The splitting of the Soret band of [RS-heme-CO]$^-$ and [RS-heme-O_2]$^-$ has been correlated with other metalloporphyrins such as Sb(III) and Bi(III) porphyrins that bear a close spectral resemblance and a theorectical interpretation for this splitting as well as the red shifting of the Soret band has been proposed.[21] The notable spectral discrepancies between the [RS-heme-O_2]$^-$ complex reported here and the oxygenated P-450 enzymic system is, however, open to speculation at this stage. Nevertheless the present results suggest that while in the ferric deoxy and ferrous CO forms of P-450 a deprotonated cysteine residue may serve as the axial ligand, the oxygenated form of P-450 *cannot* be bound to a mercaptide ion. Whether this change in axial ligation, upon oxygen binding, results from the change of mercaptide to mercaptan or replacement of mercaptide for a non-sulfur-containing ligand must await further experimentation. However, this intriguing change in axial ligation at the critical step of the enzymic reaction may be ultimately related to the activation of molecular oxygen for the hydroxylation reactions catalyzed by these systems.

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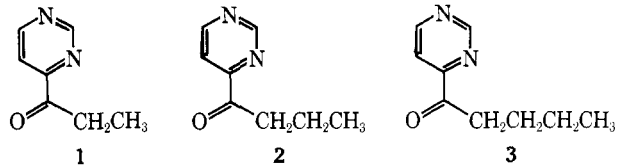
Photochemistry as a Probe of the Excited State Properties of Molecules. IV.[1] A Determination of the Relative Triplet Reactivities of the Carbon–Nitrogen and Carbon–Oxygen Chromophores of 4-Acylpyrimidines. Photochemical Cyclopropanol Formation

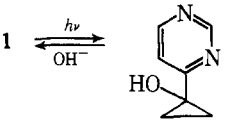
Sir:

In recent years the photochemistry arising from the C=N portion of azaaromatic molecules has received considerable attention.[4] A number of studies have compared the excited-state behavior of the C=N chromophore of aza aromatics to that of the C=O chromophore of ketones.[5] Although the studies have clearly demonstrated qualitative analogies in photochemical behavior, no quantitative comparisons of the excited-state reactivities of the two chromophores have been made. We recently reported[2] that 4-acylpyrimidines could uniquely undergo intramolecular hydrogen abstraction by way of both C=N and C=O triplets. We have since examined the relative triplet reactivities of the C=N and C=O chromophores of 4-propionylpyrimidine (**1**), 4-butyrylpyrimidine (**2**), and 4-valerylpyrimidine (**3**). In this communication we wish to report findings which indicate that the C=N and C=O triplets of 4-acylpyrimidines possess similar reactivity, but surprisingly dissimilar selectivity towards intramolecular hydrogen atom abstraction.



1 **2** **3**

Irradiations of the 4-acylpyrimidines (**1**), (**2**), and (**3**) were carried out at 313 nm in benzene as previously described.[2b] Under the photolysis conditions, ketone (**1**) was found to rearrange exclusively to 1-(4-pyrimidyl)-1-cyclopropanol (**4**). The structure of the cyclopropanol (**4**) is based on its spectral characteristics (ir (CCl_4) 2.80 μ, NMR ($CDCl_3$) methylene δ 1.42 (4 H) multiplet, hydroxyl 2.96 (1 H) broad singlet, aromatic 7.45 (1 H) doublet, 8.60 (1 H) doublet, 9.06 (1 H) singlet; mass spectrum (*m/e*) 136 M^+, 135, 108, 107, 80 (base peak), 79, 57, 55, 53, 52) and on the fact that it reverts back to ketone (**1**) upon treatment with 0.1 N NaOH. Under the same irradiation conditions, ketone (**2**) afforded a mixture of 4-acetylpyrimidine (**5**) and 1-(4-pyrimidyl)-2-methyl-1-cyclopropanol (**6**),[2b] while ketone (**3**) underwent virtually exclusive type II cleavage to 4-acetylpyrimidine (**5**).



4

Since cyclopropanol formation can occur only via γ-hydrogen abstraction by C=N triplets and type II elimination can result only from triplet C=O hydrogen abstraction,[2] each reaction can serve as a probe of the relative triplet reactivities of the two chromophores. The side chain of the pyrimidyl ketone (**1**) permits only C=N abstraction of primary hydrogen atoms. The side chain of the pyrimidyl ketone (**2**), on the other hand, allows for primary C=O hydrogen abstraction and secondary C=N hydrogen abstraction, while that of the pyrimidyl ketone (**3**) permits only secondary C=N and C=O hydrogen abstraction. The nature of the products obtained from the photolysis of ketones **1**, **2**, and **3** clearly indicates that exclusive C=N hydrogen

Table I. Quantum Yields and Triplet Reactivities[a] of 4-Acylpyrimidines

Pyrimidine	Φ_{II}[b]	Φ(Cyclopropanol formation)	Slope $Kq\tau$ (M^{-1})	$1/\tau(10^8)$ s^{-1}
(1) 4-Propionyl[c]	—	0.34[e]	75	0.67
(2) 4-Butyryl[d]	0.13	0.18	30	1.67
(3) 4-Valeryl[d]	0.26	—	4.15	12

[a] In benzene solvent, $Kq = 5 \times 10^9$ M^{-1} s^{-1}. [b] Quantum yield for 4-acetylpyrimidine formation. [c] Originally 0.01 M in ketone. [d] Originally 0.05 M in ketone. [e] In *tert*-butyl alcohol.

abstraction occurs from ketone **1**, that competitive C=N and C=O hydrogen abstraction occurs from ketone **2**, and that C=O hydrogen abstraction predominates from ketone **3**.

The photoreactions of ketones **1**, **2**, and **3** were quenched using 1,3-pentadiene. Quantitative information regarding their respective triplet reactivities was calculated from Stern-Volmer plots[6] and eq 1.

$$\Phi_0/\Phi = 1 + Kq\tau[Q] \quad (1)$$

The reaction quantum yields and triplet reactivities are summarized in Table I. The data in Table I indicate that the valerylpyrimidine triplets are about seven times more reactive towards intramolecular hydrogen abstraction than the 4-butyrylpyrimidine triplets and that the 4-butyrylpyrimidine triplets are about two and a half times more reactive than the corresponding 4-propionylpyrimidine triplets. However, since about 42% of the triplet reactivity of 4-butyrylpyrimidine (**2**) is due to the C=O chromophore and 58% to the C=N a more accurate estimate of the relative triplet carbonyl reactivity of ketone **3** to **2** (secondary vs. primary hydrogen abstraction) is 17.[7] By analogy, the relative triplet C=N reactivity of ketone **2** to **1** (secondary vs. primary hydrogen abstraction) is found to be only 1.5.[9]

When one compares the reactivities of the C=O and C=N chromophores directly, the C=O and C=N triplets are found to possess about equal reactivity towards primary hydrogen atoms (7.0×10^7 s^{-1} vs. 6.7×10^7 s^{-1}). Towards secondary hydrogens, however, the C=O triplets are found to be 12 times more reactive than the C=N triplets (12×10^8 s^{-1} vs. 0.97×10^8 s^{-1}). The latter indicates why little to no cyclopropanol formation occurs from the photolysis of 4-valerylpyrimidine (**3**).

The observed lack of selectivity of the C=N triplets of 4-acylpyrimidines towards primary vs. secondary hydrogen atom abstraction cannot be unequivocally explained on the basis of our present data. It may indicate that hydrogen abstraction by the C=N chromophore unit is more exothermic and involves a lower activation energy than that of the C=O. Such an explanation has been used to rationalize the low selectivity of certain free radicals towards abstraction of secondary vs. primary hydrogen atoms.[10] The fact that the C=N and C=O triplets exhibit about equal reactivity towards primary hydrogens, however, suggests that additional factors must influence the hydrogen abstraction process.

Triplet ketones have been compared to alkoxy radicals in terms of their selectivity towards C-H bond abstraction.[8] A similar comparison of C=N triplets to amino radicals would be of interest here. Unfortunately the scarcity of available reactivity data[11] on amino radicals does not permit such a comparison at this time.

To our knowledge this work represents the first quantitative estimation of the relative triplet reactivity of a C=O vs. C=N chromophore unit. We are presently investigating the mechanism of the C=N hydrogen abstraction process in greater detail.

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A Paramagnetic, Square-Pyramidal Nickel(II) Alkyl Complex

Sir:

A large number of nickel(II) complexes containing alkyl ligands have been prepared; however, except for one tetrahedral example, these are four- or five-coordinate,[1] diamagnetic compounds.[2] Although it is generally not stated explicitly, high-spin nickel alkyl complexes are expected to be very unstable. We have prepared a square-pyramidal, high-spin nickel(II) alkyl complex, which is stable at room temperature, by alkylation of **1**. The synthesis and properties of this unique compound are the subject of this communication.

Addition of a slight excess of dimethylmagnesium[3] to a suspension of 1 g (1.6 mmol) of **1**[4] in 25 ml of purified THF at room temperature under nitrogen produced an emerald green solution. After dissolution of all of the starting material (about 15 min), the volume of the solution was reduced to 10 ml, and 20 ml of ether was added to yield crystalline **2**. Recrystallization was by dissolution in THF followed by addition of ether. Yield, 0.57 g, 75%. Anal. Calcd for $NiC_{16}H_{35}N_4O_3SF_3$: Ni, 12.24; C, 40.08; H, 7.36; N, 11.69. Found: Ni, 12.32; C, 40.33; H, 7.35; N, 11.70. Green solutions similar to those of the methyl complex were generated using diethyl- or diphenylmagnesium in place of the dimethyl compound but products have not been isolated in pure form.

Reaction of the perchlorate salt of **1** with 1 equiv of lithi-