toreduction processes are well-known.[10] The alcohol product, L′, has been established by ^{1}H NMR and mass spectra data compared to the authentic samples of L′ synthesized independently.[11] The main result here is that visible light irradiation of the Re complexes results in the same chemistry as from direct ultraviolet irradiation of the ketones.

Sensitized photoreduction of excess ketone (ketone not initially bound to Re) requires a ligand-substitution process to exchange the reduced material for the unreacted ketone, since free ketone does no quenching of the ReLCT or ReL′CT excited state. The *fac*-[XRe(CO)$_3$L$_2$] complexes sluggishly undergo substitution reactions at 25 °C. From measurements of the rate of the reaction represented by eq 5, it would appear that dissociation of L′ (L′

$$fac\text{-}[XRe(CO)_3L_2'] + 1,10\text{-phen} \rightarrow fac\text{-}[XRe(CO)_3(1,10\text{-phen})] + 2L' \quad (5)$$

= methyl-4-pyridylmethanol, phenyl-4-pyridylmethanol) from Re occurs with a rate constant of $\sim 10^{-7}$ s^{-1}. At 50 °C, the rate constant is $\sim 10^{-4}$ s^{-1}. Thus, the ligand-exchange rate may be the rate-limiting step in the overall sensitization process, depending on the rate of excitation (light intensity) and temperature. At 25 °C and at our typical intensities of $\sim 10^{-7}$ einstein/min, thermal exchange of L′ is rate limiting. This was proven by irradiating *fac*-[IRe(CO)$_3$(4-AcPyr)$_2$] in the presence of 4-benzoylpyridine and Et$_3$N. The coordinated ketone undergoes photoreduction before any 4-benzoylpyridine is reduced.

To summarize, we find that the pyridyl ketones can be photoreduced by irradiation with wavelengths longer than absorbed by the ketones themselves. The same products and similar quantum yields are obtained from direct and sensitized photoreaction. The sensitization process involves binding the ketone to a metal to induce a low-lying M → ketone CT absorption, electron donation to the complex from some reducing agent, H$^+$/H· transfer chemistry to yield the alcohol, and exchange of the reduction product for unreacted ketone (eq 1, 2, 6, and 7).

$$fac\text{-}[XRe(CO)_3L_2]^{-}\cdot \rightarrow fac\text{-}[XRe(CO)_3LL'] \quad (6)$$

$$fac\text{-}[XRe(CO)_3LL'] \xrightarrow[\Delta]{L} fac\text{-}[XRe(CO)_3L_2] + L' \quad (7)$$

The H$^+$/H· transfer reactions giving the alcohol presumably parallel those in the direct irradiation. A difference in the Re-complex sensitization is that the odd electron in *fac*-[XRe(CO)$_3$L$_2$]$^-$· may not be totally localized on the ketone as it would be in the direct reaction (eq 8).[12] Electrochemical experiments

$$[\text{ketone}]^* + Et_3N \rightarrow [\text{ketone}]^{-}\cdot + Et_3N^{+}\cdot \quad (8)$$

show that the ketone complexes are 0.35–0.5 V more easily reduced than the free ketones, consistent with greater delocalization of the added electron density. The sensitization process outlined here should be applicable to many other photoredox reactions, and the wavelength response can be controlled, in principle, by the functionality on the metal fragment other than the L.

Acknowledgment. We thank the National Science Foundation for support of this research. M.S.W. acknowledges support as a Dreyfus Teacher-Scholar grant recipient, 1975–1980.

(11) Interestingly, pyridyl ketones appear to give the alcohol under conditions where phenyl ketones give pinacol photoreduction products: Minn, F. L.; Trichilo, C. L.; Hurt, C. R.; Filipescu, N. *J. Am. Chem. Soc.* **1970**, *92*, 3600.

(12) There is now some concern whether triplet-excited ketones are quenched by electron transfer or by H· abstraction from Et$_3$N: Inbar, S.; Linschitz, H.; Cohen, S. G. *J. Am. Chem. Soc.* **1980**, *102*, 1419.

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Methyl Reactivity in Deazalumazines[1]

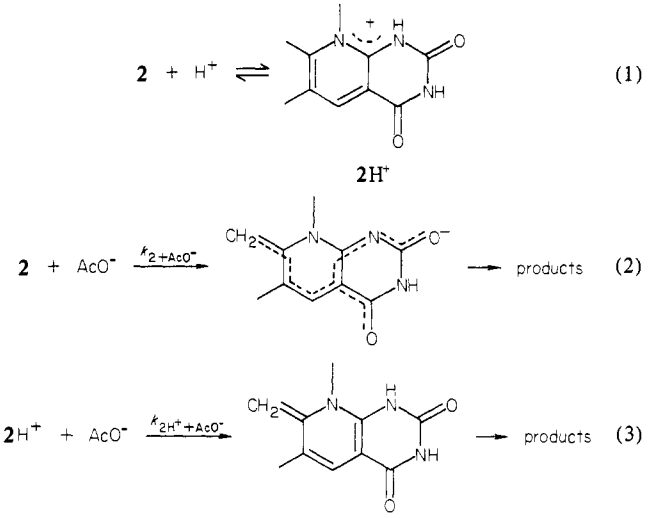
Sir:

6,7-Dimethyllumazines (e.g., **1**) give flavins both in vivo and in vitro via a mechanism involving initial proton loss from the highly reactive C-7 CH$_3$ group.[2] We have examined a series of 5-deazalumazines (**2**–**7**) in order to learn more about the activation process at C-7, since replacing N at position 5 with CH gives more opportunities for structural variation. Furthermore, 5-deazaflavins have recently been shown to be involved in the biological reduction of carbon dioxide to methane,[3] and the analogous 5-deazalumazines are of interest as possible precursors. We report herein an unusual effect of methyl substitution adjacent to the reaction site.

Compounds **2**, **3**, **5**, and **7** were prepared[4] by condensing 6-methylaminouracil with the appropriate dicarbonyl compound (or its acetal), essentially by the method of Paterson and Wood;[5] **4** and **6** were similarly prepared[4] by using the unsaturated aldehyde or acetal. These authors prepared a series of compounds closely related to those used herein and noted that both C-5 and C-7 CH$_3$ groups in deazalumazines exchange their hydrogen atoms in D$_2$O.

The structures of the isomers **2** and **4**, and **5** and **6**, made on the basis of NMR shifts and synthesis arguments, were confirmed by using the nuclear Overhauser effect. Irradiation of the N–CH$_3$ protons gave a 38% enhancement of the ring proton for **4** and a 20% enhancement of the C-7 CH$_3$ group of **5**. Assignment of the signals for the two exchanging groups in **3** was similarly made, the upfield group that was assigned to C-7 CH$_3$ giving a small enhancement (6%).

We have determined the general base- and acid-catalyzed rate constants in water for the C-5 and C-7 methyl groups (the C-6 and N-8 methyl groups do not react) by iodometry and deuterium exchange (NMR).[6] See, for example, reactions 1–3. Partitioning



(1) The financial support of the Natural Sciences and Engineering Research Council of Canada is gratefully acknowledged.

(2) (a) Paterson, T.; Wood, H. C. S. *J. Chem. Soc., Perkin Trans. 1* **1972**, 1051. (b) Plaut, G. W. E.; Beach, R. L.; Aogaichi, T. *Biochemistry* **1970**, *9*, 771.

(3) (a) Tzeng, S.; Wolfe, R.; Bryant, M. *J. Bacteriol.* **1975**, *121*, 184. (b) Eirich, D.; Balch, W.; Wolfe, R. *Biochemistry* **1978**, *17*, 4583. (c) Ashton, W. T.; Brown, R. D.; Jacobson, F.; Walsh, C. *J. Am. Chem. Soc.* **1979**, *101*, 4419.

(4) Expected NMR and UV spectra and satisfactory analytical data were obtained for all new compounds, **2**–**7**. Anal. Calcd for $C_{10}H_{11}N_3O_2$ (**2**–**4**): C, 58.53; H, 5.40; N, 20.48. Found: (**2**) C, 58.41; H, 5.40; N, 20.36; (**3**) C, 58.54; H, 5.28; N, 20.15; (**4**) C, 58.33; H, 5.30; N, 20.22. Calcd for $C_9H_9N_3O_2$ (**5**, **6**): C, 56.54; H, 4.75; N, 21.98. Found: (**5**) C, 56.46; H, 4.86; N, 21.81; (**6**) C, 56.48; H, 4.72; N, 21.75. Calcd for $C_{11}H_{13}N_3O_2$ (**7**): C, 60.26; H, 5.98; N, 19.17. Found: C, 60.06; H, 5.93; N, 19.01.

(5) Paterson, T.; Wood, H. C. S. *J. Chem. Soc., Perkin Trans. 1* **1972**, 1041. See also: Wood, H. C. S.; Wrigglesworth, R.; Yeowell, D. A.; Gurney, F. W.; Hurlbert, B. S. *Ibid.* **1974**, 1225.

(6) (a) McAndless, J. M.; Stewart, R. *Can. J. Chem.* **1970**, *48*, 263. (b) Stewart, R.; McAndless, J. M. *J. Chem. Soc., Perkin Trans. 2* **1972**, 376. (c) Srinivasan, R.; Stewart, R. *J. Am. Chem. Soc.* **1976**, *98*, 7648.

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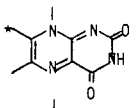
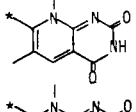
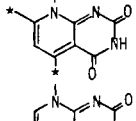
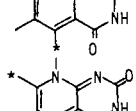
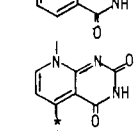
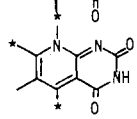
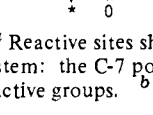
Table I. Rate Data for Proton Loss from Activated Methyl Groups[a] in Methyl Lumazines, 1–7, in Water at 35.7 °C

	Compound	pK_{SH^+}	$10^7 k_S + AcO^-$ M^{-1} sec^{-1}	$10^5 k_{SH^+} + AcO^-$ M^{-1} sec^{-1}
1		0.93	142,000[b]	238,000[b]
2		2.12	230	461
3		2.26	9.92 (7-Me 7.0) (5-Me 2.9)	13.0 (7-Me 9.2) (5-Me 3.8)
4		2.46	87.8	122
5		1.81	95.8	130
6		2.14	25.8	38.6
7		2.57	39.2 (7-Me 28) (5-Me 11)	51.2 (7-Me 36) (5-Me 15)

[a] Reactive sites shown by asterisks; lumazine numbering system: the C-7 position in **5** and the C-5 position in **6** have the reactive groups. [b] Reference 6b, $t = 34.5$ °C.

of the iodination rate between the two methyl groups in **3** was made by following the reaction in D_2O for an extended period and measuring the relative degrees of exchange with a 270-MHz spectrometer. The upfield methyl group assigned above to the C-7 position exchanged 2.4 times as fast as that at C-5. The same partition ratio was assumed to hold for **7**. The pK_{SH^+} values were required to convert the catalytic coefficients to values of $k_{SH^+ + AcO^-}$, and these were determined spectrophotometrically.

The results given in Table I show a remarkable effect of methyl substitution. Introducing a methyl group at the next ring position but one (remote substitution) has the expected deactivating effect on kinetic acidity of the reacting methyl group, whether proton loss involves the neutral compound or the cation. Comparing **2** and **7** or **3** and **5** shows that C-5 CH_3 decreases the rate of proton loss from C-7 CH_3 by factors of 8.2–14. Comparing **3** and **6** or **4** and **7** shows that C-7 CH_3 has a comparable effect on C-5 CH_3 (factors of 8.0–10.2). These results can be ascribed to the operation of a large polar effect. (Compare the still greater effect, again presumably polar in origin, when CH replaces N at position 5, i.e., **1** and **2**.)

Substituting methyl for ring hydrogen at a position *adjacent* to a reactive methyl group, however, causes an increase in the rate of proton loss. For C-7 CH_3 dissociation, compare **2** and **5** or **3** and **7**. The rate constants for the general base reaction are 2.4–4.0 times greater and for the general acid reaction 3.5–3.9 times greater when another methyl group is adjacent to the reactive methyl site. For C-5 CH_3 dissociation, compare **3** and **7** or **4** and **6**, where the effect is 3.2–3.9 times. Although these rate increases are not large in themselves, they are remarkable when one considers that the electron-donating effect of an adjacent methyl group should be markedly greater than that of a remote methyl group, where a rate *decrease* of 8–14 times was observed. The special proximity effect of methyl, whatever its origin, is thus causing a rate increase of possibly two orders of magnitude for proton loss from methyl groups at either C-5 or C-7.

Might proton loss be causing the essentially aromatic system to change to a nonplanar arrangement, thus allowing relief of steric stain? This might explain the effect at either C-5 or C-7 but not at both, since **3** is the least reactive compound of all. Furthermore, the reaction in both the general acid route (reactions 1 and 3) and general base route (reaction 2) is bimolecular, and the transition state contains an extra species, acetate ion, at the reaction site. Additionally, there appears to be no buttressing effect;[7] the rates of the tetramethyl compound **7** are in agreement with a simple additive effect of adjacent and remote methyls.

The C-7 methyl group is an activated site in lumazines (and in flavins) and is an important center for chemical condensation in these compounds.[2,8,9] Our results point to a special proximity effect of neighboring methyl (at C-6) that is the reverse of the expected steric and electronic effects[10] and that facilitates proton loss from the C-7 methyl group in such compounds.

(7) Westheimer, F. H. In "Steric Effects in Organic Chemistry"; Newman, M. S., Ed.; Wiley: New York, 1956; p 552.
(8) Weimar, W. R.; Neims, A. H. In "Riboflavin"; Rivlin, R. S., Ed.; Plenum Press: New York, 1975; Chapter 1.
(9) The lumazine that is the precursor of riboflavin in nature carries at N-8 not a methyl group as in **1** but a ribityl group, and this unit is known to have an important influence on the condensation process. See: Plaut, G. W. E.; Beach, R. L. In "Chemistry and Biology of Pteridines"; Pfleiderer, W., Ed.; de Gruyter: Berlin, 1975.
(10) For an account of the steric and electronic effects of methyl on the rate of proton loss from other compounds, see: Bordwell, F. G.; Hautala, J. A. *J. Org. Chem.* **1978**, *43*, 3116. Zoltewicz, J. A.; Helmick, L. S. *Ibid.* **1978**, *43*, 1718.

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Mercury(I)/(II): A Novel Trap for Harvesting Excited-State Energies

Sir:

Reversible excited-state electron transfer in solution, like photochemical production of hydrogen and valence isomerization, has been widely studied in connection with solar energy conversion.[1-5] Most of the studies to date have utilized systems based on eq 1–3, where a number of organic and inorganic donors (D)

$$D \xrightarrow{h\nu} {}^*D \qquad \phi' \tag{1}$$

$${}^*D + Q \xrightarrow{k_2} D^{\mp} + Q^{\pm} \tag{2}$$

$$D^{\mp} + Q^{\pm} \xrightarrow{k_b} D + Q \tag{3}$$

have been employed. Most of these systems suffer from the fact that the back thermal reaction (eq 3) is too rapid to allow efficient harvesting of the redox energy. ϕ' is the efficiency of population of the sensitizing state following excitation. An example of this

(1) (a) Jonak, G. D.; Matheson, M. S.; Meisel, D. *J. Am. Chem. Soc.* **1978**, *100*, 1449. (b) Hoselton, M. A.; Lin, C-T; Schwarz, H. A.; Sutin, N. *Ibid.* **1978**, *100*, 2383. (c) Winterle, J. S.; Kliger, D. S.; Hammond, G. S. *Ibid.* *98*, 3719.
(2) (a) Sprintschnik, G.; Sprintschnik, H. W.; Kirsch, R. P.; Whitten, D. G. *J. Am. Chem. Soc.* **1976**, *98*, 2337; **1977**, *99*, 4947. (b) Lehn, J. M.; Sauvage, J. P. *Nouv J. Chim.* **1978**, *1*, 449.
(3) (a) Lin, C-T; Bottcher, W.; Chou, M.; Creutz, C.; Sutin, N. *J. Am. Chem. Soc.* **1976**, *98*, 6536–6544. (b) Clark, W. D. K.; Sutin, N. *Ibid.* **1977**, *99*, 4676–4682. (c) Lin, C-T; Sutin, N. *J. Phys. Chem.* **1976**, *80*, 97.
(4) (a) Sutin, N.; Creutz, C. *Adv. Chem. Ser.* **1978**, *No. 168*, 1. (b) Delaive, P. J.; Lee, J. T.; Abruna, H.; Sprintschnik, H; Meyer, T. J.; Whitten, D. G. *Ibid.* **1978**, *No. 168*, 1. (c) Balzani, V.; Bolletta, F.; Gandolfi, M. T.; Maestri, M. *Top. Curr. Chem.* **1978**, *75*, 1.
(5) (a) Whitten, D. G.; DeLaive, P. J.; Foreman, T. K.; Mercer-Smith, J. A.; Schmehl, R. H.; Gianotti, C. *Sol. Energy: Chem. Convers. Storage, Symp.* **1979**, 117. (b) Thomas, J. K. *Ibid.* **1979**, 141. (c) Hoffman, M. Z.; Lichtin, N. N. *Ibid.* **1979**, 153. (d) DeGraff, B. A.; Demas, J. N.; Taylor, D. G. *Ibid.* **1979**, 189. (e) Tien, H. T.; Higgins, J.; Mountz, J. *Ibid* **1979**, 203. (f) Huatala, R. R.; King, R. Bruce; Kutal, C. *Ibid.* **1979**, 333.

0002-7863/80/1502-6169$01.00/0