (19).

***r*-1-Phenyl-1-fluoro-*c*-2-chloro-*t*-4-*tert*-butylcyclohexane (2d):** yield 17 mg (13%); white crystalline compound; mp 48–50 °C; NMR $\delta(F_1)$ −146.9 (dm, $^3J_{F_1H_6}$ = 45 Hz), $\delta((CH_3)_3)$ 1.0 (s, 9 H), δ(H) 1.7–2.3 (m, 7 H), $\delta(H_2)$ 4.3 (br s, 1 H), $\delta(C_6H_5)$ 7.3 (m, 5 H); mass spectrum (mol wt calcd for $C_{16}H_{22}ClF$ 268.1394, found 268.1390 ;, *m/e* (relative intensity) 270 (M^+ + 2, 4), 268 (M^+, 10), 212 (18), 156 (21), 155 (63), 154 (36), 135 (15), 91 (19), 85 (13), 83 (20), 77 (16), 57 (100), 41 (25).

***r*-1-Phenyl-1-fluoro-*c*-2-chloro-*c*-4-*tert*-butylcyclohexane (3d):** yield 18 mg (13%); oily compound; decomposed on heating; NMR $\delta(F_1)$ −129.7 (ddm, $^3J_{F_1H_6}$ = 14 Hz, $^3J_{F_1H_2}$ = 14 Hz), $\delta((CH_3)_3)$ 0.9 (s, 9 H), δ(H) 1.2–2.4 (m, 7 H), $\delta(H_2)$ 4.3 (ddd, 1 H, $^3J_{H_2H_{3e}}$ = 5 Hz, $^3J_{H_2H_{3a}}$ = 14 Hz, $^3J_{F_1H_2}$ = 14 Hz), $\delta(C_6H_5)$ 7.2 (m, 5 H); mass spectra (mol wt calcd for $C_{16}H_{22}ClF$ 268.1394, found 268.1400), *m/e* (relative intensity) 270 (M^+ + 2, 3), 268 (M^+, 10), 212 (16), 156 (15), 155 (43), 154 (14), 135 (18), 91 (13), 77 (11), 57 (100), 41 (20).

Acknowledgment. We thank the late Prof. J. Slivnik for xenon difluoride. The financial assistance of the Research Community of Slovenia is acknowledged.

Registry No. **1a**, 3419-73-6; **1b**, 33061-20-0; **2a**, 87830-00-0; **2b**, 87830-01-1; **2c**, 87830-02-2; **2d**, 87830-03-3; **3c**, 87830-04-4; **3d**, 87830-05-5; **4a**, 87830-06-6; **4b**, 87830-07-7; XeF_2, 13709-36-9; NBS, 128-08-5; NCS, 128-09-6; HF, 7664-39-3.

Hydroxyalkylation with α-Hydroperoxydiazenes. Alcohols from Olefins and Carbonyl Compounds from Enol Ethers

Emmanuel Y. Osei-Twum, Doug McCallion, Avtar S. Nazran, Rick Panicucci, Prabhakar A. Risbood, and John Warkentin*

Department of Chemistry, McMaster University, Hamilton, Ontario, Canada L8S 4M1

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Alkyl(1-hydroperoxy-1-methylethyl)diazenes **2a–f** [$(CH_3)_2C(OOH)N{=}NR$: **a**, R = CH_2CF_3; **b**, R = CH_2CH_2CN; **c**, R = $CH_2CH(CH_3)CN$; **d**, R = $CH_2CH_2OCH_3$; **e**, R = $CH_2CH_2OC_6H_5$; **f**, R = $CH_2CH_2CH_2OC_6H_5$)] were prepared in solution by autoxidation of the corresponding hydrazones of acetone. Thermolysis of the diazenes at 50–80 °C in alkenes leads to alcohols. For example, **2b** decomposes in 1,1-diphenylethene to afford 5-hydroxy-5,5-diphenylpentanenitrile. Alkenes with abstractable allylic hydrogens gave analogous products, but in very low yield. Thermolysis of a diazene **2** in an enol ether solvent leads to an aldehyde or a ketone. Thus, **2a** decomposes in 1-ethoxyethene and in 2-methoxypropene to afford, respectively, 4,4,4-trifluorobutanal and 5,5,5-trifluoro-2-pentanone. Yields lie in the range from 50% to 70%. The thermolysis of **2** in alkenes involves radical intermediates and radical chain hydroxyalkylation of alkene double bonds. In one chain-propagating step, R·, generated from **2**, adds to the alkene. The adduct radical so formed propagates by inducing decomposition of **2** by attack at hydroxyl oxygen. According to this mechanism, initial products from enol ethers are hemiacetals or hemiketals which do not survive the reaction conditions but decompose to the corresponding carbonyl compounds. Preliminary evidence for this mechanism is presented.

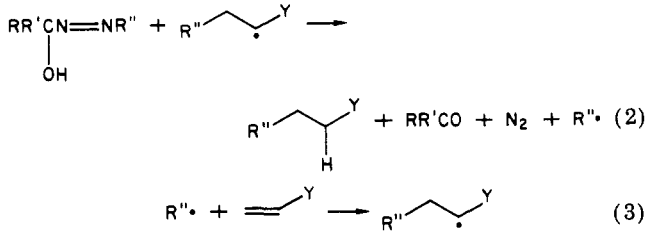
Although α-hydroperoxydiazenes (α-azo hydroperoxides, **1**) have been known for many years as the products of inadvertent or deliberate autoxidation of hydrazones[1] (eq 1), relatively little is known about their chemistry. Their

0022-3263/84/1949-0336$01.50/0

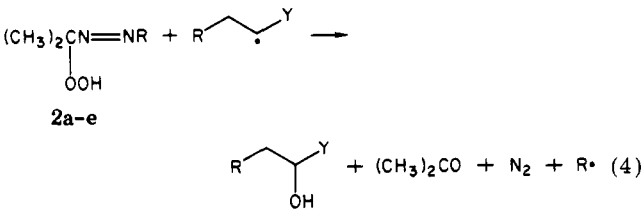
$$RR'C{=}NNHR'' \rightarrow \underset{\mathbf{1}}{RR'C(OOH)N{=}NR''} \quad (1)$$

reduction to α-hydroxydiazenes (α-azo hydroxides, α-azo carbinols) by a variety of reducing agents, including Ph_3P,[1e,2] Na_2SO_3,[3] and I^-[4] is well-known. Their application as initiators of free-radical polymerization is described in the patent literature,[5] and there are two reports of their photolysis and thermolysis to generate hydroxyl radicals in nonaqueous media.[6] For example, **1** (R = H, R′ = C_6H_5, R″ = *p*-C_6H_4Br) leads to phenols when decomposed in aromatic solvents.[6]

We had been using α-hydroperoxydiazenes for some time as sources of α-hydroxydiazenes, which are capable of hydroarylation or hydroalkylation of alkenes by a radical chain mechanism.[2,7] A key step in that mechanism is induced decomposition of the hydroxydiazene by radical attack at hydroxyl hydrogen (eq 2 and 3). It was clear

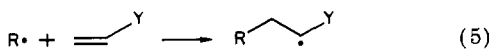


that the hydroperoxydiazenes would be interesting reagents in their own right if they too could undergo induced decomposition. By analogy with eq 2, such induced decomposition would involve hydroxyl transfer (eq 4), and the products from decomposition of **2** in alkenes (C=C—Y) would be those of overall hydroxyalkylation (eq 4 and 5).



2a-e

a, R = CH_2CF_3; b, R = CH_2CH_2CN; c, R = $CH_2CH(CH_3)CN$; d, R = $CH_2CH_2OCH_3$; e, R = $CH_2CH_2OC_6H_5$; f, R = $CH_2CH_2CH_2OC_6H_5$



We report a variety of examples of the synthesis of small molecules by radical chain reactions of alkyl(1-hydroperoxy-1-methylethyl)diazenes **2a–f** with olefins and with enol ethers.

Methods, Results, and Discussion

Monosubstituted hydrazines (Table I) were prepared by hydrazinolysis of halides or tosylates (eq 6) or by conjugate

$$H_2NNH_2 + RX \rightarrow H_2NNHR \quad (6)$$
$$X = hal, OTs$$

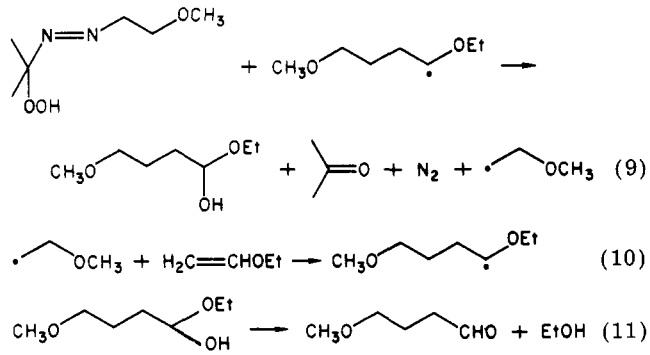
$$H_2NNH_2 + CH_2{=}CHCN \rightarrow H_2NNHCH_2CH_2CN \quad (7)$$

addition (eq 7) as described in the Experimental Section. Corresponding hydrazones of acetone (Table II) were autoxidized at about 5 °C in low-boiling petroleum ether (bp 30–60 °C) or in benzene (eq 8). The hydroperoxydiazenes

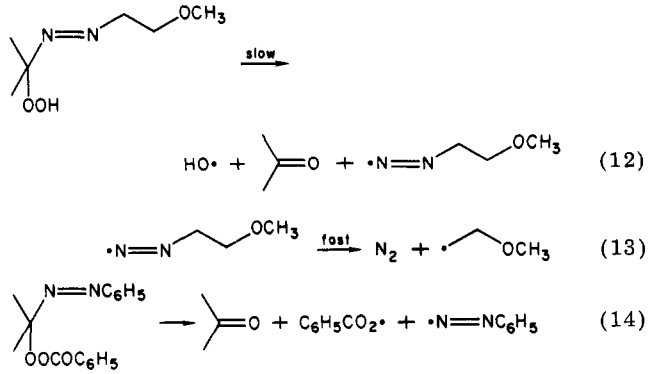
$$(CH_3)_2C{=}NNHR \xrightarrow{O_2} (CH_3)_2C(OOH)N{=}NR \quad (8)$$

so formed were freed from most of the solvent by using a rotary evaporator, with the sample bulb rotating in cold water, or by allowing a stream of dry nitrogen to impinge on the surface of the solution in a flask cooled to 5–10 °C. The desired enol ether or other alkene was then added to the neat or concentrated hydroperoxydiazene, and the resulting solution was transferred to a glass tube for degassing and sealing prior to thermolysis. **Caution**: Although we have not had any problems with hydroperoxydiazene samples as large as 0.5 g, using the procedure outlined, such compounds are undoubtedly explosive and should be handled with due care and with adequate shielding. Even modest scale runs (>100 mg ?) should probably involve the preparation of smaller batches of hydroperoxide-in-alkene which can then be combined safely for the thermolysis step.

The rapid decomposition of compounds **2** in solution at 50 °C and the poor fit of kinetic data to the first-order rate equation were initial indicators of a chain mechanism. Strong inhibition of the decomposition of **2d–f** in ethyl vinyl ether by 2,2,6,6-tetramethylpiperidin-*N*-oxyl radical (**3**) provided confirmation of the chain hypothesis. Similar samples of **2d–f** in ethyl vinyl ether, but without added **3**, decomposed without appreciable induction periods. These observations and the nature of the products (Table III) suggest the chain-carrying steps of eq 9 and 10 and



a hemiacetal decomposition step (eq 11). Initiation most likely occurs via unimolecular homolytic decomposition of the hydroperoxydiazene by a concerted first step (eq 12)



followed by fast loss of N_2 from a diazenyl radical inter-

(1) Autoxidation of hydrazones has been studied extensively. See, for example: (a) Pausacker, K. H. *J. Chem. Soc.* **1950**, 3478. (b) Criegee, R.; Lohaus, G. *Chem. Ber.* **1951**, *84*, 219. (c) Belamy, A. J.; Guthrie, R. D. *J. Chem. Soc.* **1965**, 2788. (d) Taylor, W. F.; Weiss, H. A.; Wallace, T. J. *J. Org. Chem.* **1969**, *34*, 1759. (e) Schulz, M.; Missol, U. *Z. Chem.* **1974**, *14*, 265.

(2) Chang, Y.-M.; Profetto, R.; Warkentin, J. *J. Am. Chem. Soc.* **1981**, *103*, 7189.

(3) (a) MacLeay, R. E. Japanese Kodai (Patent) 75 131 901, 1975. (b) MacLeay, R. E. U.S. Patent 4 086 224, 1978.

(4) Nazran, A. S.; Warkentin, J. *J. Am. Chem. Soc.* **1981**, *103*, 236.

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(6) (a) Tezuka, T.; Narita, N.; Ando, W.; Oae, S. *J. Am. Chem. Soc.* **1981**, *103*, 3045. (b) Tezuka, T.; Narita, N. *Ibid.* **1979**, *101*, 7413.

(7) (a) Yeung, D. W. K.; Warkentin, J. *Can. J. Chem.* **1976**, *54*, 1345. (b) Yeung, D. W. K.; Warkentin, J. *Ibid.* **1980**, *58*, 2386.

Table I. ^{1}H NMR Spectra of Alkylhydrazines (H_2NNHR) and of Their Acetone Hydrazones ($(CH_3)_2C{=}NNHR$)

R	^{1}H NMR spectral data[a]	
	H_2NNHR	$(CH_3)_2C{=}NNHR$
CH_2CF_3	3.35 (q, 2 H, J_{HF} = 9 Hz), 3.65 (s, br, 3 H)[b]	1.70 (s, 3 H), 1.89 (s, 3 H), 3.60 (m, 2 H, J_{HF} = 9 Hz, J_{HH} = 4 Hz), 4.77 (s, 1 H)[c]
CH_2CH_2CN	2.26 (t, 2 H), 3.00 (t, 2 H), 3.36 (s, br, 3 H)	1.88 (s, 3 H), 1.95 (s, 3 H), 2.65 (t, 2 H, J = 6 Hz), 3.43 (t, 2 H, J = 6 Hz), 4.75 (s, br, 1 H)
$CH_2CH(CH_3)CN$	1.30 (d, 3 H, J = 7 Hz), 2.92 (m, 3 H)	1.30 (d, 3 H, J = 7 Hz), 1.75 (s, 3 H), 1.93 (s, 3 H), 3.05 (m, 1 H), 3.25 (d, 2 H, J = 7 Hz), 4.85 (s, br, 1 H)
$CH_2CH_2OCH_3$	2.09 (t, 2 H, J = 5.8 Hz), 3.30 (s, 3 H), 3.35 (s, br, 3 H), 3.50 (t, 2 H, J = 5.8 Hz)	1.73 (s, 3 H), 1.90 (s, 3 H), 3.27 (t, 2 H, J = 5.1 Hz), 3.34 (s, 3 H), 3.50 (t, 2 H, J = 5.1 Hz), 4.75 (s, br, 1 H)
$CH_2CH_2OC_6H_5$	3.02 (t, 2 H, J = 6.0 Hz), 4.01 (t, 2 H, J = 6.0 Hz), 3.37 (s, br, 3 H), 6.94 (m, 3 H), 7.28 (m, 2 H)	1.73 (s, 3 H), 1.90 (s, 3 H), 3.50 (t, 2 H, J = 5.0 Hz), 4.05 (t, 2 H, J = 5.0 Hz), 4.88 (s, br, 1 H), 6.94 (m, 3 H), 7.28 (m, 2 H)
$CH_2CH_2CH_2OC_6H_5$	1.92 (m, 2 H), 2.87 (t, 2 H, J = 6.2 Hz), 3.35 (s, br, 3 H), 4.00 (t, 2 H, J = 5.5 Hz), 6.93 (m, 3 H), 7.30 (m, 2 H)	1.72 (s, 3 H), 1.89 (s, 3 H), 2.05 (m, 2 H), 3.31 (t, 2 H, J = 6.0 Hz), 4.05 (t, 2 H, J = 5.9 Hz), 6.92 (m, 3 H), 7.28 (m, 2 H)

[a] In $CDCl_3$ with internal Me_4Si. The numbers are δ values followed in parentheses by the multiplicity, the relative signal intensity, and, where appropriate, by the coupling constant in hertz. [b] ^{19}F chemical shift, relative to external $CFCl_3$, δ −66.3 (t, J_{FH} = 9 Hz). [c] ^{19}F chemical shift, relative to external $CFCl_3$, δ −65.9 (t, J = 9 Hz).

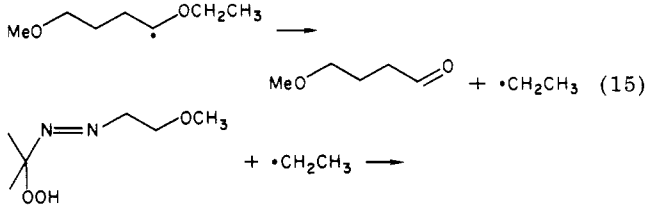
Table II. ^{1}H NMR Spectra of Hydroperoxydiazenes 2 ($(CH_3)_2C(OOH)N{=}NR$)

R	^{1}H NMR spectral data[a]
CH_2CF_3	1.40 (s, 6 H), 4.27 (q, 2 H, J_{HF} = 9 Hz), 8.80 (s, br, 1 H)[b,c]
CH_2CH_2CN	1.33 (s, 6 H), 2.83 (t, 2 H, J = 6 Hz), 4.18 (t, 2 H, J = 6 Hz), 9.08 (s, br, 1 H)[c]
$CH_2CH(CH_3)CN$	1.38 (d, 3 H, J = 7 Hz), 1.59 (s, 6 H), 3.25 (m, 1 H), 4.00 (d, 2 H, J = 7 Hz), 9.05 (s, br, 1 H)
$CH_2CH_2OCH_3$	1.32 (s, 6 H), 3.30 (s, 3 H), 3.80 (t, 2 H, J = 5.9 Hz), 4.01 (t, 2 H, J = 5.9 Hz), 9.35 (s, br, 1 H)
$CH_2CH_2OC_6H_5$	1.32 (s, 6 H), 4.19 (t, 2 H, J = 6.0 Hz), 4.48 (t, 2 H, J = 6.0 Hz), 6.94 (m, 3 H), 7.28 (m, 2 H), 9.30 (s, br, 1 H)
$CH_2CH_2CH_2OC_6H_5$	1.32 (s, 6 H), 2.23 (m, 2 H), 4.01 (2t, overlapping, 4 H), 6.91 (m, 3 H), 7.28 (m, 2 H), 9.17 (s, br, 1 H)

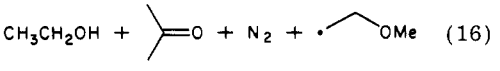
[a] In $CDCl_3$ with internal Me_4Si. The numbers are δ values followed in parentheses by the multiplicity, the relative signal intensity, and, where appropriate, by the coupling constant in hertz. [b] ^{19}F chemical shift relative to external $CFCl_3$, δ −66.8 (t, J = 9 Hz). [c] In CCl_4.

mediate (eq 13), based on analogy to the mechanism of decomposition of an α-azo perester (eq 14).[8]

Since the products isolated from reaction of **2** with enol ethers are aldehydes or ketones, an alternative mechanism has to be considered. The carbonyl compounds could possibly arise by β scission of the α-alkoxyalkyl radical of eq 15, generating an alkyl radical. The alcohol, which is

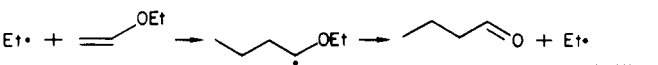


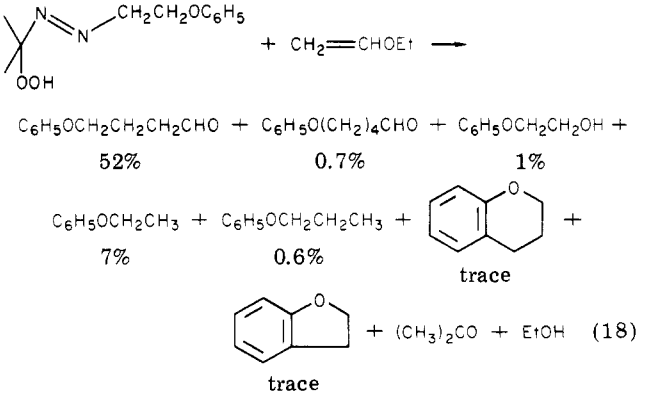
2d



a major coproduct, would then be attributed to induced decomposition of **2d** by the ethyl radical (eq 16) instead of to decomposition of a first-formed hemiacetal (or hemiketal) (eq 11).

The β-scission process is at most a minor competition step in the cases that were studied, as indicated by the absence of additional coproducts. If the processes of eq 15 and 16 were important during the thermolysis of compounds **2** in ethyl vinyl ether, then butyraldehyde should be a major coproduct, since ethyl radicals too would add to ethyl vinyl ether (eq 17). Butyraldehyde was not detected as a byproduct of any reaction with ethyl vinyl ether although trace quantities (<0.5%) could have been missed by our procedures. A careful search for minor products was carried out in the case of reaction of **1e** with ethyl vinyl ether. Equation 18 gives the products which could be

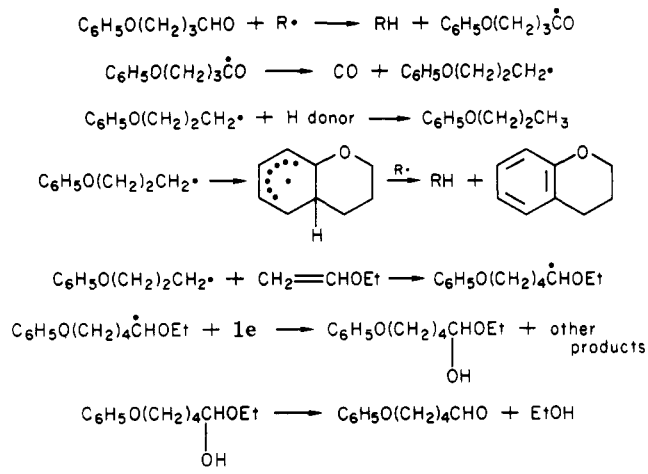




identified and the approximate yields. Particularly significant among these products were 5-phenoxypentanal, 2,3-dihydro-1,4-benzopyran, and phenyl propyl ether which probably arose from the major product by the sequence of reactions in Scheme I. Formation of 5-phenoxypentanal and phenyl propyl ether as minor byproducts provides support for the radical mechanism of formation of the major product. Abstraction of aldehyde hydrogen and subsequent decarbonylation (first steps of Scheme I) are very well-known in free-radical chemistry. The resulting 3-phenoxy-1-propyl radical should then participate in the

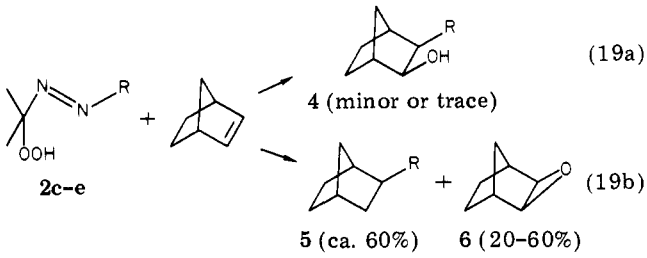
(8) Nazran, A. S.; Warkentin, J. *J. Am. Chem. Soc.* **1982**, *104*, 6405.

Scheme I



available abstraction and addition processes, leading to phenyl propyl ether, 5-phenoxypentanal, and 2,3-dihydro-1,4-benzopyran,[9] the observed minor products with one more carbon atom than would be expected from consideration of the structures of the reactants.

The thermolysis chemistry of compounds **2** in bicyclo[2.2.1]heptene (norbornene) is strikingly different from that observed with other alkenes. Although the expected products (**4**) of hydroxyalkylation of norbornene with **2c–e** were found, the major products were those of hydroalkylation (**5**), and the epoxide of norbornene (**6**, eq 19).



(19a)

(19b)

It is clear that the radical chain mechanism proposed above is less important in the case of additions of **2** to norbornene and that other processes, possibly nonradical, are contributing also. The mechanisms involved in reactions of norbornene with **2** are still under investigation.

Other alkene substrates were neither hydroxyalkylated nor epoxidized by **2**. Decomposition of **2** in tetramethylethylene gave a mixture of products suggestive of predominant abstraction of allylic hydrogen, rather than addition. 2-Cyclohexen-1-one was converted to 4-hydroxy-2-cyclohexen-1-one and other products by **2b**. Propionitrile was a major product, suggesting that H abstraction from the enone by 2-cyanoethyl radicals from **2b** is a major process that competes with addition. The ethylene ketal of cyclohexenone was also hydroxylated at the 4-position by **2b**, and again the desired product of hydroxyalkylation could not be found. Maleic anhydride in benzene was not hydroxyalkylated by **2b**.

Although it is clear that reagents **2** will hydroxyalkylate only a restricted number of alkene systems, that novel reaction could become quite useful. In view of the ease of preparation of **2**, with either simple or functionalized moieties destined to become free radicals as a result of induced decomposition, there may be considerable potential for their application in synthesis, particularly on a small scale. Although there is no reason to doubt that the hydroxyalkylations can be scaled up safely, the reader is reminded that scaling-up must be accomplished by combining small samples of hydroperoxide-in-substrate.

Details of the mechanisms by which hydroperoxydiazenes react with alkenes are under investigation. Particulars such as chain lengths, chain-termination mechanisms, and chain-transfer rate constants will be published separately.

Experimental Section

3-Hydrazinopropanenitrile and 3-Hydrazino-2-methylpropanenitrile. To hydrazine (3.8 g, 0.12 mol) in tetrahydrofuran (5 mL) was added, drop by drop with stirring at room temperature, 5.3 g (0.10 mol) of acrylonitrile. Acetic acid (5 drops) was added, and the resulting solution was stirred for 24 h. Most of the tetrahydrofuran was removed with a rotary evaporator and further distillation of volatiles was carried out at 0.1 torr, without heating. The residual 3-hydrazinopropanenitrile (8.0 g, 94%, spectral data in Table I) was pure enough for the next step. 3-Hydrazino-2-methylpropanenitrile was prepared by an analogous procedure from methacrylonitrile.

3-[(1-Methylethylidene)hydrazino]propanenitrile and 2-Methyl-3-[(1-methylethylidene)hydrazino]propanenitrile. 3-Hydrazinopropanenitrile (8.0 g, 0.094 mol) was stirred with acetone (30 mL) at room temperature for 24 h. Removal of most of the acetone with a rotary evaporator, followed by vacuum distillation of the residue, gave 10 g (85%) of 3-[(1-methylethylidene)hydrazino]propanenitrile, bp 70 °C (0.1 torr). The analogous procedure gave the second compound named in the heading. Their ^{1}H NMR spectral data are listed in Table I.

1,1,1-Trifluoro-2-hydrazinoethane. This compound, supplied as a solution in water (70% hydrazine by weight) by Aldrich Chemical Co., was used directly in the next step.

1,1,1-Trifluoro-2-[(1-methylethylidene)hydrazino]ethane. A solution of aqueous 1,1,1-trifluoro-2-hydrazinoethane containing 7.0 g (0.062 mol) of the reagent and 20 mL of ether was added slowly to a solution of acetone (6.0 g, 0.10 mole) in ether (20 mL) with stirring and cooling. The reactants were kept under nitrogen during the mixing and during a 1-h period of stirring after the addition was complete. The solution was washed three times with water, and the ether layer was dried over $MgSO_4$. Evaporation of the ether and vacuum distillation of the residue gave 7.45 g (78%) of the title hydrazone [bp 28 °C (10 torr)] with the ^{1}H NMR spectral data listed in Table I.

1-Methoxy-2-hydrazinoethane. 2-Methoxyethyl tosylate[10] (29.5 g, 0.13 mol) was added, drop by drop, to a vigorously stirred solution of hydrazine hydrate (128.6 g, 2.57 mol) in absolute ethanol (50 mL) at 0–5 °C. Addition was complete in 20 min, and stirring was continued thereafter for 2 h. After removal of the ethanol with a rotary evaporator, the residue was extracted with ether (continuous extractor) for 2 days. The ether layer was dried with Na_2SO_4, the ether was evaporated, and the residue was distilled under N_2. 1-Methoxy-2-hydrazinoethane[11] distilled at 146–147.5 °C (760 torr).

1-Methoxy-2-[(1-methylethylidene)hydrazino]ethane. Acetone (10 mL) was added slowly and with stirring to 1-methoxy-2-hydrazinoethane (9.0 g, 0.10 mol) in 20 mL of dry benzene. The resulting solution was refluxed for 20 min. After it had cooled, it was washed with water and with brine before it was dried over Na_2SO_4. Evaporation of most of the benzene followed by distillation of the residue gave the title hydrazone: 6.0 g (46%); bp

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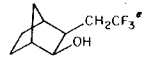
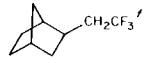
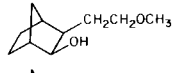
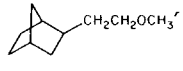
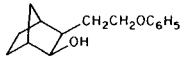
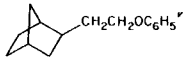
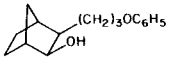
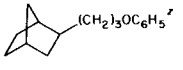
Table III. Major Products from Thermolysis of 2 in Alkenes

R in reagents 2	substrate	products: structure	yield,[a] %	products: ^{1}H NMR[b]	products: derivative
CH_2CF_3	$CH_2=C(C_6H_5)_2$	$CF_3CH_2CH_2C(OH)(C_6H_5)_2$[c]	45	2.15 (m, 4 H), 4.30 (s, 1 H), 7.21 (s, br, 10 H)	
	$CH_2=CHOC_2H_5$	$CF_3CH_2CH_2CHO$[d]	70	2.50 (m, 4 H), 9.87 (s, 1 H)	2,4-DNP (mp 179–181 °C)
	 I		14	1.04–2.53 (m, 12 H), 3.80 (d, 1 H, J = 6.7 Hz)	
			62	1.07–2.07 (m, 11 H), 2.11 (s, br, 1 H), 2.26 (s, br 1 H)	
		6[g]	60	0.63 (d, 1 H, J = 9.5 Hz), 1.18–1.47 (m, 5 H), 2.39 (s, 2 H), 2.88 (s, 2 H)	
CH_2CH_2CN	$CH_2=CHOC_2H_5$	$NC(CH_2)_3CHO$[h]	68	1.97 (m, 2 H), 2.40 (t, 2 H, J = 6.3 Hz), 2.67 (t, 2 H, J = 6.3 Hz), 9.90 (s, 1 H)[i]	
	$CH_2=C(CH_3)OCH_3$ or $CH_2=C(CH_3)OAc$	$NC(CH_2)_3COCH_3$	64	1.83 (m, 2 H), 2.13 (s, 3 H), 2.37 (t, 2 H, J = 6.7 Hz), 2.58 (t, 2 H, J = 6.7 Hz)[i]	
$CH_2CH(CN)CH_3$	$CH_2=CHOC_2H_5$	$CH_3CH(CN)(CH_2)_2CHO$[k,l]	65[j]	1.32 (d, 3 H, J = 7 Hz), 1.87 (m, 2 H), 2.67 (m and t, 3 H, $J_{triplet}$ = 7 Hz), 9.87 (s, 1 H)	2,4-DNP (mp 79–80 °C)
	$CH_2=C(CH_3)OCH_3$	$CH_3CH(CN)(CH_2)_2COCH_3$[k,m]	63	1.27 (d, 3 H, J = 7 Hz), 1.77 (m, 2 H), 2.13 (s, 3 H), 2.67 (m and t, 3 H, $J_{triplet}$ = 7 Hz)	2,4-DNP (mp 98–99 °C; MS, m/z 305 (M^+))
$CH_2CH_2OCH_3$	$CH_2=C(C_6H_5)_2$	$CH_3O(CH_2)_3C(OH)(C_6H_5)_2$[n]	40	2.07 (m, 2 H), 2.39 (t, 2 H, J = 6.3 Hz), 2.39 (s, 3 H), 3.38 (t, 2 H, J = 6.1 Hz), 7.24 (s, 10 H)	
	$CH_2=CHOC_2H_5$	$CH_3O(CH_2)_3CHO$[o]	52	1.99 (m, 2 H), 2.59 (t, 2 H, J = 6.9 Hz), 3.38 (s, 3 H), 3.47 (t, 2 H, J = 6.0 Hz), 9.85 (s, 1 H)	
	$CH_2=C(CH_3)OCH_3$	$CH_3O(CH_2)_3COCH_3$[p]	67	1.91 (m, 2 H), 2.59 (t, 2 H, J = 6.9 Hz), 2.21 (s, 3 H), 3.38 (s, 3 H), 2.24 (t, 2 H, J = 6.1 Hz)	
	I		7	q	
			64	1.0–1.6 (m, 11 H), 1.97 (s, br, 1 H), 2.19 (s, br, 1 H), 3.23 (s, 3 H), 3.25 (t, 2 H, J = 6.2 Hz)	
		6	33	0.63 (d, 1 H, J = 9.5 Hz), 1.18–1.47 (m, 5 H), 2.39 (s, 2 H), 2.88 (s, 2 H)	
$CH_2CH_2OC_6H_5$	$CH_2=CHOC_2H_5$	$C_6H_5O(CH_2)_3CHO$[s]	65	2.12 (m, 2 H), 2.67 (t, 2 H, J = 7.1 Hz), 4.01 (t, 2 H, J = 6.1 Hz), 6.94 (m, 3 H), 7.28 (m, 2 H), 9.84 (t, 1 H, J = 1.4 Hz)	2,4-DNP (mp 102–103 °C)

$CH_2CH_2OC_6H_5$	$CH_2=C(CH_3)OCH_3$	$C_6H_5O(CH_2)_3COCH_3$ [t]	76	2.10 (m, 2 H), 2.15 (s, 3 H), 2.65 (t, 2 H, J = 7.5 Hz), 3.96 (t, 2 H, J = 6.0 Hz), 6.93 (m, 3 H), 7.27 (m, 2 H)	2,4-DNP (mp 103–105 °C)
			2	*u*	
			70	1.09–1.60 (m, 15 H), 1.61–1.78 (m, 2 H), 2.04 (s, br, 1 H), 2.22 (s, br, 1 H), 3.87 (t, 2 H, J = 6.4 Hz), 6.73–6.82 (m, 3 H), 7.15 (m, 2 H)	
		6	18	0.63 (d, 1 H, J = 9.5 Hz), 1.18–1.47 (m, 5 H), 2.39 (s, 2 H), 2.88 (s, 2 H)	
$CH_2CH_2CH_2OC_6H_5$	$CH_2=CHOC_2H_5$	$C_6H_5O(CH_2)_4CHO$ [w]	60	1.83 (m, 4 H), 2.53 (t, 2 H, J = 6.0 Hz), 3.92 (t, 2 H, J = 5.7 Hz), 6.93 (m, 3 H), 7.29 (m, 2 H), 9.82 (s, 1 H)	2,4-DNP (mp 117 °C dec; MS, m/z 358)
	$CH_2=C(CH_3)OCH_3$	$C_6H_5O(CH_2)_4COCH_3$ [x]	65	1.87 (m, 4 H), 2.10 (s, 3 H), 2.59 (t, 2 H, J = 5.9 Hz), 4.00 (t, 2 H, J = 5.5 Hz), 6.96 (m, 3 H), 7.29 (m, 2 H)	2,4-DNP (mp 119 °C dec)
	I		0.5	*y*	
			64	6.93 (m, 3 H), 7.28 (m, 2 H), 3.90 (t, 2 H, J = 6.1 Hz), 2.23 (s, br, 1 H), 2.03 (s, br, 1 H), 1.06–1.88 (m, 12 H)	
		6	20		

[a] Yields are based on the amount of **2** calculated from the size of the aliquot of stock solution taken and include the assumption that autoxidation of the hydroperoxide precursor was complete. [b] $CDCl_3$ solvent, with internal Me_4Si, unless otherwise indicated. [c] Low-resolution MS, m/z 263 [$(M - OH)^+$], 262 [$(M - H_2O)^+$]. [d] IR (CCl_4) 2740 (aldehyde C–H), 1732 cm^{-1} (CO); high-resolution MS, found m/z 126.02, calcd for $C_4H_5F_3O$ m/z 126.03. [e] High resolution MS, found m/z 176.08, calcd for $C_9H_{11}F_3$ [$(M - H_2O)^+$] m/z 176.08. [f] Low-resolution MS, m/z 178 (M^+), 95 [$(M - C_2H_2F_3)^+$]. [g] Low-resolution MS, m/z 110 (M^+), 67 [$(C_5H_7)^+$], 66 [$(C_5H_6)^+$]. The ^1H NMR spectrum matched the reported spectrum.[12] [h] Known compound; spectra not reported.[13] [i] CCl_4 solvent. [j] The yield was not determined. [k] The isomeric product expected from rearrangement of the cyanoalkyl radical ($\cdot CH_2CH(CN)CH_3 \longrightarrow NCCH_2\dot{C}HCH_3$) followed by addition of the rearranged radical to the substrate was not found. It has been shown that such rearrangements of β-cyanoalkyl radicals are quite slow and that part of a previous report by two of us,[4] implying that the above rearrangement is fast in CCl_4, is in error. [l] Low-resolution MS, m/z 112 [$(M + H)^+$], 83 [$(M - CO)^+$], 82 [$(M - CHO)^+$]. [m] Low-resolution MS, m/z 126 [$(M + H)^+$], 125 (M^+), 110 [$(M - CH_3)^+$]. [n] Low-resolution MS, m/z 238 [$(M - H_2O)^+$]. [o] Low-resolution MS, m/z 74 [$(M - CO)^+$], 58 [$(M - C_2H_4O)^+$], 45 [$(C_2H_5O)^+$]. [p] IR (CCl_4) 1720 cm^{-1} (CO); low-resolution MS, m/z 104 (M^+), 89 [$(M - CH_3)^+$]; lit.[14] IR 1720 cm^{-1}. [q] This compound was not collected. Its identity was inferred from the mass spectrum and from the GC retention time which was longer than those of the coproducts. The exo,exo assignment is based on analogy only. Low-resolution MS, m/z 152 [$(M - H_2O)^+$], 95 [$(M - C_3H_7O)^+$], 45 [$(C_2H_5O)^+$]. [r] High-resolution MS, found m/z 122.11, calcd for C_9H_{14} [$(M - CH_3OH)^+$] m/z 122.11; 2,4-DNP mp 95–95.5 °C.[15] [s] IR (CCl_4) 2735 (aldehyde CH), 1728 cm^{-1} (CO); high-resolution MS, found m/z 164.08, calcd for $C_{10}H_{12}O_2$ m/z 164.08. [t] IR (CCl_4) 1718 cm^{-1} (CO); high-resolution MS, found m/z 178.10, calcd for $C_{11}H_{14}O_2$ m/z 178.10; mp 51–53 °C. [u] This compound was not collected. Its identity was inferred from the mass spectrum and from the GC retention time, which was longer than those of the coproducts. The exo,exo assignment is based on analogy. Low-resolution MS, m/z 232 (M^+), 95 [$(M - C_8H_9O)^+$], 94 [$(C_6H_6O)^+$]. [v] High-resolution MS, found m/z 216.15, calcd for $C_{15}H_{20}O$ m/z 216.15. [w] Low-resolution MS, m/z 178 (M^+), 94 [$(C_6H_6O)^+$], 85 [$(C_5H_9O)^+$]. [x] Low-resolution MS, m/z 192 (M^+), 99 [$(M - C_6H_5O)^+$], 94 [$(C_6H_6O)^+$]. [y] This compound was not collected. Its identity was inferred from the mass spectrum and from the GC retention time, which was longer than those of the coproducts. The exo,exo assignment is based on analogy. Low-resolution MS, m/z 246 (M^+), 107 [$(C_7H_7O)^+$], 95 [$(C_7H_{11})^+$], 94 [$(C_6H_6O)^+$]. [z] Low-resolution MS, m/z 230 (M^+), 137 [$(M - C_6H_5O)^+$], 107 [$(C_7H_7O)^+$], 95 [$(C_7H_{11})^+$], 94 [$(C_6H_6O)^+$].

31 °C (6 torr); ^{1}H NMR data in Table I.

1-Phenoxy-2-hydrazinoethane. 1-Bromo-2-phenoxyethane (40 g, 0.20 mol) in ethanol was dropped, during 20 min, into a solution of hydrazine hydrate (150 g, 3.0 mol) in ethanol (50 mL) at 20 °C. The resulting solution was stirred for 1 h at 20 °C and for 1.5 h at 40 °C before the ethanol was removed with a rotary evaporator. The residue was extracted continuously with ether for 48 h. Drying of the ether layer and evaporation of the solvent gave 28.9 g (95%) of the desired hydrazine (Table I), which was used without purification in the next step.

1-Phenoxy-2-[(1-methylethylidene)hydrazino]ethane. Condensation of 1-phenoxy-2-hydrazinoethane (28.9 g, 0.19 mol) with acetone (50 mL) by following procedures analogous to those described above gave 34.6 g (90%) of the title compound (Table I), bp 124–126 °C (2.5 torr).

1-Phenoxy-3-hydrazinopropane. 1-Bromo-3-phenoxypropane (5 g, 0.04 mol) in ethanol was added drop by drop to a refluxing solution of hydrazine hydrate (95%, 10 mL, ca. 0.2 mol) in ethanol during 1 h. The resulting solution was refluxed for 4 h before the ethanol was removed with a rotary evaporator. The residual material was extracted continuously for 24 h with 200 mL of ether. Drying of the ethereal extract and evaporation of the ether left 1-phenoxy-3-hydrazinopropane (Table I) as an oil in 75% yield.

1-Phenoxy-3-[(1-methylethylidene)hydrazino]propane. Condensation of the hydrazine described in the section just above with excess acetone, by procedures analogous to those described earlier for other hydrazones, gave the title compound (Table I) as an oil: 85% yield: bp 90–97 °C (0.1 torr).

Autoxidation of Hydrazones to α-Hydroperoxydiazenes. The hydrazones described above autoxidized spontaneously as solutions in petroleum ether (bp 30–60 °C) or in benzene. Undistilled hydrazones did not autoxidize reliably, in some cases absorbing O_2 only after induction periods of many hours. Samples autoxidized at one time ranged from about 5 to 30 mmol. The following procedure for oxidation of 2-methyl-3-[(1-methylethylidene)hydrazino]propanenitrile to 3-[(1-hydroperoxy-1-methylethyl)azo]-2-methylpropanenitrile is typical.

2-Methyl-3-[(1-methylethylidene)hydrazinopropanenitrile (0.65 g, 5.2 mmol) in benzene (25 mL) at 5–10 °C was exposed to oxygen from a gas buret. Uptake of oxygen was spontaneous. When the gas volume remained constant for 4 h or more, indicating completion of the reaction, an aliquot containing about 15 mg of product was removed, and the benzene was removed either with a rotary evaporator, with the rotating bulb in cold water, or with a stream of N_2 directed onto the surface of the solution in a flask contacting cold water. The ^{1}H NMR spectrum of the product (Table II) had no signals for the (*E*)- and (*Z*)-methyl groups of the starting hydrazone, indicating that autoxidation was complete.

Thermolysis of Hydroperoxides 2 in Unsaturated Substrates. In a typical procedure, a hydroperoxide sample ranging in weight from about 15 mg to 50 mg was obtained by one of the solvent-removal procedures described above. The desired olefin or enol ether (neat, about 0.5 mL/25 mg of hydroperoxide) was then added, and the resulting solution was transferred to a glass tube for degassing and sealing. For larger scale runs, several samples of hydroperoxide in alkene were combined before the degassing step.

Sealed tubes were heated at 50 °C in an oil bath for 10–24 h before they were opened for bulb-to-bulb vacuum distillation of the volatiles (acetone, enol ether, alcohol, for example) and analysis of the residue. Products were separated by analytical gas chromatography with a Varian 3700 instrument fitted with a glass column (6 ft × 2 mm i.d.) packed with OV-17 (3%) on Chromosorb W, HP 80/100. The carrier gas was N_2 at 25 mL min^{-1} except in the case of GC/MS runs, when it was He at 10 mL min^{-1}. Preparative gas chromatography was done with a Varian Aerograph A90-P3 instrument equipped with a thermal-conductivity detector and a steel column (6 ft × 4 mm i.d.) packed with OV-17 (10%) on Chromosorb W, HP 80/100. The carrier gas was helium at 20 mL min^{-1}, and the column temperature was programmed from 40 to 250 °C at a rate between 5 and 10 °C min^{-1}.

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Registry No. 2a, 87841-75-6; **2b**, 76680-63-2; **2c**, 76680-64-3; **2d**, 87841-76-7; **2e**, 87841-77-8; **2f**, 87841-78-9; *exo,exo*-**4** (R = CH_2CF_3), 87841-84-7; *exo,exo*-**4** (R = $CH_2CH_2OCH_3$), 87841-88-1; *exo,exo*-**4** (R = $CH_2CH_2OC_6H_5$), 87841-92-7; *exo,exo*-**4** (R = $CH_2CH_2CH_2OC_6H_5$), 87841-97-2; *exo*-**5** (R = CH_2CF_3), 87841-85-8; *exo*-**5** (R = $CH_2CH_2OCH_3$), 87841-89-2; *exo*-**5** (R = $CH_2CH_2OC_6H_5$), 87841-93-8; *exo*-**5** (R = $CH_2CH_2CH_2OC_6H_5$), 87841-98-3; **6**, 3146-39-2; I, 498-66-8; $H_2NNHCH_2CF_3$, 5042-30-8; $H_2NNHCH_2CH_2CN$, 353-07-1; $H_2NNHCH_2CH(CH_3)CN$, 352-16-9; $H_2NNHCH_2CH_2OCH_3$, 3044-15-3; $H_2NNHCH_2CH_2OC_6H_5$, 3184-38-1; $H_2NNHCH_2CH_2CH_2OC_6H_5$, 69781-95-9; $(CH_3)_2C{=}NNHCH_2CF_3$, 87841-79-0; $(CH_3)_2C{=}NNHCH_2CH_2CN$, 30292-77-4; $(CH_3)_2C{=}NNHCH_2CH(CH_3)CN$, 76680-62-1; $(CH_3)_2C{=}NNHCH_2CH_2OCH_3$, 87841-80-3; $(CH_3)_2C{=}NNHCH_2CH_2OC_6H_5$, 87841-81-4; $(CH_3)_2C{=}NNHCH_2CH_2CH_2OC_6H_5$, 87841-82-5; $CH_2{=}C(C_6H_5)_2$, 530-48-3; $CH_2{=}CHOC_2H_5$, 109-92-2; $CH_2{=}C(CH_3)OCH_3$, 116-11-0; $CH_2{=}C(CH_3)OAc$, 108-22-5; $CF_3CH_2CH_2C(OH)(C_6H_5)_2$, 87841-83-6; $CF_3CH_2CH_2CHO$, 406-87-1; $CF_3CH_2CH_2CHO$ (2,4-DNP), 580-10-9; $NC(CH_2)_3CHO$, 3350-74-1; $NC(CH_2)_3COCH_3$, 10412-98-3; $CH_3CH(CN)(CH_2)_2CHO$, 53146-24-0; $CH_3CH(CN)(CH_2)_2CHO$ (2,4-DNP), 87841-86-9; $CH_3CH(CN)(CH_2)_2COCH_3$, 18397-60-9; $CH_3CH(CN)(CH_2)_2COCH_3$ (2,4-DNP), 18397-61-0; $CH_3O(CH_2)_3C(OH)(C_6H_5)_2$, 87841-87-0; $CH_3O(CH_2)_3CHO$, 21071-24-9; $CH_3O(CH_2)_3COCH_3$, 17429-04-8; $C_6H_5O(CH_2)_3CHO$, 19790-62-6; $C_6H_5O(CH_2)_3CHO$ (2,4-DNP), 20034-80-4; $C_6H_5O(CH_2)_3COCH_3$, 87841-90-5; $C_6H_5O(CH_2)_3COCH_3$ (2,4-DNP), 87841-91-6; $C_6H_5O(CH_2)_4CHO$, 87841-94-9; $C_6H_5O(CH_2)_4CHO$ (2,4-DNP), 87841-95-0; $C_6H_5O(CH_2)_4COCH_3$, 65851-20-9; $C_6H_5O(CH_2)_4COCH_3$ (2,4-DNP), 87841-96-1; H_2NNH_2, 302-01-2; $CH_2{=}CHCN$, 107-13-1; $CH_2{=}C(CH_3)CN$, 126-98-7; $(CH_3)_2CO$, 67-64-1; $CH_3OCH_2CH_2OTs$, 17178-10-8; $C_6H_5OCH_2CH_2Br$, 589-10-6; $C_6H_5OCH_2CH_2CH_2Br$, 588-63-6.