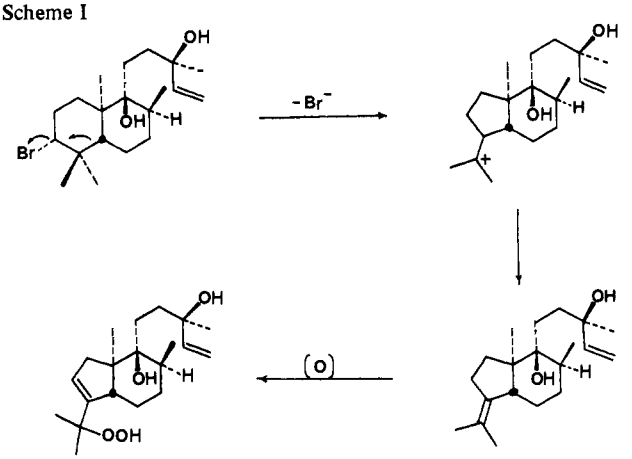
Scheme I



refined in the tangent formula. Phases were extended to the largest 200 E's, and a subsequent electron density synthesis revealed a plausible 23-atom fragment. Full-matrix, least-squares refinements with all atoms identified as carbons converged to a standard crystallographic residual of 12%.[6] Inspection of thermal parameters and bond distances indicated that four of the atoms should be identified as oxygens. In Figure 1, these are O(21), O(22), O(23), and O(24). It was also obvious that one of the carbon atoms was very poorly behaved, with a thermal parameter roughly twice as large as any of the other carbons and a carbon-carbon bond distance of 1.70 Å! This atom is roughly midway between the atoms labeled C(14) and C(15) in Figure 1. Since the ^{1}H NMR spectrum clearly showed a $-CH{=}CH_2$ group which was not present in our x-ray model, we replaced the poorly behaved atom with a disordered vinyl group. The current residual for this model is 4.9% for the observed reflections. Figure 1 presents an x-ray drawing of this model showing only one of the threefold disordered vinyl group orientations. In general, bond distances and bond angles agree well with generally accepted values. The hydroperoxide geometry is C(4)-O(23) = 1.438 (7) Å, O(23)-O(24) = 1.461 (6) Å, and ∠C(4)-O(23)-O(24) = 108.1 (4)°. The five- and six-membered rings are trans fused, and the relative stereochemistry at C(5), C(8), C(9), C(10), and C(13) is identical with that reported for **2**.[3] Additional crystallographic details can be found in the supplemental material.

We suggest that **1** and **2** are biogenetically related via solvolysis of the C(3) equatorial bromine in **2**, as depicted in Scheme I. These transformations are precedented in the solvolytic A-ring contraction reactions of 3β-tosyltriterpenes[7] and in the reactivity of ground state (enzymatic) or singlet O_2 with tetrasubstituted olefins to yield rearranged allylic hydroperoxides.

Acknowledgments. We (B.M.H. and W.F.) are grateful for financial support for this research from the National Science Foundation, Oceanography Section, under Grant No. OCE75-03824 and for NSF funding of the R/V DOLPHIN, which enabled us to collect *Laurencia* species at Catalina Island. In addition, we wish to acknowledge our use of the NMR instrumentation of the Department of Chemistry, University of California, San Diego, supported by an NIH grant, No. RR-408.

Supplementary Material Available: Fractional coordinates (Table 1), bond distances (Table 2), bond angles (Table 3), and observed and calculated structure factors (Table 4) (9 pages). Ordering information is given on any current masthead page.

References and Notes

(1) We are unaware of reports of terpenes with the hydroperoxide functionality; however, a steroidal hydroperoxide, 3α,22α-dihydroxy-7α-hydroperoxy-Δ^5-stigmastene is a natural product; see F. G. Fisher and H. Mägerlein, *Justus Liebigs Ann. Chem.*, **636**, 88 (1960). Also, it seems secure that hydroperoxides are important intermediates in prostaglandin synthesis; see (inter alia) M. Hamberg, J. Svenson, T. Wakabayashi, and B. Samuelson, *Proc. Natl. Acad. Sci. U.S.A.*, **71**, 345 (1974).

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(4) Two different collections of *L. snyderiae*, one from La Jolla and one from Santa Catalina Island, were compared. La Jolla populations contained concinndiol (**2**) as well as β-snyderol (**3**), the structure of which was reported in an earlier communication (B. M. Howard and W. Fenical, *Tetrahedron Lett.*, 41 (1976)). Santa Catalina Island populations also contained **2** and **3**, but they contained, in addition, the hydroperoxide **1** and an aromatized snyderol derivative, **4**, reported earlier as a component of *L. nidifica* (H. H. Sun, S. W. Waraszkiewicz, and K. L. Erickson, *Tetrahedron Lett.*, 585 (1976)). It thus appears that solvolysis of C(3) equatorial bromine in concinndiol results in bridgehead bond migration, while the analogous solvolytic rearrangement in the sesquiterpene **3** results in methyl migration.

3 **4**

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(8) Camille and Henry Dreyfus Foundation Teacher-Scholar Grant awardee 1972-1977.

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Nitrosoalkanes as New Ligands of Iron(II) Porphyrins and Hemoproteins

Sir:

Nitrosoalkanes or nitrosoarenes are interesting ligands because of their nitroso group which is isoelectronic with dioxygen, of their different possible modes of binding (at N or O atom, side-on or end-on), and of their low-lying π* system[1] which should be readily available for back-bonding. However, few transition metal complexes having such ligands have been reported. Most of these are nitrosoarene complexes[2-10] and only two nitrosoalkane complexes, $CoCp(C_7H_{10}N_2O_2)$[11] and $[Ru(NH_3)_5[(NO)CH_2C(CH_3)_2OH]]^{2+}$,[12] have been isolated. In addition, very recently, the reaction of aliphatic hydroxylamines with $[Fe(CN)_5(H_2O)]^{3-}$ has been reported to give complexes identified as $[Fe(CN)_5(RNO)]^{3-}$ from their spectral characteristics, by analogy with those of the $[Fe(CN)_5(ArNO)]^{3-}$ Baudisch complexes.[13]

However, nitrosoarenes bind to hemoglobin,[14] and we recently proposed that nitrosoalkanes are the exogenous ligands of the very stable "425-, 421-, and 455-nm absorbing com-

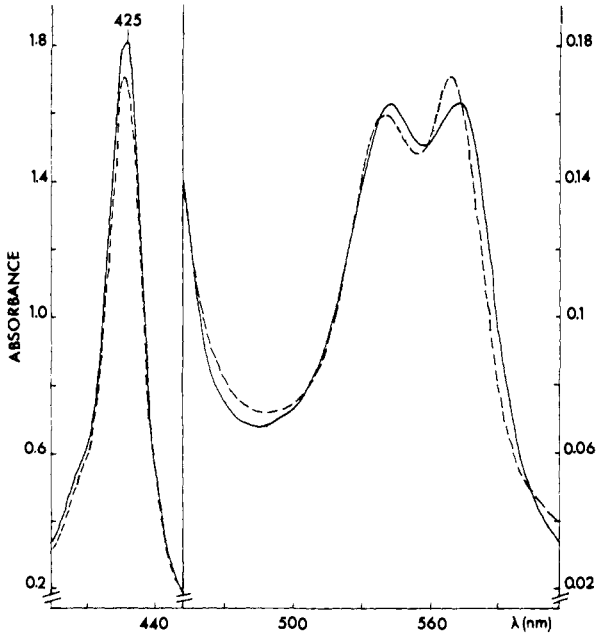

Figure 1. Electronic spectra at 25°C: - - -, FePPIXCl, 1.24×10^{-5} M in C_6H_6-DMF ($1\text{-}5 \times 10^{-3}$) after addition of 5×10^{-2} M *i*-PrNHOH and 6×10^{-4} M 1-MeIm; —, metMb, 1.12×10^{-5} M in phosphate buffer, pH 7.4, after addition of 10^{-1} M *i*-PrNHOH.

plexes" of myoglobin, hemoglobin, and cytochrome P450, which are formed for instance during oxidation of various aliphatic primary *N*-hydroxylamines in the presence of these hemoproteins.[15] In order to prove this hypothesis, we studied model reactions between iron porphyrins and aliphatic hydroxylamines, and we report here the isolation of the first metalloporphyrin complex containing a nitrosoalkane ligand and the obtention of a heme model for the nitrosoalkane-myoglobin complexes described previously.

The reaction of isopropylhydroxylamine (*i*-PrNHOH), 3×10^{-2} M in benzene, with iron(III) mesotetraphenylporphyrin chloride (FeTPPCl), 5×10^{-6} M, is very rapid, as shown by visible spectroscopy by the complete and almost immediate appearance, with isosbestic points at 412, 433, and 521 nm, of a new spectrum characterized by two maxima at 422 and 535 nm.[16] A further addition of increasing amounts of pyridine (Py) leads with isosbestic points at 423, 520, and 546 nm to a new species with maxima at 424 and 536 nm.[17] From a similar reaction performed with 0.2 M FeTPPCl, 0.8 M *i*-PrNHOH, and 0.3 M Py in $CHCl_3$, which is complete within 1 h, a purple complex I can be isolated (>90% yield). It is an $Fe^{II}TPP$ complex as indicated by the following spectral data which are similar to those of the known complex Fe(Py)$_2$[18]—visible max ($CHCl_3$, 1% pyridine) 424 nm (ϵ 250×10^3), 536 (10.5×10^3); ^{1}H NMR with three signals at δ 8.64 (s, 8), 8.06 (m, 8), 7.68 ppm (m, 12) and ^{13}C NMR with seven signals at δ 144.2, 142, 133.4, 132, 126.6, 125.7, 118.8 ppm[19] characteristic of the protons and carbons of the porphyrin ring. Complex I has two axial ligands: one pyridine (^{1}H NMR, δ 1.60, 5.22, 6.10 ppm[20]) and one ligand with an isopropyl group (^{1}H NMR δ −2.02 (d, 6, J = 7 Hz, CH_3), −0.81 ppm (hept, 1, J = 7 Hz, CH); ^{13}C NMR δ 16.02 (CH_3), 81.6 ppm (CH)) located in close proximity of the porphyrin ring as shown by the ring-current shift of the methyl signals. According to the ^{1}H NMR spectrum and elemental analysis ($C_{52}H_{40}FeN_6O$) (C, H, N) of complex I, this axial ligand should have the formula C_3H_7NO. Moreover, the mass spectrum of I does not exhibit the molecular ion[21] but two peaks at *m/e* 79 and 73 corresponding, respectively, to Py and C_3H_7NO. Furthermore, in pure pyridine, this ligand is displaced, leading to FeTPP(Py)$_2$ and acetone oxime[22] (Scheme I). The reaction

Scheme I

$$\mathrm{Fe^{III}TPPCl} \xrightarrow[CHCl_3]{(CH_3)_2CHNHOH + Py} \underset{\mathbf{I}}{\mathrm{Fe^{II}TPP(Py)[(CH_3)_2CHNO]}}$$

$$\mathbf{I} \xrightarrow[\text{solvent}]{\text{Py as}} \mathrm{Fe^{II}TPP(Py)_2} + \underset{CH_3}{\overset{CH_3}{>}}C{=}N{-}OH$$

can be followed by ^{1}H NMR and corresponds to the gradual replacement of the isopropyl signals of the ligand by those of acetone oxime quantitatively. Acetone oxime is also formed when complex I is heated in vacuo (150 °C (10^{-2} mmHg)).

Similar complexes FeTPP(L)(RNO) are obtained with L = Py, imidazole, 1-methylimidazole, and *i*-PrNH$_2$, and with R = Me, *i*-Pr, and $PhCH_2CH_2$. Nitrosoalkanes, particularly those which have a hydrogen α to the nitroso group, are especially unstable leading almost irreversibly to the corresponding dimers or tautomers.[1] Our results indicate that they are efficiently stabilized upon coordination to iron(II) porphyrins. Accordingly, complex I is stable for months in the solid state and for days in anaerobic solution (10^{-4} M in benzene). Moreover, its stability toward autoxidation in aerated solvents is quite remarkable when compared with that of other classical hexacoordinated $Fe^{II}TPP$ complexes: the half-lives of I, 10^{-4} M in MeOH or $CHCl_3$, of ~14 and 6 h, are much greater than those of FeTPP (Py)(CO) (respectively 1 and 5 min) and FeTPP(Py)$_2$ (<1 min).

Like FeTPPCl, iron(III) protoporphyrin IX (hemin, Fe^{III}PPIX) chloride is reduced by aliphatic hydroxylamines, RNHOH (R = Me, *i*-Pr, $PhCH_2CH_2$) forming heme-iron(II) nitrosoalkane complexes similar to the corresponding $Fe^{II}TPP$ complexes. The visible spectrum of the material obtained by addition of *i*-PrNHOH to hemin chloride in the presence of 1-methylimidazole (1-MeIm), which should correspond to the hexacoordinated complex, Fe^{II}PPIX(*i*-PrNO)(1-MeIm), II, by analogy to the above results, is almost superimposable on the spectrum of the hexacoordinated myoglobin (Mb)-iron(II) complex obtained by reaction of metmyoglobin-iron(III) and *i*-PrNHOH (Figure 1). Complex II is thus a good model for the "425-nm absorbing myoglobin complex" described previously,[15] confirming the protein-imidazole-iron(II)-*i*-PrNO structure that we have proposed for this Mb complex.

Nitrosoalkanes constitute a new class of ligands for iron(II) porphyrins. The stability of the Fe^{II}-RNO bond in the herein described TPP complexes may explain the inactivation of cytochrome P450 having bound nitrosoalkane ligands formed during metabolic oxidations of some amines and *N*-hydroxylamines.[15,24] The study of the nature of the bond between iron(II) and nitrosoalkanes, and the preparation of nitrosoalkane complexes of other transition metals are currently under way.

Acknowledgments. This work was supported in part by C.N.R.S. Grant ATP No. 2647 and by D.G.R.S.T. Grant No. BRD 75-7-1614.

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(16) From its spectral characteristics (^{1}H NMR, ^{13}C NMR), the corresponding complex bears the same *i*-PrNHOH-derived ligand as complex I (vide infra) and its isolation is under way.
(17) This last entity is completely formed after addition of 4×10^{-3} M Py. The addition of larger amounts of Py (4 M) leads to the formation of FeTPP $(Py)_2$.
(18) FeTPP $(Py)_2$ prepared according to J. O. Alben et al., *Biochemistry*, **7**, 624 (1968), gives three signals in ^{1}H NMR (C_5D_5N), δ 8.73 (8 H), 7.98 (8, H), 7.46 ppm (12 H), and seven signals in ^{13}C NMR (C_5D_5N, $CDCl_3$), δ 145.1, 141, 133, 132.2, 125.1, 124.6, 118.5 ppm.
(19) The NMR spectra were recorded on a Bruker WH 90 working in FT mode, in $CDCl_3$ at 23 °C (δ from TMS).
(20) At 20 °C, bound and free Py are in rapid exchange relative to the NMR time scale. At −60 °C, this exchange is slow and the signals of bound Py can then be identified and are those indicated in the text.
(21) Its higher peak (*m/e* 668) corresponds to FeTPP.
(22) The fast transformation of nitrosoalkanes, bearing a hydrogen α to NO, to the corresponding oximes in solution is well known[1] and is particularly favored in the presence of bases.
(23) It is noteworthy that the conversion of the hydroxylamine to the nitrosoalkane is a two-electron oxidation, the iron(III) porphyrin being the first one-electron oxidant. The second oxidant could be oxygen, but, as the reaction can be run under argon, it could also be the hydroxylamine itself. Accordingly, the dismutation of hydroxylamines has been reported to occur in the presence of $[Fe(CN)_5H_2O]^{3-}$ leading to the corresponding nitrosoalkane-iron(II) complexes.[13] (We thank a referee for suggesting this comment.)
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Vinyl Alcohol. A Stable Molecule

Sir:

Vinyl alcohol, the simplest member of the enol class of molecules has proved an elusive target for experimental observation. Attempts to prepare vinyl alcohol have generally produced its keto isomer acetaldehyde,[1] a result which could be taken to indicate a low energy pathway connecting the enol and keto structures. Recently, however, Saito[2] was able to prepare and identify vinyl alcohol in the gas phase. On the basis of the observation in interstellar space of structurally related molecules including CH_3OH,[3] CH_3CH_2OH,[4] CH_3CHO,[5] and CH_2=CHCN,[6] Saito suggested that vinyl alcohol CH_2=CHOH may also be an interstellar molecule. In this connection, we note that, because of the large intermolecular distances and hence infrequent collisions between molecules, the interstellar medium offers favorable conditions for the existence of molecules which are stable with respect to *intra*molecular rearrangement but which are very difficult to observe under normal laboratory conditions owing to *inter*molecular or ionic rearrangements. A relevant example is hydrogen isocyanide which was observed[7] several years ago in interstellar space but has only very recently been observed in the laboratory.[8] Theoretical calculations[9] have shown that there is indeed a large barrier to the intramolecular rearrangement of HNC to HCN. In order to assess the stability of vinyl alcohol as an isolated molecule and, in particular, to examine the likelihood of vinyl alcohol existing in the interstellar medium, it is therefore important to establish the magnitude of the barrier for rearrangement to acetaldehyde. In this paper, we apply ab initio molecular orbital theory to this problem.

Standard LCAO SCF MO theory was used with a modified

Table I. Optimized Geometric Parameters[a] for Vinyl Alcohol (I), Acetaldehyde (II), and the Transition States (IIIA, IIIB) Separating I and II

	I	IIIA	IIIB	II
Symmetry constraint	C_s	C_1	C_1	C_s
No. of independent parameters	11	15	15	10
Bond distances, Å				
C_1-C	1.312	1.448	1.413	1.537
C-O	1.390	1.293	1.378	1.217
C-H	1.089	1.097	1.098	1.104
O-H_3	0.990	(1.163)	(1.662)	
C_1-H_1	1.080	1.087	1.080	1.085
C_1-H_2	1.077	1.082	1.080	1.087
C_1-H_3		1.475	1.743	1.087
C-H_3			(1.164)	
Bond angles, degrees				
$\angle C_1CO$	126.9	102.6	124.6	124.3
$\angle C_1CH$	122.2	136.5	115.3	114.3
$\angle CC_1H_1$	122.0	108.1	119.8	110.5
$\angle CC_1H_2$	121.2	118.8	121.5	108.8
$\angle CC_1H_3$		67.1	41.7	108.8
$\angle COH_3$	105.2			
Dihedral angles, degrees				
$\angle HCC_1O$	180.0[b]	183.1	188.5	180.0[b]
$\angle H_1C_1CO$	0.0[b]	−81.8	−10.4	0.0[b]
$\angle H_2C_1CO$	180.0[b]	151.7	−183.8	120.6
$\angle H_3C_1CO$	0.0[b]	3.3	−75.3	−120.6

[a] Derived (nonindependent) values shown in parentheses. [b] Values determined by symmetry.

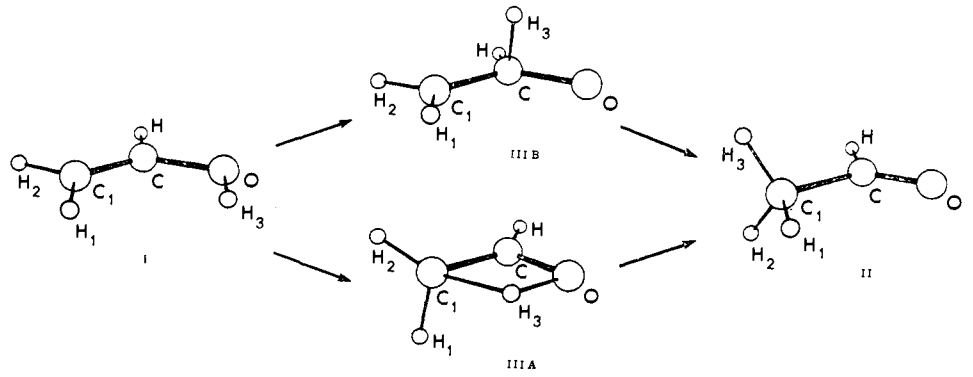

Figure 1. 1,3-Sigmatropic shift in vinyl alcohol/acetaldehyde.