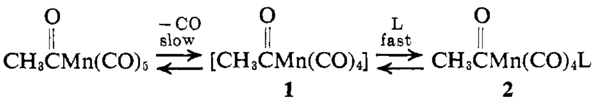
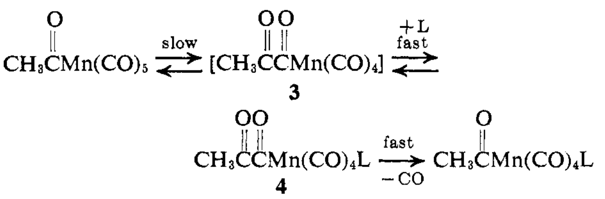
to occur by a methyl-migration mechanism.[1] Presumably, the reaction of other nucleophiles with $CH_3Mn(CO)_5$ to give $CH_3COMn(CO)_4L$ (**2**) also proceeds by a methyl-migration mechanism. On the other hand, reaction of triphenylphosphine with $CH_3COMn(CO)_5$, which follows first-order kinetics, has been proposed to occur by a dissociative mechanism, (1), involving the coordinately unsaturated intermediate **1**.[2] However, an acetyl migration mechanism, (2), analogous to the methyl-migration mechanism and involving the unsaturated pyruvoyl species **3**, is also in agreement with previous data.[1,3,4] The observation that $CH_3{}^{13}COMn(CO)_5$ reacts with $P(C_6H_5)_3$ to give $CH_3{}^{13}COMn(CO)_4P(C_6H_5)_3$ rules out a mechanism involving slow decarbonylation to give $CH_3Mn(CO)_5$ which then rapidly reacts with ligand to give $CH_3COMn(CO)_4L$. The direct displacement of CO by the entering ligand is, of course, inconsistent with the observed first-order kinetics.



$$\mathrm{CH_3\overset{\overset{O}{\|}}{C}Mn(CO)_5} \xrightleftharpoons{\substack{-\mathrm{CO}\\ \text{slow}}} \underset{\mathbf{1}}{[\mathrm{CH_3\overset{\overset{O}{\|}}{C}Mn(CO)_4}]} \xrightleftharpoons{\substack{\mathrm{L}\\ \text{fast}}} \underset{\mathbf{2}}{\mathrm{CH_3\overset{\overset{O}{\|}}{C}Mn(CO)_4L}} \quad (1)$$



$$\mathrm{CH_3\overset{\overset{O}{\|}}{C}Mn(CO)_5} \xrightleftharpoons{\text{slow}} \underset{\mathbf{3}}{[\mathrm{CH_3\overset{\overset{O}{\|}}{C}\overset{\overset{O}{\|}}{C}Mn(CO)_4}]} \xrightleftharpoons{\substack{+\mathrm{L}\\ \text{fast}}}$$

$$\underset{\mathbf{4}}{\mathrm{CH_3\overset{\overset{O}{\|}}{C}\overset{\overset{O}{\|}}{C}Mn(CO)_4L}} \xrightarrow[-\mathrm{CO}]{\text{fast}} \mathrm{CH_3\overset{\overset{O}{\|}}{C}Mn(CO)_4L} \quad (2)$$

In studying the possibility of mechanism 2, we have prepared $CH_3COCOMn(CO)_5$ (**4**, L = CO). Pyruvoyl chloride[5] (6.4 g, 60 mmol) reacted with $NaMn(CO)_5$ (95 ml, 0.62 *M*, 60 mmol) at 0° in tetrahydrofuran under a nitrogen atmosphere to produce a red solution. Evaporation of the solution to dryness followed by sublimation at 25° (0.2 mm) gave a red solid which was further purified by recrystallization from pentane–ether at −78°. The red solid is shown to be pyruvoylpentacarbonylmanganese (**4**, L = CO) (5.27 g, 33% yield, mp 76–77°) by spectral data. The ir spectrum in heptane has three metal carbonyl bands at 2116 (m), 2021 (s), and 2006 cm^{-1} (s) expected for a $Mn(CO)_5$ fragment and two carbonyl bands at 1718 and 1640 cm^{-1} attributed to the two carbonyls of the pyruvoyl group. The nmr spectrum in benzene is a single sharp singlet at δ 1.63. The uv–visible spectrum contains three maxima at 218 (ϵ 31,200), 255 (shoulder, ϵ 12,000), and 477 mμ (ϵ 62). The red color is apparently due to the pyruvoyl chromophore since $CH_3COMn(CO)_5$ shows no long-wavelength absorption, but biacetyl, a yellow compound, has a λ_{max} at 420 mμ (ϵ 19).[6] The mass spectrum (70 eV) contained no parent ion; the most intense peaks in the spectrum were *m/e* (relative intensity) 223 (12), 195 (17), 167 (13), 139 (23), 111 (28), 98 (21), 83 (35), 70 (11), 55 (98), 43 (30), 28 (100). *Anal.* Calcd for $C_8H_3O_7Mn$: C, 36.09; H, 1.13; Mn, 20.68. Found: C, 36.38; H, 1.38; Mn, 20.3

The thermal decomposition of $CH_3COCOMn(CO)_5$ in benzene has been studied by nmr using *p*-di-*tert*-butylbenzene as an internal standard. When the decomposition is carried out in a sealed tube, the products of the reaction are an equilibrium mixture of $CH_3COMn(CO)_5$ and $CH_3Mn(CO)_5$. The decomposition of $CH_3COCOMn(CO)_5$ follows first-order kinetics to over 87% reaction. At 75°, the rate of decomposition of $CH_3COCOMn(CO)_5$ is 21 times slower than the rate of decarbonylation of $CH_3COMn(CO)_5$ in benzene (Table I). The isolation of $CH_3COCOMn(CO)_5$ as a stable compound indicates that structures of this type cannot be intermediates in the substitution reactions of $CH_3COMn(CO)_5$.

Table I. Decarbonylation of Pyruvoylpentacarbonylmanganese[a]

Compound	Rate constant, sec^{-1}	Temp, °C[b]
$CH_3COCOMn(CO)_5$[c]	8.63×10^{-5}	69.0
$CH_3COCOMn(CO)_5$[c]	1.05×10^{-4}	73.0
$CH_3COCOMn(CO)_5$[c]	2.05×10^{-4}	79.5
$CH_3COCOMn(CO)_5$[c]	5.56×10^{-4}	88.0
$CH_3COMn(CO)_5$[d]	2.88×10^{-3}	75.0

[a] All rates were measured in benzene. [b] Temperatures were estimated from the nmr peak separations of ethylene glycol and are accurate to ±0.5°. [c] $\Delta H^{\ddagger} = 25.5 \pm 1$ kcal, $\Delta S^{\ddagger} = -3.4 \pm 2.9$ eu at 79.5°. [d] Rate determined by nmr analysis of aliquots taken from an open system periodically flushed with nitrogen.

An attempt to prepare $CH_3COCOMn(CO)_5$ by carbonylation of $CH_3COMn(CO)_5$ at 258 atm of CO and 80° for 9 hr failed.

Charles P. Casey,* Charles A. Bunnell
Department of Chemistry, University of Wisconsin
Madison, Wisconsin 53706

Received May 6, 1971

A Convenient General Synthesis of Alkyl Hydroperoxides *via* Autoxidation of Organoboranes

Sir:

The low-temperature autoxidation of organoboranes in tetrahydrofuran (THF) solution leads to a diperoxyborate. Following treatment with aqueous hydrogen peroxide, the corresponding alkyl hydroperoxides can be obtained in excellent yield.

Organoboranes undergo a facile autoxidation which may be stoichiometrically controlled to give essentially quantitative conversion into alcohols.[1] The reaction proceeds through the chain-carrying alkylperoxy radicals[2] (eq 1–3). This initial oxidation produces a peroxide, which may either react with a second mole of oxygen (eq 4) or undergo an intermolecular redox reaction[3] (eq 5). In concentrated solutions (~0.5 *M*)

$$R_3B + O_2 \longrightarrow R\cdot + R_2BO_2\cdot \qquad (1)$$

$$R\cdot + O_2 \longrightarrow RO_2\cdot \qquad (2)$$

$$RO_2\cdot + R_3B \longrightarrow RO_2BR_2 + R\cdot \qquad (3)$$

$$RO_2BR_2 + O_2 \longrightarrow (RO_2)_2BR \qquad (4)$$

$$RO_2BR_2 + R_3B \longrightarrow 2ROBR_2 \qquad (5)$$

---

(3) F. Calderazzo and F. A. Cotton, *Chim. Ind.* (*Milan*), **46**, 1165 (1964).

(4) F. Calderazzo and K. Noack, *Coord. Chem. Rev.*, **1**, 118 (1966).

(5) The solution of pyruvoyl chloride in ether was prepared from pyruvic acid and thionyl chloride and contained a small amount of thionyl chloride: P. Carré and P. Jullien, *C. R. Acad. Sci.*, **202**, 1521 (1936).

(6) J. G. Calvert and J. N. Pitts, Jr., "Photochemistry," Wiley, New York, N. Y., 1966, p 422.

(1) H. C. Brown, M. M. Midland, and G. W. Kabalka, *J. Amer. Chem. Soc.*, **93**, 1024 (1971).

(2) A. G. Davies and B. P. Roberts, *J. Chem. Soc. B*, 311 (1969).

(3) S. B. Mirviss, *J. Org. Chem.*, **32**, 1713 (1967).

the intermolecular reaction predominates at 0° and there is a substantial loss of peroxide content.

Control over reactions 4 and 5 would provide a useful route to alkyl hydroperoxides. Indeed, the intermolecular reaction has been minimized by using highly dilute solutions (0.01–0.05 *M*). Oxygen (2 mol) is absorbed to form a diperoxide (eq 4). The remaining boron–carbon bond was then oxidized by the addition of an oxidizing agent such as perbenzoic acid.[4]

Consequently, the autoxidation of dilute solutions of organoboranes provides a possible synthesis for alkyl hydroperoxides.[5] However, the procedure suffers from several difficulties. Thus, this synthesis utilizes huge volumes of solvent. Oxidation of the organoboranes in such dilute solutions is somewhat sluggish, so that relatively long reaction times are required. Furthermore, use of water-immiscible solvents[4] also requires utilization of less convenient oxidizing systems compatible with these solvents, such as peracids, or hydrogen peroxide dissolved in *tert*-butyl alcohol. It would be much more convenient if the synthesis could be realized using relatively concentrated solutions of the organoborane in THF, the preferred hydroboration solvent.[6]

Examination of the autoxidation of organoboranes using 0.5 *M* THF solutions has revealed that the reaction can be controlled to achieve a quantitative yield of the alcohol following treatment with sodium hydroxide at 0°.[1] Examination of the oxidation of such solutions at −78°, using the automatic gas generator[7] adapted for oxygen production,[1] revealed that the reaction is initially very fast, even at this low temperature. The first mole of oxygen is absorbed within 2–3 min. Organoboranes produced from internal disubstituted olefins, such as cyclohexene, continue to absorb oxygen, absorbing a second mole over a period of 1 hr. On the other hand, organoboranes produced from terminal olefins, such as 1-butene, fail to absorb the second mole of oxygen at this temperature. In both cases, however, warming to 0° results in the rapid absorption of a second mole of oxygen. Addition of sodium hydroxide at this point then causes oxidation of the remaining boron–carbon bond by one of the peroxide linkages (eq 6). However, addition of a 30% aqueous solution of hydrogen peroxide to the reaction mixture at 0° liberates the alkyl hydroperoxide with concurrent oxidation of the remaining boron–carbon bond (eq 7). The alkyl hydroperoxide present in the intermediate is thus recovered without loss.

$$RB(O_2R)_2 + HO^- + 2H_2O \longrightarrow 2ROH + ROO^- + B(OH)_3 \quad (6)$$

$$RB(O_2R)_2 + H_2O_2 + 2H_2O \longrightarrow ROH + 2RO_2H + B(OH)_3 \quad (7)$$

The above procedure provides the alkyl hydroperoxides in THF solution in a molar ratio of RO_2H:ROH of 2:1. For many purposes, such mixtures of hydroperoxide and alcohol may be used directly. However, if it is desirable to separate and to isolate the pure hydroperoxide, this is readily done by treating the above solution with excess aqueous potassium hydroxide. The potassium salt of the hydroperoxide dissolves in the aqueous phase leaving the alcohol behind in the organic phase. Acidification of the aqueous phase provides the pure hydroperoxides.[8,9]

The reaction was applied to a representative series of olefins with excellent results (Table I).

Table I. The Formation of Alkyl Hydroperoxides *via* Autoxidation of Organoboranes

		Product	
Olefin in R_3B[a]	Time,[b] min	% yield[c]	Hydroperoxide
1-Butene	20	92	1-Butyl
1-Octene	20	81	1-Octyl
2-Methyl-1-pentene	360	90	2-Methyl-1-pentyl
2-Butene	60	91	2-Butyl
Cyclopentene	45	95	Cyclopentyl
1-Methylcyclopentene	60	91	2-Methylcyclopentyl[d,f]
Cyclohexene	60	95	Cyclohexyl
Norbornene	75	84	Norbornyl[e,f]

[a] 10 mmol of R_3B in 20 ml of THF. [b] Time for absorption of 2.0 mol of O_2/R_3B. [c] By iodometric titration, based on a maximum of 2 mol of RO_2H/R_3B. [d] The product contained 64% trans and 36% cis isomer. [e] The product contained 80% exo and 20% endo isomer. [f] The stereochemistry was determined by analysis of the alcohol obtained after reduction of the hydroperoxide with $LiAlH_4$.

The following procedure for the preparation of cyclohexyl hydroperoxide is representative. A dry 200-ml flask equipped with a septum inlet and a magnetic stirrer with a Teflon collar was flushed with nitrogen. The flask was charged with 75 ml of dry THF and 12.3 g of cyclohexene (150 mmol) and then cooled to 0°. Hydroboration was achieved by the dropwise addition of 16.3 ml of a 3.07 *M* solution of borane in THF (150 mmol of hydride) followed by heating at 50° for 3 hr to complete the hydroboration of this relatively sluggish olefin. (Methanol, 1.0 ml, was added to facilitate the solution of 10 mmol of tri-*n*-octylborane.) The solution was cooled to −78° and attached to the automatic oxygenator which had been previously flushed with oxygen (inject 15 ml of 30% hydrogen peroxide into the generator with an empty 100-ml flask in place of the reaction flask). The system was further flushed by injecting 5 ml of 30% hydrogen peroxide into the generator. The stirrer was started and oxygen absorption was followed by reading the buret filled with standardized 3% aqueous hydrogen peroxide. In the case of terminal olefins, the solution was warmed to 0°, following the absorption of the first mole of oxygen, to complete the oxidation. With internal olefins, the oxidation was continued at −78° until absorption of oxygen stopped. The solution was then warmed to 0° with stirring. After the absorption of 2 mol of oxygen had been completed, 16.5 ml of 30% aqueous hydrogen peroxide was added dropwise. The solution was stirred at 0° for 0.5 hr. Hexane (50 ml) was then added and the solution was washed with 25 ml of water. Iodometric titration for hydroperoxide[10] gave a 95% yield.

---

(4) M. H. Abraham and A. G. Davies, *J. Chem. Soc.*, 429 (1959).

(5) G. Wilke and P. Heimbuch, *Justus Liebigs Ann. Chem.*, **652**, 7 (1962).

(6) H. C. Brown, "Hydroboration," W. A. Benjamin, New York, N. Y., 1962.

(7) C. A. Brown and H. C. Brown, *J. Amer. Chem. Soc.*, **84**, 2829 (1962). We utilized a commercial model of the hydrogenator available from Delmar Scientific Laboratories, Maywood, Ill. 60154.

(8) C. Walling and S. A. Buckler, *J. Amer. Chem. Soc.*, **77**, 6032 (1955).

(9) H. R. Williams and H. S. Mosher, *ibid.*, **76**, 2984, 2987 (1954).

(10) S. Siggia, "Quantitative Analysis *via* Functional Groups," Wiley, New York, N. Y., 1949.

The hydroperoxide was separated from the alcohol by extracting the hydroperoxide from the THF–hexane solution with four 25-ml portions of 40% potassium hydroxide. The combined aqueous extracts were washed with 50 ml of hexane and then neutralized at 0° with concentrated hydrochloric acid. The hydroperoxide was then recovered with 50 ml of hexane. The hexane was separated, dried ($MgSO_4$), and removed. There was recovered 9.5 g (82%) of cyclohexyl hydroperoxide, bp 39–40° (0.08 mm), n^{20}D 1.4645 (lit.[5] bp 42–43° (0.1 mm), n^{20}D 1.4645).

The low-temperature autoxidation of organoboranes provides a rapid, convenient synthesis of alkyl hydroperoxides. The reaction is applicable to a wide variety of derivatives. Unlike the reaction of alkyl methanesulfonates with hydrogen peroxide, which produces hydroperoxides in 10–50% yield,[9] the present procedure readily accommodates substrates which do not readily undergo nucleophilic substitution, such as cyclohexyl and norbornyl. The organoborane route also accommodates a wide variety of functional groups. Consequently, the present procedure is both convenient and broadly applicable, providing a wide variety of alkyl hydroperoxides.

(11) National Science Foundation Predoctoral Fellow.

Herbert C. Brown,* M. Mark Midland[11]
Richard B. Wetherill Laboratory, Purdue University
Lafayette, Indiana 47907

Received May 28, 1971

Electrophilic Attack at the Porphyrin Periphery

Sir:

Many examples are known of electrophilic attack at the periphery of the porphyrin nucleus.[1–3] While substitution is more facile at the β than the meso positions, attack at meso positions does occur when the β positions are blocked. It has been reported[4] that metalloporphyrins are more susceptible to electrophilic attack than are the metal-free compounds, and this has been explained by such hypotheses as dπ–pπ overlap between metal and nitrogen orbitals, stabilizing an otherwise dearomatized transition state,[5] or that bis N-protonation strongly deactivates the metal-free porphyrin to further electrophilic attack by simple electrostatic repulsion.[4] In particular it was found that in metal-free octaethylporphyrin (OEP) exchange of meso protons in neat deuteriotrifluoroacetic acid (DTFA) occurred with a half-life of 275 hr, at 90°,[6] whereas the Fe(III), Cu(II), and Pt(II) complexes of OEP underwent almost complete exchange in 1:1 DTFA–$CHCl_3$ at room temperature within 20 min, while other metalloporphyrins, such as Co(III) aetioporphyrin, showed either no exchange or demetalation under these conditions.[4] In our experience, trifluoroacetic acid which has not been carefully purified and deoxygenated rapidly effects oxidation of Co(III) porphyrins to their π-cation radicals,[7] and in order to reassess and quantitate electrophilic attack at the meso positions of porphyrins, we have examined the rate of deuterium incorporation into various octaalkyl porphyrins in refluxing deuterioacetic acid.

In this solvent the rates are sufficiently slow to be conveniently measured, and unwanted side reactions such as demetalation and oxidation to π-cation radicals do not occur. Deuterium uptake was followed by high-resolution mass spectrometry, and the ratios of each of the successively meso-deuterated species were determined from the relative intensities of the parent peaks, using appropriate corrections for metal isotopes, ^{13}C, ^{15}N, ^2H, and for the loss of H and 2H from the alkyl side chains.

In the presence of a large excess of solvent, the kinetics were assumed to be pseudo first order, such that

$$\underset{A}{PH_4} \xrightarrow{4K} \underset{B}{PH_3D} \xrightarrow{3K} \underset{C}{PH_2D_2} \xrightarrow{2K} \underset{D}{PHD_3} \xrightarrow{K} \underset{E}{PD_4}$$

where A, B... are the mole fractions of the variously deuterated species PH_4, PH_3D..., and K is the rate constant for exchange of a specific meso proton by deuterium. The kinetic equations are $-dA/dt = 4KA$, $-dB/dt = K(-4A + 3B)$, $-dC/dt = K(-3B + 2C)$, $-dD/dt = K(-2C + D)$, $dE/dt = KD$, and solutions, for the case where at $t = 0$, $B = C = D = E = 0$, and $A = A_0$, take the following symmetrical form: $A(t)/A_0 = (e^{-Kt})^4$, $B(t)/A_0 = 4(e^{-Kt})^3(1 - e^{-Kt})$, $C(t)/A_0 = 6(e^{-Kt})^2(1 - e^{-Kt})^2$, $D(t)/A_0 = 4(e^{-Kt})(1 - e^{-Kt})^3$, $E(t)/A_0 = (1 - e^{-Kt})^4$. Values of the solutions (as mole fractions) and mass spectra (based on these solutions and the observed parent peak ratios of the starting materials) were all computed *vs.* Kt. Comparison of the measured and calculated parent peak intensities (Table I) gave values of Kt which were self consistent for all mass peaks (in the parent peak region) greater than 4% of the parent peak total intensity. The octaalkyl porphyrin rates determined are given in Table II. The porphyrins studied undergo electrophilic attack at rates differing by not much more than a factor of 200, without any obvious correlation

Table I. A Comparison of the Measured and Calculated Parent Peak Intensities for the Deuteration of Co^{II}OEP in Refluxing Deuterioacetic Acid

Mass peak	Measd intensity at t = 10 min	Calcd intensity for Kt = 0.29	Measd intensity at t = 50 min	Calcd intensity for Kt = 1.55
M − 2	0.5	0.56		
M − 1	2.5	2.2	0.5	0.06
M	59	58.5	1.5	0.8
M + 1	100	100	7.5	6.9
M + 2	74	74.6	33	34.0
M + 3	31	31.7	85	86.8
M + 4	9	8.9	100	100
M + 5	2	2.0	34	34.6
M + 6	0.5	0.4	6.5	6.9
M + 7		0.05	1.5	1.4
M + 8			0.5	0.33

(1) R. Bonnett and G. F. Stephenson, *J. Chem. Soc.*, 291 (1964).

(2) H. H. Inhoffen, J. H. Fuhrhop, H. Voigt, and H. Brockmann, Jr., *Justus Liebigs Ann. Chem.*, **695**, 133 (1966).

(3) A. W. Johnson and D. Oldfield, *J. Chem. Soc. C*, 794 (1966).

(4) R. Grigg, A. Sweeney, and A. W. Johnson, *Chem. Commun.*, 1237 (1970).

(5) H. Brockmann, Jr., K. M. Bliesener, and H. H. Inhoffen, *Justus Liebigs Ann. Chem.*, **718**, 148 (1968).

(6) R. Bonnett, I. A. D. Gale, and G. F. Stephenson, *J. Chem. Soc. C*, 1168 (1967).

(7) J. Fajer, D. C. Borg, A. Forman, D. Dolphin, and R. Felton, *J. Amer. Chem. Soc.*, **91**, 4174 (1969).