can be accounted for by attack at the terminal nitrogen,[9] as shown in eq 3. These products have analogues in the reactions of other anions with N_2O.[10]

$$CH_2^{\bullet-} + N{=}N{=}O \rightarrow [{}^{\bullet}CH_2{-}N{=}N{-}O^-] \rightarrow CH_2{=}N^- + {}^{\bullet}NO \quad (3a)$$

$$\rightarrow CN^- + H_2 + {}^{\bullet}NO \quad (3b)$$

$$\rightarrow \dot{C}{=}N{=}N^- + H_2O \quad (3c)$$

Reaction with carbon disulfide also occurs by a number of channels (eq 4) reflecting the great reactivity of $CH_2^{\bullet-}$. Reaction

$$CH_2^{\bullet-} + S{=}C{=}S \rightarrow S^{\bullet-} + CH_2{=}C{=}S \quad (4a)$$

$$\rightarrow HS^- + \dot{C}H{=}C{=}S \quad (4b)$$

$$\rightarrow {}^-CH{=}C{=}S + HS^{\bullet} \quad (4c)$$

$$\rightarrow CH_2S^{\bullet-} + CS \quad (4d)$$

$$\rightarrow CS_2^{\bullet-} + CH_2 \quad (4e)$$

$$\rightarrow \text{neutral products} + e \quad (4f)$$

4a presumably occurs by addition with loss of $S^{\bullet-}$. Channels 4b and 4c result when reaction 4a is followed by hydrogen atom transfer or proton transfer, respectively, before the initial products separate. Direct carbanion attack on sulfur would lead to $CH_2S^{\bullet-}$ (eq 4d) while charge transfer would form $CS_2^{\bullet-}$ (eq 4e). Detachment (eq 4f) is, however, the major channel.

Reaction of $CH_2^{\bullet-}$ with O_2 forms $O^{\bullet-}$ exclusively (eq 5), while SO_2 produces both $SO^{\bullet-}$ (by attack on oxygen, eq 6a) and $SO_2^{\bullet-}$ (by electron transfer, eq 6b).

$$CH_2^{\bullet-} + O_2 \rightarrow O^{\bullet-} + CH_2{=}O \quad (5)$$

$$CH_2^{\bullet-} + SO_2 \rightarrow SO^{\bullet-} + CH_2{=}O \quad (6a)$$

$$\rightarrow SO_2^{\bullet-} + CH_2 \quad (6b)$$

The $CH_2^{\bullet-}$ and $O^{\bullet-}$ anions are isoelectronic species and, as such, show many parallels in reactivity. Nevertheless, there are important differences in their behavior, differences which shed light on the chemistry of both species.[11] For example, $O^{\bullet-}$ reacts with ethylene to form the vinylidene radical anion (eq 7),[12] while the

$$O^{\bullet-} + CH_2{=}CH_2 \rightarrow H_2O + {}^{-\bullet}C{=}CH_2 \quad \Delta H \simeq -10 \text{ kcal/mol} \quad (7)$$

$$CH_2^{\bullet-} + CH_2{=}CH_2 \not\rightarrow CH_4 + {}^{-\bullet}C{=}CH_2 \quad \Delta H \simeq -21 \text{ kcal/mol} \quad (8)$$

analogous process with $CH_2^{\bullet-}$ does not occur despite its greater exothermicity[13-16] (eq 8). Similarly, we have no evidence for $H_2^{\bullet+}$ abstraction by $CH_2^{\bullet-}$ with other organic compounds, for example, benzene, in striking contrast to the chemistry of $O^{\bullet-}$.[9]

As our results show, even minor, highly reactive ions can be separated and studied in the FA-SIFT. We are currently extending our investigations to the chemistry of CH^- and $C^{\bullet-}$ and examining ion production from other neutrals (e.g., SiH_4 and PH_3) which should give rise to analogous anions. It seems likely that nearly any anion bound by 8-10 kcal/mol or more can be studied by this technique.

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(8) Nitrous oxide also reacts rather slowly with other anions. For example, for $NH_2^- + N_2O$, $k = 2.9 \times 10^{-10}$ (Bierbaum, V. M.; Grabowski, J. J.; DePuy, C. H. *J. Phys. Chem.* **1984**, *88*, 1389).

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(10) Kass, S. R.; Filley, J.; Van Doren, J. M.; DePuy, C. H. *J. Am. Chem. Soc.* **1986**, *108*, 2849.

(11) For a summary of the reactions of $O^{\bullet-}$, see: Jennings, K. R. *Philos. Trans. R. Soc. London, Ser. A* **1979**, *293*, 125. Bruins, A. P.; Ferrer-Correia, A. J.; Harrison, A. G.; Jennings, K. R.; Mitchum, R. K. *Adv. Mass Spectrom.* **1978**, *7*, 355. Dawson, J. H. J.; Jennings, K. R. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 700.

(12) Lindinger, W.; Albritton, D. L.; Fehsenfeld, F. C.; Ferguson, E. E. *J. Chem. Phys.* **1973**, *63*, 3238.

(13) Reaction enthalpies were calculated at 0 K by using heats of formation from the following sources: ref 14 for $O^{\bullet-}$, C_2H_4, H_2O, and CH_4; ref 15 and 16 for ${}^{-\bullet}C{=}CH_2$; ref 1 for $CH_2^{\bullet-}$.

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Generation and Physical Properties of Enamines Related to the Key Intermediate in Thiamin Diphosphate Dependent Enzymatic Pathways

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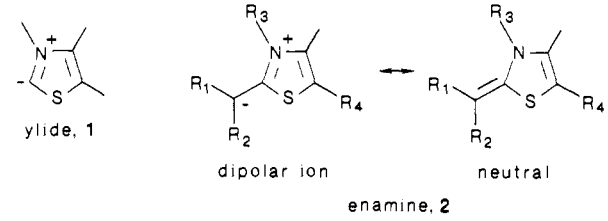
The catalytic power of the thiamin diphosphate coenzyme resides, in part, in the ability of its thiazolium ring to stabilize two intermediates: the ylide **1** and the putative enamine ($C2_\alpha$ carbanion) **2**.[1,2] We here report the first successful generation of structures analogous to the enamine **2** in model systems[3] and ^1H NMR spectroscopic characterization of such structures.



The thiazolium models **3** synthesized[4] are listed in Table I. Protection of the hydroxy group was essential to avoid base-induced decomposition. The ^1H NMR spectra could be assigned unequivocally based on comparisons between the N-CH_3 and N-CD_3 compounds and the readily detectable long-range J coupling between C4-CH_3 and C5-H. Compounds **3a** and **3b** were useful in the spectral assignments and enabled assessment of the effect of the C2-C_α oxygen on enamine structure and stability.

Treatment of **3** with about 1.2 equiv of potassium *tert*-butoxide or Na[$(CH_3)_3Si]_2N$ ((trimethylsilyl)amide, pK_a in Me_2SO is 25[5]) in anhydrous pyridine-d_5 resulted in the shift to higher fields of the N-CH_3, C4-H, and C5-H (or C5-CH_3) resonances (Table II), consistent with reduction of the aromaticity and/or of the

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(2) Krampitz, L. O. *Annu. Rev. Biochem.* **1969**, *38*, 213-240.

(3) Some model studies that implied the intermediacy of the enamine: (a) Rastetter, W. H.; Adams, J.; Frost, J. W.; Nummy, L. J.; Frowmer, J. E.; Roberts, D. B. *J. Am. Chem. Soc.* **1979**, *101*, 3785-3787. (b) Zoltewicz, J. A.; Helmick, L. S. *J. Org. Chem.* **1978**, *43*, 1718-1721, 3785-3787.

(4) Elemental analysis (C, H, N = ±0.3%) and ^1H NMR were consistent with the proposed structures.

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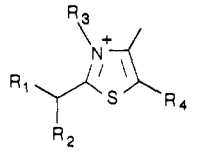
Table I. Thiazolium Compounds Synthesized



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]

			2c		
resonances	**2a**	**2b**	I	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, $[\delta] = \delta(\mathbf{3}) - \delta(\mathbf{2})$.

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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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(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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