periphery will give a shift to higher field, in analogy with ^{59}Co chemical shifts.[12] An increase in basicity of the axial base will give roughly a 10 ppm shift to higher field[13] per pK_a unit. A change in solvent polarity from that of DMF–H_2O, 90:10, to toluene gives rise to a 20 ppm upfield shift for FePF(BuIm)(CO), Table I. The effect of tilting the carbonyl relative to the heme normal can then be estimated from the chemical shifts of MbCO, 8234 ppm,[14] and Fe(PPIX)(1-MeIm)(CO), 8151 ppm.[13] In MbCO, the porphyrin is flat and the CO is tilted by about 15°.[8] In Fe(PPIX)(1-MeIm)(CO), the plane is nearly flat and the CO is linear.[15] The chemical shift difference must be due to a difference in coordination of the imidazole residues, a medium effect, and the effect of forcing the carbonyl off axis. The effect of restricted vinyl rotation can be estimated from a comparison between Fe(PPIX)(py-d_5)(CO) and Fe(meso-PIX)(py-d_5)(CO) and should introduce a small upfield shift. A nonideal coordination from histidine to iron in MbCO would suggest a downfield shift by 20–50 ppm.[13] The medium effect on going from aqueous solution to the nonpolar interior of the heme pocket would roughly cancel that, leaving a downfield shift of 50–80 ppm as the effect of tilting the carbonyl.

The magnitudes of all of these shifts are substantially smaller than the ones encountered as an effect of perturbations of the porphyrin core. In Table I, the chemical shifts are given for the picket-fence porphyrin and a series of sterically hindered iron porphyrins, derivatives of the hybrid "basket-handle" porphyrins by Momenteau and co-workers.[4] From the crystal structures of some of these, it is clear that the carbonyl lies along the heme normal and that the porphyrin is clearly ruffled; the shorter the aliphatic chain, the more it is ruffled.[7] The chemical shift varies by more than 600 ppm between the two extremes and in a seemingly regular fashion, giving a high-field shift with increased ruffling. The magnitude of the shifts is such that they can be interpreted. An upfield shift of more than 100 ppm relative to some reference compound can only be caused by perturbations of the porphyrin residue. Considering the large number of heme proteins and protein mutants under study, this should be a very helpful tool for the investigation of detailed structure. Also, we conclude from the difference in magnitude of the chemical shifts that the perturbation of the d-orbital energies are much larger than what is observed upon changing the ligands in a strictly octahedral complex.

Further information can be extracted from the substituent effects on the chemical shifts when the axial base is varied in the series of carbonyl complexes. As reported previously,[13] the ^{57}Fe NMR resonance is shifted to higher field as the electron-donating ability of the axial base is increased, in a series of Fe(PPIX)(B)(CO) complexes, completely in accordance with prediction. This is true also for the picket-fence and the "largest" basket-handle complex, but for the more tightly packed superstructures, the reverse is true, Table I. Within the framework of the Ramsey equation,[12] the high-field shift of FePF(BuIm)(CO) and FeBH12(BuIm)(CO) can be viewed as originating from an increased repulsion of the d_{z^2} orbital giving rise to an increase in ΔE and a decrease in the chemical shift. With FeBH10(BuIm)(CO) and FeBH9(BuIm)(CO), the data suggest that an increase in the electron-donating ability of the axial base causes a repulsion of the same orbital but that this leads to a decrease in ΔE. This is deduced from the fact that the chemical shift is downfield. This is only possible if the d_{z^2} orbital is no longer unoccupied and one of the previously occupied orbitals has increased its energy so much as to become unoccupied; in other words, there has been an energy level crossover. This requires, of course, that the Ramsay equation is valid under these conditions. An unequivocal proof of an energy level crossover would be to observe a paramagnetic iron(II) porphyrin complex for a certain amount of superstructure tightness, and a reversal of substituent effects for a more pronounced tightness. We were not able to observe a paramagnetic state, but in a similar class of compounds, such an observation has been made. Ellis et al.[16] reported several years ago that they observed paramagnetism in a "capped" porphyrin. They attributed this paramagnetism to nonlinear coordination of one of the axial bases. An alternative explanation is that the porphyrin core is ruffled. In the present case, it is clear that both axial ligands bind in a linear way.

The relevance of this observation is obvious when one considers the importance of spin state for ligand binding in heme proteins. Since the ruffled porphyrins are clearly biologically significant, this should be of considerable interest.

Acknowledgment. Financial support from the Swedish Natural Science Research Council is gratefully acknowledged.

Registry No. Fe(PPIX)(py-d_5)(CO), 125592-90-7; ^{57}Fe, 14762-69-7.

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Flash Photolytic Generation and Study of α-(Trimethylsilyl)vinyl Alcohol: The Effect of α-Silyl Substitution on Enol Chemistry

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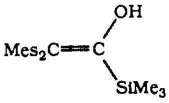
Recent interest in the chemistry of simple enols[1] has led to the prediction that α-silyl substitution should stabilize enols relative to their keto isomers markedly, and that has produced the synthesis of the first stable α-silyl enol, β,β-dimesityl-α-(trimethylsilyl)vinyl alcohol (**1**) (Mes = mesityl = 2,4,6-trimethylphenyl).[2] This enol could not be converted to its keto isomer under conditions much more drastic than required for ketonization of silicon-free analogues; it therefore certainly does possess unusual kinetic stability. However, because equilibration with the keto isomer could not be achieved, its thermodynamic stability could not be assessed and the effect of silyl substitution on keto–enol equilibria could not be determined. We report that we have now generated another α-silyl enol, the prototype substance α-(trimethylsilyl)vinyl alcohol (**2**), under conditions where this enol is converted to its keto isomer, acetyltrimethylsilane (**3**);[3] this has enabled us to evaluate the keto–enol equilibrium constant for this system as well as acidity constants of the keto and enol forms.



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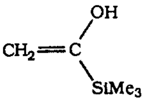

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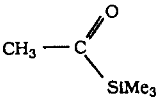

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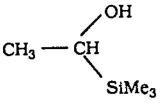

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We produced this enol by photooxidation[4] of the corresponding alcohol, α-(trimethylsilyl)ethanol (**4**),[5] using acetone as the oxidant. The two ketyl radicals formed in this reaction, eq 1, may dis-

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[1] For reviews, see: (a) Kresge, A. J. *CHEMTECH* **1986**, *16*, 250–254; *Acc. Chem. Res.* **1990**, *23*, 43. (b) Capon, B.; Guo, B.; Kwok, F. C.; Siddhanta, A.; Zucco, C. *Acc. Chem. Res.* **1988**, *21*, 135–140. (c) Rappoport, Z.; Biali, S. *Acc. Chem. Res.* **1988**, *21*, 442–449.

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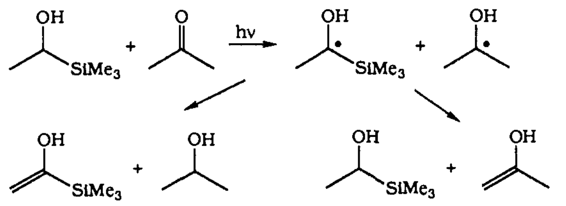
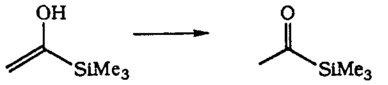


(1)

proportionate in two different ways, giving the enol of interest as well as that of acetone. We found that flash photolysis of aqueous solutions of this silyl alcohol plus acetone did produce two transient species which absorbed in the far UV, as expected of aliphatic enols. Rates of decay of both transients, monitored spectroscopically at λ = 220 nm, were accurately proportional to acid concentration in dilute perchloric acid solutions, and analysis of the data gave the hydronium ion catalytic coefficients $k_{\mathrm{H}^+}{}^{\mathrm{K}} = (5.66 \pm 0.27) \times 10^3\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$ and $k_{\mathrm{H}^+}{}^{\mathrm{K}} = (7.78 \pm 0.11) \times 10^1\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$.[6] The first of these agrees well with $k_{\mathrm{H}^+}{}^{\mathrm{K}} = (5.95 \pm 0.23) \times 10^3\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$ reported for ketonization of the enol of acetone,[7] and the second can therefore be assigned to ketonization of α-(trimethylsilyl)vinyl alcohol, eq 2. This assignment is



(2)

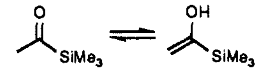
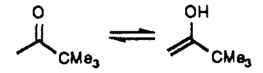
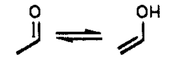
supported by identification of the corresponding ketone, acetyltrimethylsilane, as a reaction product. It is further reinforced by the solvent isotope effect, $k_{\mathrm{H}^+}{}^{\mathrm{K}}/k_{\mathrm{D}^+}{}^{\mathrm{K}} = 4.23 \pm 0.19$,[6] measured for this decay, which is in the correct direction and of the right magnitude for the ketonization of an enol,[8] as well as by the UV spectrum of the transient, which shifted from $\lambda_{\max} = 210$ nm in acidic solution to $\lambda_{\max} = 240$ nm in basic solution, as expected for conversion of an enol to its enolate ion.[9]

We also measured rates of enolization of acetyltrimethylsilane by iodine scavenging. Observed first-order rate constants determined in dilute aqueous perchloric acid solutions were accurately proportional to acid concentration and gave the catalytic coefficient, $k_{\mathrm{H}^+}{}^{\mathrm{E}} = (1.03 \pm 0.02) \times 10^{-3}\ \mathrm{M}^{-1}\,\mathrm{s}^{-1}$,[6] and the solvent isotope effect, $k_{\mathrm{H}^+}{}^{\mathrm{E}}/k_{\mathrm{D}^+}{}^{\mathrm{E}} = 0.49 \pm 0.03$;[6] an inverse isotope effect like this is consistent with a preequilibrium proton transfer mechanism[10] such as that generally accepted for the enolization of ketones.[11] Further evidence that the process being monitored is enolization was provided by the fact that $k_{\mathrm{D}^+}{}^{\mathrm{E}}$ is consistent with the rate of incorporation of deuterium into the acyl methyl group of the substrate, as determined from changes in the proton NMR spectrum of a sample dissolved in acidified D_2O.

Hydronium ion catalytic coefficients for enolization and ketonization such as those determined here may be combined to give keto–enol equilibrium constants: $K_{\mathrm{E}} = k_{\mathrm{H}^+}{}^{\mathrm{E}}/k_{\mathrm{H}^+}{}^{\mathrm{K}}$. The present results give $K_{\mathrm{E}} = (1.32 \pm 0.03) \times 10^{-5}$, $\mathrm{p}K_{\mathrm{E}} = 4.88 \pm 0.01$.[6]

The ketonization of α-(trimethylsilyl)vinyl alcohol is also catalyzed by hydroxide ion. This catalysis, however, as is typical of simple enols,[1a] becomes saturated as the hydroxide ion concentration is raised, and standard treatment of rate data obtained in this region[8a] provides the acidity constant of the enol ionizing as an oxygen acid, $K_{\mathrm{a}}{}^{\mathrm{E}} = (2.90 \pm 0.14) \times 10^{-12}$ M. Another estimate of this constant can be obtained from a spectrophotometric titration curve constructed with initial absorbances calculated by extrapolating the rate data back to zero time. The result, $K_{\mathrm{a}}{}^{\mathrm{E}} = (2.43 \pm 0.48) \times 10^{-12}$ M, agrees well with the kinetic determination. The weighted average of the two values is $K_{\mathrm{a}}{}^{\mathrm{E}} = (2.86 \pm 0.13) \times 10^{-12}$ M, $\mathrm{p}K_{\mathrm{a}}{}^{\mathrm{E}} = 11.54 \pm 0.02$.[6,12]

Table I. Comparison of the Acetyltrimethylsilane Keto–Enol System with Some Silicon-Free Analogues[a]

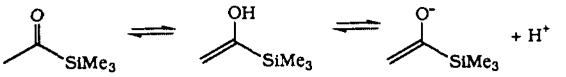
system	$\mathrm{p}K_{\mathrm{E}}$	$\mathrm{p}K_{\mathrm{a}}{}^{\mathrm{E}}$	$\mathrm{p}K_{\mathrm{a}}{}^{\mathrm{K}}$	ref
	4.88	11.54	16.42	this work
	8.33	10.94	19.27	7, 13
	8.76			4
	6.23	10.50	16.73	8b

[a] Aqueous solution, 25 °C, ionic strength = 0.10 M; acidity constants are *concentration* quotients appropriate to this ionic strength.

Enol acidity constants such as this may be combined with keto–enol equilibrium constants to provide acidity constants of the keto forms ionizing as carbon acids, $K_{\mathrm{a}}{}^{\mathrm{K}} = K_{\mathrm{E}}K_{\mathrm{a}}{}^{\mathrm{E}}$. For the present system this gives $K_{\mathrm{a}}{}^{\mathrm{K}} = (3.79 \pm 0.20) \times 10^{-17}$, $\mathrm{p}K_{\mathrm{a}}{}^{\mathrm{K}} = 16.42 \pm 0.02$.[6,12]

The present results are summarized and compared with data for related systems in Table I. It may be seen that α-silyl substitution has raised K_{E} for the present system by a substantial amount: by 3.8–3.9 pK units over that of acetone[14] or methyl *tert*-butyl ketone. This comparison provides a differential substituent effect of $\delta_{\mathrm{R}}\Delta G = 5.1$–$5.3$ kcal mol^{-1}, which is consistent with the energy difference of 6.0 kcal mol^{-1} predicted by ab initio calculation.[2]

The data of Table I show further that the silyl substituent in α-(trimethylsilyl)vinyl alcohol lowers the acidity of this substance, i.e., it raises $\mathrm{p}K_{\mathrm{a}}{}^{\mathrm{E}}$. This effect is in the direction expected from the electropositive nature of silicon and is consistent with a similar influence of the silyl substituent on the acid strength of *m*-(trimethylsilyl)phenol.[15] The silyl substituent in acetyltrimethylsilane, on the other hand, operates in the opposite direction: it raises the acidity of this substance (lowers $\mathrm{p}K_{\mathrm{a}}{}^{\mathrm{K}}$). This unexpected difference may be understood by considering ionization of the ketone as a two-stage process, enolization followed by ionization of the enol, eq 3. It has been found that substituents generally



(3)

affect the first of these stages more strongly than they do the second and that substituent effects on the overall reaction follow those on the keto–enol equilibrium;[1a,16] the acid-strengthening influence of the silyl group on the ionization of acetyltrimethylsilane is thus a reflection of its marked ability to shift the keto–enol equilibrium in favor of enol.

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support of this work.

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(6) Aqueous solution, 25 °C; ionic strength = 0.10 M.

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(12) This is a *concentration* dissociation constant appropriate to ionic strength = 0.10 M.

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(14) A statistical factor of 2, to take into account the two equivalent directions in which acetone can enolize, is included in this comparison.

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