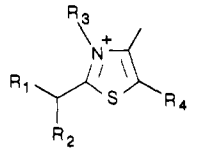
Table I. Thiazolium Compounds Synthesized



compd	R_1	R_2	R_3	R_4
3a	H	H	CH_3	H
3b	H	H	CH_3	CH_3
3c	CH_3	OCH_3	CH_3	H
3d	CH_3	OCH_3	CD_3	H
3e	CH_3	$OSi(t\text{-}C_4H_9)(C_6H_5)_2$	CH_3	H
3f	CH_3	$OSi(t\text{-}C_4H_9)(C_6H_5)_2$	CD_3	H
3g	CH_3	$OSi(CH_3)_2(t\text{-}C_4H_9)$	CH_3	$CH_2CH_2OSi(CH_3)_2$-$(t\text{-}C_4H_9)$

positive charge on the ring. Compounds **3a** and **3b** underwent quantitative and reversible deprotonation by (trimethylsilyl)amide at C2-CH_3 since (1) the resonance corresponding to C2-CH_3 was replaced by two multiplets (one proton each) and (2) neutralization of intermediates **2a** and **2b** with CF_3COOD regenerated **3a** and **3b** with diminution in the integral corresponding only to the C2-CH_3 group Potassium *tert*-butoxide was too weak to convert **3a** to **2a** and **3b** to **2b**. The pK_a at the C2-CH_3 site is therefore between 19 and 24.

Compound **3c** when treated with potassium *tert*-butoxide or (trimethylsilyl)amide gave rise to two sets of resonances for **2c**. Compound **3e** on treatment with (trimethylsilyl)amide (but not with potassium *tert*-butoxide) gave rise to only one set of resonances for **2e**. That deprotonation at C2-C_α had taken place was evident from the following: (1) the J coupling between C_2-$C_\alpha H$ and C2-$C_\beta H_3$ was lost; (2) on loss of the C2-$C_\alpha H$ resonance in base, no other resonance(s) appeared; (3) on neutralization with CF_3COOD, all resonances corresponding to **3c** and **3e** reappeared (the resonance corresponding to the C2-$C_\beta H_3$ was a singlet with a chemical shift in between the doublet resonances, subject to a small upfield shift induced by the C2-$C_\alpha D$, observed in **3c** and **3e**; and (4) on neutralization with CF_3COOH, all resonances corresponding to **3c** and **3e** reappeared.

The following could be concluded about enamine **2** in pyridine-d_5. (1) The pK_a of the biologically relevant **3c** at the C2-C_α position is lower than ca. 19,[6] a surprisingly large number considering that several thiamin diphosphate dependent enzymes must ionize this bond near pH 7.[7] The pK_a for the corresponding ionization in 2-(1-hydroxyethyl)thiamin was estimated to be 17 in H_2O.[8] (2) The barrier to rotation around the C2-C_α bond is high on the NMR time scale.[13] The temperature dependence of ^1H NMR spectra on **2a** and **2c** showed no coalescence up to 100 °C and enabled us to calculate a lower limit of ca. 18.4 kcal/mol for the barrier to rotation around the C2-C_α bond in these enamines.[14] Such a high barrier was evident even in **2a** with absolutely minimal steric constraints; hence, at least the same size barrier can be expected for any thiamin-bound enamine intermediate. The results provide direct and strong experimental support for the predominant role of the neutral resonance contribution in the electronic structure of the enamine[15] and are consistent with the observation of the highly conjugated enamine structure on pyruvate decarboxylase produced from a conjugated substrate analogue.[16]

Table II. Proton Chemical Shifts of Enamine Intermediates[a]

resonances	**2a**	**2b**	**2c** I	**2c** II	**2e**
N3-CH_3	2.68 (s) [1.36]	2.73 (s) [1.33]	2.82 (s) [1.42]	3.10 (s) [1.14]	2.70 (s) [1.36]
C4-CH_3	1.68 (d) [0.78]	1.79 (s) [0.51]	1.71 (d) [0.79]	1.68 (d) [0.82]	1.70 (d) [0.85]
C5-H	5.27 (m) [2.77]		5.35 (q) [2.88]	5.23 (q) [3.00]	5.44 (q) [2.93]
C5-CH_3		1.58 (s) [0.68]			
C2-$C_\alpha H$	4.03 (d) [-0.97] 3.77 (m) [-0.71]	4.02 (d) [-0.94] 3.76 (d) [-0.68]			
C2-$C_\beta H_3$			1.99 (s) [-0.40]	1.79 (s) [-0.20]	1.79 (s) [-0.15]
C2-$C_\alpha OCH_3$			3.49 (s) [-0.03]	3.36 (s) [0.10]	

[a] Measured in pyridine-d_5, chemical shifts measured downfield from internal $(CH_3)_4Si$ in ppm; the multiplicities are indicated in parentheses. The chemical shift difference between **3** and **2** is indicated in brackets, $[\delta] = \delta(\mathbf{3}) - \delta(\mathbf{2})$.

Acknowledgment. Financial support was provided by NSF Grant PCM-8217100, NIH-MBRS S06RR0.8223 (M. Nathanson, P.I.), the Rutgers Busch fund, and the Rutgers Research Council. We are grateful to Dr. F. J. Scheidl of Hoffmann-La Roche Inc., Nutley, NJ, for performing the elemental analyses.

Supplementary Material Available: Synthesis and analytical data for **3** (2 pages). Ordering information is given on any current masthead page.

(6) But not by much, since that of **3e** is greater than 19.
(7) Such as transketolases, but see also: Chen, G. C.; Jordan, F. *Biochemistry* **1984**, *23*, 3576-3582.
(8) Estimated[9] by relating the rate of deuterium exchange into the C_2-C_α position[10] to the pK_a via a linear free energy relationship that relates pK_a vs. such exchange rate constants in ketones.[11] A further uncertainty in comparing the acidity at the C_2-C_α in **3c** to that in 2-(1-hydroxyethyl)thiamin has to do with the apparently different inductive effects on the rate of deuterium exchange in 2-(1-hydroxyethyl)-3,4-dimethylthiazoliums (slower by at least 4 times) compared to those in 2-(1-hydroxyethyl)thiamine.[12]
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(10) Mieyal, J. J.; Votaw, R. G.; Krampitz, L. O.; Sable, H. Z. *Biochem. Biophys. Acta* **1967**, 205-208.
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(12) Gallo, A. A.; Sable, H. Z. *J. Biol. Chem.* **1976**, *251*, 2564-2570.
(13) Two resonances were observed for C2-CH_2 in **2a** and **2b**: two sets of resonances corresponding to the *E* and *Z* configurations in **2c** and one set of resonances for **2e**, similar in chemical shift to one of two sets observed for **2c**. Presumably, in **2e** the bulky silyl substituent does not allow formation of two configurations.
(14) Rahman, Atta-ur. *Nuclear Magnetic Resonance*; Springer-Verlag: New York, 1986; pp 131-133.
(15) While there is a clear uncertainty in relating the pK_a's found in pyridine-d_5 to those on the enzyme surface or even in water, the barrier height is only a lower limit even for enamine **2a** and is likely to be at least that magnitude under *all conditions* in *all* related enamines.
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Hydrogen-Bonded Cluster Carboxylic Acid: $[(\mu\text{-}H)_3(CO)_9Os_3(\mu_3\text{-}CCOOH)]_2$

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We wish to report the preparation and crystal structure of $(\mu\text{-}H)_3(CO)_9Os_3(\mu_3\text{-}CCOOH)$ (I), a hydrogen-bonded cluster carboxylic acid which was prepared from the reaction of $(\mu\text{-}H)_2(CO)_9Os_3(\mu_3\text{-}CCO)$ (II) with an H_2O-HCl mixture in CH_2Cl_2 at room temperature.

$$(\mu\text{-}H)_2Os_3(CO)_9(\mu_3\text{-}CCO) + H_2O \xrightarrow{HCl} (\mu\text{-}H)_3(CO)_9Os_3(\mu_3\text{-}CCOOH)$$

Formation of $(\mu\text{-}H)_3(CO)_9Os_3(\mu_3\text{-}CCOOH)$ is believed to take place through the hydrolysis of a chloroacyl intermediate formed in an initial reaction with HCl, analogous to the well-known reaction of ketene with H_2O in the presence of HCl.[1] The molecule

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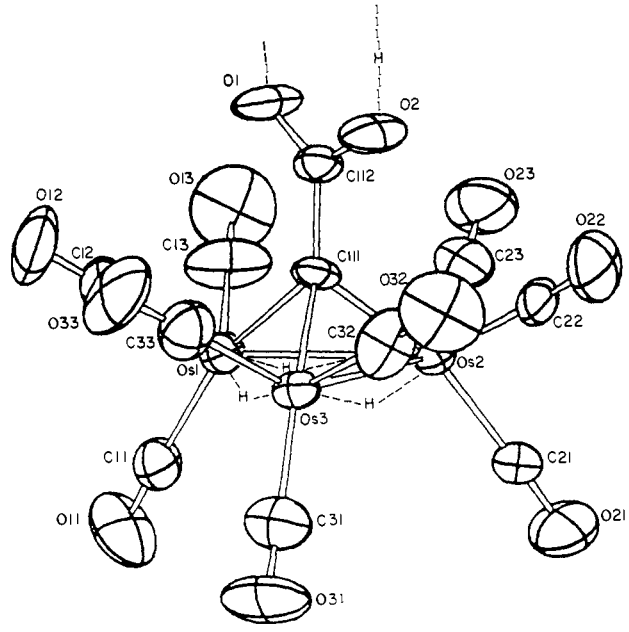

Figure 1. Molecular structure of the $(\mu\text{-H})_3(CO)_9Os_3(\mu_3\text{-CCOOH})$ unit.

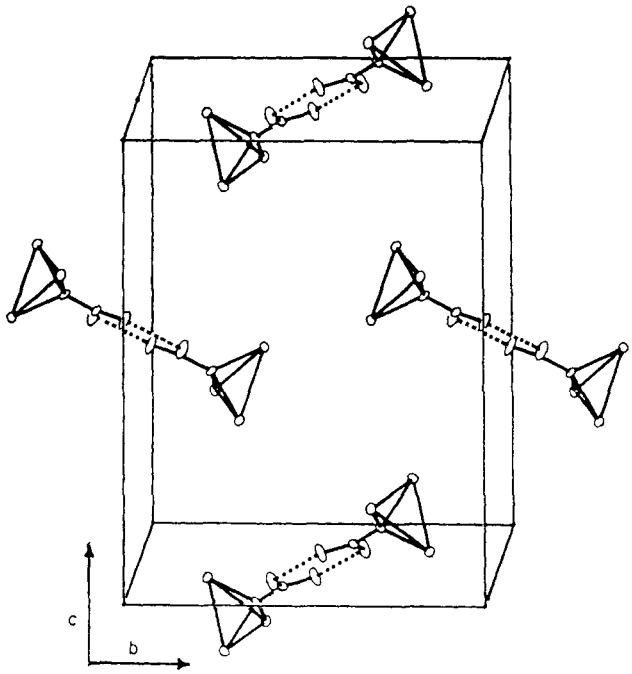

Figure 2. Packing of $[(\mu\text{-H})_3(CO)_9Os_3(\mu_3\text{-CCOOH})]_2$ dimers.

crystallizes as the hydrogen-bonded dimer $[(\mu\text{-H})_3(CO)_9Os_3(\mu_3\text{-CCOOH})]_2$.[1] Figures 1 and 2 show the structure of the $(\mu\text{-H})_3(CO)_9Os_3(\mu_3\text{-CCOOH})$ unit and the packing of the dimers, respectively. To our knowledge this is the first reported structure of a μ_3-CCOOH complex and the first evidence for hydrogen bonding. The formation of I through the reaction of II with H_2O has been reported,[2] and we have noted the very slow conversion of II to I in air. The analogous complex $(\mu\text{-H})_3(CO)_9Ru_3(\mu_3\text{-CCOOH})$[4] and also $Cp_3Co_3(\mu_3\text{-CH})(\mu_3\text{-CCOOH})$[5] have been reported based on ^1H NMR, IR, and mass spectra. Related esters $(\mu_3\text{-CCOOR})$[4-9] have also been reported, based uon ^1H NMR spectra.

To $(\mu\text{-H})_2Os_3(CO)_9(\mu_3\text{-CCO})$[3,6] (14.4 mg, 0.0166 mmol) in undried (0.005% H_2O content) degassed CD_2Cl_2 (1 mL) was added gaseous HCl (2 equiv, 0.0320 mmol). The reaction mixture was stirred at ambient temperature and then tipped into an NMR tube that was attached to the reaction vessel via a side arm. The sample was sealed under vacuum and stored at room temperature (300 K). Formation of the title compound was followed as a function of time by observing its ^1H NMR spectrum.[10] No significant increase in I was observed after a period of 3 weeks. The proton NMR spectrum suggests a 55% conversion to I. It was isolated in 47% yield (6.8 mg, 0.0077 mmol)[10] by three successive fractional crystallizations by allowing hexane to slowly diffuse into a CH_2Cl_2 solution at −10 °C. Impurities were unreacted II small amounts of $(\mu\text{-H})_3(CO)_9Os_3(\mu_3\text{-CCl})$(identified from single-crystal X-ray structure determination), and a material tentatively identified as $(\mu\text{-H})_3(CO)_9Os_3(\mu_3\text{-CCH}_2Cl)$ from the mass spectrum (calcd for $^{12}C_{11}{}^{35}Cl_1{}^1H_5{}^{16}O_9{}^{192}Os_3$ m/e 892, found m/e 892).

In the solid state the dimer $[(\mu\text{-H})_3(CO)_9Os_3(\mu_3\text{-CCOOH})]_2$ possesses C_i point symmetry.[1] Although the hydrogens were not located, their existence is established by the ^1H NMR spectrum described below.[10,11] The Os–Os distances Os(1)–Os(2) = 2.880 (1), Os(2)–Os(3) = 2.872 (1), and Os(1)–Os(3) = 2.879 (1) Å agree well with Os–Os distances observed for the Os–H–Os bonds in $(\mu\text{-H})_2(CO)_9Os_3(\mu_3\text{-CCO})$.[3] The Os–C distances Os(1)–C(111) = 2.07 (1), Os(2)–C(111) = 2.07 (1), and Os(3)–C(111) = 2.12 (1) Å are on the average 0.06 Å shorter than the corresponding bonds in $(\mu\text{-H})_2(CO)_9Os_3(\mu_3\text{-CCO})$.

For the CCOOH unit, distances and angles are as follows: C(111)–C(112) = 1.48 (2), C(112)–O(1) = 1.25 (2), C(112)–O(2) = 1.24 (2) Å; C(111)–C(112)–O(1) = 119 (1)°, C(111)–C(112)–O(2) = 121 (1)°, O(1)–C(112)–O(2) = 121 (1)°. The distance between hydrogen-bonded O(1) and O(2) atoms is 2.57 (1) Å. Although the CCOOH unit can be considered to be a precursor to acetic acid, some of its structural features more closely resemble those of benzoic acid. Benzoic acid also crystallizes as a centrosymmetric hydrogen-bonded dimer[11] while acetic acid exists as infinite hydrogen-bonded chains in the solid state.[12] The C–C bond distance of the CCOOH unit in benzoic acid is 1.48 (2) Å, equal to that of the C(111)–C(112) bond in I. The C–C bond in acetic acid is 1.54 (2) Å, a normal carbon–carbon bond length. This difference has been attributed to some double bond character between the two carbon atoms in the case of the benzoic acid.[11] Such a possibility is also reasonable in the present case. The distance between hydrogen-bonded oxygens in benzoic acid and in acetic acid is 2.64 (2) and 2.61 (2) Å, respectively. Acetic acid and benzoic acid have the same C–O distances, 1.24 (2) and 1.29 (2) Å.

Acknowledgment. We thank the NSF for support of this work through Grant CHE84-11630. D.-Y.J. thanks The Ohio State

(1) Crystal data for $[(\mu\text{-H})_3(CO)_9Os_3(\mu\text{-CCOOH})]_2$: space group $P2_1/c$, a = 8.440 (2) Å, b = 12.869 (3) Å, c = 16.8011 (4) Å, β = 100.47 (2)°, V = 1794.6 Å^3, d(calcd) = 3.268 g cm^{-3}, M, = 882.6, Z = 4, μ = 192.5 cm^{-1}. Diffraction data were collected with an Enraf–Nonius CAD4 diffractometer. Crystallographic computations were carried on a PDP 11/44 computer using SDP (structure determination package). The structure was solved by a combination of the direct method MULTAN 11/82 and difference Fourier syntheses. Full-matrix least-squares refinements were employed. R_F = 0.031 and R_{wF} = 0.041 (227 variables refined including the extinction coefficient) for 1864 reflections [$I > 3.0(I)$] of 2301 independent reflections collected over the 2θ range $4° \le 2\theta \le 55°$.

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(10) $(\mu\text{-H})_3(CO)_9Os_3(\mu_3\text{-CCOOH})$: mass spectrum calcd for $^{12}C_{11}{}^1H_4{}^{16}O_{11}{}^{192}Os_3$ m/e 888, found m/e 888; ^1H NMR (CD_2Cl_2, 30 °C, δ(Me_4Si) 0.00) 10.76 (COOH), −19.46 (Os–H–Os); ^{13}C NMR (CD_2Cl_2, 30 °C, δ ($Si(^{13}CH_3)_4$) 0.00) 165.5 (6C), 167.8 (3C), 170.1 (COOH).[13] IR (CH_2Cl_2) ν(OH) 3497 (w), ν(CO) 2128 (m, sh), 2092 (s), 2079 (sh), 2068 (m), 2031 (br, s), 1786 (w), 1639 (w, br) cm^{-1}.

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University for a Presidential Fellowship. NMR spectra were obtained at The Ohio State University Campus Chemical Instrument Center (funded in part by NSF Grant 79-10019). We thank Dr. Steven Mullen and Professor Allen Marshall for FTICR mass spectra.

Supplementary Material Available: Tables of selected bond distances, bond angles, positional parameters, and thermal parameters (4 pages); tables of observed and calculated structure factors (18 pages). Ordering information is given on any current masthead page.

Magnetic Field Effects on the Catalytic Oxidation of 2,6-Di-*tert*-butylphenol

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Although magnetic field effects in photochemical processes are well documented,[1] similar claims of magnetic perturbations on thermal reactions and biological processes suffer from irreproducibility and flawed experimental design or originate from controversial mechanisms.[2] Recent observations of CIDNP spectra in organometallic reactions indicate that radical pair formation can occur.[3a,b] We report a catalytic thermal reaction altered significantly by a laboratory magnetic field.

An applied magnetic field alters the oxidation rate of 2,6-di-*tert*-butylphenol to the corresponding benzoquinone (BQ) or diphenoquinone (DPQ) in the presence of dioxygen and a transition-metal catalyst. Reaction conditions are adjusted so that cobalt(II)bis(3-(salicylideneamino)propyl)methylamine, Co(SMDPT) ($S = {}^3/_2$), generates only BQ[4] while manganese(II)-bis(3-((5-nitrosalicylidene)amino)propyl)methylamine, Mn(5-NO_2SMDPT) ($S = {}^5/_2$), forms only DPQ.[5] Two stock solutions were prepared immediately prior to the experiment, one containing

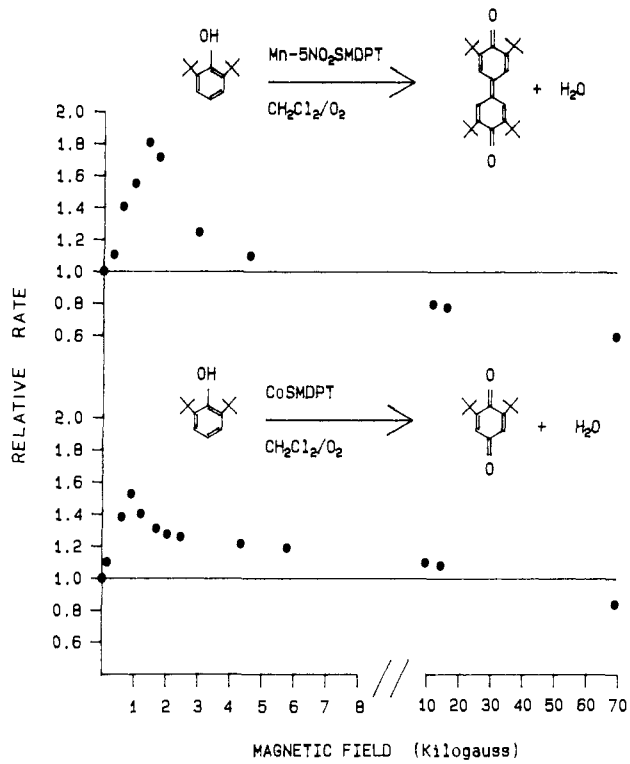

Figure 1. Relative rate of substrate oxidation vs. magnetic field strength (H). The initial rate at field H is divided by the initial rate at zero magnetic field.

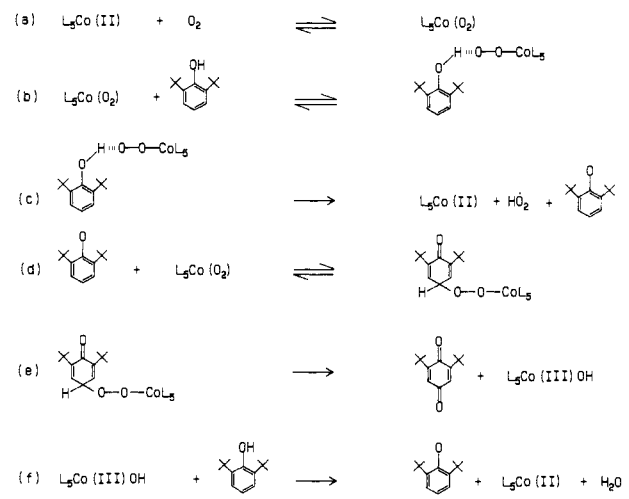

Figure 2. Mechanism of DTBP oxidation by CoSMDPT in the presence of O_2.

2,6-di-*tert*-butylphenol (DTBP) in CH_2Cl_2 and the other with the catalyst in deoxygenated CH_2Cl_2. The DTBP stock solution (0.1 mL) was syringed into a 5-mm screw cap NMR tube followed by the syringe addition of the catalyst solution (0.1 mL). Pure dioxygen was bubbled through the solution for 2 min, and the tube was sealed and placed in an air-driven turbine spinner to agitate the solution to ensure that mass transfer of O_2 into the solution is not rate limiting. An external magnetic field[6] is applied by placing the entire sample volume midway between and at the center of the 4-in. pole faces of an electromagnet. The 70.05 kG field was obtained from the superconducting magnet of a 300-Mhz Bruker NMR spectrometer. Dioxygen and DTBP are present in sufficient concentration to ensure that the rate of product formation is linear during the reaction interval, and reaction conditions were chosen to prevent formation of a precipitate.[7] The

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(6) Magnetic field strength (H, Oe) corresponds to magnetic inductance (H, G). Zero-field is approximated by the earth's field of 0.5 G.

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