Intramolecular Photochemical Hydrogen Abstraction in 2-Alkylpyrazines and 2-Alkylpyridines

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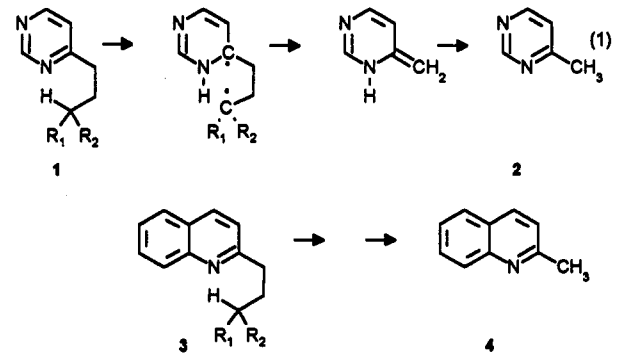
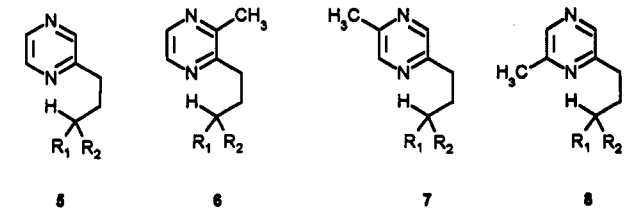
Photochemical hydrogen abstraction in 2-alkylpyrazines **5–8** and 2-alkylpyridines **9–11** proceeds analogously to the process of eq 1. Hydroxylic solvent causes quantum yields for pyrazine fragmentation products (Φ_p) to increase about 1 order of magnitude. Pyridine fragmentation takes place from both singlet and triplet states. Pyrazine fragmentations follow Stern–Volmer kinetics with modest bond strength selectivity (1°:3° ~ 1:17 for **5a** and **5c**). Methyl substitution lowers the rate of abstraction in pyrazines and trifluoromethyl substitution increases Φ_p in pyridines. It is suggested that these effects reflect changes in the $n\pi^*$ and $\pi\pi^*$ character of the reactive excited states.

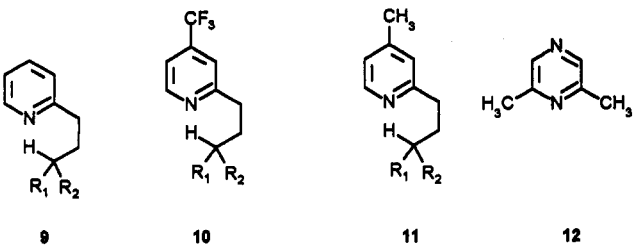
Singlet and triplet $n\pi^*$ excited states of a variety of aromatic nitrogen heterocycles mediate abstraction of hydrogen in a process analogous to the well-studied type II abstraction of carbonyl oxygen.[1-4] An earlier study from our laboratory concentrated on intramolecular triplet abstraction and fragmentation in 4-alkylpyrimidines **1a–c**, which proceed as shown in eq 1, and on the analogous



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

singlet reaction of 2-alkylquinolines **3a–c**.[3] We found that abstraction by nitrogen differs from the triplet carbonyl reaction in that Φ_2 and Φ_4 do not approach unity in hydroxylic solvent, and there is little rate difference in transferring primary, secondary, and tertiary hydrogen in the initial step for either the singlet or triplet reactions.[3] Other than our study of **1** and **3** and a few quantum yields for fragmentation in other systems,[1,2] there is little information available concerning the effects of structural change on the course of this process. In order to probe these effects and to provide data for comparison with our earlier work, we have now investigated intramolecular abstraction in a number of 2-alkylpyrazines and 2-alkylpyridines. These include compounds **5a–c** and **9a–c**, where





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

the abstracted hydrogen is varied from primary to secondary to tertiary in the parent heterocycle, as well as compounds bearing an additional ring substituent, such as **7c** and **10c**. Ring substituents alter the energies of $n\pi^*$ and/or $\pi\pi^*$ excited states of these systems, and our particular interest has been to explore the effect of these changes on rates of abstraction and quantum yields for reaction.

Preparative Experiments. The alkylpyrazines employed were **5a–c**, **6a–c**, **7c**, and **8c**, all of which have been described previously.[5,6] Following a known procedure,[5] we prepared those that are not available commercially through deprotonation of methylpyrazine or the appropriate dimethylpyrazine by sodamide in liquid ammonia and subsequent treatment with an alkyl halide. The required pyridines were **9a–c**, **10a–c**, and **11c**, all of which were available on free radical alkylation[7] of pyridine or the relevant 4-substituted pyridine. Compounds **9a**[8] and

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(1) Stermitz, F. R.; Wei, C. C.; O'Donnell, C. M. *J. Am. Chem. Soc.* **1970**, *92*, 2745.

(2) Stermitz, F. R.; Huang, W. H.; Blythin, D. J.; Hoeft, A.; Kim, D. K.; O'Donnell, C. M. *J. Heterocycl. Chem.* **1972**, *9*, 1289.

(3) (a) Prathapan, S.; Loft, S.; Agosta, W. C. *J. Am. Chem. Soc.* **1990**, *112*, 3940. More complete references to earlier work are given in this paper. (b) Prathapan, S.; Loft, S.; Agosta, W. C. *Ibid.* **1992**, *114*, 7326.

(4) Prathapan, S.; Robinson, K. E.; Agosta, W. C. *J. Am. Chem. Soc.* **1992**, *114*, 1838.

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(6) Flament, I.; Stoll, M. *Helv. Chim. Acta* **1967**, *50*, 1754. Heynes, K.; Behse, E.; Francke, W. *Chem. Ber.* **1981**, *114*, 240.

(7) Minisci, F.; Vismara, E.; Fontana, F. *Heterocycles* **1989**, *28*, 489 and references cited therein.

(8) Cocker, W.; Geraghty, N. W. A.; Shannon, P. V. R. *J. Chem. Soc., Perkin Trans. 1* **1984**, 2241.

0022-3263/94/1959-0178$04.50/0

Table 1. Quantum Yields, Selectivity, and Rates for Hydrogen Abstraction in 2-Alkylpyrazines

		in benzene					in *t*-BuOH[a]		
C–H bond	compd	$\Phi_p \times 10$	rel Φ_p per H	$k_q\tau$, M^{-1}	$1/\tau \times 10^{-7}$, s^{-1}	rel $1/\tau$ per H	$\Phi_p \times 10$	rel Φ_p per H	$k_q\tau$, M^{-1}
1°	**5a**	0.0024	(1.0)	54.7	9.2	(1.0)	0.069	(1.0)	
2°	**5b**	0.029	18	34.3	15	2.4	0.30	6.5	
		0.04[b]							
3°	**5c**	0.066	83	9.75	51	17	0.54	23	
1°	**6a**	0.095	(1.0)	367	1.4	(1.0)	0.92	(1.0)	
2°	**6b**	0.26	4.1	202	2.5	2.7	1.1	1.8	
3°	**6c**	0.57	18	138	3.6	7.1	1.5	4.9	754
1°	**7a**	0.032					0.13		349
1°	**8a**	0.026					1.1		240

[a] 9:1 *tert*-butyl alcohol–benzene. [b] From ref 2.

Table 2. Quantum Yields for Fragmentation of 2-Alkylpyridines in *tert*-Butyl Alcohol[a]

C–H bond	compd	$\Phi_p \times 10$	C–H bond	compd	$\Phi_p \times 10$
1°	**9a**	0.14	2°	**10b**	0.53
2°	**9b**	0.097	3°	**10c**	0.80
3°	**9c**	0.15	3°	**11c**	0.021
1°	**10a**	0.36			

[a] 9:1 *tert*-butyl alcohol–benzene.

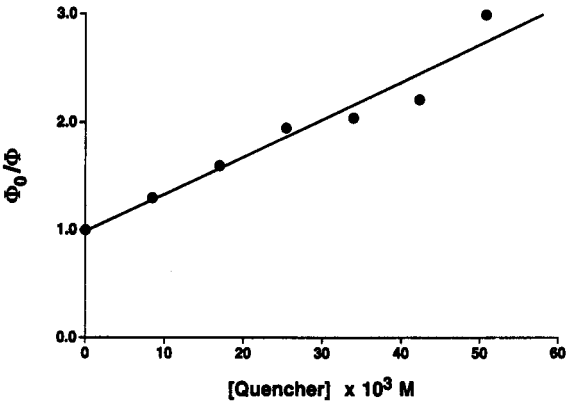

Figure 1. Stern–Volmer plot of quenching by piperylene of reaction of 2-butylpyrazine (**5b**). Irradiation in benzene at ~313 nm.

9b[9] have been described previously. These known pyridines and the pyrazines had spectroscopic properties in agreement with those previously reported.

Photochemical Results and Discussion. We have determined quantum yields (Φ_p) for fragmentation of pyrazines **5a–c**, **6a–c**, **7c**, and **8c** to methylpyrazine or the corresponding dimethylpyrazine and of pyridines **9a–c**, **10a–c**, and **11c** to the corresponding 2-methylpyridine in a merry-go-round apparatus, using 9:1 *tert*-butyl alcohol–benzene as solvent and the concomitant type II fragmentation of 2-butylquinoline to 2-methylquinoline as an actinometer.[2,3] For the pyrazines Φ_p's were also measured in benzene as solvent. Results are presented in Tables 1 and 2, along with the earlier reported[2] value for fragmentation of **5b** in benzene. We have also carried out quenching studies on the triplet states mediating fragmentation of the pyrazines, using piperylene as quencher in benzene as solvent. Results plotted as Φ_0/Φ vs [Q] demonstrated that the reactions follow Stern–Volmer kinetics.[10] Typical data are shown in Figure 1, and the resulting $k_q\tau$'s are given in Table 1. Data obtained earlier[3] for pyrimidines **1a–c** are presented in Table 3 for comparison. Preparative-scale photolyses yielded small amounts of other products in addition to the appropriate methylpyrazines, and in some cases solutions irradiated to high conversion turned red or brown, particularly with *tert*-butyl alcohol as solvent. For this reason we measured Φ_p's at ≤0.5% conversion and $k_q\tau$'s at ≤1%, using analytical gas chromatography for all analyses.

Table 3. Quantum Yields, Selectivity, and Rates for Hydrogen Abstraction in 2-Alkylpyrimidines in Water[a]

C–H bond	compd	Φ_p	rel Φ_p per H	$k_q\tau$, M^{-1}	$1/\tau \times 10^{-7}$, s^{-1}	rel $1/\tau$ per H
1°	**1a**	0.13	(1.0)	5.2	3.4	(1.0)
2°	**1b**	0.16	1.8	1.9	9.5	4.1
3°	**1c**	0.25	5.8	6.0	3.0	2.6

[a] Φ_p's in D_2O; $k_q\tau$'s in H_2O; data from ref 3.

Table 1 also includes rates of triplet deactivation ($1/\tau$) calculated on the assumption that k_q in benzene is 5×10^9 M^{-1} s^{-1}.[11,12] The derived relative rates of decay per available hydrogen atom ($1/\tau$ per H) are also given.

Quenching experiments with **9c** and **10b** indicated that fragmentation of these pyridines does not follow Stern–Volmer kinetics. As shown in Figure 2, for **9c** only ~32% of the fragmentation is quenchable and for **10b**, only ~46%. Since quantum yields for intersystem crossing (Φ_{ISC}) of pyridine and its methyl derivatives are ~0.3 from S_1 ($n\pi^*$) and much lower from S_2 ($\pi\pi^*$),[13,14] the data in Figure 2 suggest most simply that fragmentation of these pyridines takes place from both singlet and triplet $n\pi^*$ states.

The quenching data for pyrazines **5a–c** provide useful information about the effects of structure on the fragmentation reaction. Since the rates of deactivation ($1/\tau$) are large relative to the presumed intrinsic rates of decay,[15] they are a reasonable measure of the rates of hydrogen abstraction.[16] The $k_q\tau$ values for both series **5** and **6** reveal a selectivity of about 1:20 in comparing abstraction of primary and tertiary hydrogens. This is greater than the selectivity in series **1**[3] but much less than that of carbonyl triplets (~1:150).[17] We have previously noted that the low selectivity in abstraction of hydrogen by excited-state

(9) Hanessian, S.; Kagotani, M. *Synthesis* **1987**, 409.
(10) Plotted curves were least squares fit with fixed origin; error was ≤5.1%, except for **1a** (8.5%).
(11) Wagner, P. J.; Kochevar, I. *J. Am. Chem. Soc.* **1968**, *90*, 2232.
(12) The $1/\tau$ values in Table 3 were derived from $k_q\tau$'s using $k_q = 1.8 \times 10^8$ M^{-1} s^{-1}, the self-quenching constant for pyrimidine.
(13) Cundall, R. B.; Fletcher, F. J.; Milne, D. C. *Trans. Faraday Soc.* **1964**, *60*, 1146.
(14) Yamazaki, I.; Murao, T.; Yamanaka, Takaya; Yoshihara, K. *Faraday Discuss. Chem. Soc.* **1983**, *75*, 395. Yamazaki, I.; Sushida, K.; Baba, H. *J. Chem. Phys.* **1979**, *71*, 381.
(15) The intrinsic decay rate (k_{int}) of pyrazine in benzene is not known, but k_{int} is 2.2×10^5 s^{-1} in water and 7.2×10^4 s^{-1} in acetonitrile. Pyrazine triplet decays rapidly only in solvents that provide readily abstractable hydrogen: Bent, D. V.; Hayon, E.; Moorthy, P. N. *J. Am. Chem. Soc.* **1975**, *97*, 5065.
(16) This is also true for the data for **1a–c** given in Table 3 (in this regard, see ref 3b.)

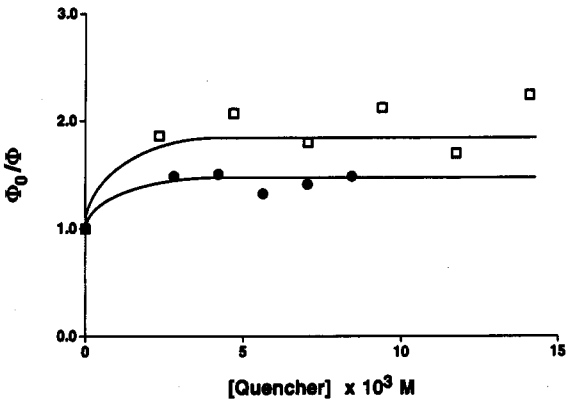

Figure 2. Stern–Volmer plot of quenching by piperylene of reaction of 2-isopentylpyridine (**9c**) (●) and 2-butyl-4-(trifluoromethyl)pyridine (**10b**) (□). Irradiation in benzene at ~313 nm.

nitrogen is in accord with earlier observations of relatively indiscriminate hydrogen abstraction by various nitrogen-centered radicals.[3] The quantum yield results for **5** and **6** indicate that Φ_p increases about 1 order of magnitude in *tert*-butyl alcohol. We also previously noted that the failure of Φ_p for abstraction by nitrogen to approach unity in hydroxylic solvent is in line with weaker hydrogen bonding by nitrogen heterocycles than carbonyl groups.[3] This modest increase in Φ_p in hydroxylic solvent may also result in part from an electronic effect. Polar solvents lower the energy of $\pi\pi^*$ states, and nonpolar solvents lower $n\pi^*$ states. The active excited state may then be more $\pi\pi^*$-like in hydroxylic solvent. We note below some evidence that biradical reversion may decrease (and Φ_p increase) as $\pi\pi^*$ character of the abstracting state increases.

The data for substituted heterocycles **6–8**, **10**, and **11** provide experimental evidence for the influence of ring substitution on the fragmentation reaction. It has been known for many years that methyl substitution on nitrogen heteroaromatics causes the energy of $n\pi^*$ triplets (E_T) to increase, and that of $\pi\pi^*$ triplets to decrease, relative to E_T's of the parent compound.[18-20] Thus, methyl substitution shifts E_T's from ~75 ($n\pi^*$) and ~79 ($\pi\pi^*$) kcal/mol in pyrazine to ~77 kcal/mol for each triplet in 2,6-dimethylpyrazine (**12**). Further substitution leads to ~76 ($\pi\pi^*$) and ~78 kcal/mol ($n\pi^*$) in tetramethylpyrazine.[19] Methyl substitution has parallel effects on E_T's of $n\pi^*$ and $\pi\pi^*$ states of aromatic ketones.[21,22] Trifluoromethyl substitution in aromatic ketones has the converse effect, lowering E_T of $n\pi^*$ triplets and raising E_T of $\pi\pi^*$ triplets.[22] We know of no comparable data concerning the effect of trifluoromethyl groups on E_T's of nitrogen heteroaromatics, but we expect the effect to parallel that observed in ketones. In general, the effects of ring substituents on $n\pi^*$ and $\pi\pi^*$ energies of singlet states in pyridines are similar to those on ketone and pyrazine triplets.[18,23]

These considerations suggest that methyl or trifluoromethyl substitution should have an observable effect on hydrogen abstraction here, since closely spaced $n\pi^*$ and $\pi\pi^*$ states of nitrogen heterocycles undergo efficient mixing[19] and fragmentation is mediated only by $n\pi^*$ states.[24] Thus methyl substitution should decrease the rate of abstraction, and trifluoromethyl substitution should increase it. This predicted effect on hydrogen abstraction has not been systematically explored in nitrogen heteroaromatics, although the related effect is known in the photochemistry of aromatic ketones.[22,25] The decrease in $1/\tau$ in methylated pyrazines **6–8** relative to **5** indicates that methylation reduces the rate of abstraction, as expected in light of the foregoing discussion.

Quantum yield results for **5** and **6** add to this picture. On methyl substitution the rate of biradical reversion decreases (Φ_p increases), and reversion becomes less sensitive to the degree of substitution at the site of abstraction (cf. rel Φ_p per H for **5** and **6**). It is not clear why more $\pi\pi^*$ character in the abstracting triplet should have these effects on biradical reversion, but it is noteworthy that both Φ_p and rel Φ_p per H for **6** are quite similar to those for **1**, where the reactive triplets also have more $\pi\pi^*$ character than those of **5**.[26]

In the pyridines methyl substitution leads to decrease in Φ_p (one case) and trifluoromethyl substitution causes a several-fold increase in Φ_p. While this observation is qualitatively in line with the above discussion, its mechanistic basis is complex. For these pyridines Φ_p's are composites of singlet and triplet processes. Furthermore, relative Φ_p's reflect relative rates of abstraction only to the extent that rates of reversion of biradical to substrate are identical, and the singlet and triplet reversion processes are unexplored in the pyridines.

We note also that the position of methylation has a sizeable effect, as shown in the $k_q\tau$ values for **6a**, **7a**, and **8a**. In **6a** this may include a steric effect, but more generally the positional effect probably reflects symmetry properties of excited-state wave functions. Electron donation to the aromatic ring by the methyl substituent has quantitatively different effects at different sites.

Overall, hydrogen abstraction is well behaved in these systems. The differences among the various heterocyclic systems that have now been examined are reasonable, and interaction of $n\pi^*$ and $\pi\pi^*$ states leads to differences in reactivity in a qualitatively understandable fashion. We are presently continuing our earlier study[4] of the related abstraction of hydrogen in acyl-substituted nitrogen aromatics, and the results reported here should facilitate our understanding of these more complex reactions.

Experimental Section

Materials and Equipment. Preparative gas chromatography (GLC) was carried out on a Varian Aerograph Model 920 gas chromatograph with a SE-30, 10-ft column on Chromosorb-W, packed in a 0.25-in. aluminum tubing. Analytical GLC was carried

(17) Wagner, P. J.; Hammond, G. S. *Advan. Photochem.* **1968**, *5*, 21. Wagner, P. J. *Acc. Chem. Res.* **1971**, *4*, 168.

(18) See, for example: Hoover, R. J.; Kasha, M. *J. Am. Chem. Soc.* **1969**, *91*, 6508. The specific spectroscopic assignments made in this paper have subsequently been modified.

(19) Hochstrasser, R. M.; Marzzacco, C. *J. Chem. Phys.* **1968**, *49*, 971.

(20) Uchida, K. Yamazaki, I.; Baba, H.; *Chem. Phys.* **1978**, *35*, 91.

(21) Yang, N. C.; McClure, D. S.; Murov, S. L.; Houser, J. J.; Dusenbury, R. *J. Am. Chem. Soc.* **1967**, *89*, 5466.

(22) Wagner, P. J.; Kemppainen, A. E.; Schott, H. N. *J. Am. Chem. Soc.* **1973**, *95*, 5604.

(23) Sarkar, S. K.; Ghoshal, S. K.; Kastha, G. S. *J. Chem. Phys.* **1982**, *76*, 825.

(24) Stermitz, F. R.; Wei, C. C.; O'Donnell, C. M. *J. Am. Chem. Soc.* **1970**, *92*, 2745. Formosinho, S. J. *J. Chem. Soc., Faraday Trans. 2* **1976**, *72*, 1332 and references cited therein. See also paper cited in ref 15.

(25) Yang, N. C.; McClure, D. S.; Murov, S. L.; Houser, J. J.; Dusenbury, R. *J. Am. Chem. Soc.* **1967**, *89*, 5466.

(26) Because T_1 ($n\pi^*$) and T_2 ($\pi\pi^*$) are more closely spaced in pyrimidines than in pyrazines, the active triplet in **1** should have considerably more $\pi\pi^*$ character than that of **5**. For pyrimidine ΔE_T is ~2.5 kcal/mol and for pyrazine it is ~4.6 kcal/mol: ref 19. See also in this regard: Fujita, M.; Ohta, N.; Takemura, T.; Baba, H. *Bull. Chem. Soc. Jpn.* **1988**, *61*, 1787.

out isothermally using internal standards on a HP-5890 temperature programmable gas chromatograph using Alltech Econo-Cap (30 m × 0.25 mm) capillary column with a film thickness of 0.25 μm. All NMR spectra were recorded on a GE Model QE-300 (300 MHz for protons) 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 IR spectrophotometer or on a Perkin-Elmer 1870 Fourier transform spectrophotometer either neat or in KBr pellets, and absorption values are given in reciprocal centimeters. Ultraviolet absorption spectra were recorded on a Cary Model 14 recording instrument. All spinning disk chromatographic separations were carried out on a Chromatotron (Harrison Model 7924 T) using silica gel coated (2- or 4-mm thick) glass rotors. Mass spectral analyses were performed on a VG-70250 magnetic sector instrument. All organic solutions obtained by workup of the reaction mixtures were washed with brine and dried over anhydrous $MgSO_4$ prior to removal of solvent. All operations were carried out under nitrogen atmosphere unless otherwise mentioned.

General Procedure for Preparative Photochemistry. Solutions of pyridines and pyrazines (0.1 M) in degassed benzene or 10% benzene in *tert*-butyl alcohol in toroidal Pyrex vessels were 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 and the residue was purified either by preparative gas chromatography or by spinning disk chromatography. All the products were identified by comparing their GLC retention times with those of authentic samples and coinjection of the reaction mixture with authentic samples.

General Procedure for Quantum Yield Measurements. (a) Degassed benzene or 10% benzene in *tert*-butyl alcohol solutions of the pyrazine samples (0.1 M) were irradiated under a nitrogen atmosphere simultaneously in a merry-go-round apparatus with a 450-W medium-pressure mercury lamp at 313-nm light (using K_2CrO_4 solution as filter). Conversions of the starting materials were 0.1 to 0.5% in all cases. A 0.2 M solution of 2-butylquinoline in benzene (4 mL) was used as an actinometer. Photolysates were analyzed by analytical gas chromatography.

(b) Degassed benzene solutions of the pyridine samples were irradiated under nitrogen atmosphere in quartz tubes in a merry-go-round apparatus in a Southern New England RPR unit at 254 nm using 2-butylquinoline as an actinometer.

General Procedure for Stern–Volmer Quenching Experiments. Degassed benzene solutions of the pyrazine samples along with various amounts of piperylene were irradiated under nitrogen atmosphere in quartz tubes in a merry-go-round apparatus using a 450-W medium-pressure mercury lamp with a K_2CrO_4 filter at 313 nm. Photolysates were analyzed by gas chromatography. Results are collected in Table 1.

Preparation of 2-Propyl-, 2-Butyl-, and 2-Isopentylpyrazine (5a–c); 2-Propyl-, 2-Butyl-, and 2-Isopentyl-3-methylpyrazine (6a–c); 2-Propyl-5-methylpyrazine (7a), and 2-Propyl-6-methylpyrazine (8a). These were prepared from the appropriate 2-methyl derivative by the route previously employed by Behum and Levine[5] in good to moderate yields.

Preparative of 4-Methyl-2-isopentylpyridine (11c). This was made by the method developed by Fontana and Minici.[7] To a mixture of 4-methylpyridine (1 mmol), 4-methylvaleric acid (3 mmol), $AgNO_3$ (0.1 mmol), and concd H_2SO_4 (2.5 mL) in 45 mL of water was added an aqueous solution of $(NH_4)_2S_2O_8$ (7.5 mmol) (25 mL) slowly over 2 h at 80 °C. The mixture was stirred for an additional 2 h. The aqueous solution was made basic with NaOH and extracted with ether (150 mL). The product **11c** was isolated (40% yield) and purified by spinning disk chromatography using 10% ethyl acetate–hexane as eluant: ^{1}H NMR ($CDCl_3$) δ 8.24 (d, 1 H, J = 4.8 Hz), 6.83 (s, 1 H), 6.76 (d, 1 H, J = 4.8 Hz), 2.64–2.59 (m, 2 H), 2.16 (s, 3 H), 1.49–1.45 (m, 3 H), 0.83–0.81 (d, J = 5.7 Hz, 6 H); ^{13}C NMR δ 162.24, 148.66, 146.73, 123.10, 121.49, 38.83, 35.96, 27.71, 22.21, 20.65; IR (neat) 3055, 3012, 2870, 1563, 1479, 1409 , 1384, 1280, 1198 cm^{-1}; HRMS m/z 163.1351 (M^+), calcd for $C_{11}H_{17}N$ 163.1362.

Preparation of 2-Butyl- and 2-Isopentylpyridine (9b,c). These were prepared by the above-mentioned procedure from pyridine and valeric acid (for **9b**) or 4-methylvaleric acid (for **9c**). **9b** has been previously reported.[9] For **9c**: ^{1}H NMR ($CDCl_3$) δ 8.52 (s, 1 H), 7.58 (t, 1 H), 7.16–7.08 (dd, 2 H), 2.81–2.76 (m, 2 H), 1.63–1.60 (m, 3 H), 0.956 (bs, 6 H); ^{13}C NMR δ 162.81, 149.15, 136.13, 122.55, 120.74, 39.04, 36.32, 27.91, 22.47; IR (neat) 2956, 2870, 1591, 1474, 1434, 1385, 1367, 1149 cm^{-1}; HRMS m/z 148.1128 [$(M - H)^+$], calcd for $C_{10}H_{14}N$ 148.1126.

Preparation of 2-Propyl-, 2-Butyl-, and 2-Isopentyl-4-(trifluoromethyl)pyridine (10a–c). These compounds were prepared by the procedure given above. 4-(Trifluoromethyl)-pyridine (instead of 4-methylpyridine) and butyric acid, valeric acid, and 4-methylvaleric acid were used. For **10a**: ^{1}H NMR ($CDCl_3$) δ 8.65 (d, 1 H, J = 5.1 Hz), 7.31 (s, 1 H), 7.27 (d, 1 H, J = 4.8 Hz), 2.83–2.78 (t, 2 H), 1.78–1.70 (q, 2 H), 0.96–0.90 (t, 3 H); ^{13}C NMR δ 163.85, 150.09, 138.61, 118.10 (q, J = 3.3 Hz), 116.38 (q, J = 3.2 Hz), 40.26, 22.76, 13.58;[27] IR (neat) 2979, 2931, 2868, 1615, 1445, 1384, 1351, 1218 cm^{-1}; HRMS m/z 189.0777 (M^+), calcd for $C_9H_{10}NF_3$ 189.0765.

For 10b: ^{1}H NMR ($CDCl_3$) δ 8.70 (d, 1 H, J = 5.1 Hz), 7.36 (s, 1 H), 7.325 (d, 1 H, J = 4.8 Hz), 2.90–2.85 (t, 2 H), 1.78–1.72 (m, 2 H), 1.46–1.38 (m, 2 H), 0.98–0.92 (t, 3 H); ^{13}C NMR δ 169.42, 164.13, 150.14, 118.25 (q, J = 3.0 Hz), 116.50 (q, J = 3.4 Hz), 38.135, 31.77, 22.40, 13.85;[27] IR (neat) 2962, 2934, 2876, 1613, 1574, 1480, 1468, 1382, 1255, 1214, 1171 cm^{-1}; HRMS m/z 203.0939 (M^+), calcd for $C_{10}H_{12}NF_3$ 203.0922.

For **10c**: ^{1}H NMR ($CDCl_3$) δ 8.68 (d, 1 H, J = 4.8 Hz), 7.29 (s, 1 H), 7.25 (d, 1 H, J = 4.8 Hz), 2.85–2.80 (m, 2 H), 1.68–1.50 (m, 3 H), 0.91 (d, J = 6.0 Hz, 6 H); ^{13}C NMR δ 177.25, 164.8, 149.86, 118.18 (q, J = 3.0 Hz), 116.47 (q, J = 3.2 Hz), 38.72, 36.01, 27.82, 22.19;[27] IR (neat) 3029, 2959, 2873, 1612, 1574, 1480, 1386, 1242 cm^{-1}; HRMS m/z 216.0992 [$(M - H)^+$], calcd for $C_{11}H_{13}NF_3$ 216.1000.

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(27) In the ^{13}C NMR spectrum of α,α,α-trifluorotoluene the CF_3 carbon appears as a very weak signal, δ 124.6 (q, J = 271.7 Hz), and C(2) and C(6) appear at δ 125.4 (q, J = 3.9 Hz): Johnson, L. F.; Jankowski, W. C. *Carbon-13 NMR Spectra*; John Wiley & Sons: New York, NY, 1972; spectrum 225. In ^{13}C NMR spectra of **10a–c** we observed no signal for CF_3 carbon.