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.[8] 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.

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## 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 $\beta$ than the meso positions, attack at meso positions does occur when the $\beta$ 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 $d\pi$–$p\pi$ 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 $\pi$-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 $\pi$-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, $^{13}C$, $^{15}N$, $^{2}H$, 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 $A$, $B\ldots$ are the mole fractions of the variously deuterated species $PH_4$, $PH_3D\ldots$, and $K$ is the rate constant for exchange of a specific meso proton by deuterium. The kinetic equations are $-\mathrm{d}A/\mathrm{d}t = 4KA$, $-\mathrm{d}B/\mathrm{d}t = K(-4A + 3B)$, $-\mathrm{d}C/\mathrm{d}t = K(-3B + 2C)$, $-\mathrm{d}D/\mathrm{d}t = K(-2C + D)$, $\mathrm{d}E/\mathrm{d}t = KD$, 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 |

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**Table II**

| Starting porphyrin | $K$, $10^{-4}$ min$^{-1}$ | $t_{1/2}$, min |
|---|---|---|
| $Co^{III}Br(NH_3)$ Aetio I[a] | 670 ± 60 | 10.5 ± 0.6 |
| $Co^{II}OEP$ | 300 ± 20 | 23 ± 2 |
| Aetio I | 69 ± 2 | 101 ± 2 |
| OEP | 50 ± 5 | 140 ± 14 |
| $Fe^{III}ClOEP$[a] | 3.0 ± 0.15 | 2300 ± 100 |

[a] In acetic acid $Co^{III}Br(NH_3)$ Aetio I porphyrin is immediately converted into the corresponding $Co^{III}Br$ Aetio I. Both the $Co^{III}Br$ Aetio I and $Fe^{III}ClOEP$ porphyrins can be recovered unchanged from refluxing acetic acid.

between these rates and either the presence or absence of metal, or the oxidation state of the metal. Also, contrary to prior reports,[4] we find that Co(III) porphyrins not only exchange, but do so faster than any of the other porphyrins examined.

It had been suggested[8] that the meso positions of metal-free porphyrins would resist attack by electron-deficient reagents, and no change in the nmr spectrum of rhodoporphyrin dimethyl ester was observed when it was treated with deuterioacetic acid at 90° for 5 hr. However, we find that metal-free porphyrins exchange at a rate comparable to the metalloporphyrins in refluxing deuterioacetic acid. Under these conditions, OEP exists 60% as the N-diprotonated species, and 40% as the neutral porphyrin. In DTFA, where the concentration of neutral porphyrin is negligible, the rate of exchange is very much slower, and it is clear that N-protonation accounts for the previously observed deactivation of metal-free porphyrins in strong acids, and that it is the neutral porphyrin which undergoes electrophilic attack. The absence of exchange with rhodoporphyrin in deuterioacetic acid is not a basic property of metal-free porphyrins, and is probably a function of the electron-withdrawing methoxycarbonyl group. The dicyano-Co(III) complex showed a rate of deuteration which increased with time, but which remained slower than the corresponding amino-bromo complex. It has been reported[9] that refluxing acetic acid converts the dicyano into the monocyano complex, and thus we conclude that the rate of electrophilic attack on a porphyrin is dependent not only upon the nature of the metal (and its oxidation state), but also upon the nature of the axial ligands.

It was recently suggested[10] that a small incorporation of deuterium into the meso positions of an Fe(III) porphyrin during its reduction, by iron powder in deuterioacetic acid–*N*-methylpyrrolidone, gave *direct* evidence for peripheral attack on the metalloporphyrin during chemical reduction. While peripheral attack on porphyrins is undoubtedly an important aspect of both their chemistry and biochemistry,[11] the 5% deuterium incorporation observed during the reduction could also be explained by an electrophilic attack on the Fe(II) complex which is isoelectronic with the cobalt(III) complex (the fastest reacting example we have observed).

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## Spin–Spin Coupling between Copper(II) Ions Bridged by Pyrazine Ligands

*Sir:*

The magnetic properties of the 1:1 copper(II) nitrate-pyrazine complex, $[Cu(C_4N_2H_4)(NO_3)_2]_n$, reflect an exchange coupling between the copper ions although, as shown schematically in Figure 1, the copper(II) ions are separated by 6.712 Å.[1] While exchange coupling across bidentate heterocyclic amine ligands has been suggested previously,[2] these results provide the first demonstration of an antiferromagnetic interaction in a system which has been characterized by structural studies, magnetic measurements collected over a wide temperature range, and epr measurements.

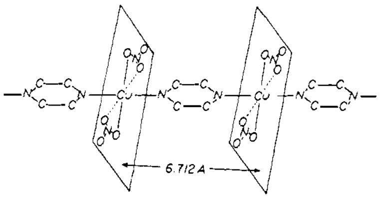

Figure 1. The structure of $[Cu(C_4H_4N_2)(NO_3)_2]_n$.

The magnetic susceptibility of a powdered sample of an analytically pure sample was determined in the temperature range 2.9–65°K using a vibrating sample magnetometer[3,4] operated at 10,000 G and calibrated with $Hg[Co(NCS)_4]$.[5] Temperatures were measured with a calibrated germanium resistance thermometer using a high-impedence ac resistance bridge, and with a gallium arsenide diode. Appropriate diamagnetic and TIP corrections[6] were applied to the experimental data. The data can be described by the Ising model for linear antiferromagnetic interactions in chains using eq 1 developed by Fisher.[7]

The equations are

$$\chi_{\perp} = \frac{Ng^2\beta^2}{8J}\left[\tanh\left(\frac{J}{kT}\right) + \left(\frac{J}{kT}\right)\operatorname{sech}^2\left(\frac{J}{kT}\right)\right] \tag{1a}$$

and

$$\chi_{\parallel} = \frac{Ng^2\beta^2}{4kT}\exp(2J/kT) \tag{1b}$$

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