Mechanism of Epoxidation of Norbornene with α-Hydroperoxy Diazenes

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Thermolysis of α-hydroperoxy diazenes **1a–1c** ($Me_2C(OOH)N{=}NR$: **1a**, R = CH_2CF_3; **1b**, R = $CH_2CH_2OCH_3$; **1c**, R = $CH_2CH_2OC_6H_5$) at 50 °C in benzene containing norbornene or in neat norbornene affords *exo*-(2*R*)-norbornane and *exo*-norbornene epoxide as major products and *exo,exo*-(2*R*)-3-hydroxynorbornane as a minor product. The reaction kinetics and the effects of deuteration of the hydroperoxy function on the distribution of products points to a radical chain process for the hydroalkylation and for the epoxidation. The other major product is formed by a competitive radical chain reaction.

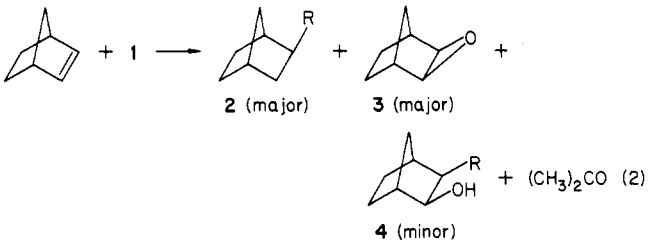
α-Hydroperoxy diazenes such as **1** were shown recently to serve as thermal hydroxyalkylating agents for a number of enol ethers and olefins[1] (eq 1). With the aid of spin

$$\underset{\mathbf{1}}{(CH_3)_2C(OOH)N{=}NR} + CH_2{=}CHY \rightarrow RCH_2CH(Y)OH + (CH_3)_2CO + N_2 \quad (1)$$

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

trapping and ESR spectroscopy it was shown that there are radical intermediates, and a radical chain mechanism was inferred from the observation that 2,2,6,6-tetramethylpiperidine-*N*-oxyl inhibits the thermolysis of **1**.[2] Scheme I shows a mechanism consistent with chain character and with the products.

Although Scheme I can account for most of the chemistry observed when **1** is decomposed in enol ethers or in alkenes without abstractable allylic hydrogens, the thermolysis of **1a–c** in norbornene took a different course,[1] yielding mainly the products of hydroalkylation (**2**) and epoxidation (**3**) with very little of the product of hydroxyalkylation (**4**) (eq 2). It was not clear why norbornene,

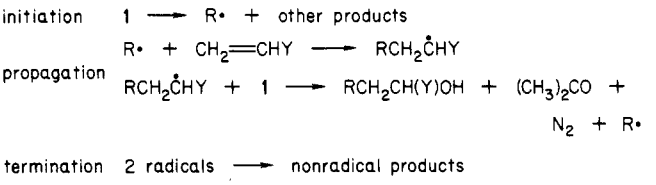


which lacks abstractable allylic hydrogen and which gives good yields in other radical addition processes,[3] should fail to hydroxyalkylate at least as efficiently as other olefins. Knowledge about the likely mechanism of the epoxidation seemed to be a prerequisite for an explanation of the observations, and we report here the results of a mechanistic study of the reactions of **1a–1c** with norbornene. Results of a similar study, with 3,3-dimethyl-1-butene as a model hindered olefin, are also reported.

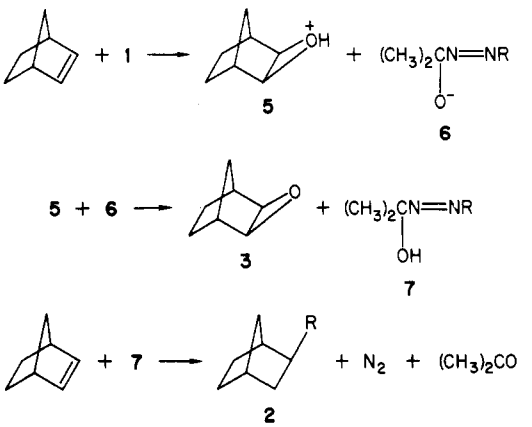
Methods, Results, and Discussion

(a) Mechanism. The three mechanisms of epoxidation by hydroperoxides that are most likely[4] are shown with

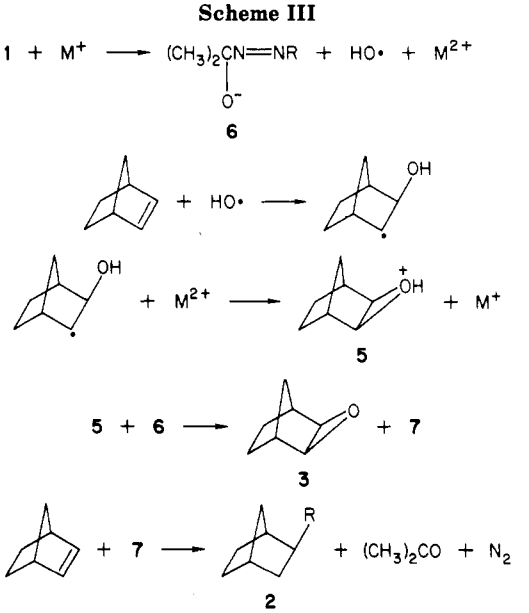
Scheme I



Scheme II



Scheme III



Schemes II–IV, for the case of norbornene and **1**.

Scheme II depicts a bimolecular reaction between norbornene and **1**, leading directly to the conjugate acid of

(1) Osei-Twum, E. Y.; McCallion, D.; Nazran, A. S.; Panicucci, R.; Risbood, P. A.; Warkentin, J. *J. Org. Chem.* **1984**, *49*, 336.
(2) Osei-Twum, E. Y.; Warkentin, J., unpublished observations.
(3) (a) Kharasch, M. S.; Friedlander, H. N. *J. Org. Chem.* **1949**, *14*, 239. (b) Weinstock, J. *Abstr. Pap. Am. Chem. Soc.* **1955**, *12th*, 19.
(4) Mechanisms involving base-catalyzed transformation of the α-hydroperoxy diazene into a dioxirane, a carboxyl oxide, or some other reactive intermediate[5-7] which then attacks the olefin are excluded from consideration because neutral solutions were used. In one experiment, with **1a** and norbornene, added pyridine did not alter the product composition.
(5) Tezuka, T.; Iwaki, M. *J. Chem. Soc., Perkin Trans. 1* **1984**, 2507.
(6) Tezuka, T.; Iwaki, M. *Heterocycles* **1984**, *22*, 725.
(7) Tezuka, T.; Iwaki, M.; Haga, Y. *J. Chem. Soc., Chem. Commun.* **1984**, 325.

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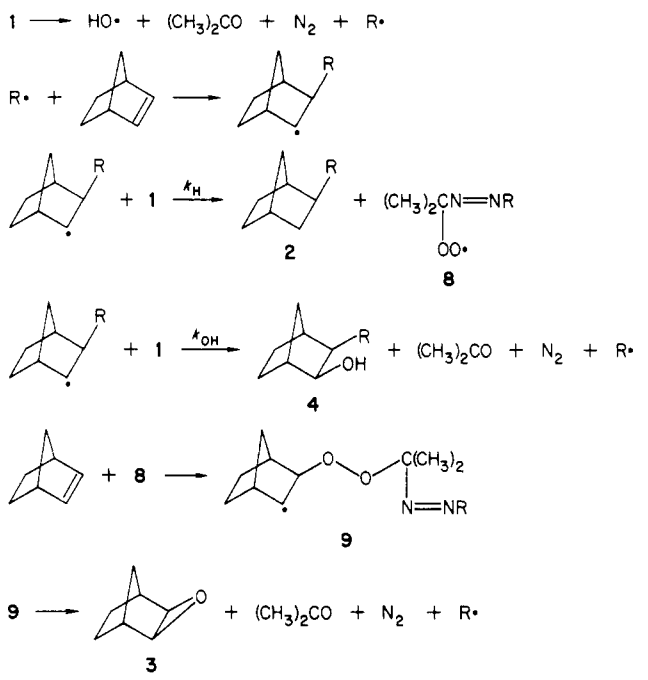
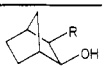
Scheme IV



norbornene epoxide **5**, ion paired with the conjugate base of α-hydroxy diazene **6**. Proton transfer between the ions leads to **3** and **7**. Epoxidation of olefins with an α-hydroperoxy ketone, ester, amide, or nitrile has been shown to be first order in both hydroperoxide and olefin,[8] suggesting a mechanism with a first step like that of Scheme II or a concerted modification in which that step leads directly to epoxide rather than its conjugate acid. Aryl α-hydroperoxy diazenes ($ArCH(OOH)N{=}NC_6H_5$) epoxidize 2,3-dimethyl-2-butene efficiently, with second-order kinetics and with aryl group substituent effects ($\rho = +1.1$, σ values) suggestive of a transition state formed by nucleophilic attack of the alkene at the hydroxyl oxygen, as suggested in Scheme II.[9] A cyclic analogue (3-bromo-4,5-dihydro-5-hydroperoxy-4,4-dimethyl-3,5-diphenyl-3*H*-pyrazole) of α-hydroperoxy diazenes also epoxidizes alkenes with second-order kinetics, presumably through a similar mechanism.[10] There is precedent also for the last line of Scheme II. Hydroalkylation of alkenes with α-hydroxy diazenes is a radical chain process[11] the chain carrying steps of which add up to the overall reaction shown in that line.

It is clear that the rate of consumption of **1** should increase with norbornene concentration if Scheme II were applicable and that a minor contribution from the hydroxyalkylation chain of Scheme I, which would be required to account for the small amount of **4** obtained (Table I), would not distort that concentration dependence significantly from first order. Pseudo-first-order plots of the rates of disappearance of **1b** at 50 °C in benzene containing norbornene in excess, as well as tetramethylpiperidine-*N*-oxyl (0.03 M) to suppress radical chain processes, were linear. A tenfold increase in the concentration of norbornene, from 0.3 to 3.0 M lead to a small decrease in $k_{obsd.}$, from $(1.5 \pm 0.5) \times 10^{-5}$ to $(1.2 \pm 0.3) \times 10^{-5}$ s^{-1}. That result cannot be accommodated within the framework of Scheme II, and that mechanism is therefore ruled out for the reaction of **1b** with norbornene.

Table I. Major Products and Yields from Reactions of 1 ($(CH_3)_2C(OOH)N{=}NR$) and ^2H-Labeled 1 with Norbornene (3 M, in Benzene)[a-c]

R	peroxy group	yield, %		
				
CH_2CF_3	OOH	60	62	14
	OOD	48	24	29
$CH_2CH_2OCH_3$	OOH	31	64	7
	OOD	22	26	18
$CH_2CH_2OC_6H_5$	OOH	54	70	2
	OOD	36	30	12

[a] Yields, determined by gas chromatography, with *exo*-2-norborneol as internal standard, are average values from four runs. They are not corrected for differences in detector response. Yields are based on moles of product per mole of hydroperoxy diazene, assayed by iodometric titration. Since 1 mol of hydroperoxy diazene can lead to more than 1 mol of norbornene derivatives, the total yields exceed 100% in some cases. [b] The 2-alkylnorbornanes (**2**) obtained from ^2H labeled hydroperoxy diazenes contained 2-exo ^2H (ca. 6 parts) 2-endo ^2H (ca. 1 part); total incorporation 50 ± 5% (see text). The exo:endo ratio and the ^2H content were determined from ^2H NMR and mass spectra, respectively. [c] Minor products were formed in each case. The competing processes, for the thermolysis of **1c** in ethyl vinyl ether, have been described.[1] Additional norbornyl products, formed in each case above in small amounts and tentatively assigned by mass spectrometry only were the appropriate 2-alkyl-3-(2-norbornyl)norbornanes and 2-hydroxy-3-(2-norbornyl)norbornane.

Scheme III shows a mechanism involving catalysis by an adventitious redox couple (M^+/M^{2+}) such as Cu^+/Cu^{2+}. One-electron transfers from cations such as cuprous copper and ferrous iron to peroxidic compounds are very well-known,[12] and the complementary reaction of Scheme III, namely, oxidation of carbon-centered radicals to cations, is also well documented.[12] Redox chemistry of the sort shown in Scheme III ought to be prevented by sequestering adventitious metal ion impurities with a reagent such as EDTA. In the present case, washing the glassware with aqueous EDTA solution did not affect either the rate of decomposition of **1b** or the distribution of products from its reactions with norbornene. Thus the redox mechanism of Scheme III is unlikely to be correct.

According to Scheme IV, all of the principal products arise from two radical chain processes that have the initiation step and the first chain-propagating step in common. Subsequent chain-carrying steps involve abstraction of either OH or H from **1** by the adduct from R· and norbornene. Abstraction of H leads to peroxy radical **8**, which adds to norbornene to form **9**. Intramolecular induced decomposition of the peroxy function (γ-scission) leads to epoxide and to the regeneration of R·.

A simple test for Scheme IV involves the use of **1** labeled with ^2H in the OOH group. Since the step labeled k_H (Scheme IV) should be subject to a primary H/D kinetic isotope effect, while that labeled k_{OH} should be insensitive to isotopic substitution because the OH bond is not broken in that step, labeling of **1** with ^2H should alter the product distribution. Yields of epoxide **3** and of hydroalkylation product **2** should be reduced and the yield of hydroxyalkylation product **4** should be enhanced as a result of using ^2H-labeled **1**. Moreover, **2** should contain deuterium.

(8) (a) Rebek, J., Jr.; McCready, R.; Wolak, W. *J. Chem. Soc., Chem. Commun.* **1980**, 705. (b) Rebek, J., Jr.; McCready, R. *J. Am. Chem. Soc.* **1980**, *102*, 5602.
(9) Baumstark, A. L.; Vasquez, P. C. *Tetrahedron Lett.* **1983**, 123.
(10) Baumstark, A. L.; Pilcher, R. S. *J. Org. Chem.* **1982**, *47*, 1141.
(11) (a) Chang, Y.-M.; Profetto, R.; Warkentin, J. *J. Am. Chem. Soc.* **1981**, 7189. (b) Yeung, D. W. K.; Warkentin, J. *Can. J. Chem.* **1980**, *58*, 2386. (c) Yeung, D. W. K.; Warkentin, J. *Can. J. Chem.* **1976**, *54*, 1345. (d) Knittel, P.; Warkentin, J. *Can. J. Chem.* **1976**, *54*, 1341. (e) Knittel, P.; Warkentin, J. *Can. J. Chem.* **1975**, *53*, 2275.
(12) Kochi, J. K. In "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 1, p 591.

The results in Table I are in accord with those expectations, although the ^2H content of **2** was less than one ^2H atom per molecule, indicating that H abstraction is not exclusively from the OOH group. Control experiments, in which **1b** was treated with H_2O instead of D_2O, did not change the product distributions from those obtained with dry **1b** and norbornene. The effects of deuteration on the product distribution are therefore not explicable in terms of effects of hydration of **1b** on the various reaction rate constants. Thus Scheme IV appears to be a viable mechanism for the formation of **2–4**.

Scheme IV is a simplified rationale that does not include minor products and other pathways to the major products. Therefore it should not be used for quantitative predictions that could be valid if Scheme IV included all of the chemistry. It does not follow from Scheme IV, for example, that the yields of **2** and **3** should be the same because an alternative channel to **8** (and hence to **3**), namely, R· + **1** → RH + **8**, is not included in the simplified scheme. Also omitted from Scheme IV are alternative routes to **2**, in which H is abstracted from sources other than the OOH group of **1**.

There is ample precedent for individual steps of Scheme IV. Abstraction of hydroperoxy hydrogen by radicals is fairly fast, with rate constant ca. 2×10^4 M^{-1} s^{-1} at 50 °C, for abstraction from *tert*-butyl hydroperoxide by a primary alkyl radical.[13] Addition of peroxy radicals to alkenes has been known for many years[14,15] and γ-scission of β-peroxyalkyl radicals, prepared by bromine abstraction from β-peroxyalkyl bromides[16] is a facile process with a rate constant near 7×10^5 s^{-1} at 25 °C.[16]

Primary kinetic isotope effects, k_H/k_D, for abstraction of hydroperoxy hydrogen by alkyl radicals are not well-known. Howard and Tong[13] estimated that $k_H/k_D \leq 2$ for abstraction by primary alkyl radicals from *tert*-butyl hydroperoxide. For the case of **1** estimates of k_H/k_D can be made, from the ratios of the yields of **2** obtained with sets of unlabeled and labeled **1**, using eq 3. The left-hand term

$$\frac{[\text{2-H}]_{OOH}}{([\text{2-H}] + [\text{2-D}])_{OOD}} = \frac{k_H[NR\cdot]_H[\text{1-H}] + nk_N[NR\cdot]_H[N]}{k_D[NR\cdot]_D[\text{1-D}] + nk_N[NR\cdot]_D[N]} \quad (3)$$

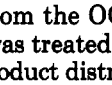
is the ratio of the yields of **2** from a set of experiments (Table I) with a given **1**. It is assumed to be equal to the ratio of rates of formation of **2**, and **2** is assumed to be formed principally by attack of adduct radicals (NR·), from addition of R· to norbornene, on **1** and on norbornene (N). The term nk_N is a stoichiometric factor for the number of hydrogens abstractable from norbornene multiplied by the corresponding rate constant. Full deuteration of **1**-D is assumed. In view of the large excess of D_2O used for the exchanges (see Experimental Section) and because loss of D by the reaction **8** + N → **1**-H must be quite slow,[17] that assumption is probably valid.

Equation 3 can be greatly simplified as follows. Reaction conditions (starting concentrations, temperature) were the same for sets of experiments summarized in Table I. It is therefore likely that the steady-state concentrations of adduct radicals, $[NR\cdot]_H$ and $[NR\cdot]_D$ were not much different. The assumption that they too were the same and the experimental finding that about 50% of the **2** obtained from **1**-D was labeled (i.e. $k_D[NR\cdot]_D[\text{1-D}] = nk_N[NR\cdot]_D[N]$) lead to eq 4. Values of k_H/k_D calculated from the data

$$\frac{k_H}{k_D} = \frac{2[\text{2-H}]_{OOH}}{([\text{2-H}] + [\text{2-D}])_{OOD}} - 1 \quad (4)$$

in Table I by using eq 4 are 4.2, 3.9, and 3.7 for **1a**, **1b**, and **1c**, respectively. The scatter presumably reflects experimental error and the approximations implied in the assumptions, rather than effects of structure of k_H/k_D. A primary kinetic isotope effect of about 4 appears to be reasonable, in view of the theoretical maximum value of 7.9 for the OH group.[19]

Table II. Yields of Epoxidation, Hydroalkylation, and Hydroxyalkylation Products from 1c and 10[a]

peroxy group	yield, %		
		C_6H_5O-$(CH_2)_4C(CH_3)_3$	C_6H_5O-$(CH_2)_3CH$-$(OH)C(CH_3)_3$
OOH	1.5	35	5
OOD	0.5	20	22

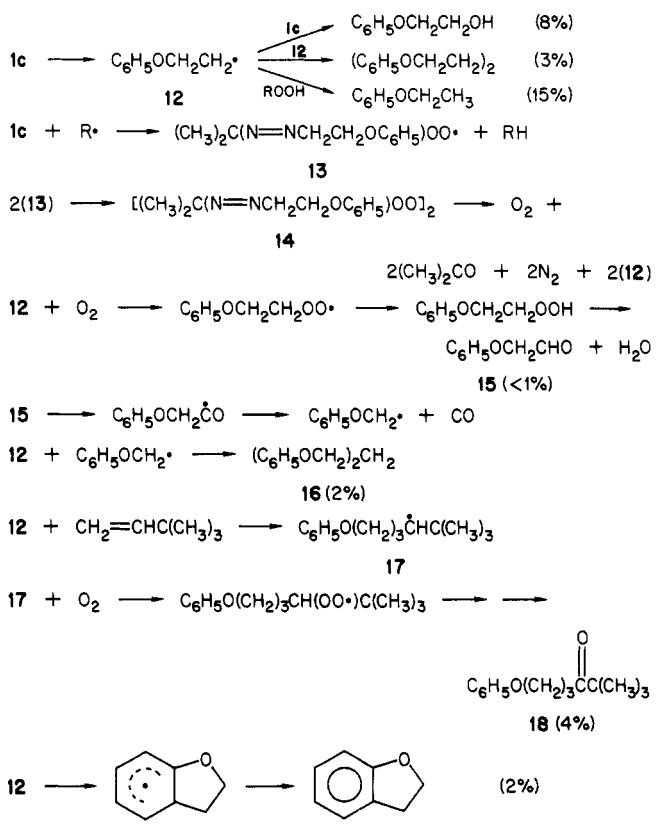
[a] Additional products and their yields, for the case of protio-**1c**, are in Scheme V.

A question remaining is why norbornene is epoxidized and hydroalkylated by **1** whereas enol ethers and 1,1-diphenylethylene are hydroxyalkylated primarily.[1] Steric hindrance at the transition state for reactions of the *exo*-2-alkyl-1-norbornyl radical is a plausible factor. For a hindered radical the free energy for substitution at oxygen of **1** could be raised, because of nonbonded interactions, to the point where reaction at the more accessible H atom becomes favored, in spite of the higher OH bond strength. A reexamination of the products from thermolysis of **1** in 1,1-diphenylethylene[1] showed that epoxidation is a competitive process there also (ca. 5% yield) as expected on the basis of the steric hindrance hypothesis.

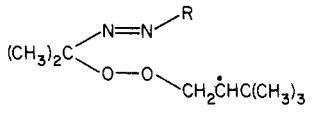
In order to test the steric hindrance hypothesis further, **1c** and its deuterium labeled (OOD) analogue were thermolyzed in neat 3,3-dimethyl-1-butene (**10**). The results, in Table II, indicate that the chemistry is qualitatively the same as that in the case of norbornene. The same trend in the yields of products as a result of ^2H labeling indicates that hydroalkylation again involves H (or D) abstraction from the hydroperoxy group. What is strikingly different, compared to the situation with norbornene, is that the peroxy radicals so formed fail to form epoxide efficiently. Although the reasons for this difference may be complex, two factors come readily to mind. First, 3,3-dimethyl-1-butene (**10**) is probably considerably less reactive than norbornene in the radical addition process. As a result, a larger fraction of the peroxy radicals generated in the presence of **10** couple with other peroxy radicals[20] or with

(13) Howard, J. A., Tong, S. B. *Can. J. Chem.* **1979**, *57*, 2755.
(14) (a) Mayo, F. R. *J. Am. Chem. Soc.* **1958**, *80*, 2497. (b) Mayo, F. R.; Miller, A. A.; Russell, G. A. *J. Am. Chem. Soc.* **1958**, *80*, 2500. (c) van Sickle, D. E.; Mayo, F. R.; Arluck, R. M. *J. Am. Chem. Soc.* **1965**, *87*, 4824, 4832.
(15) Ingold, K. U. *Acc. Chem. Res.* **1969**, *2*, 1.
(16) Bloodworth, A. J.; Courtneidge, J. L.; Davies, A. G. *J. Chem. Soc., Perkin Trans. 2* **1984**, 523.
(17) It is unlikely that initially labeled hydroperoxides lose some of the label by the process R'OO· + norbornene → R'OOH. The rate constant for $(CH_3)_3COO\cdot$ + RH (secondary) → $(CH_3)_3COOH$ is small, lying between 10^{-4} and 9×10^{-4} M^{-1} s^{-1} at 30 °C.[18] Any R'OOH formed during reaction should, in any case, have reexchanged with the D_2O left in the reaction mixture (see Experimental Section).
(18) (a) Chenier, J. H. B.; Tong, S. B.; Howard, J. A. *Can. J. Chem.* **1978**, *56*, 3047. (b) Korcek, S.; Chenier, J. H. B.; Howard, J. A.; Ingold, K. U. *Can. J. Chem.* **1972**, *50*, 2285.
(19) Value for 298 K, based only on stretching contributions to the zero-point energy difference. Bell, R. P. *Chem. Soc. Rev.* **1974**, *3*, 513.
(20) The rate constant for combination of peroxy radicals **13** at 50 °C is estimated to be at least 10^4 M^{-1} s^{-1} from the literature values for other peroxyls. Values of $2k_t$ (30 °C) for *tert*-butylperoxy,[18] cumylperoxy,[21] and 1,1-(diphenylethyl)peroxy[22] radicals are 1.2×10^3, 6×10^3, and 6.4×10^4 M^{-1} s^{-1}, respectively.

Scheme V



alkyl radicals than is the case when norbornene is the substrate. Second, the peroxy adducts (**11**) that do form from **10** may have lower rate constants for closure to epoxide (γ-scission) than their counterparts in the case of norbornene because of steric hindrance. γ-Scission of **11**



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involves a radical site of the neopentyl-type closing onto an atom from which a similarly bulky group is simultaneously leaving. The oxirane-like transition state can be expected to involve strong eclipsing interactions between those bulky groups and ring hydrogens.[23] Although generalization on the basis of a few examples is risky, it may be that norbornene is a special case, blending high addition reactivity with significant steric inhibition of subsequent intermolecular processes, for the efficient operation of the radical chain epoxidation mechanism (Scheme IV).

Examination of the minor products from thermolysis of **1c** in neat, oxygen-free **10** (Scheme V) provided support for the postulate that a significant fraction of the peroxy radicals from **1c** couple instead of adding to **10**. The product of such coupling would be the unstable tetraoxide **14** (Scheme V) which should decompose to form O_2. Minor products in Scheme V that are indicative of oxygen formation are phenoxyacetaldehyde (**15**), 1,3-diphenoxypropane (**16**), and 2,2-dimethyl-6-phenoxyhexan-3-one (**18**).

(b) Stereochemistry of Additions to Norbornene. Radical addition from the exo face of the norbornene double bond is apparently without exception.[3] On the basis of analogy and from a comparison of the ^{13}C NMR spectrum of exo-2-methylnorbornane[24] with those of **2**, compounds **2** were assigned the exo-alkyl (exo-R) geometry. In the ^2H NMR spectra of the hydroalkylation/deuterioalkylation products there were two signals, near δ 1.14 and 1.56, in an intensity ratio of about 6 to 1. The major signal was assigned to exo-3-deuterium and the minor signal to endo-3-deuterium on the basis of the following argument. In the ^1H NMR spectrum of 2-(2,2,2-trifluoroethyl)-3-hydroxynorbornane the signal from the proton at the hydroxyl-bearing carbon atom is an isolated doublet (J = 6.3 Hz) at δ 3.82,[25] coupling being to a proton absorbing at δ 1.85. Addition of D_2O removed a signal near δ 1.10 without affecting the signals at δ 3.82 and 1.85. The resonance at δ 1.85 can therefore be assigned to a CH proton, rather than OH, and the magnitude of the coupling constant indicates that it is adjacent and cis (dihedral angle near 0°) to the proton which gives rise to the δ 3.82 signal. Given the evidence that the alkyl group is in the exo position, the hydroxyl group must be exo also, and both carbon-bound protons referred to above must be in endo positions. If hydroxyl is transferred to the exo face, then H or D transfer, with smaller steric requirements, must also be predominantly to the exo face. The similarity between the ^2H spectra of the 2-alkyl-3-deuterionorbornanes then requires that in all cases reported here the preferred stereochemistry of hydroalkylation was exo,exo. The stereochemistry of hydroxyalkylation was not determined for the other hydroxyalkylation products of Table I. In each case there was only one major hydroxyalkyl derivative and on that basis alone the exo,exo structures are made likely; abrupt reversal from exo,exo to exo,endo stereochemistry with small changes in R being implausible.

Experimental Section

Proton magnetic resonance spectra were recorded with a Varian EM-390, Bruker WP-80, or Bruker WH-250 spectrometer. ^2H NMR spectra were acquired with the Bruker WH-250 instrument. The solvent was $CDCl_3$, unless otherwise stated, and the reference was tetramethylsilane.

Electron-impact mass spectra were obtained with a VG7070 mass spectrometer using either a direct insertion probe system or, for trace components, a GC column/jet separator system. The ion-source temperature was 200 °C, the accelerating voltage was 4 kV, and the electron energy was 70 eV with emission of 100 μA. All mass spectra were acquired and processed with a VG 2035 data sytem.

A Varian VISTA 6000 gas chromatograph with an off-column flash injector at 220 °C, a flame ionization detector at 300 °C, and a glass column (2.5 m × 2 mm i.d.) packed with OV-17 (3%) on Chromosorb W, HP80/100, was used for separation and for quantitative analysis of products by the internal standard technique. Carrier gas (N_2) was passed at 25 mL min^{-1}, and the oven temperature was normally programmed from 40 to 280 °C at 5° min^{-1}. The data were acquired and processed with the Varian VISTA 402 chromatographic data system.

Semipreparative gas chromatography, with a Varian Aerograph A90-P3 instrument equipped with a tc detector at 300 °C, an off-column injector at 250 °C, and a steel column (1.18 × 4 mm

(21) Howard, J. A.; Bennett, J. E.; Brunton, G. *Can. J. Chem.* **1981**, *59*, 2253.

(22) (a) Howard, J. A. *Adv. Free Radical Chem.* **1972**, *4*, 49. (b) Howard, J. A.; Chenier, J. H. B.; Yamada, T. *Can. J. Chem.* **1982**, *60*, 2566.

(23) The effect of *gem*-dialkyl substitution, at the site between the reacting atoms, is to enhance the rate constant for formation of a three-membered ring (the Thorpe–Ingold effect). Modest increases in the steric requirements at the radical site, in a series of radicals that undergo γ-scission, also leads to rate enhancement; MeCH(OO-*t*-Bu)$\dot{C}H_2$ (8×10^4 s^{-1}), MeCH(OO-*t*-Bu)$\dot{C}$HMe (1.96×10^6 s^{-1}), and EtCH(OO-*t*-Bu)$\dot{C}$HEt (6.2×10^6 s^{-1}).[16] The trend was attributed to polar effects[16] and a reversal of the trend for the case of a substituent like *tert*-butyl, where steric effects might dominate, would not be surprising.

(24) Stothers, J. B.; Tan, C. T.; Teo, K. C. *Can. J. Chem.* **1973**, *51*, 2893.

(25) Previously reported[1] as 6.7 Hz, δ 3.80.

i.d.) packed with OV-17 (10%) on Chromosorb W (HP 80/100) was used to collect major products. The carrier gas was helium, normally flowing at 20 mL min^{-1}, and the column temperature was usually programmed from 40 °C to a maximum of 300 °C.

α-Hydroperoxy Diazenes 1 and ^2H Analogues. The α-hydroperoxy diazenes used in this work have been described.[1] A ^2H analogue was prepared by stirring a benzene solution containing between 60 and 100 mg of hydroperoxy diazene with excess D_2O (3 mL) for 20 h at about 5 °C. The benzene layer, together with ca. 0.5 mL of the aqueous phase, was used directly for reactions in which benzene was the solvent. For reactions carried out in neat alkene, the benzene was removed from the hydroperoxy diazene by one of the procedures described earlier.[1]

Thermolysis of Hydroperoxy Diazenes 1 in Norbornene and in 10. The procedure for the preparation of samples and for the workup was essentially that described earlier.[1] The experiment with **1b** and norbornene, to test for redox couples, involved washing the glassware with aqueous EDTA solution, drying, and addition of solid EDTA (5 mg) to the reactants before sealing the tube. EDTA was only slightly soluble in the solution of **1b** and norbornene in benzene, and a solid EDTA phase was present throughout the thermolysis.

Kinetics of Thermolysis of 1b in Benzene Containing Norbornene. Stock solutions of hydroperoxy diazene (0.05M) in benzene containing norbornene (0.3 or 3.0 M) and tetramethylpiperidine-*N*-oxyl (TMPO, 0.03 M) were prepared, and aliquots (1.0 mL) were degassed and sealed into glass tubes, which were then heated at 50 °C in an oil bath. For analysis a tube was chilled and cut, the sample was transferred to a cold, glass-stoppered Erlenmeyer flask (125 mL), cold methanol (4 mL) and dry ice (ca. 0.1 g) were added, and the flask was swirled to displace O_2 with CO_2. Freshly prepared, saturated, aqueous KI solution (1 mL) and glacial acetic acid (15 mL) containing $FeCl_3$ (0.002%) were added, and when no more dry ice remained the flask was stoppered and kept in the dark for 10 min. Water (50 mL) was added, and the resulting solution was titrated to the starch end point with 0.01 N sodium thiosulfate solution. The volume of titrant required for a sample that had reacted to completion (six or more half-lives) was subtracted from the other titration volumes for a given kinetic run.

Products. The products of hydroalkylation and hydroxyalkylation of norbornene with **1** have been reported.[1] Additional products reported here include minor and trace components for which tentative structures were assigned on the basis of low resolution mass spectrometry alone. The mass spectra are reported in order of decreasing values of m/z; peaks smaller than 50% of the base peak (100) being omitted except for molecular ions and for peaks of high diagnostic significance, where the relative intensity is given.

***exo*-Norbornene epoxide**: ^1H NMR δ 0.63 (d, J = 9.5 Hz, 1 H); 1.18–1.47 (m, 5 H), 2.39 (s, 2 H), 2.88 (s, 2 H);[26] ^{13}C NMR δ 25.01, 26.11, 36.57, 51.26; MS, m/z 110 (M^+), 67 ($C_5H_7^+$, 100), 66 ($C_5H_6^+$).

2-(2,2,2-Trifluoroethyl)-3-(2-norbornyl)norbornane: MS, m/z 272 (M^+), 95 ($C_7H_{11}^+$, 100), 67 ($C_5H_7^+$).

2-(2-Methoxyethyl)-3-(2-norbornyl)norbornane: MS, m/z 216 ($M^+ - CH_3OH$), 188 ($M^+ - C_3H_8O$), 95 ($C_7H_{11}^+$, 100), 93 ($C_7H_9^+$), 80 ($C_6H_8^+$), 79 (not assigned), 67 ($C_5H_7^+$), 45 ($C_2H_5O^+$).

2-Hydroxy-3-(2-norbornyl)norbornane: MS, m/z 206 (M^3), 188 ($M^+ - H_2O$, 18), 95 ($C_7H_{11}^+$, 100), 80 ($C_6H_8^+$), 67 ($C_5H_7^+$).

2,3-Dihydro-4,5-benzofuran: MS, m/z 120 (M^+, 100), 94 ($C_6H_6O^+$), 91 ($C_7H_7^+$).

***tert*-Butylethylene oxide**: MS, m/z 100 (M^+), 57 ($C_4H_9^+$, 100), 41 ($C_3H_5^+$). The material that gave this mass spectrum had the same retention time on the analytical GC column as authentic *tert*-butylethylene oxide.

2,2-Dimethyl-5-phenoxypentane: MS, m/z 192 (M^+), 94, ($C_6H_6O^+$, 100), 57 ($C_4H_9^+$).

Phenoxyacetaldehyde: IR 1735 cm^{-1}; MS, m/z 136 (M^+), 94 ($C_6H_6O^+$, 100).

2,2-Dimethyl-6-phenoxyhexan-3-ol: MS, m/z 222 (M^+), 165 ($M^+ - C_4H_9$, 6), 94 ($C_6H_6O^+$), 71 ($C_5H_{11}^+$, 100).

2,2-Dimethyl-6-phenoxyhexan-3-one: IR 1712 cm^{-1}; MS, m/z 220 (M^+), 163 ($M^+ - C_4H_9$, 5), 127 ($C_8H_{15}O^+$, 100), 57 ($C_4H_9^+$).

1,3-Diphenoxypropane: MS, m/z 228 (M^+), 135 ($C_9H_{11}O^+$), 107 ($C_7H_7O^+$, 100), 77 ($C_6H_5^+$).

1,4-Diphenoxybutane: MS, m/z 242 (M^+), 149 ($C_{10}H_{13}O^+$), 107 ($C_7H_7O^+$, 100), 77 ($C_6H_5^+$).

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The Nature of the Macromolecular Network Structure of Bituminous Coals

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The macromolecular network structure of bituminous coals has been studied by using the classical solvent-swelling techniques of polymer chemistry. Solutions of nonpolar solvents in coals follow regular solution theory. Solvents which are hydrogen bond acceptors show strongly enhanced solubility (coal swelling) which correlates with the strength of the hydrogen bond between the solvent and *p*-fluorophenol. A family of network active hydrogen bonds exists in bituminous coals. In native coals, their strength appears to range from 5 to 8 kcal/mol. The use of solvent-swelling data to calculate the number average molecular weight between cross-links ($\bar{M}_c$) has been explored. It is not yet possible to calculate correct absolute values for $\bar{M}_c$, but changes in $\bar{M}_c$ can be followed. The treatment of coals as macromolecular networks is possible and provides significant new insight into their structure.

The principal component of bituminous coals, vitrinite, consists of a porous, cross-linked macromolecular network in which is dissolved a complex mixture of soluble molecules. This structure plays a dominate role in determining many of the physical properties of coals such as the various mechanical properties and mass transfer rates. Similarly, much of a coal's chemistry is determined by its macromolecular structure. The macromolecular network structure of this complex material must be fully characterized if we are to have any real hope of understanding its chemistry.

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