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Photochemical Hydrogen Abstraction by Singlet and Triplet nπ* States of Aromatic Nitrogen: Fragmentation of 4-Alkylpyrimidines and 2-Alkylquinolines

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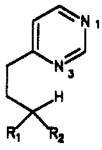
Abstract: On either direct irradiation in water or triplet-sensitized irradiation in acetone, pyrimidines **1a–c** undergo hydrogen abstraction from an nπ* triplet state, fragmentation, and rearomatization to form **5** (eq 1). Similarly, direct irradiation of quinolines **2a–c** in benzene or *tert*-butyl alcohol furnishes **6** from an nπ* singlet state. Quantum yields for products (Φ_5 and Φ_6) and Stern–Volmer quenching studies on these reactions (Tables I and II) provide mechanistic information concerning abstraction by aromatic nitrogen. Unlike Φ for abstraction by carbonyl triplets, Φ_5 and Φ_6 do not increase in hydrogen-bonding solvent, and there is little rate difference in transferring primary, secondary, and tertiary hydrogen in the initial step. Singlet and triplet abstractions show little difference in selectivity, but the singlet reaction is $\sim 10^4$ faster. Concentration studies show that fragmentation of **1a–c** is self-quenched, while reaction of **2a–c** is enhanced with increasing concentration.

Photochemical abstraction of hydrogen by aromatic nitrogen has received much less study than the related abstraction by carbonyl oxygen. In common with other fundamental properties of nitrogen heteroaromatics,[1] there is a lack of information in this area despite the biological importance of nitrogen-containing systems. In connection with related photochemical studies,[2] we have investigated intramolecular transfer of hydrogen to nitrogen in two series of heteroaromatics. The results provide information on selectivity among primary, secondary, and tertiary hydrogen that has long been available for ketones.[3,4] The systems examined are 4-alkylpyrimidines (**1**) and 2-alkylquinolines (**2**).[5] In each case isopentyl (**a**), butyl (**b**), and propyl (**c**) side chains provide tertiary, secondary, and primary hydrogen, respectively, in a position from which abstraction by nitrogen can occur through a six-membered ring, analogous to the abstraction of γ-hydrogen by carbonyl oxygen.[6,7] The overall reaction is illustrated in eq 1 for **1a**, and consists of 1,5 transfer of hydrogen, fragmentation of the resulting 1,4 biradical **3** to alkene and **4**, and tautomerization of **4** to 4-methylpyrimidine (**5**). A corresponding pathway leads from **2** to quinaldine (**6**) by way of **7**,[8] and within each series, fragmentation yields the same isoaromatic intermediate and final product for side chains **a–c**. An earlier study of the photochemistry of various quinolines included **2b**; both **6** and propylene were reported as products under preparative conditions, and the quantum yield for **6** (Φ_6) was measured for 0.2 M **2b** in benzene and in *tert*-butyl alcohol.[9] More recently, methide **7** has been identified spectroscopically as a transient on flash photolysis of **2b**.[10,11]



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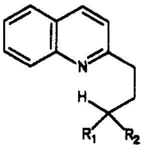

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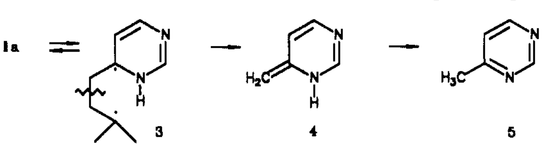
a, $R_1 = R_2 = CH_3$ b, $R = CH_3$, $R = H$ c, $R_1 = R_2 = H$



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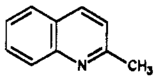

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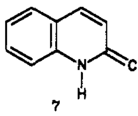

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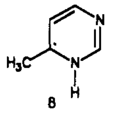

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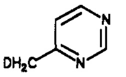

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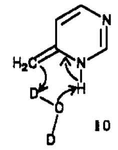

10

$C_6H_5COCH_2CH_2CHRR'$

11

a, $R = R' = H$

b, $R = R' = CH_3$

$(CH_3)_3CN{=}NC(CH_3)_3$

12

These substrates permit examination of transfer of hydrogen activated by both triplet and singlet nitrogen nπ* excited states. The lowest triplet state in pyrimidine and 4-methylpyrimidine (**5**) is a nitrogen nπ* state, which in **5** is at $\sim$84 kcal/mol;[12] as we will show, abstraction in **1** occurs from this state. The cleavage of the quinoline **2b** to **6** was already known[9] to take place from an nπ* singlet.[13] Below we discuss the selectivity for hydrogen transfer in these two series, quantum yields for products, and lifetimes of the reactive excited states.

Preparative Experiments. In earlier work[2] we prepared **1a** by a known route;[14] parallel reactions served for **1b,c**. Reaction of

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[1] Wiberg, K. B.; Nakaji, D.; Breneman, C. M. *J. Am. Chem. Soc.* **1989**, *111*, 4178.

[2] Brumfield, M. A.; Agosta, W. C. *J. Am. Chem. Soc.* **1988**, *110*, 6790.

[3] Wagner, P. J.; Hammond, G. S. *Adv. Photochem.* **1968**, *5*, 21.

[4] Wagner, P. J. *Acc. Chem. Res.* **1971**, *4*, 168.

[5] A portion of this work has appeared as a preliminary communication: Prathapan, S.; Loft, S.; Agosta, W. C. *Tetrahedron Lett.* **1988**, *29*, 6853.

[6] Wagner, P. J. In *Rearrangements in Ground and Excited States*; de Mayo, P., Ed.; Academic Press: New York, 1980; Vol. 3, Chapter 20.

[7] Padwa, A. *Chem. Rev.* **1977**, *77*, 37.

[8] A concerted pathway can also be considered here, since cleavage of **2** is a singlet reaction. For the singlet type II reaction of alkanones the 5–10% loss of stereochemistry in the alkene product has been interpreted as evidence for a stepwise mechanism involving a short-lived singlet biradical: Casey, C. P.; Boggs, R. A. *J. Am. Chem. Soc.* **1972**, *94*, 6457, and references cited therein. Fragmentation of **2a–c** is probably also stepwise, but direct evidence is lacking.

[9] Stermitz, F. R.; Wei, C. C.; O'Donnell, C. M. *J. Am. Chem. Soc.* **1970**, *92*, 2745.

[10] Pedersen, C. L. *Tetrahedron Lett.* **1982**, *23*, 1943.

[11] Less specifically pertinent references concerning hydrogen abstraction in quinolines include: Stermitz, F. R.; Seiber, R. P.; Nicodem, D. E. *J. Org. Chem.* **1968**, *33*, 1136. Stermitz, F. R.; Wei, C. C. *J. Am. Chem. Soc.* **1969**, *91*, 3103. Allan, G.; Castellano, A.; Catteau, J. P.; Lablache-Combier, A. *Tetrahedron* **1971**, *27*, 4687. Stermitz, F. R.; Huang, W. H.; Blythin, D. J.; Hoeft, A.; Kim, D. K.; O'Donnell, C. M. J. *Heterocycl. Chem.* **1972**, 9, 1288. Hata, N.; Ono, I.; Matono, S.; Hirose, *Bull. Chem. Soc. Jpn.* **1973**, *46*, 942. Hata, N.; Saito, T. *Ibid.* **1974**, *47*, 942. Ono, I.; Hata, N. *Ibid.* **1983**, *56*, 3667. Ono, I.; Fujiki, Y.; Fujinami, N.; Hoshi, T. *Chem. Lett.* **1989**, 371. General references concerning the photochemistry of pyrimidines are given in ref 2.

[12] Hochstrasser, R. M.; Marzzacco, C. *J. Chem. Phys.* **1968**, *49*, 971. Uchida, K.; Yamazaki, I.; Baba, H. *Chem. Phys.* **1978**, *35*, 91.

[13] Energies in the range 83–91 kcal/mol have been reported for the first singlet state of quinoline under various conditions: Mataga, N.; Tsuno, S. *Bull. Chem. Soc. Jpn.* **1957**, *30*, 368. Goodman, L.; Harrell, R. W. *J. Chem. Phys.* **1959**, *30*, 1131. Hadley, S. G. *J. Phys. Chem.* **1971**, *75*, 2083. Pisanias, M. N.; Christophorou, L. G.; Carter, J. G. *Chem. Phys. Lett.* **1972**, *13*, 433. Fischer, G. *J. Mol. Spectrosc.* **1974**, *49*, 201. Energies in 2-alkylquinolines should be little different: Schulman, S. G.; Capomacchia, A. C. *J. Am. Chem. Soc.* **1973**, *95*, 2763. Further discussion of quinoline S_1 and S_2 states is given below.

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Table I. Quantum Yields, Relative Triplet Lifetimes, and Abstraction Selectivity for **1a–c**

		in water[a]					in acetone	
C–H bond	cmpd	Φ_5	rel Φ_5 per H	$k_q\tau \times 10^{-2}$, M^{-1}	rel $1/\tau$	rel $1/\tau$ per H	$\Phi_5 \times 10^3$	rel Φ_5 per H
3°	**1a**	0.25	5.8	12	1.1	3.2	7.5	7.7
2°	**1b**	0.16	1.8	3.9	3.3	5.0	5.6	2.9
1°	**1c**	0.13	(1.0)	13	(1.0)	(1.0)	2.9	(1.0)

[a] Φ_5's in D_2O; $k_q\tau$'s in H_2O.

Table II. Quantum Yields, Relative Singlet Lifetimes, and Abstraction Selectivity for **2a–c**

		in benzene					in *tert*-butyl alcohol	
C–H bond	cmpd	$\Phi_6 \times 10^3$	rel Φ_6 per H	$k_q\tau \times 10$, M^{-1}	rel $1/\tau$	rel $1/\tau$ per H	$\Phi_6 \times 10^3$	rel Φ_6 per H
3°	**2a**	3.7	1.6	8.3	1.7	5.1	5.4	2.5
2°	**2b**	9.5	2.1	8.1	1.7	2.6	9.8	2.3
1°	**2c**	6.8	(1.0)	14	(1.0)	(1.0)	6.4	(1.0)

quinoline with butyllithium leads to **2b**,[9,15] and we used this method to prepare **2a–c**.. Photoproducts **5** and **6** are commercially available.

Results and Discussion

From a report that direct irradiation of **5** in methanol at 113 K leads to **8** in a monophotonic process probably involving a triplet state,[16] and from related work concerning both the quenching of pyrimidine triplets by isopropyl alcohol and the assignment of the lowest triplet of pyrimidine as an nπ* state,[17] it appeared likely that intramolecular hydrogen abstraction would occur from the lowest triplet of **1a–c**. Direct irradiation of these pyrimidines in benzene or *tert*-butyl alcohol as solvent, with a medium-pressure mercury arc lamp and either a potassium chromate solution (λ ~ 313 nm) or Pyrex glass (λ > 280 nm) as a filter, led to no reaction and recovery of starting pyrimidine. Irradiation in acetone (E_T ~ 79–82 kcal/mol)[18a] as solvent through Pyrex, however, led to slow destruction of starting material and formation of **5**, which was isolated and identified by comparison with an authentic sample. These observations indicate that the first triplet of **1** is accessible on sensitization with acetone and that this triplet mediates hydrogen transfer to N(3) as illustrated in eq 1. They imply further that this triplet is not populated on direct irradiation of **1** in benzene or *tert*-butyl alcohol. In contrast, we found that direct irradiation of **1a–c** through Pyrex in water (or deuterium oxide) as solvent did lead to **5**. This solvent effect apparently reflects differences in intersystem crossing of **1** in organic solvent and in water, and it is in accord with earlier reports that intersystem crossing of pyrimidine is poor in hexane[18b] but efficient in water (Φ_{ISC} ~ 1 at 25 °C).[17] We have determined quantum yields for formation of **5** (Φ_5) from **1a–c** in deuterium oxide and in acetone, and these are reported in Table I, along with the derived relative quantum yields per hydrogen atom (rel Φ_5/H). Results in deuterium oxide are for ~0.05 M solutions at low conversion. Results in acetone are for ~0.04 M solutions; Φ_5's in acetone are only 2–3% as large as those in water, and this difference can be attributed largely to the inefficiency of this endothermic (2–5 kcal/mol) triplet sensitization.[19] Relative Φ_5's were essentially unchanged at ~0.02 M **1** in acetone. Measurements in deuterium oxide were made with a physical actinometer; those in acetone were carried out in a merry-go-round apparatus with the concomitant formation of acetophenone from type II elimination of valerophenone as a chemical actinometer.[20] Formation of **5** was estimated by nuclear magnetic resonance (NMR) spectroscopy or analytical gas chromatography.

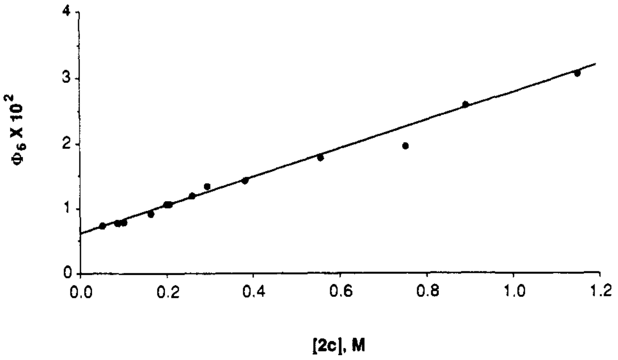

Figure 1. Quantum yield (Φ_6) for formation of quinaldine (**6**) as a function of concentration of 2-propylquinoline (**2c**) irradiated in benzene.

Quinolines **2a–c** underwent fragmentation on direct irradiation in benzene and in *tert*-butyl alcohol, as expected.[9] Quantum yields (Φ_6 and rel Φ_6/H, Table II) were determined in a merry-go-round apparatus for ~0.01 M solutions, relative to the reported Φ_6 for **2b** in benzene (Φ_6 = 0.015 at 0.20 M);[9] formation of **6** was determined gas chromatographically.

These quantum yields refer to the overall reactions of eq 1 and the corresponding processes for **2**, reflecting both selectivity in hydrogen transfer and reversion of the biradical to ground-state reactant. In addition, some self-quenching occurs with the pyrimidines (see below).[17] Tautomerization of the isoaromatic intermediate (**4** or **7**) is not expected to contribute to differences in measured selectivity within a series, since the same methide is formed and aromatizes under virtually identical conditions from each substrate. Equilibrium strongly favors the aromatic system for both series,[21] although the rate of aromatization should be slow in hydrocarbon solvent, since for conversion of **7** to **6**, $k = 72$ s^{-1} in cyclohexane.[10] This slow hydrogen shift could lead to secondary photolytic destruction of the methide (λ_{max} ~ 395 nm for **7**),[10] but we noted no effect at low conversion. NMR measurements on 4-methylpyrimidine formed from **1a** in deuterium oxide indicated that this material was essentially all **9**. We conclude that under these conditions aromatization of **4** occurs with solvent participation, as shown in **10**.

Interpretation of the product quantum yields (Φ_p's) in Tables I and II is mechanistically complex, as noted above, but some interesting points emerge. As with the type II reaction of phenones **11a,b**,[4] there is no great variation of Φ_p with side chain in either series. However, the effect of hydroxylic solvent on Φ_p of the ketones is absent with **1** and **2**. In 12 phenones of the general structure **11**, Φ_p for acetophenone formation is 0.09–0.50 in benzene but in all cases approaches unity in *tert*-butyl alcohol as solvent.[4,22] This has been interpreted as suppression of biradical reversion through hydrogen bonding of the hydroxy group of the biradical to a solvent that is a Lewis base, and this behavior is believed to be quite general in triplet hydrogen transfer.[4,23,24] Thus the quantum yield for initial abstraction of hydrogen (Φ_{br}) in *tert*-butyl alcohol, and presumably also in benzene, is unity, and the solvent influences only biradical reversion. In the fragmen-

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[14] Bredereck, H.; Gompper, R.; Morlock, G. *Chem. Ber.* **1957**, *90*, 942. These authors report preparation of **1c**.

[15] Evans, J. C. W.; Allen, C. F. H. In *Organic Syntheses*; Wiley: New York, 1943, Collect. Vol. II, p 517.

[16] Castellano, A.; Catteau, J. P.; Lablache-Combier, A. *Photochem. Photobiol.* **1974**, *20*, 27.

[17] Bent, D. V.; Hayon, E.; Moorthy, P. N. *J. Am. Chem. Soc.* **1975**, *97*, 5065, and references cited therein.

[18] (a) Schmidt, M. W.; Lee, E. K. C. *J. Am. Chem. Soc.* **1970**, *92*, 3579, and references cited therein. Zuckermann, H.; Schmitz, B.; Haas, Y. *J. Phys. Chem.* **1988**, *92*, 4835. (b) Cohen, B. J.; Goodman, L. *J. Chem. Phys.* **1967**, *46*, 713.

[19] A rule of thumb suggests that the rate of energy transfer decreases an order of magnitude for each 1.4 kcal/mol of endothermicity: Turro, N. J. *Modern Molecular Photochemistry*; Benjamin-Cummings: Menlo Park, CA, 1978; p 311.

[20] Wagner, P. J. *J. Am. Chem. Soc.* **1967**, *89*, 5898.

[21] For the equilibrium **7** ⇌ **6**, log *K* is 9.9: Cox, R. A.; Stewart, R.; Cook, M. J.; Katritzky, A. R.; Tack, R. D. *Can. J. Chem.* **1976**, *54*, 900. For **4** ⇌ **5** log *K* may be even larger, since for the corresponding equilibrium in 2-picoline log *K* is 13.3: Cook, M. J.; Katritzky, A. R.; Linda, P.; Tack, R. D. *J. Chem. Soc., Perkin Trans. 2* **1972**, 1295. Chua, S.-O.; Cook, M. J.; Katritzky, A. R. *Ibid.* **1973**, 2111.

[22] Wagner, P. J.; Kemppainen, A. E. *J. Am. Chem. Soc.* **1968**, *90*, 5896.

[23] Wagner, P. J. *Tetrahedron Lett.* **1967**, 1753; **1968**, 5385.

[24] Wagner, P. J. *Acc. Chem. Res.* **1989**, *22*, 83.

tation of **1** and **2**, however, Φ_p does not approach unity in hydroxylic solvent. Several reasons for this difference come to mind. First, hydrogen bonds to a Lewis base by NH are significantly weaker than those by OH,[25] so that reversion of the biradical should be less effectively suppressed in hydrogen-bonding solvents. Second, unlike the behavior of phenones **11**, Φ_{br} for **1** and **2** is not unity, since, as we discuss below, abstraction is relatively slow. In this circumstance, an upper limit to Φ_p is set by the value of Φ_{br}, regardless of the effectiveness of hydrogen bonding in suppressing reversion. Finally there is an important consideration that applies only to the singlet reaction of **2**. As we noted above,[8] this fragmentation could conceivably be concerted. It is more likely that the singlet biradical lifetime here is simply too short (see below) to permit effective solvation. This latter explanation has been offered[26] for the similar lack of solvent effect in the type II reaction of singlet alkanones.[23,26] The close similarity of Φ_6 in benzene and *tert*-butyl alcohol supports the conclusion that these abstraction reactions involve direct hydrogen atom transfer as discussed above, rather than initial electron and then proton transfer, for which a solvent effect is expected.[27]

There is a concentration effect on Φ_6 in cleavage of quinolines **2** that should be noted. Figure 1 shows that, for fragmentation of **2c** on irradiation at ~313 nm (potassium chromate filter) in benzene to low conversion (<1%), Φ_6 increases linearly over a greater than 20-fold increase in concentration of **2c** (0.051–1.15 M).[28,29] It is unlikely that this behavior involves the triplet of **2c**, since for quinoline T_1 is a phosphorescent $\pi\pi^*$ state,[30,31] from which hydrogen abstraction and cleavage should not occur.[9,17,32] Quinoline forms a singlet excimer,[33] and the rise in Φ_6 probably reflects an effect of this excimer on fragmentation. One possible explanation is that formation of **6** directly from the excimer is more efficient than from the monomer. An alternative possibility is that the excimer significantly alters the interaction between S_1 and S_2. It is known that the spacing and ordering of these two states in quinoline are medium-dependent, that in hydrocarbon solvent S_1 is an $n\pi^*$ state that lies slightly below the $\pi\pi^*$ S_2 state,[34] and that S_1 and S_2 are vibronically coupled.[35,36] The coupling of these two states leads to rapid internal conversion ($S_1 \rightarrow S_0$) and consequently a short intrinsic lifetime for S_1 ($\tau_{int} \sim 10^{-10}$ s);[31,35] this interaction has been studied in some detail in quinoline and designated the "proximity effect". It is enhanced by vibrational excitation, which leads to an even higher rate of internal conversion.[31,37,38] If the formation of excimer effectively reduces S_1–S_2 vibronic coupling or increases the rate of $S_2 \rightarrow S_1$ internal conversion, this could lead to an increase in Φ_6. In our studies on **2a–c** the concentration of **2** has been ≤0.05 M, where this effect should be minimal.[39]

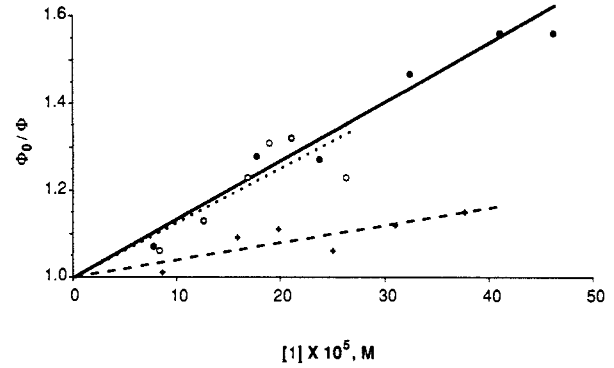

Figure 2. Stern–Volmer plots of self-quenching of formation of 4-methylpyrimidine (**5**) on irradiation of **1a–c** in water: (○) 4-isopentylpyrimidine (**1a**); (+) 4-butylpyrimidine (**1b**); (●) 4-propylpyrimidine (**1c**).

We have carried out quenching experiments on the excited states involved in fragmentation of **1a–c** and **2a–c**. Since ground-state pyrimidine efficiently quenches pyrimidine triplets in water,[17] it was convenient to determine quenching for **1a–c** by measuring formation of **5** in water at low conversion as a function of initial concentration, [**1**]. A plot of [**1**]/[**5**], which is the reciprocal of the yield of **5**, against [**1**] gives a straight line that extrapolates acceptably to zero, as expected for such a curve.[40a] Plots of $1/\Phi$ against [**1**] are linear for each reactant, and their extrapolation to infinite dilution yielded Φ_0's, which were then used in plots of Φ_0/Φ against [**1**] (Figure 2).[40b] The slopes of these curves gave $k_q\tau$'s (Table I) for **1a–c** according to the Stern–Volmer equation (eq 2).[40c] As with ketones,[4] the processes known to determine

$$\Phi_0/\Phi = 1 + k_q[\mathbf{1}]\tau \qquad (2)$$

τ are intrinsic decay in the absence of chemical reaction ($k_{int} = 1/\tau_{int}$) and hydrogen abstraction (k_{abs}) (eq 3). Contrary to the

$$1/\tau = \sum k_i \simeq k_{int} + k_{abs} \qquad (3)$$

situation with ketones,[4] however, the $k_q\tau$'s obtained for **1a–c** reveal that abstraction is too slow for k_{int} to be neglected in estimating k_{abs}; this can be appreciated from the following considerations. The maximum k_q observed for quenching of pyrimidine triplets by various agents in water is ~7.0 × 10^9 M^{-1} s^{-1} (for quenching by KBr);[17] assuming this value for k_q in the self-quenching of **1c** gives 0.19 μs as a reasonable lower limit for τ of **1c**. For self-quenching of pyrimidine, k_q is reported to be 1.5 × 10^8 M^{-1} s^{-1} (±15%),[17] and accepting this as k_q for **1c** yields 8.7 μs as a more probable τ for **1c**. These two values bracket 1.4 μs, the reported[17] τ_{int} of pyrimidine under these conditions, and differ from it by less than an order of magnitude. We conclude that for **1a–c**, k_{int} and k_{abs} are of comparable magnitude.[41] Since the actual values of k_q and k_{int} for **1a–c** are unknown, k_{abs} cannot be evaluated accurately. However, $k_q\tau$ for **1a–c** can yield a reasonable measure of selectivity in hydrogen abstraction. This will be given by the relative rates of triplet decay (rel $1/\tau$), and these, as well as rel

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[25] Cf. the weaker hydrogen bond to fluoride ion with NH than with OH: Clark, J. H.; Miller, J. M. *J. Am. Chem. Soc.* **1977**, *99*, 498.

[26] Yang, N. C.; Elliot, S. P. *J. Am. Chem. Soc.* **1969**, *91*, 7550. Yang, N. C.; Elliot, S. P.; Kim, B. *Ibid.* **1969**, *91*, 7551.

[27] Closs, G. L.; Miller, J. R. *Science* **1988**, *240*, 440.

[28] For 2-alkylquinolines $\epsilon_{313} \sim 2100$, so that solutions ≥0.001 M are effectively opaque.

[29] The data of Figure 1 are shown fitted (±4%) to ($y = ax + b$, $a = 2.08 \times 10^{-5}$, $b = 6.23 \times 10^{-3}$); Φ_6 extrapolated to infinite dilution is then 0.0062.

[30] Hadley, S. G. *J. Phys. Chem.* **1971**, *75*, 2083.

[31] Okajima, S.; Lim, E. C. *J. Chem. Phys.* **1978**, *69*, 1929.

[32] Formosinho, S. J. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 1332, and references cited therein.

[33] Monomer and excimer fluorescence have been studied and are well behaved: Perkampus, H.-H.; Kortüm, Z. *Phys. Chem. (Frankfurt) Neue Folge* **1967**, *56*, 73. Blaunstein, R. P.; Gant, K. S. *Photochem. Photobiol.* **1973**, *18*, 347.

[34] The S_1–S_2 gap in hydrocarbon solvent has not been reported, but in the gas phase, where the $n\pi^*$ state is also S_1, the gap is 1804 cm^{-1} (5.2 kcal/mol): Hiraya, A.; Achiba, Y.; Kimura, K.; Lim, E. C. *J. Chem. Phys.* **1984**, *81*, 3345.

[35] Lim, E. C. In *Excited States*; Lim, E. C., Ed.; Academic Press: New York, 1977; Vol. 3, p 305, and references cited therein.

[36] This led to considerable confusion in earlier reports: Ross, I. G. In *Photochemistry of Heterocyclic Compounds*; Buchardt, O., Ed.; Wiley: New York, 1976, pp 34–35.

[37] Lai, T.; Lim, E. C. *Chem. Phys. Lett.* **1979**, *62*, 507.

[38] Wassam, W. A., Jr.; Lim, E. C. *J. Chem. Phys.* **1978**, *68*, 433.

[39] We confirmed the earlier report (ref 9) that for **2b** (0.20 M) in benzene Φ_6 is unaffected (±1.7% in our hands) by addition of piperylene (0.50 M). At the concentrations (typically ~0.01 M) and conversions (≤1%) employed in the present work, however, there is an *increase* in Φ_6 of 15–20% in the presence of piperylene (≥0.2 M). With piperylene present solutions remain colorless on irradiation, but without it there is slight visible coloration even at 1% conversion. Values of Φ_6 reported below were obtained in the absence of piperylene. This process has no effect on selectivity in hydrogen abstraction.

[40] (a) These plots for **1a–c** (not shown) were made to provide a simple check of the data. (b) We chose to present Figure 2 in this form (Φ_0/Φ versus [**1**]) because it is the presentation most familiar to organic chemists. Wagner, P. J. In *Creation and Detection of the Excited State*; Marcel Dekker: New York, 1971; Vol. 1, Part A, p 173. (c) Curves in Figure 2 are least-squares fit with fixed origin; error is in the range 4–12%.

[41] Use of the reported value of k_q for self-quenching of pyrimidine (1.5 × 10^8 M^{-1} s^{-1} [17]) for self-quenching of **1** yields τ's for **1a–c** slightly greater than the τ_{int} reported for pyrimidine, suggesting that for **1a–c** either k_q (cf. eq 2) or τ_{int} (cf. eq 3) or both are somewhat greater than the values of k_q and τ_{int} reported for pyrimidine.

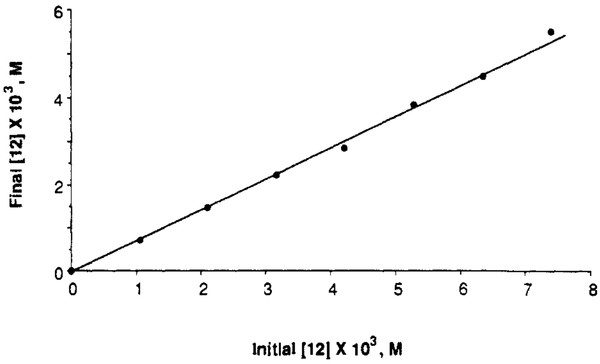

Figure 3. Destruction of **12** on quenching fragmentation of **2a**. Final [**12**] as a function of initial [**12**] after irradiation for 1 h at $\lambda \sim 313$ nm, where **2a** absorbs essentially all light.

$1/\tau$'s per hydrogen available for transfer (rel $1/\tau$ per H), are shown in Table I. Since the $k_q\tau$'s are all of similar magnitude and both k_q and k_{int} are reasonably assumed to be very similar for all three pyrimidines, the effect of neglecting k_{int} on the estimated *relative* rates is minor. The noteworthy result is that triplet nitrogen in **1a–c** abstracts primary, secondary, and tertiary hydrogen all at very similar rates; unlike carbonyl oxygen, nitrogen here shows little sensitivity to carbon–hydrogen bond strength. Owing to this, the steric and entropic differences in transfer of primary, secondary, and tertiary hydrogen should be more discernible in the reaction at nitrogen than at oxygen. This fact provides an explanation for the observed slightly faster abstraction of secondary hydrogen in **1b**, which is favored by both steric and entropic factors, than of tertiary hydrogen in **1a**, which is favored by its lower bond strength.

Identification of a satisfactory singlet quencher for **2a–c** was troublesome. Biacetyl had no effect on the reaction, and di-*tert*-butyl nitroxide[42] behaved anomalously. Azo-*tert*-butane (**12**)[43] appeared to be an attractive possibility, since quenching of the fluorescence of naphthalene and triphenylene by **12** has been attributed to singlet electronic energy transfer, largely by electron exchange with only a small contribution from dipole–dipole coupling; in benzene k_q is 5.2×10^9 M^{-1} s^{-1} for naphthalene and 6.3×10^9 for triphenylene.[44] While **12** quenched the fragmentation of **2a–c** satisfactorily and we did adopt it as the quencher of choice, it presented a problem in that it is efficiently destroyed on excitation to S_1 during the quenching process. This fact, together with the low quantum yield (Φ_6) of the reaction being quenched, requires that Stern–Volmer studies be done at very low conversion with a correction for loss of quencher during reaction. Figure 3 shows the relationship between initial and final concentrations of **12** over 1 h in a typical quenching of fragmentation of **2a**. Irradiation was at $\lambda \sim 313$ nm where **2a** absorbs essentially all the light, conversion was low (<1%), and the solutions remained opaque. Under these conditions, as Figure 3 shows, the rate of loss of **12** is first order in [**12**]. This indicates that at low conversion of **2a–c** a correction for first-order destruction of **12** should suffice for kinetic plots. We measured [**12**] before and after irradiation for each determination in quenching **2a–c**, and from this we calculated k for destruction of **12** and the time-average [**12**] present. For example, in one 60-min run involving **2c** and various concentrations of **12**, 35% of **12** was destroyed in all samples; from this the mean value of [**12**] over this period is 81% of its initial concentration.[45a] Plots of Φ_0/Φ for fragmentation of **2a–c** against corrected values of [**12**] at ~0.2% conversion are shown in Figure 4, and derived $k_q\tau$'s (eq 2) are given in Table II.[45b] These data are only semiquantitative, owing to the error in measuring the small amount of **6** formed. It will be noted that the error introduced by correction for destruction of the quencher is comparable for the three substrates, since $k_q\tau$'s are very similar for **2a–c**. For this reason the use of mean [**12**] should have negligible effect on the *relative* values derived below.

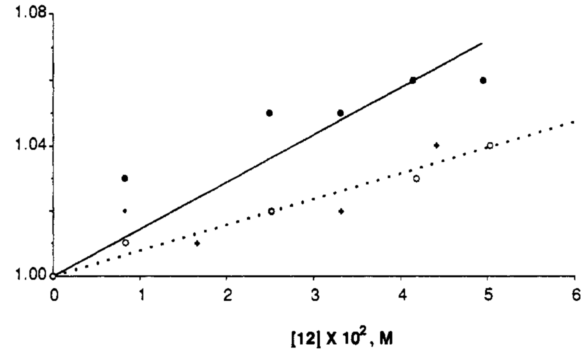

Figure 4. Stern–Volmer plots of quenching by azo-*tert*-butane (**12**) of the formation of quinaldine (**6**) on irradiation of **2a–c** in benzene: (○) 2-isopentylquinoline (**2a**); (+) 2-butylquinoline (**2b**); (●) 2-propylquinoline (**2c**). Curves for **2a** and **2b** are virtually coincident, and only the curve for **2a** is shown. [**12**] is corrected for its sensitized decomposition during reaction (cf. Figure 3); see text for details.

In view of the short lifetime of quinoline singlet ($\tau_{int} \sim 10^{-10}$ s),[31,35] k_{int} cannot be neglected in evaluation of k_{abs} for **2a–c**. For k_{int} to be negligible would require k_{abs} to be $> \sim 10^{11}$ s^{-1} and would imply that k_q is $> 10^{11}$ M^{-1} s^{-1} for quenching of **2** by **12**. However, the observed k_q's for singlet quenching by azoalkanes in hydrocarbon solvent are of the order of 10^{10} M^{-1} s^{-1}, even when dipole–dipole quenching is favored.[43] As with **1a–c** above, true values of k_q and k_{int} for **2a–c** are unknown, so that k_{abs} cannot be evaluated accurately, but $k_q\tau$ can yield a good estimate of selectivity in hydrogen transfer. Rel $1/\tau$'s and rel $1/\tau$'s per H in **2a–c** are collected in Table II. Here again there is a spread of only ~5-fold in selectivity for abstraction of primary, secondary, and tertiary hydrogen.

Thus, neither singlet nor triplet nitrogen is very sensitive to carbon–hydrogen bond strength, but the singlet hydrogen transfer in **2a–c** is $\sim 10^4$ faster than triplet transfer in **1a–c**. As we have noted above, various problems limit the accuracy and precision of our data for both **1** and **2**. The main purpose in this initial exploration, however, has been to determine the relative behavior of these different substrates. Our findings may be compared with the behavior of ketones. Study of alkanones with primary, secondary, and tertiary γ-hydrogens has shown that the singlet reaction is ~10 times faster and that the triplet is ~10 times more selective.[4,26] We note that in the present work comparison is between two distinct aromatic series, so that the large difference in rate of hydrogen abstraction necessarily incorporates effects of both spin state and structure.

Finally, it is interesting to compare the selectivity of these excited nitrogen aromatics toward abstraction of hydrogen with the selectivity of appropriate aminyl radicals ($R_2N^\bullet$). For triplet ketones **11** the relative reactivities of primary, secondary, and tertiary hydrogen are 1:22:165, and toward *tert*-butoxy radical these reactivities are 1:13:70.[3,4] Although little information is available concerning the reactivity of aminyl radicals in solution,[46,47] what is known is in good accord with our results. Dimethylaminyl is a "feeble" abstracting agent in hydrocarbon solvents.[48] It fails to abstract hydrogen from cumene or toluene at room temperature but does so to some extent at 134 °C; under these latter conditions, the reaction is roughly 2–3 times faster with cumene than with toluene, implying a difference in rate of reaction of primary and tertiary hydrogen of less than 10-fold.[46]

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(42) Green, J. A., II; Singer, L. A. *J. Chem. Phys.* **1973**, *58*, 2690; *J. Am. Chem. Soc.* **1974**, *96*, 2730.

(43) Engel, P. S.; Fogel, L. D.; Steel, C. *J. Am. Chem. Soc.* **1974**, *96*, 327.

(44) Wamser, C. C.; Lou, L.; Mendoza, J.; Olson, E. *J. Am. Chem. Soc.* **1981**, *103*, 7228.

(45) (a) Variations in light intensity lead to some variation in the relative time-average [**12**] from run to run; these values are typical. Destruction of **12** was uniform for **2a–c** when all three quinolines were irradiated simultaneously in a merry-go-round apparatus. Mean values for [**12**] were calculated by using first-order kinetics and the mean value theorem. (b) Curves in Figure 4 are least-squares fit with fixed origin; error is in the range 4–17%.

(46) Michejda, C. J.; Hoss, W. P. *J. Am. Chem. Soc.* **1970**, *92*, 6298.

(47) Golden, D. M.; Solly, R. K.; Gac, N. A.; Benson, S. W. *J. Am. Chem. Soc.* **1972**, *94*, 363.

(48) Mackay, D.; Waters, W. A. *J. Chem. Soc. C* **1966**, 813.

Lack of selectivity also characterizes hydrogen abstraction by imidyl $[(RCO)_2N^\bullet]$[49] and bis(trialkylsilyl)aminyl $[(R_3Si)_2N^\bullet]$[50] radicals in solution, and by aminyl $(H_2N^\bullet)$[51] in the gas phase. The low selectivity in the photochemistry of **1a–c** and **2a–c** is in good qualitative agreement with these limited observations.

Experimental Section

Materials and Equipment. Preparative gas chromatography (GLC) was carried out on a Varian Aerograph Model 920 gas chromatograph with (a) 10% OV101, 5-ft column on Chromosorb-P or (b) 25% Carbowax, 10-ft column on Chromosorb-W, packed in 0.25-in. aluminum tubing. Analytical GLC was carried out isothermally using internal standards on a HP-5890 temperature-programmable gas chromatograph with (a) Ultra-1 25 m × 0.2 mm capillary column with a film thickness of 0.33 μm or (b) OV-225 25 m × 0.25 mm capillary column with a film thickness of 0.25 μm. All NMR spectra were recorded on either a Varian Model T-60 (60 MHz) or a Nicolet/Oxford Model NT-300 (300 MHz) spectrometer and are reported in parts per million downfield from tetramethylsilane employed as an internal standard (δ). Infrared spectra were recorded on a Perkin-Elmer Model 237B grating infrared spectrophotometer. Ultraviolet absorption spectra were recorded on a Cary Model 14 recording spectrophotometer. The physical actinometer used was a Photon Technology International Model Q1 Quantacount instrument. Mass spectral analyses were performed by The Rockefeller University Mass Spectrometric Biotechnology Resource on a VG-70250 magnetic sector instrument. Organic solutions obtained by workup of reaction mixtures were dried by washing with brine prior to treatment with anhydrous sodium or magnesium sulfate.

Preparation of 4-(3-Methylbutyl)-, 4-Butyl-, and 4-Propylpyrimidine (1a–c). These were prepared by following the route previously used for **1a**[2] and **1c**. For **1b** this requires 1-chloro-1-hepten-3-one, which was prepared by a known[52] procedure. For **1b**: ^1H NMR ($CDCl_3$) δ 9.1 (1 H), 8.6 (1 H), 7.1 (1 H), 2.7 (2 H), 1.1–1.9 (4 H), 0.9 (3 H); IR (CCl_4) 2960, 1582, 1555, 1475, 1388, 1315, 995 cm^{-1}; Anal. ($C_7H_{12}N_2$) C, H, N.

Preparation of 2-(3-Methylbutyl)-, 2-Butyl-, and 2-Propylquinoline (2a–c). These were prepared from quinoline, isopentyl bromide (for **2a**), butyl bromide (for **2b**), or propyl bromide (for **2c**), and lithium according to the procedure reported[9,15] for preparation of **2b**; yields, ~95%. After purification by distillation and preparative gas chromatography, **2b**[9] and **2c**[53] had spectroscopic properties in agreement with those on record. For **2a**: ^1H NMR ($CDCl_3$) δ 7.2–8.2 (m), 2.9 (t, J = 7 Hz), 1.4–2.0 (m), 1.0 (d, J = 7 Hz); IR (CCl_4) 2960, 2910, 1620, 1600, 1500, 1467, 1424, 1383, 1368, 1305, 1110 cm^{-1}; Anal. ($C_{14}H_{17}N$) C, H, N.

Preparative Photochemistry A. 4-Alkylpyrimidines 1a–c. An acetone solution of the appropriate alkylpyrimidine (0.5 mmol in 75 mL) in a toroidal Pyrex vessel was irradiated with the output from a Hanovia 450-W medium-pressure mercury lamp in a Pyrex-jacketed immersion well, until all the starting material was consumed. Solvent was removed by distillation through a 75-cm Vigreux column; the residue was passed through a short silica column and further purified by preparative gas chromatography (70 °C). The material thus purified had ^1H NMR and IR spectra identical with those of authentic 4-methylpyrimidine (**5**).

B. 2-Alkylquinolines 2a–c. Irradiation of **2a–c** was carried out in benzene and in *tert*-butyl alcohol solution as described for **1a–c** above, except that the concentration was 0.02 M and a potassium chromate filter solution was employed. Purified product was spectroscopically identical with authentic quinaldine (**6**).

Quantum Yield Measurements A. 4-Alkylpyrimidines 1a–c in Acetone. Degassed solutions of **1a–c** in acetone-d_6 (~0.04 M, 0.5 mL) were irradiated simultaneously in a merry-go-round apparatus with the lamp set up described above for 4.25 h. The photolysates were analyzed by ^1H NMR. Conversions were 5–12%. Relative Φ_5's obtained in this manner were converted to absolute Φ_5's by using the valerophenone actinometer at 313 nm.[20] A 0.04 M solution of **1a** in acetone (4 mL) and a 0.1 M solution of valerophenone in benzene (4 mL) were irradiated simultaneously as above for 4 h. Photolysates were analyzed by analytical gas chromatography. Conversion of **1a** was 0.33%; conversion of valerophenone was 6.5%. Results are given in Table I.

B. 4-Alkylpyrimidines 1a–c in Water. Measurements were made on a physical actinometer at 313 nm. A solution of the appropriate 4-alkylpyrimidine in D_2O (~27 mM in 3 mL) was used in each case. Analysis was carried out by ^1H NMR. Separate NMR measurements showed that the product was **9**. Conversions were 9–12%. Results are given in Table I.

C. 2-Alkylquinolines 2a–c in Benzene. By use of the same lamp apparatus with potassium chromate filter described above, solutions of **2a–c** (0.01 M) in benzene were irradiated in a merry-go-round. Product **6** was determined gas chromatographically. Conversions were in the range 1–2%. The conversion of **2b** to **6** in benzene (0.20 M) served as actinometer.[9] Results are given in Table II.

D. 2-Alkylquinolines 2a–c in *tert*-Butyl Alcohol. The experiments described in C were repeated in *tert*-butyl alcohol. Analysis, conversion, and actinometer were as described for experiments in benzene. Results are given in Table II.

Concentration Dependence of Φ_5 for 2c. Solutions of **2c** in benzene at concentrations from ~0.05 to 1.2 M were irradiated and analyzed as described above. Results are given in Figure 1.

Quenching Experiments. A. 4-Alkylpyrimidines 1a–c. Aqueous solutions of **1a–c** (0.02–0.12 M) were irradiated in quartz tubes in a merry-go-round apparatus in a Southern New England RPR unit at 254 nm. The photolysates were analyzed gas chromatographically. Results are given in Table I and Figure 2.

B. 2-Alkylquinolines 2a–c. Benzene solutions of **2a–c** (0.01 M) were irradiated for 1 h in the presence of azo-*tert*-butane (0.001–0.006 M) in quartz tubes in a merry-go-round apparatus by use of the lamp with potassium chromate filter described above. Photolysates were analyzed gas chromatographically; results are collected in Table II and Figure 4.

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(49) Skell, P. S.; Tanko, J. M. *J. Org. Chem.* **1986**, *51*, 4959, and references therein.

(50) Cook, M. D.; Roberts, B. P.; Singh, K. *J. Chem. Soc., Perkin Trans. 2* **1983**, 635.

(51) Demissy, M.; Lesclaux, R. *J. Am. Chem. Soc.* **1980**, *102*, 2897.

(52) Price, C. C.; Pappalardo, J. A. In *Organic Syntheses*; Wiley: New York, 1963; Collect. Vol. IV, p 186. Belil, C.; Pascual, J.; Serratosa, F. *Tetrahedron* **1964**, *20*, 2701.

(53) Cervinka, O.; Fabryova, A.; Matouchova, L. *Collect. Czech. Chem. Commun.* **1963**, *28*, 535.