Substituent Effects on Photochemical Hydrogen Abstraction in 2-Acylpyridines, 2-Acylpyrazines, and 4-Acylpyrimidines

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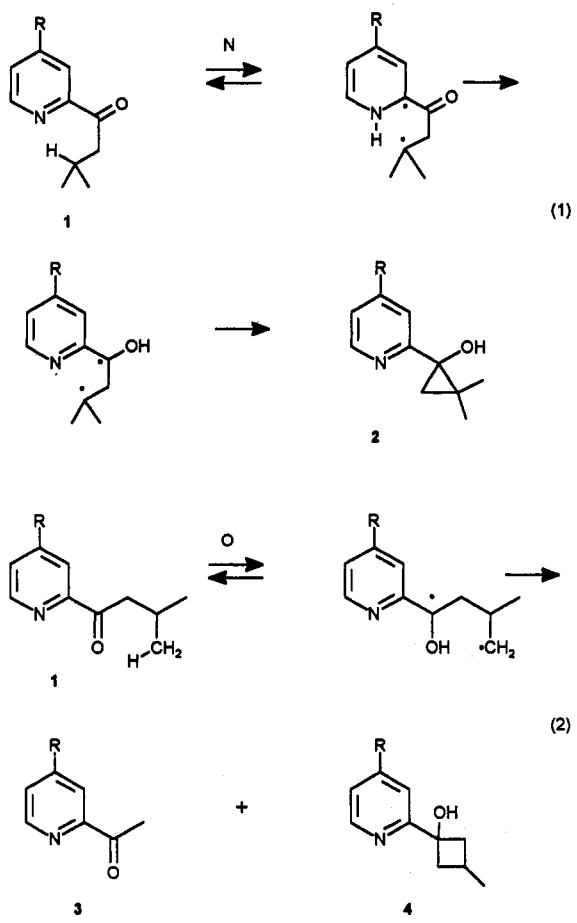
Stern–Volmer quenching of the photochemistry of **1c** indicates that N- and O-abstraction (eqs 1 and 2, respectively) are quenched at different rates (Figure 1). For quenching of **2c** $k_q\tau$ is 157 M^{-1} and for **3c**, 64 M^{-1}. When **1c** is sensitized with triplet sensitizers of increasing E_T, N-abstraction increases (Table 1). These data indicate that N- and O-abstraction in **1c** take place from distinguishable triplet states. Survey of Φ_p's of ring-substituted ketones **1b–d**, **6d**, **7a,b,d**, **8b**, **9b,d**, **10b**, and **11d** demonstrates the effect of substitution on the competition between N- and O-abstraction (Table 2). For methyl- and diacyano-substituted ketones, the results can be understood simply in terms of shifts in E_T of the $n\pi^*$ and $\pi\pi^*$ states of the heterocycle. The photochemistry of all these ketones requires consideration of interactions among three triplet states.

Heteroaromatic ketones such as 2-acylpyridines, in which the acyl substituent is adjacent to nitrogen, can undergo competitive abstraction of hydrogen by nitrogen (N-abstraction) and by oxygen (O-abstraction) on direct irradiation.[1-3] The reactions of 2-isovalerylpyridine[3] (**1a**) shown in eqs 1 and 2 are typical. We found earlier that

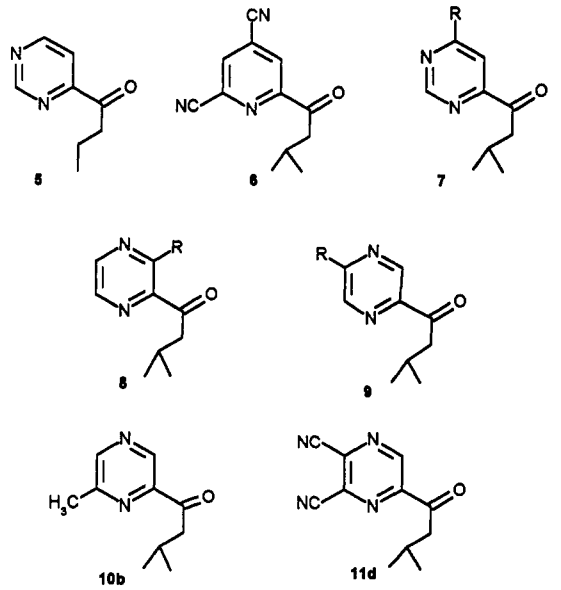


(1)

(2)

a, R = H; **b**, R = CH_3; **c**, R = CF_3; **d**, R = CN

Stern–Volmer quenching of these reactions of **1a**[3] gives identical $k_q\tau$ values for products of abstraction by both nitrogen and oxygen, indicating that these competitive processes are mediated either by a single triplet with electron deficiency on both nitrogen and oxygen or by two triplets that interconvert rapidly. Alexander had previously described similar results for analogous reactions of 4-butyrylpyrimidine (**5**).[1] In further exploring this matter we have now discovered that two distinguishable triplets



a, R = H; **b**, R = CH_3; **c**, R = CF_3; **d**, R = CN

mediate N- and O-abstraction in 2-isovaleryl-4-(trifluoromethyl)pyridine (**1c**).[4] These findings are discussed in the first part of the paper below. Thereafter, we discuss susbstituent effects on N- and O-abstraction and also note chemical transformations and a new photochemical reaction.

Preparative Reactions. The compounds employed in this work were pyridines **1b–d** and **6d**, pyrimidines **7a,b,d**, and pyrazines **8b**, **9b,d**, **10b**, and **11d**, which we

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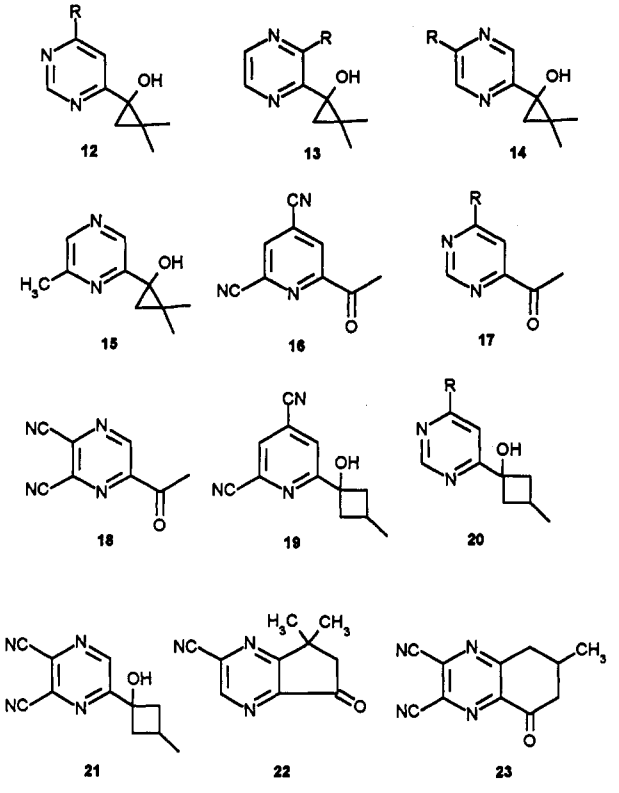
(4) A portion of this work has appeared as a preliminary communication: Rao, C. J.; Agosta, W. C. *Tetrahedron Lett.* **1993**, *34*, 6713.

0022-3263/94/1959-2125$04.50/0

prepared by free radical acylation of the appropriate heterocycle following a known procedure.[5] In addition to commercially available compounds, the substrates for this acylation reaction included pyridine-2,4-dicarbonitrile[6] and 4-pyrimidinecarbonitrile,[7] which were available through known methods, and pyrazine-2,3-dicarbonitrile, which we prepared from the commercially available diamide using the Burgess reagent.[8] Acylation of 2-methylpyrazine yielded a separable mixture of **8b**, **9b**, and **10b**, along with a minor amount of diacylated material. Details are given in the Experimental Section.

Photochemical Products. The photoproducts obtained were cyclopropanols **2a–d**, **12a,b,d**, **13a,b**, **14b,d**, and **15**, methyl ketones **3a–d**, **16**, **17a,b,d**, and **18**, cyclo-



a, R = H; b, R = CH_3; c, R = CF_3; d, R = CN

butanols **4a–d** and **19–21**, and **22** and **23**. These compounds were isolated by spinning disk chromatography and characterized spectroscopically. We were able to separate two of the diastereomeric mixtures of cyclobutanols; in these cases we characterized the isomers separately and assigned their stereochemistry. Most ketones were irradiated both in benzene and in *tert*-butyl alcohol–benzene, and not all products were observed in both solvents. Details are given in the Experimental Section.

Stern–Volmer Quenching of 1c. Irradiation of 0.1 M solutions of **1c** in benzene furnishes **2c** (Φ_p 0.13), **3c** (0.28), and **4c** (0.14). For O-abstraction, Φ_p's are concentration dependent, increasing ~60% as the concentration is increased to 0.4 M. This concentration effect on Type II reactions of pyridyl ketones has been observed previously and presumably results from hydrogen bonding of the hydroxy-substituted biradical with the pyridine nitrogen of a second molecule of substrate.[9] The Φ_p's for N-abstraction do not increase with concentration, and this behavior is in accord with the relatively small enhancement of N-abstraction observed in hydroxylic solvent.[10,11] Quenching of these processes with piperylene[3,9] indicated that they followed Stern–Volmer kinetics and that N- and O-abstraction were quenched at different rates. From the data shown in Figure 1, we calculate that $k_q\tau$ is 157 M^{-1} for quenching of **2c**, and 64 M^{-1} for **3c**. This result implies that under these conditions abstraction of hydrogen is mediated by two distinguishable triplets that do not equilibrate rapidly relative to quenching. The quenching constant (k_q) has not been measured for these reactions, but on the assumption[9] that under these conditions k_q is 5×10^9 M^{-1} s^{-1}, lifetimes (τ) are 31 ns for the triplet leading to **2c** and 13 ns for that leading to **3c**. These quenching results are solvent dependent. In 9:1 *tert*-butyl alcohol–benzene the measured $k_q\tau$'s for quenching **2c** and **3c** are 73 and 57 M^{-1}, respectively. In methanol they are 29 and 13 M^{-1}.[12,13]

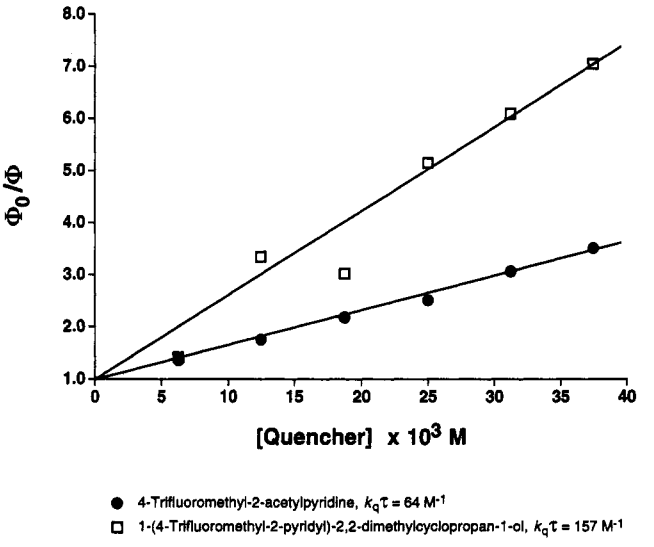


Figure 1. Stern–Volmer plot of quenching by piperlyene of formation of **2c** (□) and **3c** (●) on irradiation of **1c** in benzene at ~313 nm.

Triplet sensitization experiments with **1c** in benzene provide independent evidence for two distinguishable triplets. Table 1 gives the results of irradiating 0.035 M solutions of **1c** in benzene containing phenone triplet sensitizers of different E_T, along with a similar solution in acetone.[14] These results show that the relative yield of **2c** increases as sensitizer E_T increases, consistent with **2c** originating from a discrete triplet of energy higher than that leading to **3c** and **4c**. The carbonyl triplet quenches

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(12) Concomitant formation of red-orange byproducts discolor the reaction solutions even at low conversion in *tert*-butyl alcohol–benzene. This effect was absent in methanol and almost absent in benzene.

(13) For comparison, $k_q\tau$ for quenching photoelimination of valerophenone by 2,5-dimethyl-2,4-hexadiene is 36 M^{-1} in benzene and 61 M^{-1} in ethanol. The value in ethanol is reduced by concomitant photoreduction which decreases τ somewhat: Wagner, P. J.; Kochevar, I. *J. Am. Chem. Soc.* **1968**, *90*, 2232.

Table 1. Triplet Sensitization of 1c

sensitizer	E_T, kcal/mol[a]	ratio of Φ_p's: $\Phi_{2c}/(\Phi_{3c} + \Phi_{4c})$
4-benzoylpyridine	67.1	0.0
benzophenone	68.6	0.053
1-tetralone	72.2	0.078
1-indanone	75.0	0.18
acetone	79–82	0.29

[a] See ref 14.

4-benzoylpyridine inefficiently but quenches benzophenone and 1-tetralone efficiently, suggesting that the carbonyl E_T is ~69–70 kcal/mol. This implies that the trifluoromethyl group at C(4) has little effect on the carbonyl E_T of **1c**, since the reported[9,15] E_T of 2-acetylpyridine is ~70 kcal/mol. This small effect would be in line with the lack of effect of a 3-trifluoromethyl substituent on E_T of acetophenone.[16] The results in Table 1 do not permit an accurate estimate of the nitrogen nπ^* E_T of **1c**, but the ring substituents in **1c** should lower the pyridine nπ^* state E_T (84–85 kcal/mol[17,18]) to roughly 72–77 kcal/mol.[3,9,16] In summary, these sensitization data taken with the Stern–Volmer quenching experiments described above constitute good evidence that irradiation of **1c** in benzene leads to states chemically identifiable as discrete nitrogen and carbonyl nπ^* triplets. It is not yet clear whether these triplets interconvert in competition with these abstraction reactions. In other solvents these states may equilibrate rapidly and/or mix differently, and, as is already known for **1a**,[3] the situation may be different for other ketones.

We turn now to the effect of ring substituents on the competition between N- and O-abstraction. Earlier we found that in simple acyl-substituted pyridines and pyrimidines such as **1** and **5**, as well as in related pyrazines and pyridazines, there is a correlation between the observed photochemistry and the triplet energy (E_T) of T_1 (nπ^*) of the parent heterocyclic ring.[3] The excited state or states responsible for these reactions result from interaction of the ring $\pi\pi^*$ state and the oxygen and nitrogen nπ^* states, all of which have E_T in the range of 70–85 kcal/mol. The nitrogen and oxygen nπ^* states mediate hydrogen abstraction; the ring $\pi\pi^*$ state does not. Our results showed that N-abstraction increases with decreasing nπ^* E_T of the parent heterocycle. Ring nπ^* E_T thus influences these competitive photochemical processes in a qualitatively straightforward way. These results suggested that substituents on the heteroaromatic ring might also influence competitive N- and O-abstraction reactions in an understandable fashion. It is well known that ring substituents on nitrogen heteroaromatics can shift the energies of both the nitrogen nπ^* and the ring $\pi\pi^*$ states.[3,17–21] If this is the case, the effectiveness of two competitive photochemical pathways could be controlled through manipulation of triplet energies by simple ring substitution. This possibility interested us as a way of influencing the course of a chemical reaction.

Table 2. Photochemical Products from Ketones 1 and 6–11

series	compd	subst	quantum yields for products, Φ_p[a] Φ_N	Φ_O	Φ_{Ac}	Φ_{cb}	Φ_N/Φ_O
pyridine[b]	1c[c]	H	0.31	0.63	0.54	0.088	0.49
	1b	CH_3	0.061	0.84	0.68	0.16	0.073
	1c	CF_3	0.17	0.75	0.51	0.24	0.27
	1d	CN	0.35	0.36	0.26	0.099	0.97
	6d	$(CN)_2$	0.00	0.61	0.44	0.17	only O
pyrimidine[b]	7a	H	0.47	0.38	0.38	0.0	1.2
	7b	CH_3	0.28	0.62	0.45	0.17	0.45
	7d	CN	0.53	0.30	0.30	0.0	1.8
pyrazine[d]	8a	H	0.37	~0.0	~0.0	0.0	only N
	8b	CH_3	0.088	~0.0	~0.0	0.0	only N
	9b	CH_3	0.23	~0.0	~0.0	0.0	only N
	9d	CN	0.50	~0.0	~0.0	0.0	only N
	10b	CH_3	0.27	~0.0	~0.0	0.0	only N
	11d	$(CN)_2$	0.0	0.27	~0.27	0.0	only O

[a] $\Phi_N = \Phi_p$ for cyclopropanol, $\Phi_{Ac} = \Phi_p$ for methyl ketone, $\Phi_{cb} = \Phi_p$ for cyclobutanol, $\Phi_O = (\Phi_{Ac} + \Phi_{cb})$. [b] In 9:1 *t*-BuOH–$C_6H_6$. [c] From ref 3. [d] In C_6H_6.

Such an effect would be in accord with earlier observations. It has been known for many years that substituents on the aromatic ring of simple aromatic ketones (phenones) can shift the energies of both carbonyl (nπ^*) and ring ($\pi\pi^*$) states and thereby influence the reactivity of T_1 in O-abstraction.[16,22] Similarly, we have recently found that substituent shifts affect excited state reactivity in N-abstraction in ring-substituted 2-alkylpyridines and -pyrazines.[10] There is a noteworthy difference between these earlier studies of aromatic ketones and alkyl heteroaromatics and the present study of heterocyclic ketones. Both earlier studies concerned the efficiency of a single reaction, while the present study deals with the partitioning of reactivity between two competing reactions.

Our present results demonstrate that ring substitution can influence competitive N- and O-abstraction in a simple fashion. Irradiation of ketones **1** and **6–11** led to some or all of the expected cyclopropanol, methyl ketone, and cyclobutanol products, as reported above. Quantum yields for the products are gathered in Table 2, along with the ratio Φ_N/Φ_O as a measure of competitive N- and O-abstraction. Three different substituents are represented, cyano, methyl, and trifluoromethyl. Each of these should have a different effect on the excited states involved in these reactions. Cyano-substitution lowers the energy of both nπ^* and $\pi\pi^*$ states in pyridine[23] and in aromatic ketones.[15,21] Methyl substitution raises nπ^* and lowers $\pi\pi^*$ energies in both nitrogen heteroaromatics[17,19,20] and in aromatic ketones.[16,22] Trifluoromethyl substitution lowers nπ^* and raises $\pi\pi^*$ energies in aromatic ketones,[16] and we asssume a similar inductive effect operates in nitrogen heteroaromatics.[10]

The data in Table 2 demonstrate the effect of substituents on N- and O-abstraction, and the results for methyl and dicyano substitution are qualitatively in line with expectation. In **1b**, **7b**, **8b**, **9b**, and **10b** a methyl

(14) (a) Phenone concentrations were adjusted so that sensitizers absorbed ≥97% of the light; acetone (as solvent) absorbed ~93%. (b) Phenone E_T's: Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973. See also ref 22 in this regard. (c) Acetone E_T: Schmidt, M. W.; Lee, E. K. C. *J. Am. Chem. Soc.* **1970**, *92*, 3579, and ref cited therein. Zuckermann, H.; Schmitz, B.; Haas, Y. *J. Phys. Chem.* **1988**, *92*, 4835.

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(17) 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.

(18) Evans, D. F. *J. Chem. Soc.* **1957**, 3885. Buma, W. J.; Groenen, E. J. J.; van Hemert, M. C. *J. Am. Chem. Soc.* **1990**, *112*, 5447, and ref cited therein.

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

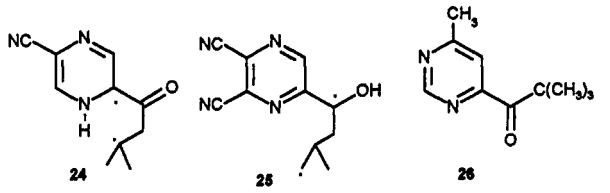
(22) Yang, N. C.; McClure, D. S.; Murov, S. L.; Houser, J. J.; Dusenbury, R. *J. Am. Chem. Soc.* **1967**, *89*, 5466.

(23) T_1 and T_2 of pyridine are closely spaced at 84–85 kcal/mol (ref 18). In ethanol, 4-cyanopyridine has T_1 ($\pi\pi^*$) 80.7 kcal/mol and T_2 (nπ^*) 82.4 kcal/mol (ref 21), indicating that a 4-cyano group lowers the $\pi\pi^*$ state of pyridine somewhat more than the nπ^* state.

substituent causes a marked reduction in Φ_N, consistent with increased $\pi\pi^*$ character in the nitrogen triplet. In **6d** and **11d** N-abstraction is suppressed completely. This suggests that two cyano groups lower the ring $\pi\pi^*$ energy well below the nitrogen $n\pi^*$ triplet in these compounds so that the latter state is inaccessible; that is, in **6d** and **11d** the ring $\pi\pi^*$ triplet is T_2 and the nitrogen $n\pi^*$ triplet is T_3. Dicyanopyrazine **11d** is the only known pyrazyl ketone structurally capable of 1,5 N-abstraction of hydrogen in which that reaction is absent. As indicated in Table 2, all other pyrazines examined here gave essentially only N-abstraction.[24]

The shifts in E_T's caused by methyl and dicyano substitution affect triplet characteristics sufficiently that the results can be understood simply, and the effects thus have predictive value. The behavior of **1c**, **1d**, and **7d** is not explainable in these simple terms. One important factor that has been omitted in this simple analysis is that Φ_p's also reflect reversion of the two competitively formed biradicals (eqs 1 and 2).[25] In simple alkyl-substituted heterocycles there is some evidence that reversion of the biradical is affected by changing $n\pi^*$ and $\pi\pi^*$ character of the nitrogen triplet,[10] but it is not yet clear how important this effect is in these ketones. Doubtless other factors are also involved.

Other Reactions. In addition to furnishing the expected products, two of the pyrazyl ketones underwent novel cyclization reactions on irradiation in *tert*-butyl alcohol–benzene. From **9d** we obtained ~24% of **22**, and from **11d**, ~8% of **23**.[26] Only one mode of abstraction operates in both **9d** and **11d**. In **9d**, products arise only from N-abstraction, by way of biradical **24**, while in **11d** there is only O-abstraction, by way of **25**. We assume that the cyano substituents favor cyclization of these biradicals to bicyclic dihydropyrazines that then aromatize oxidatively to **22** and **23**.



On treatment with methanolic sodium hydroxide, cyclopropanol **12b** opened cleanly to give *tert*-butyl ketone **26**, in keeping with previous experience.[3,27] Exposure of **2d** to silica gel in hot benzene led to cleavage of the cyclopropane ring in the direction opposite to the opening of **12b**, with formation of **1d** as the only product. This change in the regiochemistry of cleavage of a cyclopropanol on going from basic to acidic catalysis has been known for many years, but the complete regiospecificity observed with **2d** is unusual.[27]

Not surprisingly, the hydrogen abstraction reactions of these ketones are more complicated than those of the related alkyl-substituted heterocycles, where only the ring $\pi\pi^*$ and nitrogen $n\pi^*$ states intereact to control the photochemistry.[10,11] In the ketones three states play a role; carbonyl $n\pi^*$ (T_1), and nitrogen $n\pi^*$ and ring $\pi\pi^*$ (T_2 and T_3) states all influence the photochemistry. A complete understanding here will require both spectroscopic studies on these ketones and further photochemical investigations.

(24) In some cases there were very small gas chromatographic peaks possibly indicative of methyl ketones.

(25) The biradical formed on N-abstraction is assumed to revert to the substrate in analogy to the behavior of the Type II biradical: Wagner, P. J.; Hammond, G. S. *Adv. Photochem.* **1968**, *5*, 21. Wagner, P. J. *Acc. Chem. Res.* **1971**, *4*, 168.

(26) These cyclization products were not observed on irradiation in benzene and so do not affect the results in Table 2.

(27) DePuy, C. H. *Acc. Chem Res.* **1968**, *1*, 33, and references cited therein.

Experimental Section

Materials and Equipment. Preparative gas chromatography (GLC) was carried out on a Varian Aerograph Model 920 gas chromatograph using a SE-30, (10 or 12 ft × 0.25 in.; Chromosorb-W) column. Analytical GLC was carried 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) or a Nicolet/Oxford Model NT-360 (360 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 as KBr pellets; 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 after 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. Unless otherwise indicated, pure compounds were obtained as colorless oils.

1. Preparation of 4-Methyl-(1b), 4-(Trifluoromethyl)-(1c), 4-Cyano-2-isovalerylpyridines (1d) and 4,6-Dicyano-2-isovalerylpyridine (6d).[5] 2,4-Dicyanopyridine was prepared by adaptation of the reported procedure.[6] **1b** was prepared by the reaction of 4-methylpyridine (232 mg, 2.5 mmol), sodium salt of 4-methyl-2-oxoisovaleric acid (800 mg, 5.2 mmol), silver nitrate (34 mg, 0.20 mmol), ammonium persulfate (1.2 g, 5.2 mmol), and concd H_2SO_4 (3.0 mL) in 30 mL of water and 30 mL of dichloromethane at 40 °C for 3 h to give **1b** (yield 30%; bp 78 °C/0.5 mm). **1c**,[4] **1d**, and **6d**[5] were prepared using a similar procedure. For **1b**: ^{1}H NMR ($CDCl_3$) δ 8.53 (1 H), 7.86 (1 H), 7.2 (1 H), 3.08 (2 H, d, J = 6.8 Hz), 2.42 (3 H), 2.33 (1 H, septet, J = 6.8 Hz), 1.00 (6 H, d, J = 6.4 Hz); ^{13}C NMR ($CDCl_3$) δ 201.9, 153.6, 148.5, 148.0, 127.6, 122.5, 46.4, 24.6, 22.6, 20.9; IR (neat) 3054, 2958, 2871, 1696, 1601, 1560, 1469, 1384, 1366, 1301, 1166, 1041, 924, 864, 769; MS m/z 178.1277 ($(M+H)^+$; calcd for $C_{11}H_{16}NO$, 178.1232). For **1d**: yield 80%, recrystalized from *n*-hexane, mp 62–63 °C; ^{1}H NMR ($CDCl_3$) δ 8.85 (1 H), 8.25 (1 H), 7.7 (1 H), 3.10 (2 H, d, J = 7.7 Hz), 2.31 (1 H, septet, J = 7.7 Hz), 1.0 (6 H, d, J = 7.7 Hz); ^{13}C NMR ($CDCl_3$) δ 199.7, 154.4, 149.8, 127.8, 123.4, 121.5, 115.8, 46.2, 24.6, 22.6; IR (KBr) 3087, 3067, 2955, 2868, 2241, 1698, 1597, 1547, 1472, 1394, 1358, 1227, 1158, 1027, 935, 867, 852, 750; MS m/z 189.1023 ($(M + H)^+$, calcd for $C_{11}H_{13}N_2O$, 189.1028).

2. Preparation of 4-isovalerylpyrimidine (7a) and 6-Cyano-(7b) and 6-Methyl-4-isovalerylpyrimidine (7d). Pyrimidine-4-carbonitrile was prepared by adaptation of the procedure reported earlier.[7] This involved the reaction of 4-chloropyrimidine (450 mg, 3.9 mmol) with a solution of trimethylamine in benzene (20%, 20 mL) to give corresponding quaternary ammonium chloride (433 mg, 64%) which was directly converted to pyrimidine-4-carbonitrile (300 mg, 68%) by treatment with tetraethylammonium cyanide (470 mg, 3.0 mmol) in dichloromethane under nitrogen. **7a** (466 mg, 71%, bp 62 °C/0.5 mm) was obtained from the reaction of pyrimidine (322 mg, 4 mmol), sodium salt of 4-methyl-2-oxovaleric acid (1.84 g, 12.0 mmol), silver nitrate (67 mg, 0.4 mmol), ammonium persulfate (2.7 g, 12 mmol), concd H_2SO_4 (2 mL) in 30 mL of water, and 30 mL of dichloromethane at 40 °C for 3 h. **7b** and **7c** were prepared by using similar procedure. For **7a**: ^{1}H NMR ($CDCl_3$) δ 9.36 (1 H) 8.97 (1 H, d, J = 5.1 Hz), 7.89 (H, d, J = 5.1 Hz), 3.07 (2 H, d,

J = 6.6 Hz), 2.31 (1 H, septet, J = 6.6 Hz), 1.01 (6 H, d, J = 6.6 Hz); ^{13}C NMR ($CDCl_3$) δ 200.9, 159.0, 158.8, 117.2, 46.2, 24.7, 22.7; IR (neat) 3056, 2960, 2932, 2873, 1707, 1574, 1549, 1467, 1389, 1368, 1305, 1290, 1241, 1178, 1065, 1021, 950, 891, 866, 764; MS m/z 164.0933 (M^+; calcd for $C_9H_{12}N_2O$, 164.0949). For **7b**: yield 65%, bp 68 °C/0.5 mm. ^{1}H NMR ($CDCl_3$) δ 9.21 (1 H), 7.75 (1 H), 3.05 (2 H, d, J = 6.9 Hz), 2.63 (3 H), 2.30 (1 H, septet, J = 6.9 Hz), 0.99 (6 H, d, J = 6.9 Hz); ^{13}C NMR ($CDCl_3$) δ 202.0, 169.4, 159.1, 158.6, 117.0, 46.6, 24.8, 24.4, 22.7; IR (neat) 3056, 2964, 2872, 1705, 1584, 1535, 1467, 1389, 1368, 1311, 1238, 1162, 1042, 865, 691; MS m/z 178.1088 (M^+; calcd for $C_{10}H_{14}N_2O$, 178.1106). For **7d**: yield 60%, bp 95 °C/0.5 mm; ^{1}H NMR ($CDCl_3$) δ 9.49 (1 H), 8.21 (1 H), 3.07 (2 H, d, J = 6.9 H z), 2.30 (1 H, septet J = 6.9 Hz), 1.02 (6 H, d, J = 6.9 Hz); ^{13}C NMR ($CDCl_3$) δ 199.0, 160.3, 159.6, 143.1, 120.6, 115.0, 46.1, 24.5, 22.5; IR (neat) 3066, 2961, 2933, 2874, 2246, 1712, 1575, 1533, 1468, 1388, 1373, 1340, 1230, 1151, 1030, 910, 853, 782, 696; MS m/z 189.0906 (M^+; calcd for $C_{10}H_{11}N_3O$, 189.0902).

3. Preparation of 2-Methyl-3-isovaleryl-, 2-Methyl-5-isovaleryl-, 2-Cyano-5-isovaleryl-, 2-Methyl-6-isovaleryl-, and 2,3-dicyano-5-isovalerylpyrazines. (8b, 9b, 9d, 10b, and 11d). [(Methoxycarbonyl)sulfamoyl]triethylammonium hydroxide (Burgess reagent)[8] was used to prepare pyrazine-2,3-carbonitrile. This involved stirring of pyrazine-2,3-dicarboxamide (166 mg, 1.0 mmol) in 10 mL of THF and Burgess reagent (2.38 g, 10 mmol) under argon for 3 h to give pyrazine-2,3-dicarbonitrile (120 mg, 90%). Compounds **8b**, **9b**, and **10b** were prepared from the reaction of 2-methylpyrazine (1.12 g, 12 mmol), sodium salt of 4-methyl-2-oxovaleric acid (1.82 g, 12 mmol), ammonium persulfate (2.7 g, 12 mmol), silver nitrite (194 mg, 1.2 mmol), and concd H_2SO_4 (2 mL) in 50 mL of water and 50 mL of dichloromethane at 40 °C for 1 h. These products were separated by preparative gas chromatography and characterized individually. Pyrazines **9d** and **11d** were prepared by using the same procedure. For **8b**: ^{1}H NMR ($CDCl_3$) δ 8.59 (1 H, d, J = 2.1 Hz), 8.48 (1 H, d, J = 2.1 Hz), 3.06 (2 H, d, J = 6.9 Hz), 2.81 (3 H), 2.26 (1 H, septet, J = 6.9 Hz), 0.98 (6 H, d, J = 6.9 Hz); ^{13}C NMR ($CDCl_3$) δ 203.0, 154.1, 147.6, 145.5, 140.6, 48.3, 24.8, 23.1, 22.6; IR (neat) 3049, 2964, 2936, 2879, 1701, 1553, 1531, 1467, 1396, 1294, 1166, 1074, 1003, 946, 854, 755; MS m/z 178.1110 (M^+; calcd for $C_{10}H_{14}N_2O$, 178.1106). For **9b**: ^{1}H NMR ($CDCl_3$) δ 9.10 (1 H, d, J = 1.08 Hz), 8.48 (1 H), 3.04 (2 H, d, J = 6.8 Hz), 2.65 (3 H), 2.30 (1 H, septet, J = 6.8 Hz), 0.98 (6 H, d, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$) δ 203.0, 154.0, 147.6, 145.5, 140.6, 48.3, 24.8, 23.1, 22.6; IR (neat) 2957, 2931, 2873, 1694, 1576, 1459, 1402, 1367, 1299, 1176, 1038, 1010, 915, 878; MS m/z 178.1119 (M^+; calcd for $C_{10}H_{14}N_2O$, 178.1106). For **9d**: yield 86%, bp 102 °C/0.5 mm; ^{1}H NMR ($CDCl_3$) δ 9.30 (1 H, d, J = 1.44 Hz), 8.97 (1 H, d, J = 1.44 Hz), 3.08 (2 H, d, J = 6.8 Hz), 2.30 (1 H, septet, J = 6.8 Hz), 1.02 (6 H, d, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$) δ 199.5, 148.3, 146.8, 143.8, 132.9, 114.8, 46.5, 24.6, 22.5; IR (KBr) 3050, 3020, 2910, 2890, 2820, 2220, 1700, 1545, 1448, 1408, 1372, 1350, 1270, 1212, 1190, 1148, 1010, 980, 922, 903, 860; MS m/z 190.1006 ((M + H)$^+$; calcd for $C_{10}H_{12}N_3O$, 190.0980). For **10b**: ^{1}H NMR ($CDCl_3$) δ 9.00 (1 H), 8.60 (1 H), 3.07 (2 H, d, J = 6.8 Hz), 2.64 (3 H), 2.30 (1 H, septet, J = 6.8 Hz), 0.99 (6 H, d, J = 6.8 Hz); ^{13}C NMR ($CDCl_3$) δ 203.0, 154.0, 147.3, 140.4, 46.4, 24.7, 22.7, 21.4; IR (neat) 3039, 2964, 2879, 1701, 1577, 1469, 1368, 1304, 1177, 1047, 1013, 950; MS m/z 178.1105 (M^+; calcd for $C_{10}H_{14}N_2O$, 178.1106). For **11d**: yield 73%, ^{1}H NMR ($CDCl_3$) δ 9.45 (1 H), 3.09 (2 H, d, J = 7.2 Hz) 2.30 (1 H, septet, J = 7.2 Hz), 1.01 (6 H, d, J = 7.2 Hz); ^{13}C NMR ($CDCl_3$) δ 197.8, 147.4, 145.6, 135.5, 132.5, 112.5, 112.3, 46.6, 24.6, 22.5; IR (neat) 3060, 2963, 2934, 2875, 2243, 1706, 1547, 1523, 1468, 1425, 1396, 1371, 1351, 1304, 1137, 1109, 1024, 957, 877; MS m/z 214.0815 (M^+; calcd for $C_{11}H_{10}N_4O$, 214.0885).

Preparative Photochemistry. All preparative experiments were carried out using a Hanovia 450-W medium-pressure mercury arc lamp with a uranium glass filter ($\lambda > 340$ nm). Yields were determined gas chromatographically. Irradiations were carried out using toroidal Pyrex vessels in a 10:1 mixture of degassed *tert*-butyl alcohol and benzene.

A. 4-Methyl-2-isovalerylpyridine (1b). A solution (50 mL) of **1b** (177 mg, 1.0 mmol) was irradiated for 5 h. Solvent was evaporated under reduced pressure and the residue was subjected to spinning-disk chromatography. Four products were isolated, purified, and identified as the ketone **3b**, cyclopropanol **2b**, and two cyclobutanols **4b$_1$** (*trans*-3-methyl-1-[2-(4-methylpyridyl)]-1-cyclobutanol) and **4b$_2$** (*cis*-3-methyl-1-[2-(4-methylpyridyl)]-1-cyclobutanol). The stereochemistry of **4b$_1$** and **4b$_2$** was assigned tentatively on the basis of ^{1}H NMR. In **4b$_1$**, the tertiary hydrogen at C(3) of the cyclobutanol appears further downfield than **4b$_2$** owing to its proximity to the hydroxyl group.[28] For **3b**: ^{1}H NMR ($CDCl_3$) δ 8.82 (1 H), 7.78 (1 H), 7.28 (1 H), 2.7 (3 H), 2.4 (3 H); IR (neat) 3056, 2928, 2872, 1698, 1599, 1411, 1354, 1283, 1191, 825; MS m/z 136.0781 ((M + H)$^+$; calcd for $C_8H_{10}NO$, 136.0762). For **2b**: ^{1}H NMR ($CDCl_3$) δ 8.38 (1 H, d, J = 5.04 Hz), 7.44 (1 H), 6.97 (1 H, d, J = 5.04 Hz), 2.82 (3 H), 1.64 (1 H), 1.58 (1 H, d, J = 5.7 Hz), 1.36 (3 H), 0.92 (1 H, d, J = 5.7 Hz), 0.85 (3 H); IR (neat) 3361, 3058, 2978, 2921, 1606, 1563, 1453, 1368, 1301, 1194, 1155, 1091, 999, 978, 825; MS m/z 176.1074 ((M − H)$^+$, calcd for $C_{11}H_{14}NO$, 176.1075). For **4b$_1$**: ^{1}H NMR ($CDCl_3$) δ 8.36 (1 H, d, J = 5.0 Hz), 7.30 (1 H), 7.00 (1 H, d, J = 4.6 Hz), 2.81 (1 H, m), 2.48 (2 H, m), 2.40 (3 H), 2.15 (2 H, m), 1.62 (1 H), 1.20 (3 H, d, J = 6.8 Hz); IR (neat) 3365, 3055, 2952, 2926, 2866, 1563, 1471, 1454, 1419, 1379, 1298, 1241, 1156, 999, 954, 827; MS m/z 176.1064 ((M − H)$^+$, calcd for $C_{11}H_{14}NO$ 176.1075). For **4b$_2$**: ^{1}H NMR ($CDCl_3$) δ 8.36 (1 H, d, J = 5.0 Hz), 7.34 (1 H), 7.03 (1 H, d, J = 5.0 Hz), 2.62 (2 H, m), 2.41 (3 H), 2.20 (3 H, m), 1.56 (1 H), 1.25 (3 H, d, J = 6.4 Hz); IR (neat) 3404, 2950, 2921, 2858, 1606, 1563, 1457, 1379, 1244, 1152, 992, 950, 829; MS m/z 176.1057 ((M − H)$^+$; calcd for $C_{11}H_{14}NO$ 176.1075).

B. 4-(Trifluoromethyl)-2-isovalerylpyridine (1c). A solution (50 mL) of **1c** (231 mg, 1.0 mmol) was irradiated for 2 h. Solvent was removed and the residue was subjected to preparative gas chromatography to obtain the ketone **3c**, the cyclopropanol **2c**, and a mixture of cyclobutanols **4c**.

C. 4-Cyano-2-isovalerylpyridine (1d). A solution (50 mL) of **1d** (188 mg, 1.0 mmol) was irradiated for 7 h. Solvent was removed under pressure and the residue was subjected to spinning-disk chromatography. Three products were isolated and identified as ketone **3d**, the cyclopropanol **2d**, and a mixture of cyclobutanols **4d**. For **3d**: mp 99 °C; ^{1}H NMR ($CDCl_3$) δ 8.87 (1 H), 8.25 (1 H), 7.70 (1 H), 2.74 (3 H); ^{13}C NMR ($CDCl_3$) δ 198.0, 154.2, 149.9, 127.9, 123.3, 121.6, 115.8, 25.5; IR (KBr) 3127, 3089, 2982, 2928, 2239, 1702, 1591, 1545, 1468, 1405, 1356, 1290, 1276, 1180, 1088, 993, 926, 865; MS m/z 147.0539 ((M + H)$^+$, calcd for $C_8H_7N_2O$, 147.0558). For **2d**: ^{1}H NMR ($CDCl_3$) δ 8.89 (1 H), 7.87 (1 H), 7.35 (1 H), 3.4 (1 H), 1.56 (1 H, d, J = 6.1 Hz), 1.38 (3 H), 1.00 (1 H, d, J = 6.1 Hz), 0.89 (3 H); IR (neat) 3095, 3070, 3030, 2991, 2927, 2871, 2239, 1593, 1550, 1470, 1399, 1305, 1254, 1212, 1181, 1154, 1078, 1019, 904, 869, 841; MS m/z 189.1007 ((M + H)$^+$; calcd for $C_{11}H_{13}N_2O$, 189.1028). For **4d**: ^{1}H NMR ($CDCl_3$) δ 8.72 (1 H), 7.77 (1 H), 7.41 (1 H), 3.84 (1 H), 2.87 (1 H, m), 2.50 (2 H, m), 2.25 (2 H, m), 1.20 (3 H, d, J = 6.8 Hz); IR (neat) 3413, 3065, 3031, 2955, 2928, 2867, 2240, 1594, 1551, 1469, 1417, 1379, 1298, 1152, 1020, 912; MS m/z 189.1006 ((M + H)$^+$, calcd for $C_{11}H_{13}N_2O$, 189.1028).

D. 2,4-Dicyano-6-isovalerylpyridine (6d). A solution (10 mL) of **6d** (42 mg, 0.20 mmol) was irradiated for 20 h, solvent was removed under reduced pressure, and the residue was subjected to spinning-disk chromatography. Three products were isolated and identified as the ketone **16** and the cyclobutanols **19a$_1$** (*trans*-3-methyl-1-[2-(2,4-dicyanopyridyl)]-1-cyclobutanol) and **19a$_2$** (*cis*-3-methyl-1-[2-(2,4-dicyanopyridyl)]-1-cyclobutanol). The stereochemistry of **19a$_1$** and **19a$_2$** was assigned tentatively on the basis of ^{1}H NMR. In **19a$_1$**, the tertiary hydrogen at C(3) of the cyclobutanol appears further downfield than in **19a$_2$** owing to its proximity to the hydroxyl group.[28] For **16**: mp 108 °C, ^{1}H NMR ($CDCl_3$) δ 8.44 (1 H), 8.07 (1 H), 2.77 (3 H); ^{13}C NMR ($CDCl_3$) δ 196.0, 155.2, 134.4, 131.9, 126.3, 123.5, 115.0, 114.0, 25.4; IR (neat) 3085, 2248, 1705, 1592, 1549, 1407, 1365, 1315, 1244, 1216, 904; MS m/z 172.0528 ((M + H)$^+$, calcd for $C_9H_6N_3O$, 172.0511). For **19a$_1$**: ^{1}H NMR ($CDCl_3$) δ 8.07 (1 H), 7.79 (1 H), 2.75 (2 H, m), 2.41 (1 H, m), 2.09 (2 H, m), 1.56 (1 H), 1.28 (3 H, d, J = 6.8 Hz); IR (neat) 3489, 3085, 2955, 2928, 2872, 2248, 1599, 1556, 1457, 1414, 1400, 1248, 1177, 1063, 921; MS m/z 214.1008 ((M + H)$^+$, calcd for $C_{12}H_{12}N_3O$, 214.0980). For **19a$_2$**: ^{1}H NMR ($CDCl_3$) δ 8.06 (1 H), 7.76 (1 H), 2.88 (2 H, m), 2.36 (3 H, m), 1.57 (1 H), 1.23 (3 H, d, J = 6.4 Hz); IR (neat) 3475, 3082, 2955, 2929, 2867,

(28) For an analogous stereochemical assignment, see: Jain, R.; Sponsler, M. B.; Coms, F. D.; Dougherty, D. A. *J. Am. Chem. Soc.* **1988**, *110*, 1356.

2248, 1595, 1550, 1455, 1401, 1236, 1179, 1120, 1034, 985; MS *m/z* 214.0955 ((M + H)$^+$, calcd for $C_{12}H_{12}N_3O$, 214.0980).

E. 4-Isovalerylpyrimidine (7a). A solution (50 mL) of **7a** (164 mg, 1.00 mmol) was irradiated for 2 h. Removal of solvent followed by spinning-disk chromatography gave three products and were identified as the ketone **17a**, cyclopropanol **12a**, and cyclobutanols **20a**. For **17a**: ^{1}H NMR ($CDCl_3$) δ 9.34 (1 H), 8.96 (1 H, d, J = 5.1 Hz), 7.86 (1 H, dd, J = 5.1 Hz, J = 1.2 Hz), 2.70 (3 H); ^{13}C NMR ($CDCl_3$) δ 199.0, 159.0, 158.9, 158.6, 117.2, 25.5; IR (KBr) 3092, 3049, 2936, 1702, 1581, 1553, 1475, 1396, 1361, 1290, 1177, 1162, 1106, 1070, 992, 957, 872; MS *m/z* 122.0482 (M$^+$, calcd for $C_6H_6N_2O$, 122.0481). For **12a**: ^{1}H NMR ($CDCl_3$) δ 9.24 (1 H, d, J = 1.2 Hz) 8.86 (1 H, d, J = 5.4 Hz), 7.69 (1 H, dd, J = 5.4 Hz, J = 1.2 Hz), 1.56 (1 H, d, J = 4.5 Hz), 1.38 (3 H), 1.05 (1 H, d, J = 6.0 Hz), 0.97 (3 H); IR (neat) 3388, 2950, 2936, 1584, 1542, 1471, 1393, 1308, 1201, 1152, 1116, 1081, 1019, 978; MS *m/z* 164.0945 (M$^+$, calcd for $C_9H_{12}N_2O$, 164.0949). For **20a**: ^{1}H NMR ($CDCl_3$) δ 9.24 (1 H, d, J = 1.2 Hz), 8.86 (1 H, d, J = 5.4 Hz), 7.69 (1 H, dd, J = 5.4 Hz, J = 1.2 Hz), 2.85 (1 H, m), 2.46 (2 H, m), 2.21 (2 H, m), 1.56 (3 H, d, J = 6.0 Hz); IR (neat) 3420, 2957, 2928, 2872, 1584, 1549, 1471, 1393, 1308, 1244, 1159, 1081, 953; MS *m/z* 164.0881 (M$^+$; calcd for $C_9H_{12}N_2O$, 164.0949).

F. 6-Methyl-4-isovalerylpyrimidine (7b). A solution (20 mL) of **7b** (75 mg, 0.4 mmol) was irradiated for 2 h. Solvent was removed under reduced pressure and residue was subjected to spinning-disk chromatography. Three products were separated and identified as the ketone **17b**, the cyclopropanol **12b**, and the diastereomeric mixture of cyclobutanols **20b**. For **17b**: ^{1}H NMR ($CDCl_3$) δ 9.22 (1 H), 7.76 (1 H), 2.72 (3 H), 2.63 (3 H); IR (neat) 3084, 3059, 2968, 2928, 1699, 1592, 1537, 1439, 1245, 1036, 993, 869; MS *m/z* 136.0641 (M$^+$, calcd for $C_7H_8N_2O$, 136.0636). For **12b**: ^{1}H NMR ($CDCl_3$) δ 8.94 (1 H), 7.30 (1 H), 2.51 (3 H), 1.56 (1 H, d, J = 5.7 Hz), 1.37 (3 H), 1.26 (1 H), 0.99 (1 H, d, J = 5.7 Hz), 0.95 (3 H); IR (neat) 3261, 2973, 2928, 2871, 1592, 1537, 1448, 1384, 1316, 1256, 1154, 979, 896; MS *m/z* 178.1096 (M$^+$, calcd for $C_{10}H_{14}N_2O$, 178.1107). For **20b**: ^{1}H NMR ($CDCl_3$) δ 9.02 (1 H), 7.38 (1 H), 2.82 (1 H, m), 2.57 (3 H), 2.41 (2 H, m), 2.18 (2 H, m), 1.69 (1 H), 1.25 (3 H, d, J = 6.3 Hz); IR (neat) 3333, 2976, 2929, 1593, 1538, 1444, 1383, 1276, 1184, 1149, 1035, 958; MS *m/z* 178.1106 (M$^+$, calcd for $C_{10}H_{14}N_2O$, 178.1106).

G. 4-Cyano-6-isovalerylpyrimidine (7d). A solution (50 mL) of **7d** (189 mg, 1.0 mmol) was irradiated for 4 h. Solvent was removed under reduced pressure and the residue was subjected to spinning-disk chromatography to obtain the ketone **17d**, the cyclopropanol **12d**, and a mixture of cyclobutanols **20d**. For **17d**: ^{1}H NMR ($CDCl_3$) δ 9.49 (1 H, d, J = 1.2 Hz), 8.20 (1 H, d, J = 1.2 Hz) 2.74 (3 H); IR (neat) 3066, 2976, 2935, 2342, 1702, 1576, 1534, 1383, 1366, 1231, 1153, 1033, 910, 857; MS *m/z* 147.0429 (M$^+$, calcd for $C_7H_5N_3O$, 147.0432). For **12d**: ^{1}H NMR ($CDCl_3$) δ 9.16 (1 H), 7.99 (1 H), 1.56 (1 H, d, J = 5.1 Hz), 1.41 (3 H), 1.25 (1 H, d, J = 5.4 Hz), 1.04 (3 H); IR neat 3389, 3093, 2958, 2929, 2872, 2246, 1575, 1460, 1379, 1248, 1177, 1114, 986; MS *m/z* 189.0894 (M$^+$, calcd for $C_{10}H_{11}N_3O$, 189.0902). For **20d**: ^{1}H NMR ($CDCl_3$) δ 9.29 (1 H), 7.93 (1 H), 2.87–2.09 (6 H, m), 1.24 (3 H); IR (neat) 3409, 2967, 2928, 2872, 1581, 1531, 1460, 1418, 1311, 1269, 1177, 992, 957, 893; MS *m/z* 189.0898 (M$^+$, calcd for $C_{10}H_{11}N_3O$ 189.0902).

H. 2-Methyl-3-isovalerylpyrazine (8b). A solution (50 mL) of **8b** (178 mg, 1.0 mmol) was irradiated for 7 h. Analysis of photolysate indicated a >87% conversion along with <10% of unreacted **8b**. Solvent was removed under reduced pressure and subjected to spinning-disk chromatography. The product was separated and identified as cyclopropanol **13b**. For **13b**: ^{1}H NMR ($CDCl_3$) δ 8.28 (1 H), 8.18 (1 H), 3.68 (1 H), 2.67 (3 H), 1.43 (3 H), 1.33 (1 H, d, J = 5.7 Hz), 0.76 (1 H, d, J = 5.4 Hz), 0.70 (3 H); ^{13}C NMR ($CDCl_3$) δ 155.9, 154.1, 142.2, 140.1, 109.8, 64.6, 24.2, 21.8, 21.5, 19.8; IR (neat) 3205, 3077, 2985, 2943, 2872, 1531, 1453, 1404, 1357, 1304, 1166, 1088, 974, 911, 868, 737; MS *m/z* 178.1113 (M$^+$, calcd for $C_{10}H_{14}N_2O$, 178.1106).

I. 2-Methyl-5-isovalerylpyrazine (9b). A solution (10 mL) of **9b** (35 mg, 0.2 mmol) was irradiated for 5 h. Analysis of photolysate showed a >92% conversion along with <2% of unreacted **9b**. Removal of solvent followed by spinning-disk chromatography gave **14b**. For **14b**: ^{1}H NMR ($CDCl_3$) δ 8.58 (1 H), 8.34 (1 H), 3.90 (1 H), 2.54 (3 H), 1.47 (1 H, d, J = 5.7 Hz), 1.38 (3 H), 0.83 (1 H, d, J = 5.7 Hz), 0.85 (3 H); IR (neat) 3354, 2992, 2936, 2878, 1492, 1456, 1399, 1315, 1166, 1074, 1038, 974, 896; MS *m/z* 179.1184 ((M + H)$^+$, calcd for $C_{10}H_{15}N_2O$, 179.1184).

J. 2-Cyano-5-isovalerylpyrazine (9d). A solution (50 mL) of **9d** (189 mg, 1.0 mmol) was irradiated for 5 h. Analysis of photolysate indicated >88% of **14d** along with >4% of acetyl compound. Solvent was removed under reduced pressure and the residue was subjected to spinning-disk chromatography. Two products were separated and identified as the cyclopropanol **14d** and 2-cyano-7,7-dimethyl-7*H*-cyclopentapyrazin-5(6*H*)-one **22**. For **14d**: ^{1}H NMR ($CDCl_3$) δ 9.02 (1 H), 8.77 (1 H), 1.79 (1 H, d, J = 5.7 Hz), 1.43 (3 H), 1.11 (1 H, d, J = 5.7 Hz),0.97 (3 H); IR (neat) 3435, 3085, 2985, 2943, 2248, 1553, 1528, 1471, 1372, 1308, 1216, 1159, 1031, 925; MS *m/z* 188.0816, ((M − H)$^+$, calcd for $C_{10}H_{10}N_3O$, 188.0824). For **22**: ^{1}H NMR ($CDCl_3$) δ 9.01 (1 H), 2.84 (2 H), 1.54 (6 H); ^{13}C NMR ($CDCl_3$) δ 200.3, 176.7, 151.2, 145.8, 131.3, 114.8, 51.5, 39.0, 28.0; IR (neat) 3080, 2980, 2940, 2880, 2240, 1730, 1572, 1538, 1472, 1460, 1410, 1390, 1370, 1312, 1261, 1245, 1183, 1123, 1072; MS *m/z* 187.0478 (M$^+$, calcd for $C_{10}H_9N_3O$, 187.0745).

K. 2-Methyl-6-isovalerylpyrazine (10b). A solution (10 mL) of **10b** (35 mg, 0.2 mmol) was irradiated for 5 h. Analysis of photolysate indicated >91% conversion along with >5% of unreacted **10b**. Solvent was removed under reduced pressure and subjected to spinning-disk chromatography. The product was separated and identified as the cyclopropanol **15**. For **15**: ^{1}H NMR ($CDCl_3$) δ 8.45 (1 H), 8.25 (1 H), 4.1 (1 H), 2.52 (3 H), 1.49 (1 H, d, J = 5.7 Hz), 1.38 (3 H), 0.95 (1 H, d, J = 5.7 Hz), 0.88 (3 H); IR (neat) 3326, 2999, 2928, 2872, 1538, 1460, 1418, 1382, 1297, 1265, 1180, 1102, 1024, 989, 875; MS *m/z* 178.1109 (M$^+$, calcd for $C_{10}H_{14}N_2O$, 178.1107).

L. 2,3-Dicyano-5-isovalerylpyrazine (11d). A solution of **11d** (35 mg, 0.16 mmol in 10 mL) was irradiated for 5 h. Solvent was removed under reduced pressure and the residue was subjected to spinning-disk chromatography. Three products were identified as the ketone **18**, the diastereomeric mixture cyclobutanols **21**, and 2,3-dicyano-7,8-dihydro-7-methylquinoxalin-5(6*H*)-one (**23**). For **18**: ^{1}H NMR ($CDCl_3$) δ 9.46 (1 H), 2.78 (3 H); IR (neat) 3054, 2966, 2934, 2249, 1702, 1663, 1546, 1431, 1405, 1371, 1346, 1294, 1183, 1131, 1093, 1023, 960; MS *m/z* 172.0390 (M$^+$, calcd for $C_8H_4N_4O$, 172.0385). For **21**: ^{1}H NMR ($CDCl_3$) δ 9.20 (1 H), 2.93 (2 H, m), 2.43 (2 H, m), 2.11 (1 H), 1.69 (1 H), 1.24 (3 H, d, J = 6.6 Hz); IR (neat) 3506, 2977, 2928, 2866, 2251, 1550, 1524, 1453, 1427, 1347, 1246, 1224, 1168, 1119, 1094, 1036, 932; MS *m/z* 214.0859 (M$^+$, calcd for $C_{11}H_{10}N_4O$, 214.0854). For **23**: ^{1}H NMR ($CDCl_3$) δ 3.45 (1 H, m), 3.08 (2 H, m), 2.66 (2 H, m), 1.28 (3 H, d, J = 6.3 Hz); ^{13}C NMR ($CDCl_3$) δ 192.2, 161.6, 143.6, 134.5, 132.3, 112.2, 112.3, 46.9, 39.9, 27.9, 20.7; IR (neat) 2957, 2930, 2877, 2246, 1717, 1537, 1523, 1455, 1422, 1404, 1365, 1308, 1204, 1166, 1054, 933; MS *m/z* 212.0695 (M$^+$, calcd for $C_{11}H_8N_4O$, 212.0698).

Quantum Yield Measurements. All measurements were made at $\lambda \sim 313$ nm in either a mixture (9:1) of *tert*-butyl alcohol and benzene or benzene in a merry-go-round with the concomitant formation of acetophenone from valerophenone in the same solvent as the actinometer. Conversion was limited to <5%. Quantitative determination of the various photoproducts was made on an analytical gas chromatograph employing suitable internal standards. Calibration experiments indicated that the amount of these compounds could be accurately determined by this method.

Sensitized Irradiation of 1c. Samples **1c** (0.035 M) in benzene in the presence of (a) 4-benzoylpyridine (0.7 M), (b) benzophenone (0.5 M), (c) 1-tetralone (0.9 M), (d) 1-indanone (1.6 M), (e) samples of **1c** (0.037 M) of acetone, and (f) no sensitizer were irradiated in a merry-go-round at $\lambda \sim 313$ nm for 6 h. Photolysates were analyzed by gas chromatography. Results are furnished in Table 1.

Quenching Experiments. A. 2-Isovalerylpyridine (**1a**) (0.2 M) and 4-(trifluoromethyl)-2-isovalerylpyridine (**1c**) (0.2 M) both in benzene (4 mL) containing varying amounts of piperylene (0–0.05 M) were irradiated in a merry-go-round at λ >340 nm (4 h for **1a** and 5 h for **1c**). Quantitative determination of **3a**, **2c**, **3c**, and **4c** was made on an analytical GC. A Stern–Volmer plot of the data gave slopes 118, 157, 64, and 69 M^{-1} for **3a**, **2c**, **3c**, and **4c**, respectively.

B. Similar experiments were carried out for **1c** in methanol and a mixture of *tert*-butyl alcohol/benzene (9:1). A Stern–

Volmer plot of the data gave slopes 29, 13, 21 M^{-1} in methanol and 73, 57, 62 M^{-1} in *tert*-butyl alcohol/benzene (9:1) for **2c**, **3c**, and **4c**, respectively.

Rearrangement of Cyclopropanol 2d to 1d. A mixture of **2d** and **4d** (37 mg, 0.2 mmol) was refluxed in benzene in the presence of silica gel (1.0 g) for 12 h. Silica gel and solvent were removed, and the residue was subjected to spinning-disk chromatography. The products were isolated and identified as **1d** and **4d**, respectively.

Rearrangement of Cyclopropanol 12b to 26. Treatment of **12b** (37 mg, 0.2 mmol) with 1% methanolic sodium hydroxide at room temperature for 48 h gave ketone **26** (30 mg, 80%) as the only isolable product. For **26**: ^{1}H NMR ($CDCl_3$) δ 9.14 (1 H), 7.58 (1 H), 2.60 (3 H), 1.42 (9 H); ^{13}C NMR ($CDCl_3$) δ 206.6, 169.0, 160.7, 157.2, 118.1, 44.2, 27.0, 24.4; IR (neat) 2965, 2931, 2879, 1693, 1585, 1533, 1482, 1461, 1393, 1310, 1262, 1150, 1045, 861; MS *m/z* 178.1103 (M^+, calcd for $C_{10}H_{14}N_2O$, 178.1107).

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