the other ring protons so that no useful coupling constant data is available. On these bases, **2a** was assigned the *Z* structure and **2b** the *E* structure. The stereochemical assignments were confirmed by ^{13}C chemical shifts for which a reasonably close analogy to the present system exists in a study of methyl-substituted phosphetanes.[13] Steric interaction between the methyl groups of the *Z* isomer gives rise to resonances at higher field for both the SiMe (δ −7.0) and the C_2–Me (δ 15.6) relative to the SiMe (δ −2.3) and C_2–Me (δ 17.3) of the *E* isomer. This high field shift is also observed for the C_2 resonance of the *Z* isomer. The assignments made here are contrary to those proposed by Dubac and Mazerolles, who had in hand only a 50:50 mixture of **2a** and **2b**.[4]

Free radical chlorination using CCl_4 and benzoyl peroxide was carried out on **2a** to give **1a**. The reaction was greater than 95% stereospecific, as determined by nmr. Similarly, **2b** gave **1b**. Since this reaction goes through a silyl radical intermediate,[14] **2a** can be presumed to arise from **1a** with retention of configuration.[15–20] ^1H chemical shifts of the Si–Me groups in the chlorides offer some additional evidence, using reasoning similar to that applied to the hydrides, that **1a** has the *E* structure and **1b** the *Z* structure. This assignment again is in contrast to one made previously.[21] Perhaps surprisingly, the assignment means that the original ring closure to form silacyclobutane gives a somewhat greater amount of *E* isomer, with cis methyl groups, than of *Z* isomer, whereas conformational analysis indicates that methyl is appreciably larger than chlorine.[22]

The stereochemical assignments lead to the firm conclusion that reduction of Si–Cl by $LiAlH_4$ in the silacyclobutane ring system proceeds with retention of configuration. Acyclic[1a] and nonstrained cyclic[1b] silicon chlorides in contrast undergo reduction with almost complete inversion. The angle strain effect is thus confirmed, and we offer the following simple rationalization. "Normal" (SN2 Si)[1a] attack on the backside of Si (relative to the leaving group) occurs with the same stereochemical constraints as SN2 attack on carbon; namely, the entering and leaving groups are apical and the other substituents equatorial. Attack on one of the other three faces of the approximate tetrahedron about silicon (flank attack)[23] leads to retention of configuration. Flank attack can be induced by coordination of the leaving group to some portion of the entering group (SNi Si)[1a,24] or, as in the angle strain cases, by the inability of the substituents about Si to occupy their normal equatorial positions in the SN2 Si transition state because of prohibitive increase in angle strain.

Acknowledgment. Support of this work by a grant from the National Science Foundation is gratefully acknowledged. Cmr spectral data were obtained by Miss Barbara Ervine of Varian Associates during the visit of the CFT-20 mobile laboratory on the LSU campus.

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Unusual Metalloporphyrins. XXIII.[1] Fluxional Behavior of Out of Plane Organometalloporphyrins[2]

Sir:

Fluxional molecules[3] of both transitional[3–5] and nontransitional[6,7] organometallic compounds have received considerable attention in the past decade. Most

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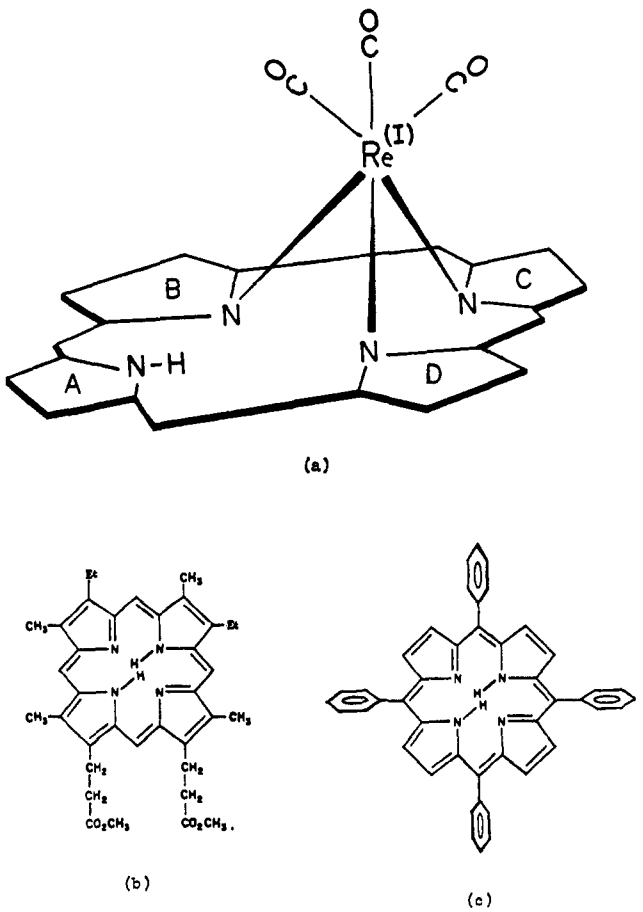

Figure 1. (a) Proposed structure for $HTPPRe(CO)_3$ (I) and $HMPRe(CO)_3$ (II) (phenyl and alkyl substituents are left out of the porphine ring for clairty); (b) mesoporphyrin IX dimethyl ester, H_2MP; (c) *meso*-tetraphenylporphine, H_2TPP.

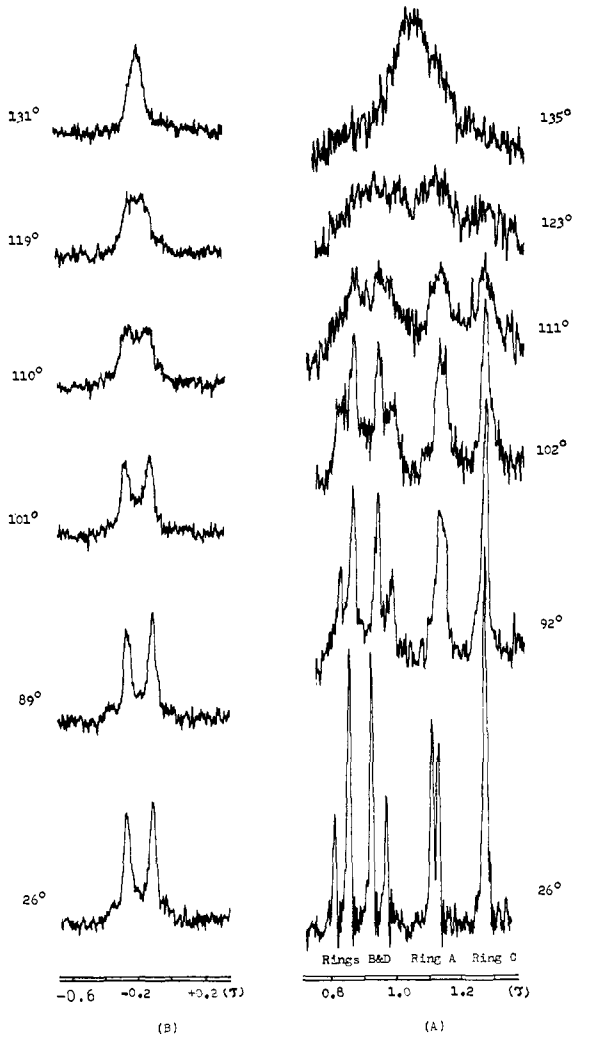

Figure 2. The 100-MHz variable temperature ^1H nmr spectra for (A) β-pyrrole protons of $HTPPRe(CO)_3$ (I) and (B) bridge methine protons of $HMPTc(CO)_3$ (III) (both in $C_2H_2Cl_4$ and temperature in °C).

investigations have been concerned with molecules containing unsaturated carbocycles;[4,6] however, a few examples are known for heteroatomic species and in particular those complexes with nitrogen or oxygen donor atom ligands.[5,7] We wish to report a variable-temperature ^1H nmr study of the fluxional character of three out of plane organometalloporphyrin compounds.

(Monohydrogen *meso*-tetraphenylporphinato)tricarbonylrhenium(I),[1] $HTPPRe(CO)_3$ (I), (monohydrogen mesoporphyrin IX dimethyl esterato)tricarbonylrhenium(I),[8] $HMPRe(CO)_3$ (II), and (monohydrogen mesoporphyrin IX dimethyl esterato)tricarbonyltechnetium(I),[9] $HMPTc(CO)_3$ (III), were prepared as previously reported. All three compounds were characterized by elemental analyses, molecular weight determinations, visible absorption, infrared, proton magnetic resonance, and mass[10] spectra. Due to the observed similarity in both their chemical and physical properties, it would not be unreasonable to assume that the three organometalloporphyrin compounds have similar structures. A single-crystal X-ray diffraction analysis is presently being investigated in this laboratory.[11] A structure similar to that of μ-[*meso*-tetraphenylporphinato]bis[tricarbonylrhenium(I)],[12] $TPP[Re(CO)_3]_2$, in which the metallo groups are sitting out of the porphyrin plane, has been proposed for these three organometalloporphyrin compounds.[1,8,9] The ^1H nmr spectral data of compound I are in agreement with the proposed structure (Figure 1a).[1]

Due to the different substituents on the porphine ring (Figure 1b and c), the ^1H nmr spectrum of I at room temperature is much more simple than that of II and III (all measured in $CDCl_3$). Besides the two multiplets for the phenyl protons, an upfield N–H peak (τ 14.0) and three different types of β-pyrrole proton peaks (an AB quartet, τ 0.87; a doublet, τ 1.12; and a sharp singlet, τ 1.28) were observed for compound I as previously reported (Figure 2A).[1] For compounds II and III, the alkyl substituents on the porphine ring give rise to overlapping multiplet nmr signals; however, an upfield N–H peak (τ 15.0) and two singlets for the bridge methine protons (centered at τ −0.17) are clearly distinguishable (Figure 2B). These ^1H nmr spectral data show the nonequivalence of the β-pyrrole protons[13]

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in compound I and also the bridge methine protons[14] in II and III at room temperature.

Temperature-dependent ^1H nmr spectral changes for I and III dissolved in 1,1,2,2-tetrachloroethane (bp 146°) are shown in Figure 2. As the temperature is raised, the peaks broaden, coalesce, and gradually sharpen. The changes have all been shown to be completely reversible with temperature. Compound II gives spectral changes similar to those of III. These results illustrate that the compounds I–III display a fluxional behavior.

The above fluxional phenomenon is best explained by the intramolecular rearrangement of the metal–carbonyl group among the four ring nitrogens of porphyrin and also movement of the N–H; it can also be regarded as an intramolecular substitution at rhenium or technetium. A solution containing II and excess free mesoporphyrin IX dimethyl ester in relative amounts 1:2.5 showed no broadening of the free ligand bridge methine proton peak in the fast exchange region for compound II. Free ligand is thus not involved in the exchange process in this system. The colescence temperatures, moreover, were not shifted by changes in the concentrations of the complexes within the standard deviations of the experiment (*ca.* ±5°). These results lend support to the fact that the thermal rearrangement process is intramolecular rather than intermolecular. Dissociation and recombination of the metal–carbonyl moieties and the porphyrin ligand or interchanges of two such ligands between two molecules at high temperature are ruled out due to the fact that attempts at the conversion of $Mp[Re(CO)_3]_2$ to compound II by reflux in decalin (bp 195°) with excess porphyrin were unsuccessful.[8]

The free energy of activation, $\Delta G^{\pm} = 19.3 \pm 2$ kcal/mol, was estimated[15] for III from the coalescence of the bridge methine proton signals.

Further studies are now being undertaken to more fully elucidate the nature and scope of these fluxional characters for out of plane organometalloporphyrin compounds.

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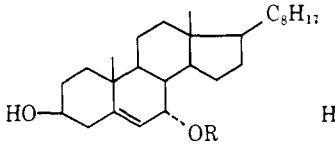
Sterol Metabolism. XXIX. On the Mechanism of Microsomal Lipid Peroxidation in Rat Liver[1]

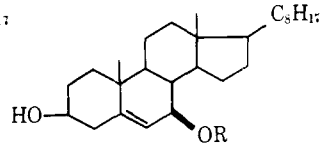
Sir:

Speculation on the participation of electronically excited (singlet) molecular oxygen in enzymic oxidations is current, such participation having been suggested for the actions of soybean lipoxygenase[2] and horseradish peroxidase[3] and for mammalian liver NADPH-dependent microsomal[4] and mitochondrial[5] lipid peroxidations. However, experimental evidence does not infer such participation for lipoxygenase[6,7] or peroxidase,[6] and the claim associated with lipoxygenase[2a] has been retracted.[8] Moreover, singlet molecular oxygen is not implicated in the oxidation of xenobiotic substances by mammalian liver microsomes.[9]

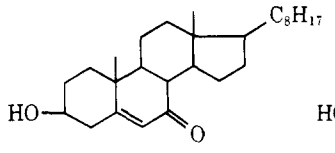
We have now examined the NADPH-dependent hepatic microsomal lipid peroxidation system using cholesterol as a probe to test the participation of singlet molecular oxygen.[10] Cholesterol oxidation in this system previously yielded cholest-5-ene-3β,7α-diol (Ia),



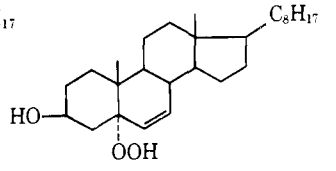
Ia, R = H
b, R = OH



IIa, R = H
b, R = OH



III



IV

cholest-5-ene-3β,7β-diol (IIa), 3β-hydroxycholest-5-en-7-one (III), and 5α-cholestane-3β,5,6β-triol.[11] Hydroperoxides, though suspected, have not heretofore been demonstrated.[11a,c] However, we have established cholesterol 7α-hydroperoxide (Ib) and 7β-hydroperoxide (IIb) but not 3β-hydroxy-5α-cholest-6-ene 5-hydroperoxide (IV) as initial products of cholesterol oxidation by air[12] and by lipoxygenase and peroxidase.[6] Subse-

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