Multiple nπ* Triplet Reactions in the Photochemistry of Alkyl-Substituted Acylpyrazines, Ketones with Four Low-Lying Zero-Order Triplets

C. Janakiram Rao and William C. Agosta*

Laboratories of The Rockefeller University, New York, New York 10021-6399

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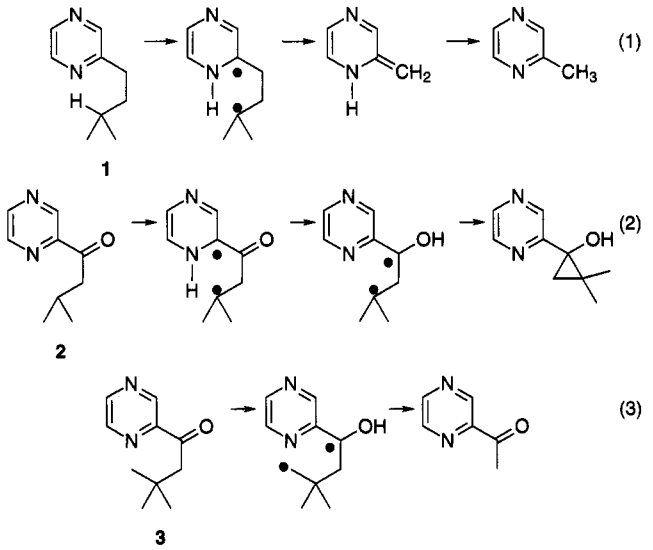
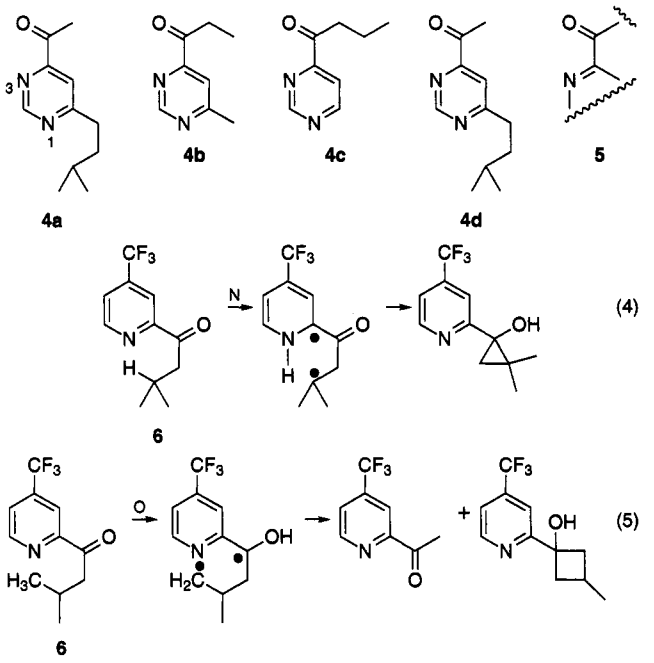
Irradiation of **7a-c** and **11a-c** leads to triplet-state abstraction of hydrogen by both nitrogen and oxygen with formation of the products shown in Schemes 1 and 2. Stern–Volmer quenching studies yield indistinguishable $k_q\tau$'s for abstraction by carbonyl oxygen and adjacent nitrogen in **11a**, and also for intermolecular comparisons both of abstraction by nitrogen in **11b** and **11c**, and also of abstraction by oxygen in **7a** and nitrogen in **7b**. Reactions of **7a** and **11a** are sensitized by acetone, but fragmentation of **7c** is not.

Irradiation of appropriate alkylpyrazines (as **1**) leads to abstraction of γ-hydrogen by nitrogen (N-abstraction) and subsequent fragmentation (eq 1).[1] A parallel reaction of acylpyrazines (as **2**) leads efficiently to cyclopropanols (eq 2).[2] In **2**, competing γ-abstraction by carbonyl oxygen is very minor (1–2%), but in appropriate molecules that lack γ_N-hydrogen for N-abstraction (as **3**), abstraction of γ_O-hydrogen by oxygen (O-abstraction) occurs efficiently with subsequent Type II fragmentation (eq 3) and/or formation of cyclobutanols.[2] In these pyrazines, as in similarly constituted pyridines and pyrimidines, both the aromatic π,π* triplet and the n,π* triplets on nitrogen and oxygen have energies (E_T) in the range ~70–85 kcal/mol.[1-5] Although there have been studies on the photophysics and spectroscopy of these triplets,[6] the photochemical behavior resulting from interactions among these states is not yet thoroughly understood. There has been some success, however, in identifying triplets having specific photochemical activities. For example, in 4-acyl-6-alkylpyrimidines, such as





4a-c, N- and O-abstraction from the C(4) acyl substituent by N(3) and by the carbonyl group are mediated by a triplet or triplets whose energy is ~70 kcal/mol, while abstraction by N(1) from the C(6) alkyl group is mediated by a different triplet, E_T ~80 kcal/mol.[2,5,7] It is also known that Stern–Volmer quenching of **4c** and several other similarly constituted simple 4-acylpyrimidines[5] and 2-acylpyridines[2,3] furnishes the same $k_q\tau$'s for both N- and O-abstraction. This indicates that in these compounds with partial structure **5** either the two abstraction processes are mediated by a single triplet or that the two reactive nitrogen and oxygen triplets are in equilibrium. A single known exception to this behavior is 4-trifluoromethyl-2-isovalerylpyridine (**6**). Here N-abstraction (eq 4) proceeds from a triplet having E_T ~72–77 kcal/mol and $k_q\tau$ ~157 M^{-1}, and O-abstraction (eq 5) from a distin-

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(6) Extensive references are given in refs. 2–4.

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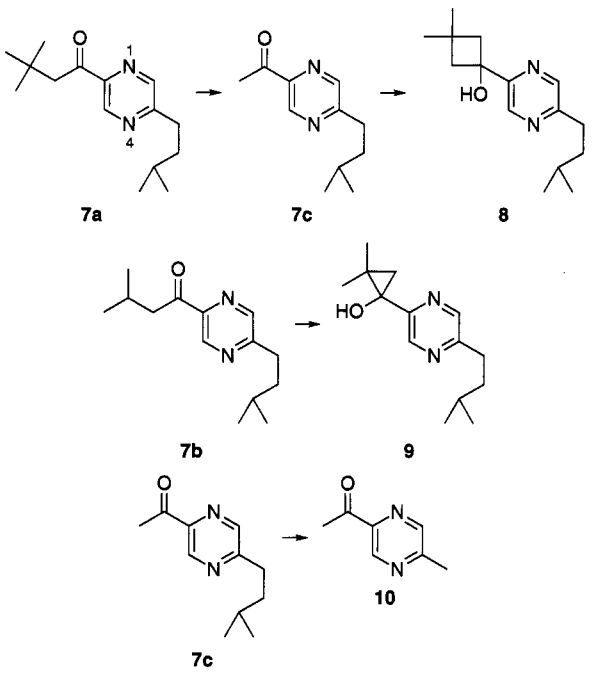
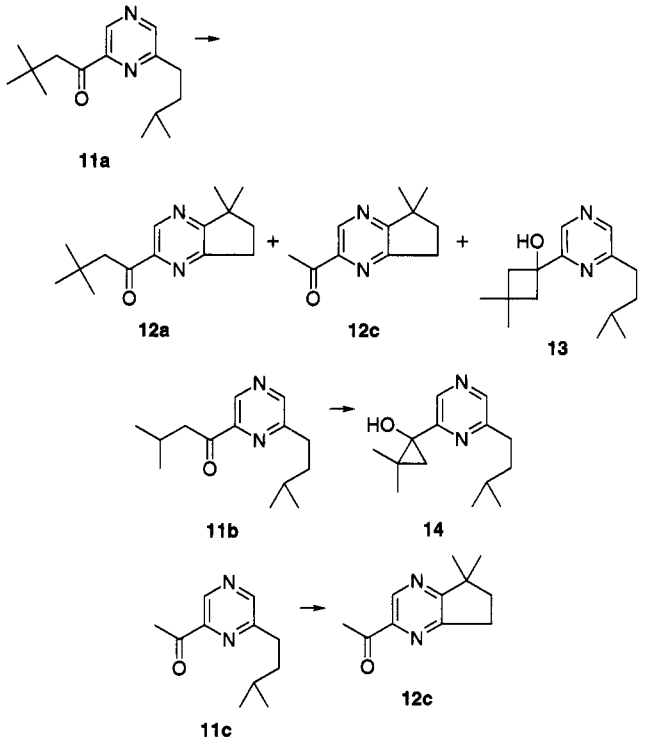
Scheme 1



Scheme 2



guishable triplet, E_T ~69–70 kcal/mol[8] and $k_q\tau$ ~64 M^{-1}.[3] Triplet sensitization of **6** with a series of sensitizers of differing E_T's leads to differing ratios of N- and O-abstraction, providing independent evidence for the two distinguishable triplets in this compound.[3] The significance of the exceptional behavior of **6** is not yet clear, but it suggests most simply that in the other heterocyclic ketones that have been examined N- and O-abstraction are mediated by two equilibrating triplets.

In view of these earlier results, we wished to investigate the photochemistry of substituted pyrazines of the general structures **7** and **11** (Scheme 1). Each of these structural types offers the possibility of O-abstraction and two different N-abstraction reactions. In **7** independent N-abstraction by each nitrogen atom is feasible, while in **11** N-abstraction by N(1) from both the C(2) and C(6) substituents should be possible. Because the two nitrogens in both **7** and **11** are in unlike environments, these ketones possess three low-lying zero-order n,π^* triplets [one each on oxygen, N(1), and N(4)]. These three states, as well as the π,π^* triplet, should all lie in the range E_T ~70–85 kcal/mol,[2,3] so that interactions among these four zero-order triplets should determine the physical properties of the observable states and the photochemical reactivity of the compounds. As a consequence, the photochemistry of **7** and **11** should provide an informative comparison with the behavior of pyrimidines **4**. We describe below the preparation and photochemistry of **7a-c** and **11a-c**.

Preparative Experiments. Ketones **7a-c** and **11a-c** were available on free radical acylation of isopentylpyrazine,[1] following a procedure previously described.[2,9] Each acylation reaction gave a mixture of the two position isomers **7** and **11**, along with the corresponding 2-acyl-3-isopentylpyrazine and diacylated products. Spinning-disk chromatography of the total reaction products yielded a mixture of **7** and **11**, which was then separated by preparative gas chromatography to furnish pure ketones for characterization and irradiation.

Table 1. Quantum Yields and Stern–Volmer Quenching Data for Photoproducts from 7 and 11 in *tert*-Butyl Alcohol–Benzene

ketone	product	Φ_P	$k_q\tau$, M^{-1}	abstraction by
7a	**7c**	0.60	400	O
	8	0.20		O
7b	**9**	0.45	401	N(1)
7c	**10**	0.05		N(4)
11a	**12a**	0.20	95	N(1)
	12c	0.23		N(1),O
	13	0.06	93	O
11b	**14**	0.42	71	N
11c	**12c**	0.33	85	N

Photochemical Results. For preparative purposes each ketone was irradiated (λ > 340 nm) in 9:1 *tert*-butyl alcohol–benzene as solvent and the products isolated and purified by spinning-disk chromatography. Structures of these products, as shown in Schemes 1 and 2, are based on IR, ^1H and ^{13}C NMR, and high resolution mass spectra. O-abstraction yielded both cyclobutanols and Type II fragmentation products; N-abstraction from alkyl chains yielded bicyclic compounds and fragmentation products, while N-abstraction from acyl chains gave cyclopropanols. We have previously reported bicyclic products analogous to **12a,c** from both N- and O-abstraction in cyano-substituted pyrazines and have suggested that they arise from cyclization of the initial biradical onto the aromatic ring, followed by rearomatization with loss of hydrogen.[3] The other types of products are well known.[1-5] Conversion of **11a** to **12c** requires both N- and O-abstraction. We previously reported a similar double abstraction reaction of **4d**.[7] Table 1 gives quantum yields (Φ_p's) and $k_q\tau$'s derived from Stern–Volmer quenching for several of these products. A typical Stern–Volmer plot is shown in Figure 1. Data were obtained in 9:1 *tert*-butyl alcohol–benzene. Quantum yields were measured

(8) E_T of other 2-acylpyridines is known to be ~70 kcal/mol: (a) Wagner, P. J.; Capen, G. *Mol. Photochem.* **1969**, *1*, 173. (b) Arnold, D. R. *Adv. Photochem.* **1968**, *6*, 301.

(9) Sakamoto, T.; Yamanaka, H. *Chem. Pharm. Bull.* **1980**, *28*, 571. Sakamoto, T.; Ono, T.; Sakasai, T.; Yamanaka, H. *Ibid.* **1980**, *28*, 202. Fontana, F.; Minisci, F.; Nogueira Barbosa, M. C.; Vismara, E. *J. Org. Chem.* **1991**, *56*, 2866.

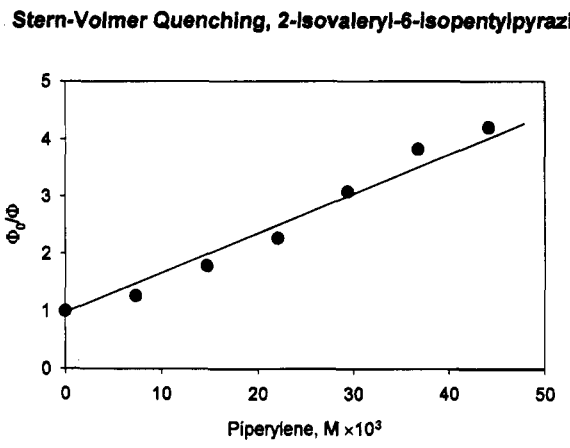


Figure 1. Stern–Volmer plot of piperylene quenching of formation of cyclopropanol **14** on irradiation (λ ~313 nm) of 2-isovaleryl-6-isopentylpyrazine (**11b**) in 9:1 *tert*-butyl alcohol–benzene.

in a merry-go-round apparatus with valerophenone as actinometer;[10] piperylene was employed for Stern–Volmer quenching studies.[2,8a]

Quenching experiments showed that formation of all products is quenched by piperylene. Development of the coloration (usually red) that typically accompanies irradiation of alkyl- and acylpyrazines in *tert*-butyl alcohol[1-3] is also quenched under these conditions. Irradiation of acetylpyrazine[2] and methylpyrazine under the same conditions produces no coloration, strongly suggesting that formation of the colored side products follows initial hydrogen abstraction.[11]

The reactions of **7a** and **11a** were sensitized in acetone as solvent and triplet sensitizer. In contrast, fragmentation of **7c** was not sensitized under these conditions, suggesting that the reactive triplet on N(4) in **7c** is too energetic to be sensitized by acetone. Acetone E_T is 79–82 kcal/mol,[12] and some sensitization should occur if energy transfer is no more than 1–2 kcal/mol endothermic.[13] Failure of **7c** to fragment under these conditions suggests then that the N(4) triplet has E_T > 81 kcal/mol.

Through sensitization experiments we have found that E_T for T_1 of simple acylpyrazines is ~66–67 kcal/mol. Cyclization (eq 2) of isovalerylpyrazine (**2**)[2] was sensitized relatively efficiently by benzophenone (E_T 69.2 kcal/mol, Φ_{rel} 0.80) and 2-benzoylpyridine (67.4, Φ_{rel} 0.77), but inefficiently by 3,4–methylenedioxyacetophenone (65.9, Φ_{rel} < 0.21).[14] For **7** and **11**, E_T should be 1–2 kcal/mol higher owing to the increase in n,π^* triplet energies expected on alkyl substitution of the ring.[1,15] These estimates of triplet energies are given in Table 2 along with data reported[2,7] earlier for 4-acylpyrimidines.

Discussion

The results in Table 1 indicate that in **7a-c** and **11a-c**, N-abstraction by N(1) cannot be differentiated from O-abstraction by Stern–Volmer quenching. This is true for the competitive reactions of **11a** to give **12a** (N-abstraction) and **13** (O-abstraction) and also true for the intermolecular comparison of N-abstraction from the acyl chain in **11b** and from the alkyl chain in **11c**. Similarly the intermolecular comparison of O-abstraction in **7a** and N-abstraction in **7b** indicates that these reactions proceed from states that are indistinguishable by Stern–Volmer quenching. We make these intermolecular comparisons because O-abstraction is essentially absent where abstraction by N(1) is possible, as in **7b**, and because N-abstraction from the alkyl chain does not occur in **11b**. The close structural similarity of the ketones in each series assures that the triplet states being compared should have quite similar energies and configurations. We conclude that in competing N- and O-abstraction these acylpyrazines behave like most other ketones having partial structure **5** that have been examined. Ketone **6** remains an exception.

Table 2. Estimated Triplet Energies (E_T's) of 4a–c and 7a–c

compds	triplet species	E_T, kcal/mol
4a–c	N(1)	79–82
	N(3), O	70–71
7a–c	N(1)	>81
	N(4), O	~68
pyrimidine	N(1), N(3)	82[a]
pyrazine	N(1), N(4)	75[b]

[a] References 15 and 16. [b] References 15 and 17.

We turn now to the energies of the reactive triplets of **7a-c.** The data in Table 2 reveal that E_T's of the upper reactive states are similar in pyrazines **7a-c** and pyrimidines **4a-c** and essentially independent of E_T of the parent heterocycle (82 for pyrimidine[15,16] and 75 kcal/mol for pyrazine[15,17]). Earlier, when the only data available were those for **4a-c**, it appeared that the upper reactive triplet of **4a-c** correlated with T_1 of pyrimidine.[2,7] With the addition of the present data for **7a-c**, the energy of this upper reactive triplet appears to be essentially independent of parent E_T. Energies of the lower triplets, on the other hand, do appear to reflect E_T of the parent heterocycle. These effects supplement our previous findings that in acyl-substituted pyridines, pyrimidines, pyrazines, and pyridazines having partial structure **5** there is a correlation between E_T of the parent heterocycle (all n,π^* T_1's) and the observed photochemistry. Related studies demonstrated that E_T of the π,π^* triplet (T_2 of the parent heterocycle) also significantly influences the behavior of the triplets of these ketones.[3]

Experimental Section

Materials and Equipment. Preparative gas chromatography (GLC) was carried out on a Varian Aerograph Model 920 gas chromatograph using an SE-30, (10 ft or 12 ft x 0.25 in.; Chromosorb-W) column. Analytical GLC was carried out isothermally using internal standards on a HP-5890 temperature-programmable gas chromatograph using an Alltech Econo-Cap (30 m x 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 down field from tetramethylsilane employed as an internal standard (δ). Infrared spectra were recorded on a Perkin-Elmer Model 237B grating IR Spectro-

(10) Wagner, P. J. *J. Am. Chem. Soc.* **1967**, *89*, 5898.
(11) Colored side products of undetermined structure are also formed on irradiation of acylpyridines: See ref 8a.
(12) 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.
(13) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin/Cummings Publishing Co.: Menlo Park, CA, 1978; Chapter 9.
(14) Sensitizer E_T's are taken from: Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973. Sensitizers absorbed ≥91% of the light.
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(16) Uchida, K. Yamazaki, I.; Baba, H.; *Chem. Phys.* **1978**, *35*, 91. Vogler, H. *Z. Naturforsch.* **1986**, *41A*, 959.
(17) Evans, D. *J. Chem. Soc.* **1959**, 2753. Lee, J.; Li, F.; Bernstein, E. R. *J. Phys. Chem.* **1983**, *87*, 260.

photometer 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. Purity was established for all compounds except **9** and **14** by NMR spectra. Cyclopropanols **9** and **14** were too unstable to obtain pure.

Preparation of 2-Isopentyl-5-(3,3-dimethy-1-oxobutyl)- and 2-Isopentyl-6-(3,3-dimethy-1-oxobutyl)pyrazines (7a, 11a).[2,9] Compounds **7a** and **11a** were prepared from the reaction of 2-isopentylpyrazine (0.750 g, 5 mmol), 3,3−dimethylbutyraldehyde (0.650 g, 6.5 mmol) in 7.5 mL of water, *tert*-butyl hydroperoxide (70%) (2 mL), and ferrous sulfate (2.8 g, 10 mmol) in 10 mL of water, acetic acid (7.5 mL) and conc. H_2SO_4 (1.5 mL), stirred for 3 h at −5 °C. These products were separated along with 2-isopentyl-5-(3,3-diethyl-1−oxobutyl)-pyrazine and diacetylatedpyrazine by preparative gas chromatography and characterized individually. For **7a:** ^{1}H NMR ($CDCl_3$) δ 9.12 (1 H, d, J = 1.2 Hz), 8.47 (1 H, d, J = 1.2 Hz), 3.09 (2 H, s), 2.91−2.86 (2 H, m), 1.63−1.67 (3 H, m), 1.06 (9 H, s), 0.96 (6 H, d, J = 6.3 Hz); ^{13}C NMR ($CDCl_3$) δ 201.3, 161.4, 146.3, 142.9, 142.6, 48.6, 38.3, 33.7, 31.6, 30.0, 27.9, 22.4; IR (neat) 2956, 2871, 1691, 1570, 1521, 1467, 1431, 1387, 1366, 1255, 1228, 1169, 1063, 1032, 1008, 970; MS m/z 248.1898 (M^+; calcd for $C_{15}H_{24}N_2O$, 248.1888). For **11a**: ^{1}H NMR ($CDCl_3$) δ 9.00 (1 H, s), 8.57 (1 H), 3.11 (2 H, s), 2.91−2.86 (2 H, m), 1.69−1.64 (3 H, m), 1.06 (9 H, s), 0.98 (6 H, d, J = 5.7 Hz); ^{13}C NMR ($CDCl_3$) δ 201.8, 156.7, 147.7, 146.9, 140.6, 48.6, 38.2, 33.1, 31.6, 30.0, 27.6, 22.42; IR (neat) 2957, 2871, 1694, 1573, 1530, 1467, 1411, 1366, 1266, 1230, 1171, 1068, 1013, 915, 875; MS m/z 248.1895 (M^+; calcd for $C_{15}H_{24}N_2O$, 248.1888).

Preparation of 2-Isopentyl-5-isovaleryl- and 2-Isopentyl-6-isovalerylpyrazines (7b, 11b).[2,9] Compounds **7b** and **11b** were prepared from the reaction of 2-isopentylpyrazine (4.5 g, 30 mmol), 2-oxo-4-methylvaleric acid sodium salt (5.5 g, 36 mmol), ammonium persulfate (6.84 g, 30 mmol), silver nitrite (0.5 g, 3 mmol), and concd H_2SO_4 (5 mL) in 100 mL of water and 100 mL of dichloromethane at 40 °C for 1 h. These products were separated along with 2−isopentyl-3-isovalerylpyrazine and starting material by spinning-disk chromatography and characterized individually. For **7b:** ^{1}H NMR ($CDCl_3$) δ 9.12 (1 H, d, J = 1.2 Hz), 8.48 (1 H, d, J = 1.2 Hz), 3.04 (2 H, d, J = 6.9 Hz) 2.92−2.87 (2 H, m), 2.31 (1 H, septet J = 6.6 Hz), 1.68−1.62 (3 H, m), 1.01 (6 H, d, J = 6.6 Hz), 0.97 (6 H, d, J = 6.3 Hz); ^{13}C NMR ($CDCl_3$) δ 201.1, 161.6, 145.5, 142.9, 142.8, 46.5, 38.3, 33.7, 27.8, 24.7, 22.7 22.3; IR (neat) 2958, 2872, 1698, 1570, 1522, 1469, 1399, 1386, 1368, 1296, 1222, 1170, 1038, 1007; MS m/z 234.1731 (M^+; calcd for $C_{14}H_{22}N_2O$, 234.1732. For **11b**: ^{1}H NMR ($CDCl_3$) δ 9.01 (1 H, s), 8.59 (1 H, s), 3.06 (2 H, d, J = 6.9 Hz), 2.92−2.86 (2 H, m), 2.29 (1 H, septet J = 6.9 Hz), 1.71−1.62 (3 H, m), 1.02−0.97 (12 H, m); ^{13}C NMR ($CDCl_3$) δ 201.7, 156.9, 147.0, 146.9, 140.5, 46.4, 38.1, 33.1, 27.7, 24.8, 22.7 22.4; IR (neat) 2958, 2931, 2872, 1699, 1574, 1530, 1468, 1412, 1386, 1367, 1338, 1303, 1172, 1035, 1014, 952, 918; MS m/z 234.1731 (M^+; calcd for $C_{14}H_{22}N_2O$, 234.1732).

Preparation of 2-Isopentyl-5-acetyl- and 2-Isopentyl-6-acetylpyrazines. (7c, 11c).[2,9] Compounds **7c** and **11c** were prepared from the reaction of 2−isopentylpyrazine (1.5 g, 10 mmol), pyruvic acid (1.76 g, 20 mmol), ammonium persulfate (6.84g, 30 mmol), silver nitrite (0.5g, 3 mmol), and conc. H_2SO_4 (3 mL) in 50 mL of water and 50 mL of dichloromethane at 40 °C for 1 h. These products were separated along with 2-isopentyl-3-acetylpyrazine and diacetylatedpyrazines by preparative GLC and characterized individually. For **7c:** ^{1}H NMR ($CDCl_3$) δ 9.05 (1 H, d, J = 1.2 Hz), 8.41 (1 H, d, J = 1.2 Hz), 2.82 (2 H, m), 2.62 (3 H, s), 1.58 (3 H, m), 0.88 (6 H, d, J = 6.3 Hz); ^{13}C NMR ($CDCl_3$) δ 199.3, 161.9, 145.5, 143.0, 142.8, 38.3, 33.8, 27.9, 25.8, 22.4; IR (neat) 2957, 2872, 1705, 1570, 1521, 1471, 1421, 1368, 1269, 1170, 1099, 1028, 957; MS m/z 192.1267 (M^+; calcd for $C_{11}H_{16}N_2O$, 192.1262). For **11c**: ^{1}H NMR ($CDCl_3$) δ 9.02 (1 H, s), 8.60 (1 H, s), 2.92−2.86 (2 H, m), 2.71 (3 H, s), 1.69−1.64 (3 H, m), 0.98 (6 H, d, J = 6.3 Hz); ^{13}C NMR ($CDCl_3$) δ 199.9, 157.1, 147.3, 146.8, 140.4, 38.2, 33.2, 27.8, 25.8, 22.4; IR (neat) 2964, 2936, 2865, 1701, 1577, 1535, 1471, 1421, 1357, 1294, 1173, 1123, 1017, 960; MS m/z 192.1258 (M^+; calcd for $C_{11}H_{16}N_2O$, 192.1262).

Preparative Photochemistry. All preparative experiments were carried out using a Hanovia 450-W medium-pressure mercury arc lamp with a uranium glass filter (λ > 340 nm). Yields were determined gas chromatographically. Irradiations were carried out using toroidal Pyrex vessels or quartz tubes in a 9:1 mixture of degassed *tert*-butyl alcohol and benzene.

A. 2-Isopentyl-5-(3,3-dimethyl-1-oxobutyl)pyrazine (7a). A solution (30 mL) of **7a** (155 mg, 0.62 mmol) was irradiated for 4 h. Analysis of photolysate indicated 75% conversion. Solvent was removed under reduced pressure and the residue was subjected to spinning-disk chromatography. Two products were isolated and identified as ketone **7c**, and the cyclobutanol **8.** For **7c**: ~51%, data as given above. For **8**: ~19%, ^{1}H NMR ($CDCl_3$) δ 8.75 (1 H, d, J = 1.2 Hz), 7.35 (1 H, d, J = 1.2 Hz), 3.87 (1 H, s), 2.84−2.78 (2 H, m), 2.49 (2 H, d, J = 13.5 Hz), 2.24 (2 H, d, J = 13.8 Hz), 1.64−1.60 (3 H, m), 1.41 (3 H, s), 1.20 (3 H, s), 0.96 (6 H, d, J = 6.3 Hz); ^{13}C NMR ($CDCl_3$) δ 157.2, 155.8, 141.8, 140.8, 70.9, 49.4, 38.6, 33.1, 30.4, 29.8, 27.8, 22.4;[18] IR (neat) 3371, 2956, 2927, 2868, 1551, 1480, 1468, 1385, 1367, 1269, 1211, 1171, 1031, 937; MS m/z 248.1901 (M^+; calcd for $C_{15}H_{24}N_2O$, 248.1888).

B. 2-Isopentyl-5-isovalerylpyrazine (7b). A solution (10 mL) of **7b** (128 mg, 0.54 mmol) was irradiated in quartz tubes for 7 h. After irradiation the solution turned blue, and analysis showed 75% conversion. Solvent was evaporated under reduced pressure and the residue was subjected to spinning-disk chromatography. The product was isolated with 80% purity and identified as **9**. Cyclopropanol **9** could not be purified further even after repetitive chromatography. It also decomposes rapidly on preparative gas chromatography. For **9**: yield 62 mg, 65%, ^{1}H NMR ($CDCl_3$) δ 8.60 (1 H, d, J = 1.50 Hz), 8.33 (1 H, d, J = 1.50 Hz), 3.89 (1 H, bs), 2.87−2.76 (2 H, m), 1.62−1.58 (3 H, m), 1.55 (1 H, d, J = 5.7 Hz), 1.38 (3 H, s), 0.96−0.93 (7 H, m), 0.86, (3 H, s); IR (neat) 3303, 2957, 2871, 1529, 1483, 1469, 1385, 1367, 1306, 1251, 1227, 1167, 1079, 1037, 910; MS m/z 234.1731 (M^+; calcd for $C_{14}H_{22}N_2O$, 234.1732).

C. 2-Isopentyl-5-acetylpyrazine (7c). A solution (10 mL) of **7c** (50 mg, 0.26 mmol) was irradiated for 72 h. During irradiation the solution turned red, and analysis of it showed 20% conversion. Solvent was evaporated under reduced pressure and the residue was subjected to spinning-disk chromatography. Only one product was isolated and identified as **10**. For **10**: 5 mg, 70% ^{1}H NMR ($CDCl_3$) δ 9.11 (1 H, s), 8.51 (1 H, s), 2.70 (3 H, s), 2.67 (3 H, s); ^{13}C NMR ($CDCl_3$) δ 199.3, 157.8, 145.4, 143.3, 142.7, 25.8, 22.0; IR (neat) 3046, 2972, 2929, 2873, 1696, 1574, 1479, 1417, 1364, 1296, 1178, 1098, 1032, 954, 910; MS m/z 136.0641 (M^+; calcd for $C_7H_8N_2O$, 136.0636).

D. 2-Isopentyl-6-(3,3-dimethyl-1-oxobutyl)pyrazine (11a). A solution (50 mL) of **11a** (175 mg, 0.70 mmol) was irradiated for 20 h. Analysis of photolysate indicated 70% conversion. Solvent was removed under reduced pressure and the residue was subjected to spinning-disk chromatography. Three products were isolated and identified as the ketones **12a**, **12c** and the cyclobutanol **13**. For **12a**: ~31%, ^{1}H NMR ($CDCl_3$) δ 8.96 (1 H, s), 3.10 (2 H, s), 3.05 (2 H, t, J = 7.8 Hz) 2.10 (2 H, t, J = 7.5 Hz) 1.35 (6 H, s), 1.07 (9 H, s); ^{13}C NMR ($CDCl_3$) δ 201.5, 168.5, 157.1, 146.2, 141.8, 48.7, 42.5, 37.6, 31.5, 30.0, 29.0, 27.0; IR (neat) 2954, 2869, 1690, 1564, 1466, 1365, 1230, 1176, 1134, 1095, 1020, 939, 899; MS m/z

(18) Signals for geminal dimethyl substituents on cyclobutane apparently do not separate.

246.1734 (M^+; calcd for $C_{16}H_{22}N_2O$, 246.1732). For **12c**: ~30%, data as given below. For **13:** ~13%, ^1H NMR ($CDCl_3$) δ 8.66 (1 H, s), 8.32 (1 H, s), 4.31 (1 H, s), 2.83–2.78 (2 H, m), 2.48 (2 H, d, J = 13.8 Hz), 2.25 (2 H, d, J = 13.5 Hz), 1.65–1.61 (3 H, m), 1.42 (3 H, s), 1.23 (3 H, s), 0.95 (6 H, d, J = 6.3 Hz); ^{13}C NMR ($CDCl_3$) δ 159.0, 155.5, 141.9, 138.7, 70.7, 49.8, 38.2, 33.1, 30.4, 29.8, 27.9, 27.8, 22.5; IR (neat) 3381, 2956, 2927, 2868, 2248, 1534, 1467, 1415, 1385, 1367, 1269, 1218, 1187, 1160, 1056, 965; MS m/z 248.1884 ((M^+; calcd for $C_{16}H_{24}N_2O$, 248.1888).

E. 2-Isopentyl-6-Isovalerylpyrazine (11b). A solution (15 mL) of **11b** (220 mg, 0.60 mmol) was irradiated in quartz tubes for 9 h. During irradiation the solution turned green, and analysis showed 50% conversion. Solvent was removed and the residue was subjected to spinning-disk chromatography to obtain **14** with 85% purity. Cyclopropanol **14** could not be purified further even after repetitive chromatography. It also decomposes rapidly on preparative gas chromatography. For **14**: yield 80 mg, 72%, ^1H NMR ($CDCl_3$) δ 8.50 (1 H, s), 8.23 (1 H, s), 4.25 (1 H, bs), 2.81–2.74 (2 H, m), 1.61–1.52 (4 H, m), 1.38 (3 H, s) 0.99–0.92 (7 H, m) 0.89 (3 H s); ^{13}C NMR ($CDCl_3$) δ 155.8, 144.3, 141.0, 139.8, 63.2, 38.2, 33.2, 27.7, 26.3, 25.5, 22.4, 20.8, 20.6; IR (neat) 3278, 2956, 2870, 1533, 1467, 1415, 1385, 1367, 1299, 1179, 1107, 1016; MS m/z 234.1726 (M^+; calcd for $C_{14}H_{22}N_2O$, 234.1732).

F. 2-Isopentyl-6-acetylpyrazines (11c). A solution (50 mL) of **11c** (192 mg, 1.0 mmol) was irradiated for 5 h. Solvent was removed and the residue was subjected to spinning-disk chromatography to obtain **12c.** For **12c**: yield 67 mg, 67%, mp 64 °C; ^1H NMR ($CDCl_3$) δ 8.98 (1 H), 3.07 (2 H, t, J = 7.2 Hz), 2.70 (3 H, s), 2.11 (2 H, t, J = 7.2 Hz) 1.35 (6 H, s); ^{13}C NMR ($CDCl_3$) δ 199.6, 169.0, 157.5, 146.2, 141.7, 42.5, 37.6, 29.0, 26.9, 26.0; IR (neat) 3054, 2963, 2869, 1699, 1565, 1459, 1424, 1372, 1358, 1318, 1269, 1178, 1127, 1082, 1018, 962; MS m/z 190.1099 (M^+; calcd for $C_{11}H_{14}N_2O$, 190.1106).

Quantum Yield Measurements. All measurements were made at λ ~313 nm in a mixture (9:1) of *tert*-butyl alcohol and benzene in a merry-go-round with the concomitant formation of acetophenone from valerophenone in ethanol as the actinometer. Conversion was limited to <5%. Quantitative determination of the various photoproducts was made on analytical GLC employing suitable internal standards.

Quenching Experiments. Solutions of **7a-c** and **11a-c** (0.02 M) in a mixture (9:1) of *tert*-butyl alcohol and benzene (1.4 mL) containing varying amounts of piperylene (0–0.05 M) were irradiated in a merry-go-round at λ >340 nm (0.5 h for **7a** and **7b,** 3.75 h for **11a,** 0.5h for **11b** and 0.75 h for **11c**). Quantitative determination of **7c, 9, 12a, 13, 14** and **12c** were made on an analytical GLC. A Stern–Volmer plot of the data gave slopes 400, 401, 95, 93, 71, 85 M^{-1} for **7c, 9, 12a, 13, 14** and **12c** respectively.

Irradiation of 2-Methylpyrazine. A solution of 2-methylpyrazine (0.1 M) was irradiated at λ >340 nm but was isolated unchanged after 24 h irradiation.

Sensitized Irradiation of 2-Isovalerylpyrazine. Samples of 2-isovalerylpyrazine (0.02 M) in a mixture (9:1) of *tert*-butyl alcohol and benzene in the presence of (a) benzophenone(0.7 M), (b) benzoylpyridine (0.55 M), (c) 3,4-(methylenedioxy)-acetophenone (0.21 M), and (d) no sensitizer were irradiated at λ ~313 nm in a merry-go-round for 0.6 h. GC analysis of the photolysate indicated the formation of cyclopropanol (eq 2), as discussed in the text.

Acetone Sensitized Irradiation of 7a, 7c, and 11a. Samples of **7a, 7c,** and **11a** (0.02 M) in (a) acetone and (b) a mixture (9:1) of *tert*-butyl alcohol and benzene were irradiated in a merry-go-round at λ ~313 nm for 0.5–4 h. Photolysates were analyzed by gas chromatography. In the results below, ratios a:b refer to the relative amounts of product formed under (a) acetone-sensitized and (b) unsensitized conditions. For **7a** only O-abstraction product was formed in the ratio of 0.33:1.0 (a:b); for **7c** no reaction was observed; and for **11a** N-abstraction product was formed in the ratio of 0.90:1.0 (a:b) and O-abstraction products were formed in the ratio of 2.4:1.0 (a:b).

Control Experiment. Quartz tubes containing **11a** (0.02 M) in a mixture (9:1) of *tert*-butyl alcohol and benzene were irradiated simultaneously for 0.5 h in a merry-go-round apparatus at distances of 3.8 and 7.5 cm from the light source (λ >340 nm). Analysis indicated product distribution and relative yields were identical at the two distances. The ratio of light intensities was 3.89.

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Supplementary Material Available: Copies of ^1H NMR spectra of all new compounds (13 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.