

mL of pyridine. The solution was cooled in a vigorously stirred ice slurry. Finely ground *N*-ethylbenzoxazolium fluoroborate (500 mg, 2.14 mmol) was added in one portion. The mixture was stirred for 45 min at 0 °C and for 15 min at room temperature; 150 mL of ether was added, the reaction mixed well, and the solid collected by filtration. The product was washed with water and ether and dried under vacuum to give 1.67 g (86%) of the active ester as an amorphous white powder: ¹H NMR (Me₂SO-*d*₆) δ 1.08 (3 H, t, 7 Hz), 1.37 (9 H, s), 7.13–7.77 (19 H, m). The ester was used without further purification although HPLC (linear gradient 50% aqueous MeOH to MeOH in 15 min, 1.5 mL/min, 20.0 mL) showed minor impurities.

The above ester (832 mg, 0.7 mmol) was dissolved in 9 mL of trifluoroacetic acid and the resultant mixture allowed to stand for 30 min. The solution was evaporated and the oil rubbed with ether to form a white solid. The product was collected on a filter, washed with ether, and dried under vacuum to give a quantitative amount of the salt (896 mg) as a white powder. This was dissolved in 18 mL of DMF and added dropwise over 4.5 h to 680 mL of dry pyridine. The solution was stirred for 65 h. The solution was concentrated to approximately 15 mL, and the peptide was precipitated by adding 10 volumes of ether. The mixture was chilled in an ice bath and the product collected, washed with ether, and dried. The peptide was dissolved in ca. 0.5 mL of Me₂SO and precipitated with 10 volumes of water. The mixture was chilled in an ice bath and the product collected, washed with water and ether, and dried. Final yield was 646 mg (90% from active ester) of a solid: HPLC (linear gradient 50% aqueous MeOH to MeOH in 15 min) 1.5 mL/min, 17.5 mL; ¹H NMR (Me₂SO-*d*₆) δ 2.56–2.83 (6 H, m), 3.51–3.96 (18 H, m), 4.38 (3 H, m), 7.30 (15 H, d), 7.99 (3 H, t, 5.7 Hz), 8.18 (3 H, d, 6.2 Hz), 8.73 (3 H, t, 5.3 Hz). Anal. Calcd for C₄₂H₅₁O₉N₉S₃: C, 54.70; H, 5.58; N, 13.67; S, 10.43. Found: C, 54.67; H, 5.64; N, 13.50; S, 10.25.

cyclo-(L-Pro-Gly-L-Cys(Meb))₃ (16). The *N*-ethylsalicylamide ester of Boc(>ly-L-Cys(Meb)-L-Pro)₃-OH was prepared as a crude white solid in 99% yield by a procedure analogous to that described above: ¹H NMR (Me₂SO-*d*₆) δ 1.38 (9 H, s), 2.68–2.87 (3 H, m), 4.19–4.33 (3 H, m), 4.63–4.79 (3 H, m), 6.86 (6 H, d + d), 6.99 (1 H, t, 6.2 Hz), 7.24 (6 H, d + d), 7.95–8.32 (5 H, m), 12.42 (1 H, 6, s). Anal. Calcd for C₅₉H₇₉O₁₅N₉S₃: C, 56.66; H, 6.37; N, 10.08; S, 7.69. Found: C, 56.64; H, 6.42; N, 9.93; S, 7.81.

(The required nonapeptide acid was prepared by a ((3 + 3) + 3) synthesis entirely analogous to that reported for the glycine analogue.)

Unpurified active ester (527 mg, 0.35 mmol) was dissolved in 2.7 mL of 4.8 M HCl in tetrahydrofuran and 0.3 mL of anisole. The solution was kept at room temperature for 45 min and then evaporated; 3 mL of tetrahydrofuran was added, and the solution was evaporated. A foam was obtained that was rubbed with pentane-tetrahydrofuran (4:1) to give a pale yellow powder. The

powder was collected by centrifugation, washed, and dried under vacuum over P₂O₅ and KOH. The salt was dissolved in 5 mL of DMF and added dropwise, over 2 h, to 500 mL of pyridine at room temperature. The solution was stirred for 90 h. The crude product, a yellow oil, was obtained by evaporating the solvent. The oil was dissolved in 2 mL of methanol and precipitated, in a centrifuge tube, with 20 mL of water. A gum was obtained that was rubbed with 10 mL of 0.5 N HCl and then with 10 mL of water. The gum was kept under vacuum over P₂O₅ until it became a solid. The solid was dissolved in 2 mL of dichloromethane and precipitated, in a centrifuge tube, with 20 mL of hexane. The solvent was decanted, and the product was rubbed with hexane. These operations removed most of the salts and phenolic materials. The peptide was purified by medium-pressure LC. The sample was loaded onto an E. Merck Size C column in chloroform and eluted with chloroform-methanol (85:10) at a flow rate of 300 mL/h; 16-mL fractions were collected and examined by TLC. Appropriate fractions were pooled and evaporated. The product was kept under high vacuum to yield 201 mg (50% based on ester): HPLC (MeOH-H₂O (8:2)) 1.0 mL/min, 8.7 mL; ¹H NMR (Me₂SO-*d*₆) δ 2.67–2.93 (6 H, m), 3.62 (9 H, s), 4.90 (3 H, m), 6.79 (6 H, d, 8.4 Hz), 7.16 (6 H, d, 8.4 Hz), 7.71 (3 H, d, 9.3 Hz), 8.61 (3 H, t, 5.7 Hz). Anal. Calcd for C₅₄H₆₉O₁₂N₉S₃·CH₃OH: C, 56.73; H, 6.32; N, 10.83; S, 8.26. Found: C, 56.17; H, 6.27; N, 10.73; S, 8.94.

cyclo-(Gly-L-Cys-Gly)₃ Triply Bridged by 1,3,5-Tris(thiomethyl)benzene (5). The experimental procedure of Stewart and Young for sodium in liquid-ammonia reactions was followed. Small pieces of sodium were added to a refluxing mixture of 15 (184 mg, 1.2 mmol) in 50 mL of ammonia, freshly distilled from sodium, until a permanent light blue color was obtained. After 3 min, 1,3,5-tris(bromomethyl)benzene²⁰ (72 mg, 0.2 mmol) in 1 mL of ether was added. The solution was stirred at reflux for 4 h. Ammonium chloride (130 mg) was added, and then ammonia was evaporated under a stream of nitrogen. The white residue was dissolved in a mixture of DMF (1 mL), water (0.5 mL), and methanol (0.5 mL) and purified by preparative HPLC (Whatman Magum-9 ODS-2, MeOH-H₂O (55:45), 3.0 mL/min, 84–105 mL).

The product was dissolved in DMF (4 mL) and precipitated with ether (30 mL) to give 44 mg (29% based on 15) of a white powder: HPLC (MeOH-H₂O (45:55)) 1.5 mL/min, 10.5 mL; ¹H NMR (Me₂SO-*d*₆) δ 3.37–3.91 (18 H, m), 4.20 (3 H, m), 7.14 (3 H, s), 7.30 (3 H, d, 5.3 Hz), 7.82 (3 H, t, 5.3 Hz), 8.94 (3 H, t, 3.7 Hz); ¹³C NMR (Me₂SO-*d*₆) δ 52.5, 128.9, 136.9, 169.3, 169.8, 172.6. Anal. Calcd for C₃₀H₃₉O₉N₉S₃·H₂O: C, 45.96; H, 5.27; N, 16.08; S, 12.27. Found: C, 46.00; H, 5.32; N, 16.08; S, 12.27.

Acknowledgment. Financial support from the National Science Foundation (Grant 8116986) is gratefully acknowledged.

Generation and Chemistry of Cyclohexyloxy Radicals[†]

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Received June 12, 1985

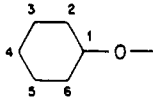
In this paper we report our work on cyclohexyloxy radicals from dicyclohexyl hyponitrite (CyON₂OCy) and the related CyO· sources dicyclohexyl peroxydicarbonate [(CyOCO₂)₂] and dicyclohexyl peroxide (CyO₂Cy), including the ¹³C and ¹H NMR spectra of the radical sources, the kinetics of DCHN decomposition over a wide range of temperature (followed by both UV and chemiluminescence), ESR spin-trapping studies, the kinetics of hydrogen atom abstraction from a variety of substrates by CyO·, and the effect of CyO· radical source on product composition. We have also investigated the effects of dissolved O₂ on DCHN decomposition in cyclohexane and comment on the source of the observed chemiluminescence.

The study of alkoxy radicals is a subject of continuing interest.¹⁻³ They can be generated by thermal or photochemical decomposition of peroxides, peresters, nitrates,

nitrites, and hypohalite compounds or by the metal-catalyzed decomposition of hydroperoxides. Many of these

[†] Contribution No. 3797.

(1) Howard, J. A., Williams, G. H., Eds. *Adv. Free-Radical Chem.* 1972, 4, 49.

Table I. ^{13}C Chemical Shifts^a for Dicyclohexyl Hyponitrite and Related Compounds


compd	$-\text{OCO}-$	C ₁	C ₂ ,C ₆	C ₃ ,C ₅	C ₄
CyON ₂ OCy (DCHN)		81.3	31.6	23.7	25.5
CyO ₂ Cy (DCHP)		81.1	30.8	24.0	25.9
(CyOCO ₂) ₂ (DCPD)	152.8	80.6	31.3	23.4	25.1
CyOCy		74.7	33.4	24.6	25.9

^aFor solutions of about 5% by weight in CDCl₃, measured downfield from Me₄Si.

Table II. ^1H Chemical Shifts^a of Dicyclohexyl Hyponitrite and Related Compounds

compd	>CHO-	-(CH ₂) ₂ ^b	-(CH ₂) ₃ ^c
CyON ₂ OCy	4.33	1.80	1.51
CyO ₂ Cy	3.96	1.80	1.42
(CyOCO ₂) ₂	4.82	1.77	1.54
CyOCy	3.34	1.80	1.32

^aFor solutions of about 5% by weight in CDCl₃. Run at 90 MHz. ^bHydrogens on carbons C₂ and C₆. ^cHydrogens on carbons C₃, C₄, and C₅.

sources have the disadvantage of forming other radical species. Hyponitrites, which can decompose cleanly to give alkoxy radicals and N₂, are a relatively new source, and have been the focus of a recent series of papers by Mendenhall and co-workers.⁴⁻⁷

While a considerable amount is known about the rates of generation and subsequent chemistry of tertiary alkoxy radicals, especially *tert*-butoxy, little is known about secondary alkoxy radicals.⁸ Our interest in oxy radicals in general and cyclohexyloxy radical in particular stems from continuing studies of the mechanism of autoxidation of cyclohexane.^{9,10} In this paper we report our work on dicyclohexyl hyponitrite (DCHN, CyON₂OCy) and the related cyclohexyloxy radical sources dicyclohexyl peroxycarbonate (DCPD, (CyOCO₂)₂) and dicyclohexyl peroxide (DCHP, CyO₂Cy). We report here the ^{13}C and ^1H NMR spectra of the CyO· radical sources, the kinetics of DCHN decomposition over a wide range of temperature (followed by both UV and chemiluminescence), ESR spin-trapping studies, the kinetics of hydrogen atom abstraction from a variety of substrates by CyO·, and the effect of CyO· radical source on product composition. We have also investigated the effects of dissolved O₂ on DCHN decomposition in cyclohexane and comment on the source of the observed chemiluminescence.

(2) Kochi, J. K. In "Free Radicals"; Kochi, J. K., Ed.; Wiley: New York, 1973; Vol. 2, pp 665-710.

(3) Gray, P.; Shaw, R.; Thynne, J. C. J. "Progress in Reaction Kinetics"; Porter, G., Ed.; Pergamon Press: Oxford, 1967; Vol. 4, p 63.

(4) Mendenhall, G. D.; Stewart, L. C.; Scaiano, J. C. *J. Am. Chem. Soc.* **1982**, *104*, 5109.

(5) Ogle, C. A.; VanderKooi, K. A.; Mendenhall, G. D.; Lorprayoon, V.; Cornilsen, B. C., *J. Am. Chem. Soc.* **1982**, *104*, 5114.

(6) Ogle, C. A.; Martin, S. W.; Dziobak, M. P.; Urban, M. W.; Mendenhall, G. D., *J. Org. Chem.* **1983**, *48*, 3728.

(7) Chen, H.-T. E.; Mendenhall, G. D. *J. Am. Chem. Soc.* **1984**, *106*, 6375.

(8) For a very recent compilation of rate data on alkoxy radical reactions see: Howard, J. A.; Scaiano, J. C. *Landolt-Bornstein New Series Group II*; Fischer, H., Ed.; New York, 1984; Vol. 13d, pp 6-127.

(9) Described in part at the Industrial and Engineering Division, Annual Meeting of the American Chemical Society, Washington, DC, Sept 1979.

(10) Druliner, J. D.; Kitson, F. G.; Rudat, M. A.; Tolman, C. A. *J. Org. Chem.* **1983**, *48*, 4951 and other papers to be published.

Table III. Rate Constants for First-Order Decomposition of Dicyclohexyl Hyponitrite in Cyclohexane

temp, °C	k, s ⁻¹	temp, °C	k, s ⁻¹
24.5	2.5 × 10 ⁻⁶	69.0	1.3 × 10 ⁻³
50.0	1.2 × 10 ⁻⁴	80.0	4.5 × 10 ⁻³ ^a
59.0	4.0 × 10 ⁻⁴		

^aMeasured by chemiluminescence in cyclohexane or benzene, with or without O₂.

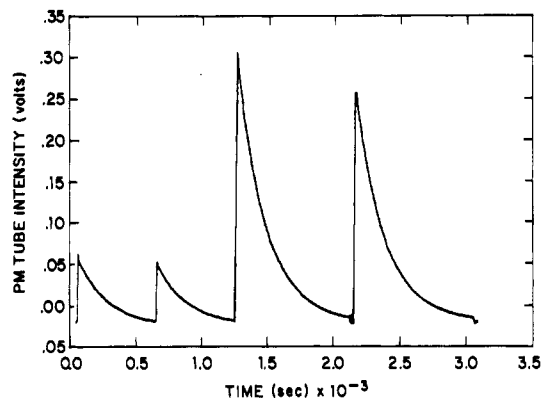


Figure 1. Chemiluminescence-repeated DCHN injections into a solution of 10⁻³ M 9,10-dibromoanthracene at 80 °C. The initial DCHN concentrations after mixing were 10⁻³, 10⁻³, 5 × 10⁻³, and 5 × 10⁻³ M, respectively.

Spectroscopic Properties

The 22.63- and 75.70-MHz $^{13}\text{C}\{^1\text{H}\}$ spectra of DCHN, DCHP, and DCPD show four resonances in a 1:2:1:1 intensity ratio with chemical shifts given in Table I. Also included for reference are the corresponding shifts for dicyclohexyl ether. Carbons C1 and C4 are readily assigned by their relative intensities and chemical shifts. C2C6 and C3C5 are assigned on the basis of their relative positions, with the greater shift of C2C6 due to stronger perturbation by the oxygen atom.

The 90-MHz ^1H NMR spectra of the same compounds show resonances in a 1:4:6 intensity ratio, with chemical shifts given in Table II. At 300 MHz the C3, C4, and C5 hydrogens of DCHN are resolved and show two multiplets of equal intensity at 1.3 and 1.5 ppm. In addition, the coupling of the α -hydrogen to the axial and equatorial β -hydrogens is cleanly resolved to give $J_{ax} = 9.4$ Hz and $J_{eq} = 3.6$ Hz. The observation of a clean triplet of triplets with DCHN suggests that only one regioisomer about the N=N double bond is present, consistent with the conclusions of Kiefer and Traylor¹¹ and Ogle et al.⁵ The observation of a broadened α -hydrogen peak for DCHP at 300 MHz indicates much freer rotation about the O-O bond.

The UV absorption spectrum of DCHN in cyclohexane shows an absorption maximum at 226 nm ($\epsilon 7.1 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$). The extinction coefficient compares well with those reported by Mendenhall et al.⁶ for a variety of hyponitrites. The earlier value of $6.2 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1}$ for di-*tert*-butyl hyponitrite reported by Kiefer and Traylor¹¹ may have been a misprint.

Kinetics of Thermal Decomposition of DCHN

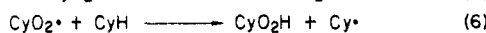
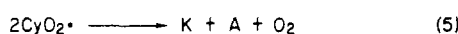
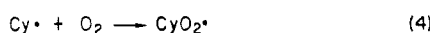
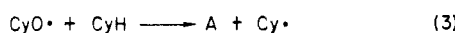
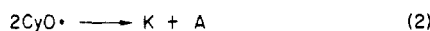
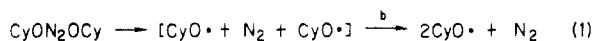
The thermal decomposition of dicyclohexyl hyponitrite was conveniently monitored in cyclohexane over the range of 25- to 70 °C by following the disappearance of the UV absorption maximum at 226 nm or at 80 °C by following the chemiluminescence of the reaction.

(11) Kiefer, H.; Traylor, T. G. *Tetrahedron Lett.* **1966**, 6163.

The reaction rate was independent of initial DCHN concentration over the range 10^{-2} – 10^{-4} M and was found to be first order over 3–5 half-lives. Table III shows the first-order rate constants covering a range of half-lives from 3 days at 25 °C to less than 3 min to 80 °C. A good linear Arrhenius plot was obtained, whose slope gives $E_a = 28.4$ kcal/mol. The corresponding transition-state parameters of $\Delta H^\ddagger = 27.5$ kcal/mol and $\Delta S^\ddagger = +8$ eu seem reasonable for a bond-breaking process.

Figure 1 shows a typical chemiluminescence experiment at 80 °C in which successive injections of DCHN in benzene were made into a solution containing 10^{-3} M 9,10-dibromoanthracene (DBA), under N_2 . The DBA does not affect the rate of the reaction but substantially increases the intensity of the light output.¹² The first two injections each gave initial DCHN concentrations of 10^{-3} M, while the second two gave 5×10^{-3} M. The volumes added were small enough that the temperature perturbation was less than 0.3 °C. The rate constants taken from the light-decay curves are the same for all four runs, within experimental error, while the computer-integrated areas beneath the peaks are proportional to $[DCHN]_0$ (with a proportionality constant in our system of 14 ± 2 V s M⁻¹).

Similar experiments in benzene under air, cyclohexane under N_2 , or cyclohexane under air at 80 °C all gave the same rates. The areas under the curves were the same except for cyclohexane and air, where the integrated areas were 3 times as large (42 ± 5 V s M⁻¹). The increased light emission in cyclohexane in the presence of O_2 can be understood in terms of reactions 1–6, where K represents



ketone (cyclohexanone) and A alcohol (cyclohexanol). Path a in reaction 1 represents recombination of the oxy radicals before they can escape the solvent cage. Reactions 1a, 2, and 5 are exothermic enough to produce K in an electronically excited state.¹³ In cyclohexane, reaction 3 is so fast (see below) that reaction 2 cannot compete; thus, the observed chemiluminescence in cyclohexane under N_2 must be solely due to disproportionation of $CyO\cdot$ in the cage. In the presence of O_2 , $Cy\cdot$ formed in (3) is rapidly scavenged to produce $CyO_2\cdot$ in (4), which reacts with itself in (5). The tripling of chemiluminescence intensity with O_2 indicates that reaction 5 contributes twice as much light as (1a). Reactions 1–5 are supported by ESR studies and product analyses described below. Reaction 6 does not significantly affect the light produced, since the $Cy\cdot$ formed is rapidly converted back to $CyO_2\cdot$ in the presence of O_2 . The cyclohexyl hydroperoxide formed in (6) is quite stable at 80 °C in the absence of added metal catalysts. Computer simulations of cyclohexane autoxidation initiated by

(12) The use of DBA has been described by several authors: (a) Vassilev, R. F. *Prog. React. Kinet.* 1967, 4, 305. (b) Kellogg, R. E. *J. Am. Chem. Soc.* 1969, 91, 5433. (c) Richardson, W. H.; Burns, J. H.; Price, M. E.; Crawford, R.; Foster, M.; Slusser, P.; Anderregg, J. H. *J. Am. Chem. Soc.* 1978, 100, 7596.

(13) Reactions 2 and 5 are estimated to be exothermic by 91 and 97 kcal/mol, respectively, using bond dissociation energies in: Kerr, J. A. *Chem. Rev.* 1966, 66, 465. Group additivities given by: Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976.

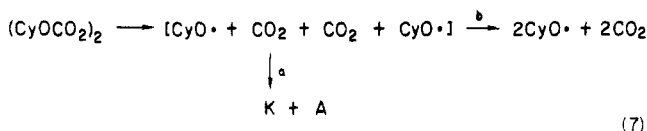
Table IV. ESR Spectral Data^a for Radical Adducts of Nitroso-*tert*-butane

radical	adduct	<i>g</i>	<i>a</i> (N)	<i>a</i> (H)	<i>a</i> (¹³ C)	<i>a</i> (¹⁷ O)
<i>t</i> -Bu·	III	2.00526	15.47		3.7	
CyO·	IV	2.00526	28.66			4.3
HCO(CH ₂) ₄ CH ₂ ·	VI	2.00598	15.38	10.43,		
				0.5		
Cy·	VII		14.82	~0.5		
<i>t</i> -BuO·	XI	2.0053	27.2			

^a Hyperfine coupling constants are in Gauss. In *o*-dichlorobenzene at 25 °C.

DCHN at 80 °C, using the simple model of reactions 1 and 3–6 with appropriate rate constants, show that the chain lengths are short at this temperature;¹⁴ the propagation rate constant of 0.2 M⁻¹ s⁻¹¹⁵ for (6) is not large relative to the termination (5) with $2k_t = 2 \times 10^6$ M⁻¹ s⁻¹.¹⁶

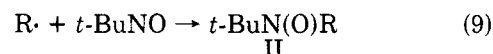
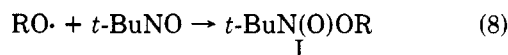
Our observation of much weaker chemiluminescence from DCPD than from DCHN in cyclohexane under N_2 is consistent with the greater separation of the $CyO\cdot$ radicals generated (eq 7), resulting in a smaller fraction of cage recombination.



ESR Studies

Cyclohexyloxy radicals, like other alkoxy radicals, cannot be observed by ESR spectroscopy in solution because the unpaired electron on oxygen is in an orbitally degenerate system and possesses a large orbital angular momentum about the C–O axis. This leads to strong spin–orbit coupling, a very anisotropic *g* tensor, and short spin-relaxation times.¹⁷ The ESR signal, already weak because of low steady-state radical concentrations, is broadened beyond detection over a wide range of the magnetic field.

We resorted, therefore, to the spin-trapping technique using nitroso-*tert*-butane (NTB, 2-methyl-2-nitrosopropane; Aldrich) as the radical scavenger.^{18,19} We chose this spin trap since we can easily distinguish between trapping an alkoxy radical (eq 8) or an alkyl radical (eq 9). Alkoxy radical adducts (I) are characterized by a nitrogen hyperfine splitting of about 28 G while adducts of alkyl radicals (II) have smaller nitrogen splittings of about 15 G.



In a series of experiments, equal volumes of an *o*-dichlorobenzene solution of NTB (0.02 M) and a freshly made *o*-dichlorobenzene solution of DCHN (0.02 M) were mixed under nitrogen in a glovebox. An aliquot of the

(14) The calculated chain lengths, defined as the moles of cyclohexane reacted per mole of radicals generated, were 1.2 and 1.5 for initial DCHN concentrations of 5×10^{-3} and 10^{-3} M, respectively. Rate constants used were $k_1 = 4.5 \times 10^{-3}$ s⁻¹ (this work), $k_3 = 1.8 \times 10^{-6}$ M⁻¹ s⁻¹ (this work), $k_4 = 10^9$ M⁻¹ s⁻¹, $k_5 = 10^6$ M⁻¹ s⁻¹, and $k_6 = 0.2$ M⁻¹ s⁻¹. For this calculation k_{1a} and k_2 were set to zero and $[O_2]$ was assumed to be 10^{-3} M.

(15) Estimated from $\log A = 9.4$ (per active hydrogen) and $E_a = 17.7$ kcal/mol for *tert*-BuO₂· + CyH (reported by: Korček, S.; Chenier, J. H. B.; Howard, J. A.; Ingold, K. U. *Can. J. Chem.* 1972, 50, 2285).

(16) McCarthy, R. L.; MacLachlan, A. *Trans. Faraday Soc.* 1961, 57, 1107.

(17) Symons, M. C. R. *J. Am. Chem. Soc.* 1969, 91, 5924.

(18) Perkins, M. J. *Adv. Phys.-Org. Chem.* 1980, 17, 1.

(19) Janzen, E. G. *Acc. Chem. Res.* 1971, 4, 31.

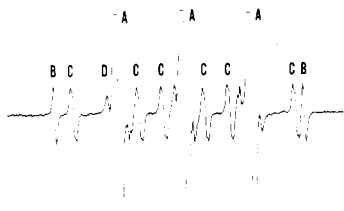
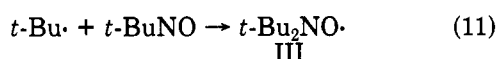
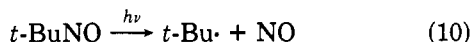


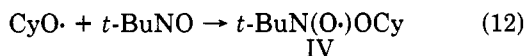
Figure 2. ESR spectrum obtained after heating at 50 °C for 1 min a solution of DCHN and NTB in *o*-dichlorobenzene. Lines labeled A–C are due to $(t\text{-Bu})_2\text{NO}\cdot$ (III), $t\text{-BuN}(\text{O}\cdot)\text{OCy}$ (IV), and $t\text{-BuN}(\text{O}\cdot)(\text{CH}_2)_5\text{CHO}$ (VI), respectively.

mixed solution in an ESR tube was heated in an oil bath for 1 min and then cooled quickly to ambient temperature by plunging it briefly into dry ice/acetone. The sample was handled in near darkness during this procedure to avoid the ready formation of di-*tert*-butyl nitroxide (III) by visible light^{18,19} (eq 10 and 11). A control experiment

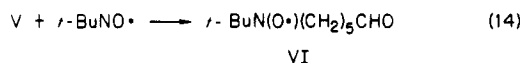
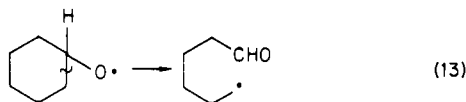


at 120 °C without the hyponitrite showed only traces of III, which were already present before the heating. Brief exposure to normal room light, however, brought out a strong three-line spectrum of III with clearly visible ¹³C satellites. (Spectral data are given in Table IV.)

The spectrum obtained with DCHN after 1 min at 50 °C is shown in Figure 2. The three strongest lines labeled A with $a(\text{N}) = 15.50$ G together with their ¹³C satellites (e.g., line D) clearly belong to III. The lines labeled B are part of a nitrogen triplet ($a(\text{N}) = 28.66$ G) whose central line is buried under the central A line. This spectrum belongs to the spin adduct of the cyclohexyloxy radical IV (eq 12). The lines labeled C are part of a nine-line trip-



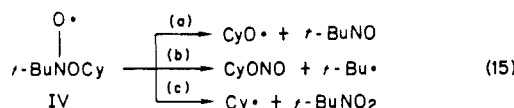
let-of-triplets pattern ($g = 2.00598$) of which three lines coincide almost exactly with A lines. The pattern arises from a hyperfine interaction with one nitrogen (15.38 G) and two equivalent protons (10.43 G) and is characteristic of a spin adduct of a primary alkyl radical, i.e. radical V formed by β -scission of the cyclohexyloxy radical and spin trapping (eq 13 and 14). The larger 1:2:1 triplet (10.43



G) is associated with the two protons of the CH₂ group attached to the nitrogen atom in VI, and the weak triplet (0.5 G) is associated with the protons of the next CH₂ group.

If the heating temperature is increased, VI grows markedly while IV decreases and can no longer be observed after 1 min at 100 °C. As is the case with other alkoxy radical adducts to NTB,¹⁸ IV is thermally unstable and decays at appreciable rates even at ambient temperature.

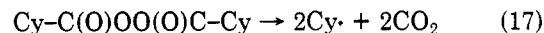
Three fragmentation modes (reaction 15) for IV can be considered.^{18,20} The formation of appreciable concentra-



tions of III in these experiments is consistent with the cleavage of the N–C bond to give cyclohexyl nitrite and a *tert*-butyl radical (path b) that is then trapped by NTB (reaction 11). Fission of the O–C bond to give a cyclohexyl radical (path c), on the other hand, can be excluded since no detectable amounts of VII were observed (eq 16). A



spectrum of VII uncontaminated by other radicals can be obtained by briefly heating in the dark at 50 °C a dilute benzene solution of dicyclohexyl carbonyl peroxide (0.01 M), a clean source of cyclohexyl radicals (eq 17), and NTB (0.01 M). It consists of a nitrogen triplet of 14.82 G further split into a group of at least nine incompletely resolved lines with an approximate splitting of 0.5 G.

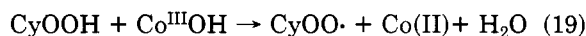
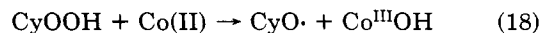


The instability of IV makes it very difficult to extract kinetic information from experiments in which CyO· is generated. The steady growth of lines C due to VI, as the thermolysis of DCHN is carried out at higher temperatures, is consistent with an increasing tendency of cyclohexyloxy radicals to undergo β -scission (reaction 13) at higher temperatures, in agreement with earlier studies on the fragmentation of other alkoxy radicals,²¹ and is consistent with a moderate activation energy for the cleavage reaction.

The CyO· radical can also be trapped by NTB in a variety of other reactions where this radical is formed. In all cases, increasing amounts of the primary alkyl radical V resulting from β -scission of cyclohexyloxy radicals are trapped if the reactions are carried out at higher temperatures. An example is the thermolysis of DCPD (reaction 7) in benzene under conditions similar to those described above.

Another example, of particular interest to the oxidation of cyclohexane, is the cobalt-catalyzed decomposition of cyclohexyl hydroperoxide. In a typical experiment, carried out with the usual precautions not to expose the NTB solution to room light or oxygen, 0.5 μL of cyclohexyl hydroperoxide is added to 1 mL of a benzene solution of NTB (0.01 M) in a 5-mm ESR tube. The resulting solution shows traces of III and IV when examined by ESR. After addition of 2 μL of an 0.02 M benzene solution of cobalt octoate, however, the spectra of III and IV increase in intensity by factors greater than 100. Only traces of VI are seen in the room-temperature experiment. The addition of the catalyst can be carried out at higher temperatures through a rubber septum, keeping the ESR tube in an oil bath. The reaction is quenched by plunging the tube briefly into dry ice/acetone. As the temperature increases, IV decreases while III and VI increase, in complete agreement with the results for the thermal decomposition of DCHN.

The cobalt-catalyzed decomposition of cyclohexyl hydroperoxide produces both cyclohexyloxy and cyclohexylperoxy radicals in the well-known Haber–Weiss catalytic cycle (eq 18 and 19).²² Additional CyO₂· radicals



are also formed in the ensuing radical chain decomposition

(20) Perkins, M. J.; Roberts, B. P. *J. Chem. Soc., Perkin Trans. 2* 1974, 297.

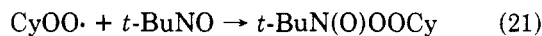
(21) Walling, C.; Clark, R. T. *J. Am. Chem. Soc.* 1974, 96, 4530.

(22) Sheldon, R. A.; Kochi, J. K. *Adv. Catal.* 1976, 25, 272.

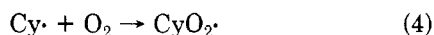
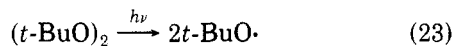
of the hydroperoxide (eq 20). No evidence was obtained



in the above experiment, however, for the trapping of $\text{CyO}_2\cdot$ radicals, presumably because their addition to NTB (eq 21) is followed very rapidly by the fission of the O-O bond with the formation of a diamagnetic 2-methyl-2-nitropropane and a cyclohexyloxy radical (eq 22).²³

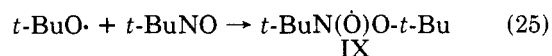


Cyclohexylperoxy radicals can be detected directly by photolysis in the ESR cavity at -100°C of an oxygen-saturated mixture of cyclohexane, di-*tert*-butyl peroxide, and cyclopropane (1:1:3, v/v/v). The latter is used as a low-temperature inert solvent; cyclohexane freezes at $+6^\circ\text{C}$. The reactions taking place are shown in eq 23, 24, and 4.



The spectrum of the cyclohexylperoxy radical at -120°C is a doublet of 4.0 G splitting with linewidths of 1.9 G and a g value of 2.0147. The doublet splitting is due to the hydrogen atom on the substituted carbon. When the light is shut off, the doublet decays slowly at -120°C but much more rapidly as the temperature is raised. Increasing the temperature also markedly broadens the lines. At 25°C only a single broad line with a width of 18 G can be observed, which decays instantaneously, no doubt by reaction 5, as the light is shut off. We also obtained the spectrum of ^{17}O -labeled cyclohexylperoxy radicals in an analogous experiment in which the solution was saturated with oxygen containing 43.9% $^{17}\text{O}^{18}\text{O}$ and 35.6% $^{18}\text{O}_2$. Two ^{17}O -labeled peroxy radicals can then be formed, i.e. $\text{Cy}^{17}\text{O}^{18}\text{O}\cdot$ (VIIIa) and $\text{Cy}^{18}\text{O}^{17}\text{O}\cdot$ (VIIIb). Accordingly, the spectrum showed two sets of ^{17}O satellite lines: one with relatively narrow linewidths and ^{17}O coupling of 18.1 G that we attribute to species VIIIa and one with much broader linewidths and 23-G coupling that we assign to species VIIIb.

The above experiments were repeated with added NTB spin trap ($\sim 0.01\text{ M}$). The visible light, which causes the decomposition of the spin trap,^{18,19} was removed by passing the light beam through a 5-cm cell containing a $\text{Co}(\text{SO}_4)_2/\text{Ni}(\text{SO}_4)_2$ aqueous solution. Surprisingly, under conditions that had led to substantial concentrations of cyclohexylperoxy radicals without NTB (irradiation at -100°C), only *t*-butoxy radicals were trapped. The same result was observed in a control experiment in which no cyclohexane was used. The spectrum of IX (eq 25) consists



of a nitrogen triplet with a splitting of 27.2 G and $g = 2.0053$. If the same sample was briefly exposed to UV light at room temperature, the spectrum of Figure 3A was obtained, showing a second wider nitrogen triplet of 29.04 G splitting and the same g factor (-100°C), clearly assignable to IV. We conclude that if a $\text{CyO}_2\cdot$ adduct to NTB is formed in this experiment, it can have only a fleeting

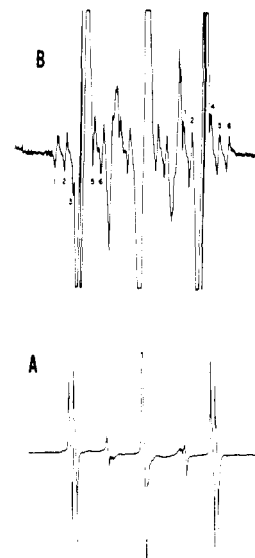


Figure 3. ESR spectra of oxygen-saturated solutions containing di-*tert*-butyl peroxide, NTB, cyclohexane, and cyclopropane, after brief exposure to UV light: (A) using normal O_2 ; (B) using O_2 enriched with ^{17}O .

existence. The most probable decomposition pathway is the cleavage of the O-O bond (eq 22) to produce $\text{CyO}\cdot$, which is subsequently trapped by the NTB. Cyclohexyloxy radicals might also be generated by the nonterminating reaction of two cyclohexylperoxy radicals (eq 26), though this reaction is not likely to be important at 25°C .



The above experiment with room-temperature illumination was repeated using oxygen enriched in ^{17}O . The spectrum obtained (Figure 3B) shows six ^{17}O satellite lines with a splitting of 4.3 G centered around the lines belonging to IV. As expected, no ^{17}O enrichment of the *tert*-butoxy spin adduct IX took place.

Kinetics of H Atom Abstraction by $\text{CyO}\cdot$

Nanosecond time-resolved excimer laser flash photolysis has been used to measure the absolute rate constants for hydrogen atom abstraction by cyclohexyloxy radical from -5 to $+40^\circ\text{C}$. Dicyclohexyl peroxide (DCHP) solutions in chlorobenzene were used as the source of cyclohexyloxy radicals. The optical spectrum of DCHP contains a weak, tailing absorption out to about 320–330 nm that is accessible by either the XeF (258-nm) or XeCl (308-nm) laser lines available with an excimer laser; in all of our experiments we used the XeCl excimer line. Because $\text{CyO}\cdot$ only weakly absorbs at short wavelengths, a probe had to be added that would compete for $\text{CyO}\cdot$ and produce an intermediate whose absorbance could be measured at longer wavelength.

The experimental method used here parallels that used by Scaiano et al.²⁴ for determining the absolute rates for the *tert*-butoxy radical. Dicyclohexyl peroxide is photolyzed by a 15-ns laser pulse in the presence of diphenylmethanol (DPM) and a second substrate (SH). Abstraction of a hydrogen from the α position of DPM produces the diphenylketyl radical, which absorbs strongly at 540 nm. Measurement of the rate of buildup of optical density at 540 nm after the laser pulse, as a function of [SH] at

(23) (a) Pfab, *J. Tetrahedron Lett.* 1978, 843. (b) Broekhoven, F. J. G.; Bolsman, Th. A. B. M.; de Boer, Th. *J. Recl. Trav. Chim., Pays-Bas* 1977, 96, 12.

(24) (a) Paul, H.; Small, R. D., Jr.; Scaiano, J. C. *J. Am. Chem. Soc.* 1978, 100, 4520. (b) Malatesta, V.; Scaiano, J. C. *J. Org. Chem.* 1982, 47, 1455. (c) Mendenhall, G. D.; Stewart, L. C.; Scaiano, J. C. *J. Am. Chem. Soc.* 1982, 104, 5109.

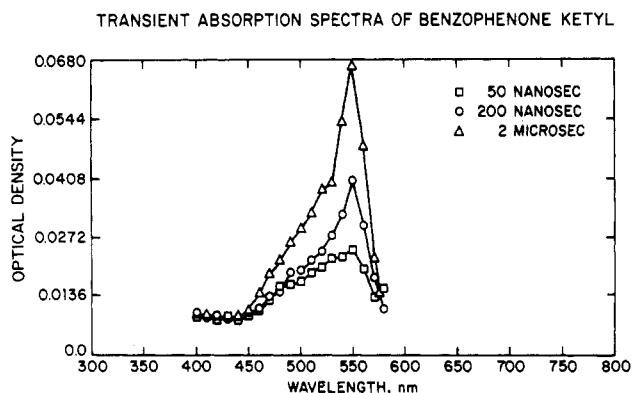


Figure 4. Transient absorption spectra of benzophenone ketyl at various times after the laser pulse.

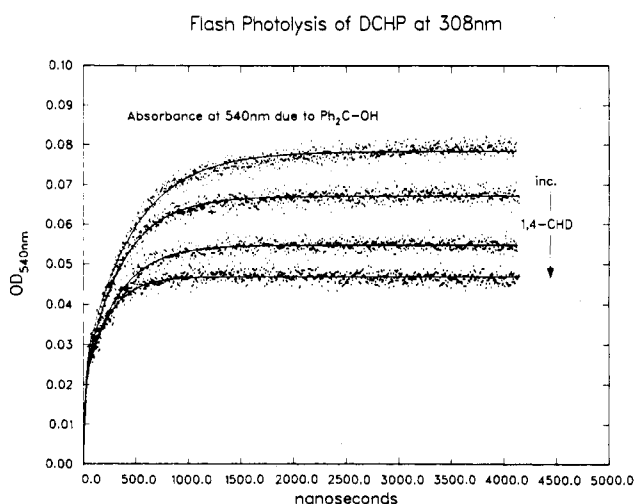


Figure 5. Family of transient curves for increasing 1,4-cyclohexadiene concentrations.

Table V. Bimolecular Rate Constants for the Reactions of the Cyclohexyloxy Radical

substr SH	k_2 (25 °C), $M^{-1} s^{-1}$	E_a , kcal/mol	A , $M^{-1} s^{-1}$
cyclohexane	$(8.0 \pm 1.5) \times 10^6$	3.2 ± 1.0	$(1.78 \pm 0.33) \times 10^8$
cyclohexanol	$(2.6 \pm 1.4) \times 10^6$	3.8 ± 1.7	$(1.61 \pm 0.89) \times 10^9$
1,4-cyclo- hexadiene	$(4.4 \pm 0.5) \times 10^7$		
diphenyl- methanol	$(7.9 \pm 0.4) \times 10^6$	4.1 ± 1.5	$(7.98 \pm 0.40) \times 10^9$
toluene	$(4.6 \pm 1.0) \times 10^6$	3.0 ± 1.0	$(7.26 \pm 1.62) \times 10^7$
cyclohexane- d_{12}	$(3.9 \pm 1.8) \times 10^6$	1.5 ± 1.0	$(4.88 \pm 2.19) \times 10^6$
toluene- d_3	$(9.4 \pm 1.9) \times 10^4$		

constant [DPM], gives an observed pseudo-first-order rate constant from which the bimolecular rate constant for the reaction of cyclohexyloxy and SH can be obtained (eq 27). The absorption spectrum can be generated by measuring the transient as a function of wavelength; that shown in Figure 4 and agrees with the reported spectrum of benzophenone ketyl.²⁵

$$k_{\text{obsd}} = (k_0 + k_2'[\text{DPM}]) + k_2[\text{SH}] \quad (27)$$

A typical family of transient curves in the presence of 1,4-cyclohexadiene is shown in Figure 5. Note that as the substrate concentration increases, the maximum OD value

Table VI. Absolute Rate Constants for Reaction of Oxy Radicals with Cyclohexadiene at 25 °C

oxy radical	k_2 , $M^{-1} s^{-1}$	ref
$t\text{-BuO}\cdot$	5.40×10^7	24a
$t\text{-BuO}\cdot$	$(4.32 \pm 0.17) \times 10^7$	this work
$\text{CyO}\cdot$	$(4.12 \pm 0.15) \times 10^7$	this work

Table VII. Amounts of Monobasic Acid Products and Dibasic Acid Products from Thermolysis of DCHP in Freon 113 at 160 °C

atm	monoalcohol ^a			dialcohol ^a HO(CH ₂) _x OH: x =		
	C ₄ OH	C ₅ OH	C ₆ OH	4	5	6
N ₂	8	6	58	0	0	3
O ₂	8	0	0	2	1	11

^a Numbers refer to relative GC peak areas for terminal alcohol products following exhaustive reduction of product solutions with LiAlH₄.

decreases. Analyzing these data according to eq 28, as shown in Figure 6, results in the data in Table V.

$$k_{\text{obs}} = k + k_2[\text{SH}] \quad k = k_1 + k_2'[\text{DPM}] \quad (28)$$

Table V shows that the rate constants for bimolecular hydrogen abstraction by $\text{CyO}\cdot$ fall in a narrow range of 10^5 – $10^7 M^{-1} s^{-1}$ for substrates ranging from the relatively unreactive cyclohexane to the highly reactive diphenylmethanol and 1,4-cyclohexadiene. The measured activation energies are all rather small, about 3 kcal/mol, giving an increase in rate constant in going from 25 to 150 °C of only a factor of 4.4.

On a molecular basis (not corrected for the number of hydrogens), cyclohexanol reacts twice as fast as cyclohexane with $\text{CyO}\cdot$. From calculations of heats of reaction for the abstraction of hydrogen from cyclohexane ($\Delta H_r = -10.2$ kcal/mol) and from the non- α positions of cyclohexanol ($\Delta H_r = -10.0$ kcal/mol),²⁶ we expect these two types of hydrogens to be about equally reactive. Therefore, after correcting for the number of hydrogens, we find that the α -hydrogen of cyclohexanol is about 10 times more reactive than the other hydrogens in the molecule. From a selectivity standpoint then, the chance of reaction at the α position (to give monosubstituted product) is equal to the probability of reaction at all other positions in the molecule (to give disubstituted products).

The small deuterium kinetic isotope effects measured for cyclohexane and toluene of about 3–4 suggest a non-symmetrical transition state. The Hammond rule states that reactions with low activation energies have transition states early on the reaction coordinate (reactant-like) and that those with high activation energies have transition states late on the reaction coordinate (product-like).²⁷ Thus, the combination of kinetic isotope effect and activation energies leads us to believe that hydrogen abstractions by $\text{CyO}\cdot$ have early transition states.

The conclusions reached above for $\text{CyO}\cdot$ agree with conclusions in the literature for *tert*-butoxy radical.²⁴ Small but possibly significant differences in the rate constants reported for *tert*-butoxy and those found here for $\text{CyO}\cdot$ led us to repeat the determination of k_2 for 1,4-cyclohexadiene with *tert*-butoxy with our experimental

(26) (a) Benson, S. W. "Thermochemical Kinetics", 2nd ed.; Wiley: New York, 1976. (b) Kerr, J. A. *Chem. Rev.* 1966, 66, 465.
(27) Hammond, G. S. *J. Am. Chem. Soc.* 1955, 77, 334.

(25) Beckett, A.; Porter, G. *Trans. Faraday Soc.* 1963, 59, 2038.

Table VIII. Decomposition Reaction Products from Thermolysis of CyOOCy (DCHP), CyON=NOCy (DCHN), and CyOC(O)OOC(O)OCy (DCPD) in Cyclohexane

compd (concn, M)	no. of sep ^a atoms	temp, °C	time, ^b h	reactn products, M				
				K	A	DCHP	CyCy	K/A
DCPD (0.094)	4	80	1	0.0056	0.16	trace	0.022	0.035
DCHN (0.098)	2	80	1	0.014	0.17	0.004	0.026	0.082
DCHN (0.048)	2	150	1	0.009	0.050		0.006	0.18
DCHP (0.048)	0	150	4	0.009	0.029			0.31

^aThe number of atoms separating incipient CyO· radicals. ^bExperiments carried out in 10-cm³ glass tubes sealed under vacuum.

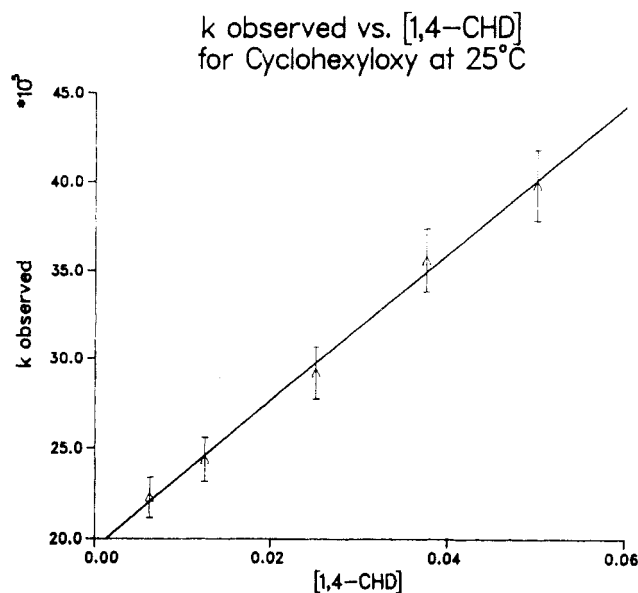
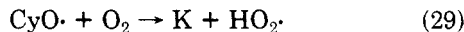


Figure 6. The value of k_{obsd} as a function of 1,4-cyclohexadiene concentration for hydrogen abstraction by CyO· at 25 °C.

apparatus. Previous results have indicated that calibration differences from one apparatus to another are significantly higher than the local precision that can be achieved.²⁸ Our results (Table VI) indeed indicate that k_2 for cyclohexyloxy and *tert*-butoxy are identical within experimental error.

Product Studies

Several aspects of the chemistry of CyO· radicals in solution were considered. In addition to H-atom abstraction (3), disproportionation to give K and A (eq 1a and 2), and β cleavage to give ring-opened ω -formyl radical V (13), two additional possible reactions were examined. These were attack of O₂ on CyO· (29) and dimerization to give DCHP (30).



A series of reactions was carried out involving the generation of CyO· radicals in F-113 solvent by thermolysis of 1% DCHP at 160 °C under either N₂ or 500 psi O₂. The major products under N₂, K and A, indicated that >90% of the reactions involved disproportionation (2) or H-atom abstraction from starting materials or products. The dependence of K/A ratios on the presence of O₂ was large, K/A = 1/4 (under N₂) vs. K/A = 13/1 and K/A = 17/1 (duplicate experiments with 500 psi O₂ in F-113). Control experiments were run using DCHP in F-113 but also containing 0.25% cyclopentyl alcohol. As expected, no cyclopentanone was formed under N₂. Under 500 psi O₂, however, about 80% of the cyclopentanol was converted to cyclopentanone. The corresponding high cyclo-

hexanone/cyclohexanol ratios can thus be explained by autoxidation of A, without invoking O₂ attack on CyO· radicals by reaction 29. The presence of O₂ also affected the distribution of ring-opened aldehydic and acidic products.¹⁰ Results of GC analysis showed that predominantly monobasic acids and aldehydes formed under N₂, whereas mostly dibasic products formed under O₂ (Table VII).

The effect of the number of atoms separating potential CyO· radicals was briefly examined with DCHP (0 atoms), DCHN (2 atoms), and DCPD (4 atoms) (Table VIII). As expected, the amounts of cage products—DCHP and K—were less from DCPD than from DCHN at 80 °C. Also, the amount of noncage product Cy-Cy was greater for DCHN than for DCHP, at 150 °C; the higher K/A ratio for DCHP reflects a greater fraction of disproportionation of CyO· radicals when generated right next to each other in the solvent cage.

Experimental Section

Instrumentation. ¹H and ¹³C NMR spectra were recorded on a Nicolet NMC360WB or Bruker WH-90 spectrometer. ESR measurements were made on a Bruker ER420 spectrometer. Chemiluminescence measurements were done using an EMI Gencom, Inc., type S-11 photomultiplier tube operated at -1.25 kV dc, in turn connected to a variable-voltage amplifier for signal recording. GC analyses were performed on a Varian Model 3700 instrument equipped with a flame ionization detector and either a 25-M Carbowax 20M glass capillary column or a 2m 1/4 in. glass column packed with Supelco Inc., 10% SP-1220, acid washed, on Chromasorb W-HP 80/100.

Warning! Dialkyl hyponitrites, alkyl hydroperoxides, and dialkyl peroxides can decompose vigorously and exothermically and should be handled with care in small amounts.

Preparation of Dicyclohexyl Hyponitrite (DCHN).³⁰ Freshly dried silver hyponitrite³¹ (3.2 g, 0.012 mol) was added as a powder over 5 min to an ice-cooled stirred solution of cyclohexyl iodide (4.86 g, 0.023 mol) in 10 mL of hexane. Stirring was continued for 4 h as the mixture warmed to room temperature. The resulting suspension was filtered with the aid of additional hexane (5.44 g of AgI recovered, 100% theoretical) and cooled to -78 °C to give crystalline dicyclohexyl hyponitrite. After recrystallization, 0.365 g (14%) of dicyclohexyl hyponitrite was recovered. ¹H NMR (300 MHz): 4.25 (1 H), 1.95 (2 H); 1.75 (2 H), 1.30 (3 H), 1.15 (3 H). ¹³C NMR: 81.08 (C1), 31.37 (C2C6), 25.23 (C4), 23.49 (C3C5) ppm. IR: 1454 (m), 1366 (m), 1045 (m), 1017 (m), 998 (s) cm⁻¹. CI-MS: (M⁺) *m/e* 226.

Preparation of Cyclohexyl Hydroperoxide. Cyclohexyl hydroperoxide can be prepared by reaction of cyclohexylmagnesium chloride with O₂, according to the procedure of Walling.³²

Preparation of Dicyclohexyl Ether. Dicyclohexyl ether was prepared by hydrogenation of diphenyl ether using 5% Ru on carbon as catalyst at 100 °C and 7500 psi H₂.

Preparation of Dicyclohexyl Peroxides. Dicyclohexyl peroxide was purified from partially oxidized cyclohexane. Briefly,

(30) Mendenhall, G. D., private communication. For potential hazards with dialkyl hyponitrites, cf. ref 4.

(31) (a) Mendenhall, G. D. *J. Am. Chem. Soc.* 1974, 96, 5000. (b) Partington, J. R.; Shah, C. C. *J. Chem. Soc.* 1932, 2589.

(32) Walling, C.; Buckler, S. A. *J. Am. Chem. Soc.* 1953, 75, 4372.

(28) Turro, N. J.; Lehr, G. F.; Butcher, J. A.; Moss, R. A.; Gao, W. J. *Am. Chem. Soc.* 1982, 104, 1754.

(29) Scaiano, J. C. *J. Am. Chem. Soc.* 1980, 102, 7747.

after extraction with caustic and vacuum distillation at $\sim 70^\circ\text{C}$ (0.1 mm), the crude product was recrystallized twice from methanol at -78°C . The resulting sample was pure by packed column GC and by both ^1H and ^{13}C NMR. ^1H NMR (300 MHz): 3.90 (1H), 1.95 (2H), 1.75 (2H), 1.1-1.6 ppm (6H). ^{13}C NMR: 80.86 (C1), 30.53 (C2C4), 25.66 (C6), 23.77 (C3C5). DCHP can also be prepared by reaction of KO_2 with cyclohexyl toluenesulfonate.³³

Laser Flash Photolysis Experiments. Flash experiments were performed essentially as described by Scaiano et al.^{24,29} Transients were collected by means of a RCA Model 4840 photomultiplier operated at -900 V dc and terminated into 50 ohms at the input of a Tektronix Model 7912AD transient digitizer. A differential amplifier was used to allow expansion and offsetting of weak signals so that maximum digital resolution was possible. A total of 1024 channels of data was collected at a scan rate of 5 ns/channel. Individual, single-shot transients were transferred to the DEC-MINC computer and subsequently averaged, analyzed,

plotted, and transferred to a DECSYSTEM-10 computer for storing and further analysis.

Samples for flash photolysis were prepared from stock solutions by serial dilution into 1 cm by 1 cm fluorescence cells with graded seals. The samples were degassed with an argon purge for 20-30 min at 0°C and sealed by means of serum stoppers. The concentration of DCHP was no higher than 10 v/v%, which gave an OD at 308 nm of 1.0.

Diphenylmethanol was triply sublimed and used promptly after purification. Chlorobenzene was used as received and gave equivalent results to freshly distilled material. 1,4-Cyclohexadiene was used as received. Other reagents were of the highest purity available and were generally distilled prior to use.

Acknowledgment. We are indebted to G. D. Mendenhall for an initial sample of DCHN and for instructions for its synthesis prior to publication. We are also grateful to a reviewer for pointing out the likelihood of autoxidation of A to K as the explanation of the high K/A ratios observed when DCHP was decomposed under 500 psi O_2 .

(33) Druliner, J. D. *Synth. Commun.* 1983, 13, 115.

New Routes to Hexafluorocyclopentadiene and Related Compounds¹

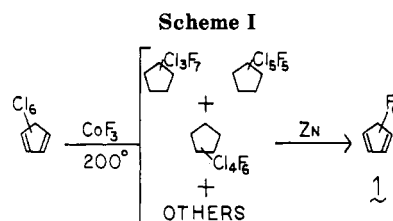
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Received August 20, 1985

Hexafluorocyclopentadiene (1) has been synthesized in two steps from pentafluorophenol (2) by fluorination followed by flash vacuum pyrolysis of the resulting hexafluorocyclohexadienones 3 and 4. Similar pyrolysis of 6-chloropentafluorocyclohexadienone (13) gave an equilibrium mixture of 1- and 2-chloropentafluorocyclopentadiene (15 and 16), presumably via the 5-chloro isomer. Flash vacuum pyrolysis of tetrafluoro-*o*-benzoquinone (17) yielded tetrafluorocyclopentadienone (20). Hexafluorocyclopentadiene was also prepared via a ring-expansion route which entailed cycloaddition (accompanied by rearrangement) of bromotrifluoroethylene to tetrafluorocyclopropene followed by reductive debromofluorination.

As a versatile diene in the Diels-Alder reaction, hexafluorocyclopentadiene (1) is an important basic building block in organofluorine chemistry.² The compound was first synthesized by Banks, Haszeldine, and Walton in 1963,³ and it has been prepared subsequently by a variety of methods.⁴⁻⁶ With the exception of a modified version of the original synthesis,^{2c,e} all of these routes give low yields. The Banks approach, shown in Scheme I, entails fluorination of hexachlorocyclopentadiene over cobaltic fluoride at 200°C , fractionation of the product, and dechlorination with zinc of the tetrachloro fraction. Recycling of other fractions from the fluorination is required to obtain good yields (up to 42% overall). The appa-



ratus required for the fluorination is a stirred-bed steel reactor which is available in very few laboratories. We were thus stimulated to seek a route to hexafluorocyclopentadiene which is simple, efficient, and capable of execution in an ordinary laboratory. Though there remains room for improvement, we have developed an attractive alternative to the Banks synthesis.

Whereas all previous approaches to hexafluorocyclopentadiene have proceeded from starting materials having five-membered rings, we began with pentafluorophenol. This compound is quite expensive, but it is easily prepared from the much cheaper hexafluorobenzene in yields exceeding 90%.⁷ The key idea for this synthesis was suggested by work of DeJongh's group, who found that high-temperature flow pyrolysis of *o*-benzoquinone⁸ and

(1) This paper is based on the Ph.D. Dissertations of R. R. Soelch (1984) and G. M. Mauer (1983), Dartmouth College.

(2) (a) Banks, R. E.; Haszeldine, R. N.; Prodgers, A. *J. Chem. Soc., Perkin Trans. 1* 1973, 596-598. (b) Banks, R. E.; Birks, L. E.; Haszeldine, R. N. *J. Chem. Soc. C* 1970, 201-203. (c) Banks, R. E.; Bridge, M.; Haszeldine, R. N. *Ibid.* 1970, 48-49. (d) Banks, R. E.; Harrison, A. C.; Haszeldine, R. N.; Orrell, K. G. *Ibid.* 1967, 1608-1621. (e) Banks, R. E.; Harrison, A. C.; Haszeldine, R. N. *Ibid.* 1966, 2102-2106. (f) Banks, R. E.; Harrison, A. C.; Haszeldine, R. N. *J. Chem. Soc., Chem. Commun.* 1966, 338-339. (g) Banks, R. E.; Harrison, A. C.; Haszeldine, R. N. *Ibid.* 1965, 41-42.

(3) Banks, R. E.; Haszeldine, R. N.; Walton, J. B. *J. Chem. Soc.* 1963, 5581-5583.

(4) Moore, E. P. U.S. Patent 3686336, 1972; *Chem. Abstr.* 1973, 78, P3832u.

(5) Harris, J. F., Jr. U.S. Patent 3449304, 1969.

(6) Burdon, J.; Hodgins, T. M.; Perry, D. R. A.; Stephens, R.; Tatlow, J. C. *J. Chem. Soc.* 1965, 808-810.

(7) National Polychemicals, Inc. Br. Patent 887691, 1962; *Chem. Abstr.* 1962, 56, 11788e.

(8) DeJongh, D. C.; Van Fossen, R. Y.; Bourgeois, C. F. *Tetrahedron Lett.* 1967, 271-275.