Triplet States Mediating Hydrogen Abstraction in 4-Acylpyrimidines, 2-Acylpyridines, 2-Acylpyrazines, and 3-Acylpyridazines

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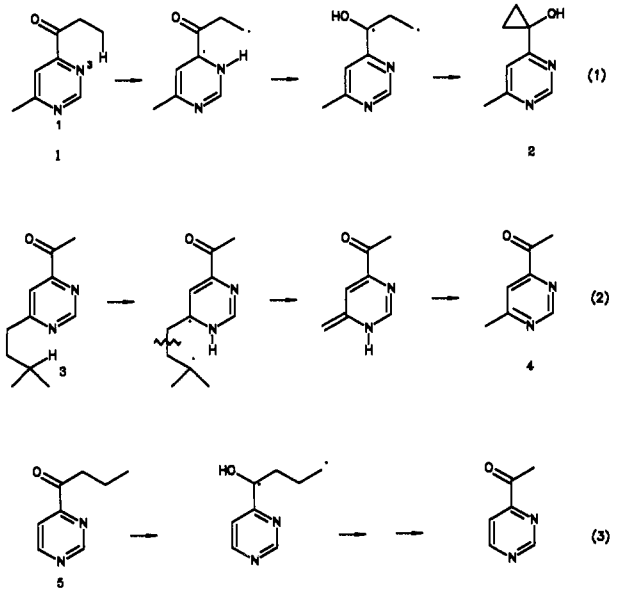
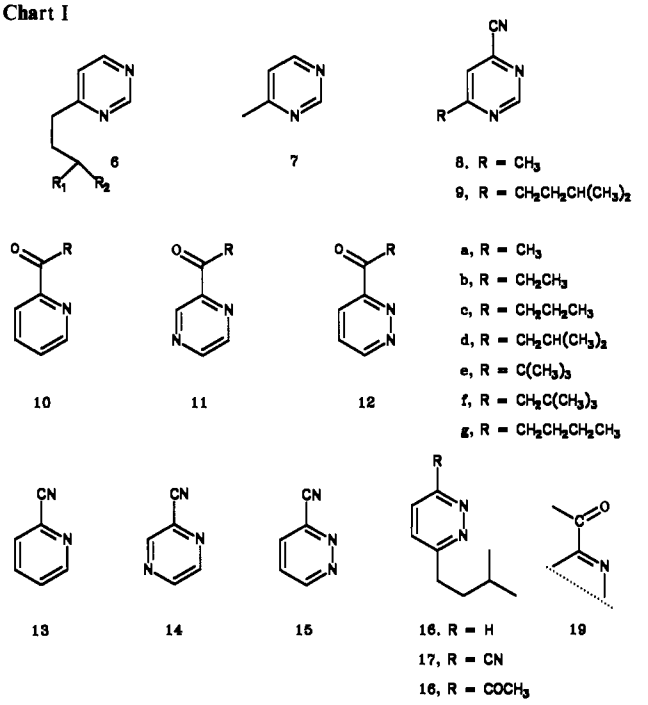
Abstract: Irradiation of **9** leads to hydrogen abstraction by N(1) and fragmentation to **8** from a triplet with E_T ~78 kcal/mol. Irradiation of 2-acylpyridines (**10**) leads to abstraction by both nitrogen and oxygen (cf. eq 4), with the same Stern-Volmer $k_q\tau$ for the two processes. Irradiation of 2-acylpyrazines (**11**) can lead to abstraction by either nitrogen (Φ_{27} 0.77 from **11b**) or oxygen (Φ_{11a} 0.95 from **11f**). 3-Acylpyridazine **12d** is unreactive on direct irradiation or triplet sensitization with sensitizer E_T ~70 kcal/mol; it furnishes a small amount of **12a** on sensitization by acetone. Ketone **18** is recovered unchanged from irradiation under all conditions used with **12d**. These observations suggest a correlation between the photochemistry of each of these compounds and the energy of the $n\pi^*$ triplet of the heteroaromatic ring. The nature of the excited state(s) responsible for hydrogen abstraction by nitrogen and oxygen in these ketones is discussed.

We have previously reported that two distinct $n\pi^*$ triplets mediate hydrogen abstraction by nitrogen in 4-acyl-6-alkylpyrimidines such as **1** and **3**.[1] Direct irradiation ($\lambda > 340$ nm) of **1** and **3** or their triplet sensitization by aromatic ketones leads to an $n\pi^*$ triplet (E_T ~70-71 kcal/mol). In **1** this state is responsible for hydrogen abstraction by N(3) from the C(4) side chain and isomerization to cyclopropanol **2** (eq 1). Ketone **3** does



not fragment from this state under either these direct or sensitized conditions. However, triplet sensitization of **3** by acetone (E_T 79-82 kcal/mol[2]) or direct irradiation of **3** through Vycor ($\lambda > 200$ nm) leads to hydrogen abstraction by N(1), cleavage of the C(6) side chain, and formation of **4** (eq 2) in a reaction occurring from an upper $n\pi^*$ triplet with E_T 79-84 kcal/mol. In addition, direct irradiation of 4-butyrylpyrimidine (**5**) and related ketones results in two competing triplet reactions that show identical quenching behavior; these are hydrogen abstraction by nitrogen as in eq 1 and the type II cleavage (eq 3) typical of aromatic ketones.[3] We were interested in exploring the nature of the triplet states that mediate these three distinct reactions. Very little information

Chart I



characterizing excited states and their photochemical properties is available for nitrogen heteroaromatic systems,[4] owing in part to the large number and complex interrelations of these states.[5]

An earlier proposal concerning the triplets responsible for two of these reactions came from Alexander and Jackson. On observing hydrogen abstraction by both nitrogen and oxygen in ketones such as **5**, they suggested that the two processes were mediated either by a single "vibronically mixed triplet state which undergoes abstraction by both ... carbonyl and ... nitrogen" or else by two equilibrating, nearly isoenergetic $n\pi^*$ triplets, one a carbonyl state and the other a nitrogen state.[3] They also noted that if the second explanation was correct, the participating nitrogen state could be the pyrimidine $n\pi^*$ triplet state, shifted energetically close to the carbonyl triplet by the electronegative 4-acyl substituent. During the years since this suggestion, others

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(2) 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.
(3) Alexander, E. C.; Jackson, R. J., Jr. *J. Am. Chem. Soc.* **1974**, *96*, 5665; **1976**, *98*, 1609.
(4) Malkin, Y. N.; Kuz'min, V. A. *Uspekhi Khimii* **1990**, *59*, 279; *Russ. Chem. Rev.* **1990**, *59*, 164.
(5) 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.

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have confirmed the original report[6] that T_1 is an $n\pi^*$ state with E_T ~82 kcal/mol for pyrimidine[7,8] and ~84 kcal/mol for 4-methylpyrimidine,[7] and we have found that simple 4-alkylpyrimidines (**6**, R_1, R_2 = alkyl, H) undergo fragmentation from T_1[6,9,10] to form 4-methylpyrimidine (**7**)[11] (Chart I).

In seeking additional experimental details about these triplet states, we have now carried out two types of studies. First, in order to assess the suggestion that the active triplet mediating abstraction by nitrogen in 4-acylpyrimidines is the ring nitrogen $n\pi^*$ state, we have determined the effect of electronegative substitution on E_T in pyrimidines. This has involved examination of 6-isopentyl-4-pyrimidinecarbonitrile (**9**). In the second investigation we have explored the photochemistry of 2-acylpyridines (**10**), 2-acylpyrazines (**11**), and 3-acylpyridazines (**12**). Since triplets of all these heteroaromatic ketones result from interaction of their conjugated carbonyl and heteroaromatic ring chromophores,[12] triplet properties in each case should reflect the properties of these contributing chromophores. As is explained below, ketones **10–12** provide systems in which E_T of the ring nitrogen $n\pi^*$ state is greater than, approximately the same as, and less than E_T of an isolated carbonyl group (~74 kcal/mol for acetaldehyde,[13] 79–82 kcal/mol for acetone[2]). These studies demonstrate a relationship between ring $n\pi^*$ triplet energy and the triplet photochemical properties of all four series of ketones, and they have improved understanding of competing abstraction by oxygen and nitrogen in these systems. Details are given below. We first describe preparation of the necessary compounds and then discuss their photochemistry.

Preparative Experiments. Preparation of 6-methyl-4-pyrimidinecarbonitrile (**8**) followed a previously described route,[14] and we adapted the same procedures for the isopentyl homologue **9**. Details are in the Experimental Section. We followed an earlier route to 2-propionylpyridine (**10b**) that involved a Grignard reaction on nitrile **13**[15] and used the same method for **10c–e**. Ketone **10a** is commercially available. Free-radical acylation of pyrazine furnished **11a–d**. The method had been used in the past for **11a,b**.[16] A Grignard reaction on nitrile **14** furnished **11f**. Grignard reactions also served for preparation of 3-propionylpyridazine (**12b**) and 3-isobutyrylpyridazine (**12d**) from **15**.[17] Synthesis of the alkylated pyridazyl ketone **18** employed known procedures. The sequence began with addition of isopentyllithium to pyridazine and subsequent oxidative rearomatization to furnish **16**.[18] This was converted to nitrile **17** on reaction with *p*-toluenesulfonyl chloride and trimethylcyanosilane in the presence of aluminum chloride, followed by base.[19] Addition of methylmagnesium iodide to **17** then yielded ketone **18**.[17] These various substrates were purified by preparative gas chromatography.

Photochemical Experiments. One of Alexander's suggestions had been that the triplet that mediates abstraction by nitrogen in **5** could be the pyrimidine nitrogen triplet, the energy of which would be lowered by 4-acyl substitution.[3] In order to evaluate this possibility, we investigated the photochemistry and properties of **9**. For our purposes, **9** offered the advantage that the cyano group is a strongly electronegative substituent that will reduce E_T of ring triplet states,[20] but unlike a carbonyl group, it will not introduce any new low-lying triplet states of its own that will mix substantially with the ring states.[21] Furthermore, since cyano is considerably more electronegative than acyl (χ_{CN} = 3.3, χ_{COR} = 2.85[22]), E_T of **9** should indicate approximately the maximum zero-order effect of an acyl group on E_T of pyrimidine.

On direct irradiation at λ ~313 nm in 90% *tert*-butyl alcohol–10% benzene, **9** undergoes fragmentation to **8** (Φ_8 0.10), in a reaction analogous to the conversion of **6** to **7**.[23] This process is sensitized efficiently by acetone, slowly by indanone (E_T ~75.7 kcal/mol[24]), and not at all by propiophenone (E_T ~74.6 kcal/mol[25]) or *m*-methoxyacetophenone (E_T ~72.4 kcal/mol[26a]). As expected from these results, nitrile **8** fails to quench the type II fragmentation of valerophenone (E_T ~74.3 kcal/mol[25]) in benzene. In general, the rate of triplet–triplet energy transfer falls to zero when the process is endothermic by ~3 kcal/mol, so that these observations imply that E_T of **8** and **9** is ~78 kcal/mol.[26b] The cyano substituent then lowers E_T of a 4-alkylpyrimidine by ~6 kcal/mol, and we consider it unlikely that an acyl group would have a much greater zero-order effect. The shift of ~11 kcal/mol required by Alexander's suggestion is improbable, and we conclude that the triplet responsible for hydrogen abstraction by nitrogen in 4-acylpyrimidines is not correlated with the nitrogen triplet (T_1) of pyrimidine. It is likely instead that the *upper* nitrogen triplet in 4-acylpyrimidines (E_T 79–84 kcal/mol)[1] is related to T_1 of pyrimidine (E_T ~82 kcal/mol) and 4-alkylpyrimidines (E_T ~84 kcal/mol), with the understanding that in 4-acylpyrimidines there may be some perturbation of this state by the carbonyl chromophore. In this case, the zero-order effect of the acetyl group is a very reasonable ΔE_T of 0–5 kcal/mol.

These results led us to focus attention on the possibility that in 4-acylpyrimidines a single triplet mediates abstraction by both nitrogen and oxygen and suggested that exploration of the photochemistry of related acyl-substituted heterocycles could be worthwhile. The 2-acylpyridines (**10**), 2-acylpyrazines (**11**), and 3-acylpyridazines (**12**) provide three appropriate series. All these compounds share with 4-acylpyrimidines partial structure **19**, with the acyl group adjacent to ring nitrogen, and all are derived from heteroaromatic parents in which T_1 is a state of known energy with $n\pi^*$ character.[27] We turned first to the 2-pyridyl ketones **10**. T_1 of pyridine is a mixed $n\pi^*$ and $\pi\pi^*$ state,[28] and E_T in solution is ~84–85 kcal/mol.[5,29] On direct irradiation, pyridine

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(10) Castellano, A.; Catteau, J. P.; Lablache-Combier, A. *Photochem. Photobiol.* **1974**, *20*, 27.
(11) Prathapan, S.; Loft, S.; Agosta, W. C. *Tetrahedron Lett.* **1988**, *29*, 6853; *J. Am. Chem. Soc.* **1990**, *112*, 3940.
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(14) Hermann, K.; Simchen, G. *Liebigs Ann. Chem.* **1981**, 333.
(15) Prasad, K. B.; Shaw, S. C. *Chem. Ber.* **1965**, *98*, 2822.
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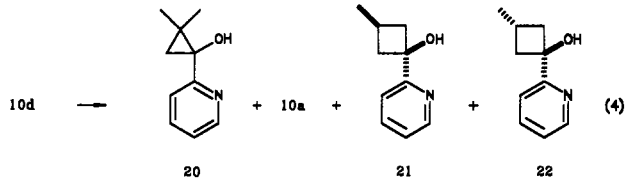
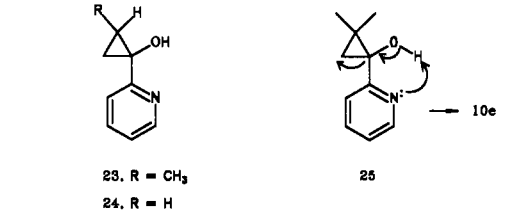
(17) Robba, M. *Ann. Chim.* **1960**, *5*, 351. Nakagome, T.; Castle, R. N. *J. Heterocycl. Chem.* **1968**, *5*, 379.
(18) Letsinger, R. L.; Lasco, R. *J. Org. Chem.* **1956**, *21*, 812.
(19) Dostal, W.; Heinisch, G. *Heterocycles* **1986**, *24*, 793.
(20) For example, a cyano group lowers the energy of the lowest $n\pi^*$ and $\pi\pi^*$ triplets of pyridine by 1–13 kcal/mol, depending on the site of substitution and the solvent: Reference 5. Sarkar, S. K.; Ghoshal, S. K.; Kastha, G. S. *J. Chem. Phys.* **1982**, *76*, 825 and references cited therein. Similarly, a cyano group lowers E_T of benzene 7–8 kcal/mol: Takei, K.; Kanda, Y. *Spectrochim. Acta* **1962**, *18*, 201.
(21) Wagner, P. J.; Capen, G. *Mol. Photochem.* **1969**, *1*, 173.
(22) Wells, P. R. *Prog. Phys. Org. Chem.* **1968**, *6*, 111. The corresponding σ values are σ_{CN} = 0.70 and σ_{COR} = 0.47: March, J. *Advanced Organic Chemistry*, 3rd ed.; Wiley: New York, 1985, p 244.
(23) Quantum yields were determined in a merry-go-round apparatus with the concomitant formation of acetophenone from type II elimination of valerophenone as a chemical actinometer: Wagner, P. J. *J. Am. Chem. Soc.* **1967**, *89*, 5898.
(24) Amrein, W.; Larsson, I.-M.; Schaffner, K. *Helv. Chim. Acta* **1974**, *57*, 2519. Catalani, L. H.; Wilson, T. *J. Am. Chem. Soc.* **1987**, *109*, 7458.
(25) Murov, S. L. *Handbook of Photochemistry*; Marcel Dekker: New York, 1973.
(26) (a) Yang, N. C.; McClure, D. S.; Murov, S. L.; Houser, J. J.; Dusenbury, R. *J. Am. Chem. Soc.* **1967**, *89*, 5466. (b) This rule of thumb comes from observations of energy transfer between a wide variety of types of compounds. The estimated E_T of **8** and **9** may be slightly high, because the rate of energy transfer between phenones (~10^9 M^{-1} s^{-1}) is somewhat lower than the rate of diffusion in nonviscous solvent (~10^{10} M^{-1} s^{-1}): Mirbach, M. F.; Ramamurthy, V.; Mirbach, M. J.; Turro, N. J.; Wagner, P. J. *Nouv. J. Chim.* **1980**, *4*, 471 and references cited therein.
(27) A review of relevant reactions of such heterocycles is available: Mariano, P. S. *Org. Photochem.* **1987**, *9*, 1.
(28) There is experimental and theoretical evidence that T_1 of pyridine is a nonplanar state of mixed $n\pi^*$ and $\pi\pi^*$ character, and it has been suggested that these findings may be relevant to other aza aromatics: Buma, W. J.; Groenen, E. J. J.; van Hemert, M. C. *J. Am. Chem. Soc.* **1990**, *112*, 5447 and references cited therein.
(29) Evans, D. F. *J. Chem. Soc.* **1957**, 3885.

abstracts hydrogen from solvent in a reaction partially quenched by oxygen.[30] Since Φ_{ISC} for pyridine is 0.9,[31] at least some of this hydrogen abstraction likely occurs by way of the triplet. The T_1's of pyridine and pyrimidine then have similar energies and probably show similar photochemical behavior. Previous studies on specific 2-pyridyl ketones have located E_T for the first triplet of 2-acetylpyridine at ~70 kcal/mol[32] and have shown that 2-valerylpyridine (**10g**) undergoes type II reactions analogous to valerophenone in both polar and nonpolar solvents.[21] These properties are parallel to those of 4-pyrimidyl ketones, with the important difference that no cyclopropanol products from abstraction by nitrogen were reported from **10g**.[21]

Under our conditions, preparative irradiation of **10d** furnished four products (eq 4).[33] These were the cyclopropanol **20** from abstraction by nitrogen (cf. eq 1) and the three products of abstraction by oxygen, **10a**, **21**, and **22**. Similarly, 2-butyrylpyridine (**10c**) gave the two diastereomers of **23**, **10a**, and essentially no cyclobutanol. Two ketones that cannot undergo type II reaction, 2-propionylpyridine (**10b**) and 2-pivalylpyridine (**10e**), gave cyclopropanols **24** and **20**, respectively. These products were best



20 21 22



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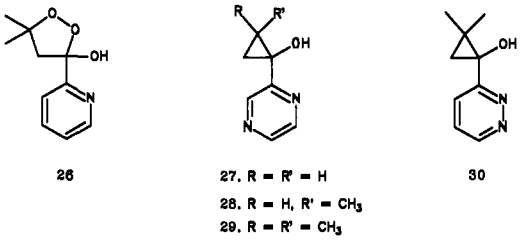

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purified by column or spinning-disk chromatography on silica gel, since the cyclopropanols decomposed on attempted preparative gas or thin-layer chromatography. Structures could be assigned from spectroscopic properties, together with the following observations. Cyclopropanol **20** opened on heating or on treatment with base to yield **10e**. The base-catalyzed cleavage of cyclopropanols and the regiospecificity leading to **10e** rather than **10d** have numerous precedents.[3,34] We assume that thermal opening of **20** benefits from intramolecular catalysis (cf. **25**) and thus is also base-catalyzed. 2-Acetylpyridine (**10a**) was identical with an authentic sample. The diastereomers of **23** were not separately characterized.

Cyclopropanol **20** was quite sensitive to oxidation, and on column chromatography over silica gel in air it added a molecule of oxygen to furnish a new crystalline compound. ^1H and ^{13}C NMR spectra of this substance indicated that the pyridine ring was still intact, and its IR spectrum (KBr pellet) showed hydroxyl but no carbonyl absorption. These and other spectroscopic data suggest that this oxidation product is peroxy hemiacetal **26**. Somewhat related reactions have been observed in the past,[34,35] but air oxidation of **20** occurs with surprising ease.

Table I. Data for Photochemical Reactions of Ketones **10–12**

ketone	product	quantum yield, Φ_p in *t*-BuOH[a]	quantum yield, Φ_p in C_6H_6	$k_q\tau$, M^{-1}
10b	**24**	0.48	0.083	
10d	**10a**	0.54	0.26	32.5[a]
	20	0.31	0.029	32.6[a]
	21 + 22	0.088	0.022	
10e	**20**	0.70	0.28	
10g[b]	**10a**		0.17	27[c]
11b	**27**	0.77	0.059	
11f	**11a**	0.95		

[a] In 90% *tert*-butyl alcohol–10% benzene. [b] Reference 21. [c] In benzene.

We measured quantum yields for these reactions of **10b,d,e** in 9:1 *tert*-butyl alcohol–benzene and in benzene[23] and also carried out Stern–Volmer quenching studies on formation of **20** and **10a** from **10d** in 9:1 *tert*-butyl alcohol–benzene. The results appear in Table I, along with earlier data[21] for **10g**. The most significant point is that within experimental error $k_q\tau$'s for quenching the formation of **20** and **10a** are equal, in agreement with the reported[3] behavior of **5**. We discuss the significance of this finding later. Another point of interest is that on going from *tert*-butyl alcohol to benzene, all Φ_p's decrease. A similar solvent effect exists in the photochemistry of 4-acylpyrimidines.[3]

We turned next to ketones **11**. T_1 of pyrazine is an $n\pi^*$ state at ~75–76 kcal/mol in solution,[6,36] and it mediates abstraction of hydrogen from aliphatic alcohols and hydrocarbons.[9,37] Since we were aware of no previous reports on the photochemistry of acylpyrazines, we first irradiated **11a** ($\lambda > 340$ nm). This ketone was recovered unchanged, and we conclude that no unforeseen transformations occur with this chromophore under our conditions. Irradiation of **11b–d** gave the corresponding cyclopropanols **27**, **28** (both diastereomers), and **29**, respectively (cf. eq 1). These products had spectroscopic properties comparable to those of previously encountered 4-pyrimidinyl- and 2-pyridinylcyclopropanols. Type II reaction was very minor, with **11c** and **11d** yielding ~1% and ~2%, respectively, of **11a**.[38] Nonetheless, similar irradiation of **11f**, where only abstraction by oxygen is sterically favored, led to efficient type II cleavage and formation of **11a**. Quantum yields for products (Φ_p) from both **11b** and **11f** are high (Table I).[23] As with the pyridines and pyrimidines noted above, Φ_p from **11d** is lower in benzene. We also noted that, in hexane as solvent, **11d** furnished no **27** and underwent only slow destruction of starting material and **11f** underwent type II abstraction of hydrogen very slowly.

Finally, we investigated the 3-acylpyridazines (**12**). There are reports that on direct irradiation pyridazine does not abstract hydrogen from solvent,[9,39] although Φ_{ISC} is 0.66.[40] Pyridazine triplet also fails to sensitize biacetyl phosphorescence, and these properties have been accounted for by its unusually short lifetime (τ_T <100 ns at room temperature).[40] Most interestingly, E_T of

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(31) Terazima, M.; Azumi, T. *Chem. Phys. Lett.* **1988**, *153*, 27.
(32) Arnold, D. R. *Adv. Photochem.* **1968**, *6*, 301.
(33) Unless otherwise indicated, preparative irradiations were carried out in 95% *tert*-butyl alcohol–5% benzene with $\lambda > 340$ nm, and quantum yield determination were performed at λ ~313 nm.
(34) DePuy, C. H. *Acc. Chem. Res.* **1968**, *1*, 33.
(35) Hoell, D.; Lex, J.; Müller, K. *J. Am. Chem. Soc.* **1986**, *108*, 5983.
(36) Evans, D. *J. Chem. Soc.* **1959**, 2753. Lee, J.; Li, F.; Bernstein, E. R. *J. Phys. Chem.* **1983**, *87*, 260.
(37) Lablache-Combier, A.; Planckaert, B. *Bull. Soc. Chim. Fr.* **1974**, 225. Jinguji, M.; Hosako, Y.; Obi, K. *J. Phys. Chem.* **1979**, *83*, 2551. In addition, intramolecular abstraction of side-chain hydrogen occurs in 2-butylpyrazine and related compounds: Stermitz, F. R.; Huang, W. H.; Blythin, D. J.; Hoeft, A.; Kim, D. K.; O'Donnell, C. M. *J. Heterocycl. Chem.* **1972**, *9*, 1289.
(38) The small yields of **11a** made it impossible to carry out accurate determination of $k_q\tau$'s for hydrogen abstraction by nitrogen and oxygen in **11c,d**.
(39) Castellano, A.; Catteau, J. P.; Lablache-Combier, A.; Planckaert, B.; Allan, G. *Tetrahedron* **1972**, *28*, 3511.
(40) Terazima, M.; Yamauchi, S.; Hirota, N. *J. Chem. Phys.* **1986**, *84*, 3679 and references cited therein. Terazima, M.; Azumi, T. *Chem. Phys. Lett.* **1988**, *145*, 286.

pyridazine is 64–69 kcal/mol,[6,41] well below E_T of a simple carbonyl triplet.

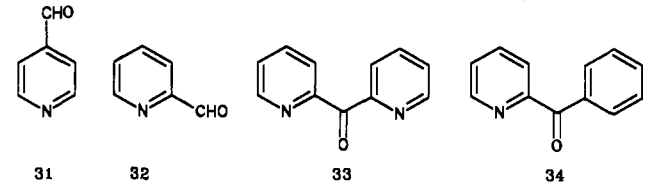
Ketone **12d** was recovered unchanged both from direct irradiation ($\lambda > 313$ nm) and from triplet sensitization using **10a** ($E_T \sim 70$ kcal/mol[32]) as the sensitizer.[42,43] Direct irradiation of **12d** in the presence of *cis*-piperylene did not lead to formation of detectable amounts of *trans*-piperylene. These observations indicate that the triplet sensitized by **10a** leads to no products from type II abstraction by carbonyl oxygen or from abstraction by N(2).[44] They suggest further that, like pyridazine itself, T_1 of **12d** has a short lifetime.

In contrast, irradiation of **12d** ($\lambda > 280$ nm) in acetone as solvent led to acetone-sensitized formation of a small amount (~10%) of cyclopropanol **30**. However, acetone-sensitized irradiation of **12f**, in which only abstraction of hydrogen by oxygen is sterically favored, led to no reaction and essentially complete recovery of unreacted starting material. Parallel experiments with 3-acetyl-6-isopentylpyridazine (**18**) gave no reaction on direct irradiation ($\lambda > 280$ nm) or on sensitization by acetone; in all cases **18** was recovered unchanged. These observations suggest that although T_1 leads to no hydrogen abstraction, 3-acylpyridazines have an upper $n\pi^*$ triplet that mediates abstraction of hydrogen by N(2) but not by oxygen. In **18** neither triplet leads to observable chemistry, implying that there is no abstraction of hydrogen by N(1).

Discussion of the Photochemistry of 10–12. In principle, it seems likely that the unperturbed triplets of the heteroaromatic ring and the carbonyl group mix to produce one or more low-lying $n\pi^*$ triplets, the properties of which depend upon both the properties and the relative energies of the contributing states.[12,45] The present results can be most simply explained by postulating that one of the states produced by this mixing has electron deficiency on both carbonyl oxygen and the adjacent ring nitrogen and that this state is thus capable of mediating hydrogen abstraction by either heteroatom. The difference in reactivity of acylpyrazines in comparison with that of 4-acylpyrimidines and 2-acylpyridines is then correlated with increasing contribution to the properties of this ketone triplet by the ring triplet as E_T of the ring triplet decreases. Ketones derived from pyridine and pyrimidine ($E_T \sim 84$ kcal/mol) show similar reactivity at nitrogen and oxygen. In contrast, ketones derived from pyrazine, where E_T is lower (~75 kcal/mol), react preferentially at nitrogen but if that is blocked, react efficiently at oxygen.

Alternative possible explanations require more triplets. Initial mixing of unperturbed states could produce two nearly isoenergetic $n\pi^*$ triplets, one predominantly a nitrogen triplet and the other predominantly a carbonyl triplet. If vibronic coupling of these two states occurs, one possible result is a lower state with reactivity at nitrogen and oxygen. As noted earlier, the possibility of a mixed state of this sort was pointed out by Alexander.[3] If the two $n\pi^*$ triplets remain discrete, ΔE_T must still be small enough that they exist in rapid equilibrium in order to explain both the quenching data for **5**[3] and **10d** and also the behavior of pyrazyl ketones **11b,f**. The noted solvent effect on Φ_p's is consistent with any of the above explanations.[45]

Experimental information relevant to these possibilities is scarce. In comparison with phenyl ketones, relatively little is known about the triplet states of heteroaromatic ketones. There is evidence that, at 1.4 K in matrices of *p*-xylene or other aromatics, the phosphorescent state of the three pyridinecarboxaldehdyes is an $n\pi^*$ state centered on the carbonyl group. In 4-pyridinecarboxaldehyde (**31**), there is some mixing of carbonyl and ring states



31 32 33 34

in this triplet, but in the C(2)-substituted isomer **32** emission occurs from an essentially pure carbonyl $n\pi^*$ state.[46] Under the same conditions, the phosphorescent states of di-2-pyridyl ketone (**33**) and 2-benzoylpyridine (**34**) are also carbonyl $n\pi^*$ states, but here there is an indication of interaction of carbonyl and nitrogen by means of spatial overlap of nonbonding orbitals.[46] A recent study of all six dipyridyl ketones reveals that the three 2-pyridyl compounds have physical properties different from the other isomers, with the nearby nitrogen increasing the $n\pi^*$ character of excitation.[47] The investigators suggested that in these compounds with nearby nitrogen T_1 is a carbonyl $n\pi^*$ state with the nitrogen $n\pi^*$ triplet ~0.5 eV (~11.5 kcal/mol) higher and in thermal equilibrium with T_1. Taken together, these observations point to some sort of local interaction between carbonyl and nitrogen in T_1 of 2-acylpyridines. It is not yet evident how this description applies to our ketones, but in any event, it does not lead to clear choices among the possible explanations for their reactive states. Additional chemical and physical information concerning the triplets of these ketones is needed.

The behavior of the pyridazyl ketones (**12**) suggests that in this case heteroaromatic and carbonyl triplet mixing has produced two nonequilibrating low-lying states. These triplets show no carbonyl character in their photochemical behavior, and this is in line with the above correlation of ketone triplet properties with heteroaromatic triplet energy. E_T for pyridazine is ~67 kcal/mol,[41] which is much lower than for the other heterocycles, so that it is reasonable that ring triplet properties dominate in the triplets of 3-acylpyridazines.

Summary. This work has shown that the reactive upper nitrogen triplet of 4-acylpyrimidines is comparable to T_1 of pyrimidine in energy and photochemical properties. It has also provided evidence in 3-acylpyridazines **12** for an upper triplet that leads to product from hydrogen abstraction by N(2) but not oxygen. Most significantly, this work indicates that in four series of heteroaromatic ketones photochemical properties can be correlated with the energy of the nitrogen heteroaromatic triplet that interacts with a carbonyl triplet to form the triplet states of these ketones.

Experimental Section

Materials and Equipment. Preparative gas chromatography (GLC) was carried out on a Varian Aerograph Model 920 gas chromatograph with (a) a 10% OV101, 5-ft column on Chromosorb-P, (b) a 25% Carbowax, 10-ft column on Chromosorb-W, or (c) an XF 150, 20.5-ft column on Chromosorb-P 60/80, packed in 0.25-in. aluminum tubing. Analytical GLC was carried out isothermally using internal standards on a HP-5890 temperature-programmable gas chromatograph with (a) an Ultra-1 25 m × 0.2 mm capillary column with a film thickness of 0.33 μm or (b) an OV-225 25 m × 0.25 mm capillary column with a film thickness of 0.25 μm. Spinning disk chromatography was performed on a Chromatotron Model 7924T instrument. All NMR spectra were recorded on either a Varian Model T-60 (60 MHz) or a Nicolet/Oxford Model NT-300 (300 MHz) spectrometer and are reported in parts per million downfield from tetramethylsilane employed as an internal

(41) The triplet energy of pyridazine is strongly influenced by the polarity of the medium: Marzzacco, C. J. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 771 and references cited therein. Linnell; Raab, F.; Clifford, R. *J. Phys. Chem.* **1964**, *68*, 1999. Coad, P.; Coad, R. A.; Wilkins, C. L. *Ibid.* **1963**, *67*, 2815. From these reports we estimate E_T of pyridazine under our conditions (*tert*-butyl alcohol containing 5–10% benzene) to be ~67 kcal/mol.

(42) Efficient energy transfer takes place from **10** to **12**. On direct irradiation of **10f** undergoes typical type II cleavage with formation of **10a**. Added **12d** quenches this reaction following Stern–Volmer kinetics with a $k_q\tau$ of 27 M^{-1} s^{-1}. Conversion was ≤4%, and the quencher (**12d**) absorbed <3% of the light (λ ~313 nm). Quenching of the type II cleavage of 2-valerylpyridine by piperylene gives the same $k_q\tau$.[21]

(43) In the sensitized irradiation of **12d**, the sensitizer (**10a**) absorbed ~67% of the light (λ ~313 nm).

(44) 3-Isopentylpyridazine (**16**) is also recovered unchanged from both direct and triplet-sensitized irradiation: Prathapan, S. Unpublished observations in this laboratory. The photochemistry of **16** is still under investigation.

(45) For a relevant discussion concerning the chromophore of the benzoyl system and phenyl ketones derived from it, see: Wagner, P. J.; Kemppainen, A. E.; Schott, H. N. *J. Am. Chem. Soc.* **1973**, *95*, 5604.

(46) Latas, K. J.; Power, R. K.; Nishimura, A. M. *Chem. Phys. Lett.* **1979**, *65*, 272.

(47) Favaro, G.; Masetti, F.; Romani, A. *J. Photochem. Photobiol. A* **1990**, *53*, 41.

standard (δ). Infrared spectra were recorded on a Perkin-Elmer Model 237B grating spectrophotometer or a Perkin-Elmer Model 1800 Fourier transform instrument. Ultraviolet absorption spectra were recorded on a Cary Model 14 recording spectrophotometer. Mass spectral analyses were performed by The Rockefeller University Mass Spectrometric Biotechnology Resource on a VG-70250 magnetic sector instrument. Organic solutions obtained by workup of reaction mixtures were dried by washing with brine prior to treatment with anhydrous sodium or magnesium sulfate. Unless otherwise indicated, products were obtained as colorless oils. Compounds purified by gas chromatography are estimated from analytical gas chromatography to be ≥98% pure. Compounds purified by column or spinning band chromatography are estimated from NMR spectra to be ≥95% pure.

Preparation of 6-(3-Methylbutyl)-4-pyrimidinecarbonitrile (9). Nitrile **9** was prepared by adaptation of the procedure reported for **8**.[14] This involved the reaction of thiourea (1.52 g, 0.02 mol) with the ethyl ester of 6-methyl-3-oxoheptanoic acid[48] (3.72 g, 0.02 mol) in the presence of sodium methoxide (2.4 g, 0.044 mol) in methanol to give the corresponding thiouracil (3.0 g, 75%), which was reduced directly to 6-isoamyluracil (0.85 g, 34%) with Raney nickel (20 g) in aqueous ammonia. For the uracil: ^{1}H NMR ($CDCl_3$) δ 8.1 (1 H), 6.3 (1 H), 2.6 (2 H), 1.6 (3 H), 0.94 (6 H); IR ($CDCl_3$) 2954, 2865, 1664, 1607, 1415 cm^{-1}. The uracil (0.83 g, 0.005 mol) was treated at reflux with phosphorus oxychloride (15 mL) to give 0.59 g (63%) of 6-chloro-4-(3-methylbutyl)-pyrimidine: ^{1}H NMR ($CDCl_3$) δ 8.9 (1 H), 7.2 (1 H), 2.8 (2 H), 1.6 (3 H), 0.95 (6 H); IR ($CDCl_3$) 2954, 2865, 1567, 1529, 1415 cm^{-1}; MS m/z 185.0842 ((M + H)$^+$; calcd for $C_9H_{14}N_2Cl$, 185.0846). The chloropyrimidine (0.55 g, 0.003 mol) was treated with a 20% solution of trimethylamine in benzene (10 mL) to give the corresponding quaternary ammonium chloride (0.585 g, 81%) which was converted directly to **9** (361 mg, 86%) by treatment with tetraethylammonium cyanide (470 mg, 0.003 mol) in dry methylene chloride. For **9**: ^{1}H NMR ($CDCl_3$) δ 9.2 (1 H), 7.5 (1 H), 2.9 (2 H), 1.6 (3 H), 0.95 (6 H); ^{13}C NMR ($CDCl_3$) δ 174.5, 160.0, 141.7, 124.1, 116.3, 38.2, 36.6, 28.5, 23.0; IR (CCl_4) 3060, 2960, 2871, 1581, 1531, 1464, 1387 cm^{-1}; MS m/z 176.1193 ((M + H)$^+$; calcd for $C_{10}H_{14}N_3$, 176.1188).

Preparation of 2-Propionyl-, 2-Butyryl-, 2-(3-Methylbutyryl)-, 2-(2,2-Dimethylpropionyl), and 2-(3,3-Dimethylbutyryl)pyridine (10b–f). These were prepared by following the route previously used for **10a,b**[15] involving the addition of the nitrile **14** to the corresponding Grignard reagent. For **10c**: ^{1}H NMR ($CDCl_3$) δ 8.7 (1 H), 8.1 (1 H), 7.9 (1 H), 7.5 (1 H), 3.1 (2 H), 1.8 (2 H), 1.0 (3 H); IR (CCl_4) 3056, 2965, 2936, 2870, 1701, 1573, 1466, 1445, 1306 cm^{-1}; MS m/z 149.0829 (M$^+$; calcd for $C_9H_{11}NO$, 149.0841). For **10d**: ^{1}H NMR ($CDCl_3$) δ 8.7 (1 H), 8.1 (1 H), 7.9 (1 H), 7.5 (1 H), 3.1 (2 H), 2.3 (1 H), 1.0 (6 H); IR (CCl_4) 3054, 2954, 2865, 1698, 1589, 1464, 1367 cm^{-1}; MS m/z 163.1008 (M$^+$; calcd for $C_{10}H_{13}NO$, 163.0997). For **10e**: ^{1}H NMR ($CDCl_3$) δ 8.6 (1 H), 7.9 (1 H), 7.8 (1 H), 7.4 (1 H), 1.45 (9 H); IR (CCl_4) 3050, 2954, 2920, 1697, 1589, 1472 cm^{-1}; MS m/z 164.1076 ((M + H)$^+$; calcd for $C_{10}H_{14}NO$, 164.1075). For **10f**: ^{1}H NMR ($CDCl_3$) δ 8.7 (1 H), 8.0 (1 H), 7.8 (1 H), 7.4 (1 H), 3.2 (2 H), 1.1 (9 H); IR (CCl_4) 3054, 2954, 2876, 1694, 1561, 1478 cm^{-1}; MS m/z 177.1176 (M$^+$; calcd for $C_{11}H_{15}NO$, 177.1154).

Preparation of 2-Acetyl-, 2-Propionyl-, 2-Butyryl-, 2-(3-Methylbutyryl)-, and 2-(3,3-Dimethylbutyryl)pyrazine (11a–d,f). **11a–d** were prepared by the free-radical acylation of pyrazine as reported earlier for **11a,b**.[16] For **11c**: ^{1}H NMR ($CDCl_3$) δ 9.2 (1 H), 8.8 (1 H), 8.6 (1 H), 3.2 (2 H), 1.8 (2 H), 1.0 (3 H); IR (CCl_4) 3055, 3007, 2935, 2875, 1699, 1584, 1570, 1464, 1362 cm^{-1}; MS m/z 150.0792 (M$^+$; calcd for $C_8H_{10}N_2O$, 150.0793). For **11d**: ^{1}H NMR ($CDCl_3$) δ 9.2 (1 H), 8.7 (1 H), 8.6 (1 H), 3.1 (2 H), 2.3 (1 H), 1.0 (6 H); IR (CCl_4) 3054, 2948, 2870, 1703, 1572, 1470, 1403, 1364 cm^{-1}; MS m/z 164.0935 (M$^+$; calcd for $C_9H_{12}N_2O$, 164.0950). **11f** was prepared in a 10% yield by the addition of the nitrile **14** (2.1 g, 0.02 mol) to neopentylmagnesium bromide (0.021 mol) followed by treatment with acid. For **11f**: ^{1}H NMR ($CDCl_3$) δ 9.2 (1 H), 8.7 (1 H), 8.6 (1 H), 3.1 (2 H), 1.1 (9 H); IR (CCl_4) 3077, 2921, 2850, 1694, 1571, 1411, 1365 cm^{-1}; MS m/z 179.1182 ((M + H)$^+$; calcd for $C_{10}H_{15}N_2O$, 179.1184).

Preparation of 3-Acetyl-, 3-Propionyl-, 3-(3-Methylbutyryl)-, and 3-(3,3-Dimethylbutyryl)pyridazine (12a,b,d,f). Preparation of **12a,b,d,f** involved the addition of 3-pyridazinecarbonitrile (**15**) to the corresponding Grignard reagent as reported earlier for **12a**.[17] For **12b**: ^{1}H NMR ($CDCl_3$) δ 9.3 (1 H), 8.1 (1 H), 7.7 (1 H), 3.4 (2 H), 1.3 (3 H); IR (CCl_4) 3054, 2976, 2931, 1709, 1570, 1381 cm^{-1}; MS m/z 136.0666 (M$^+$; calcd for $C_7H_8N_2O$, 136.0637). For **12d**: ^{1}H NMR ($CDCl_3$) δ 9.3 (1 H), 8.1 (1 H), 7.7 (1 H), 3.3 (2 H), 2.4 (1 H), 1.0 (6 H); IR (CCl_4) 3058, 2980, 2941, 1706, 1574, 1553, 1460 cm^{-1}; MS m/z 164.0965 (M$^+$; calcd for $C_9H_{12}N_2O$, 164.0950). For **12f**: ^{1}H NMR ($CDCl_3$) δ 9.3 (1 H), 8.2 (1 H), 7.7 (1 H), 3.4 (2 H), 1.1 (9 H); IR (CCl_4) 3054, 2976, 2931, 1706, 1575, 1553, 1460 cm^{-1}; MS m/z 179.1173 ((M + H)$^+$; calcd for $C_{10}H_{15}N_2O$, 179.1184).

Preparation of 3-(3-Methylbutyl)pyridazine (16). Isoamyllithium prepared from isoamyl bromide (3.75 g, 0.025 mol) and lithium (0.35 g, 0.05 mol) was added to a solution of pyridazine (2.0 g, 0.025 mol) in ether at −15 °C over a 3-h period. The mixture was stirred at room temperature overnight and then quenched by adding cold water. The organic layer was separated, and the crude 3-(3-methylbutyl)-2,3-dihydropyridazine obtained after the removal of solvent was oxidized[18] with potassium permanganate (1.0 g) in acetone (250 mL) to give 3.5 g (93%) of **16**. For **16**: ^{1}H NMR ($CDCl_3$) δ 9.1 (1 H), 7.4 (2 H), 3.0 (2 H), 1.7 (3 H), 0.98 (6 H); IR (CCl_4) 3058, 2953, 2930, 1583, 1468, 1453; MS m/z 150.1162 (M$^+$; calcd $C_9H_{14}N_2$, 150.1157).

Preparation of 6-(3-Methylbutyl)-3-pyridazinecarbonitrile (17).[19] A mixture of **16** (3.0 g, 0.02 mol), trimethylsilyl cyanide (4.0 g, 0.04 mol), and anhydrous aluminum chloride (10 mg) in dry methylene chloride (50 mL) was stirred under nitrogen for 0.5 h. A solution of *p*-toluenesulfonyl chloride (7.6 g, 0.04 mol) in dry methylene chloride (50 mL) was added over 3 h. Solvent was removed under reduced pressure, and the residue was treated with ethanol and cooled in a freezer. The solid separated out was collected by filtration and purified by column chromatography followed by recrystallization from a mixture (1:4) of ether and hexane to give 1.6 g (24%) of 2-(4-*p*-toluenesulfonyl)-6-(3-methylbutyl)-2,3-dihydro-3-pyridazinecarbonitrile, which was treated with 1,8-diazabicyclo[5.4.0]undec-7-ene (1.21 g, 0.008 mol) in dry THF to give 0.88 g (95%) of **17**, mp 33–35 °C, after flash chromatography. For **17**: ^{1}H NMR ($CDCl_3$) δ 7.8 (1 H), 7.5 (1 H), 3.1 (2 H), 1.7 (3 H), 1.0 (6 H); IR (KBr) 3060, 2957, 2931, 2869, 2245, 1574, 1545, 1472 cm^{-1}; MS m/z 176.1183 ((M + H)$^+$; calcd for $C_{10}H_{14}N_3$, 176.1188).

Preparation of 3-Acetyl-6-(3-methylbutyl)pyridazine (18). The ketone **18** was prepared in a 55% yield by the reaction of methylmagnesium iodide with **17** under conditions analogous to those employed for **12a**.[17] For **18**: ^{1}H NMR ($CDCl_3$) 8.0 (1 H), 7.5 (1 H), 3.1 (2 H), 2.9 (3 H), 1.7 (3 H), 0.98 (6 H); IR (neat) 3057, 2958, 2930, 2871, 1702, 1579, 1468, 1370 cm^{-1}; MS m/z 193.1342 ((M + H)$^+$; calcd for $C_{11}H_{17}N_2O$, 193.1341).

Preparative Photochemistry. All preparative experiments were carried out using the output from a Hanovia 450-W medium-pressure mercury lamp with a uranium glass filter (λ >340 nm). Yields were determined gas chromatographically. Irradiation were carried out in quartz tubes in a 19:1 mixture of degassed *tert*-butanol and benzene.

A. 6-(3-Methylbutyl)-4-pyrimidinecarbonitrile (9). Exhaustive irradiation of **9** (15 mg, 0.1 mmol in 4 mL) gave 6 mg (60%) of **8** as a crystalline solid, mp 41–42 °C, after preparative GLC (previously reported as a liquid), identical with an authentic sample prepared as previously reported.[14]

B. 2-Propionylpyridine (10b). A solution of **10b** (13.5 mg, 0.1 mmol in 4 mL) was irradiated for 5 h. Removal of the solvent followed by flash chromatography over silica gel gave 11 mg (81%) of the cyclopropanol **24**, mp 75–76 °C, after flash chromatography. For **24**: ^{1}H NMR ($CDCl_3$) δ 8.5 (1 H), 7.8 (1 H), 7.2 (1 H), 7.1 (1 H), 1.4 (2 H), 1.2 (2 H); IR (CCl_4) 3588, 3394, 3011, 1590, 1567, 1489 cm^{-1}; MS m/z 136.0767 ((M + H)$^+$; calcd for $C_8H_{10}NO$, 136.0762).

C. 2-Butyrylpyridine (10c). A solution of **10c** (15 mg, 0.1 mmol in 4 mL) was irradiated for 6 h. GLC analysis of the photolysate indicated that **10a** and **23** (a 1:1 mixture of two isomers) were formed in a 1:9 ratio. For **23**: IR (neat) 3144, 3017, 2981, 1596, 1567, 1477, 1296 cm^{-1}; MS m/z 149.0829 (M$^+$; calcd for $C_9H_{11}NO$, 149.0841).

D. 2-(3-Methylbutyryl)pyridine (10d). A solution of **10d** (165 mg, 1 mmol in 60 mL) was irradiated for 8 h. Solvent was removed under pressure, and the residue was subjected to spinning-disk chromatography. Four products, identified as the ketone **10a**, the cyclopropanol **20**, and the cyclobutanols **21** and **22**, were isolated and purified. For **20**: ^{1}H NMR ($CDCl_3$)$_3$ δ 8.5 (1 H), 7.4 (1 H), 7.3 (1 H), 7.1 (1 H), 1.4 (3 H), 1.2 (1 H), 0.93 (1 H), 0.84 (3 H); IR (CCl_4) 3586, 3385, 2954, 2860, 1575, 1540, 1489, 1406 cm^{-1}, MS m/z 163.0980 (M$^+$; calcd for $C_{10}H_{13}NO$, 163.0997). For **21** and **22** IR and NMR spectra were virtually identical: ^{1}H NMR ($CDCl_3$) δ 8.5 (1 H), 7.8 (1 H), 7.5 (1 H, 4.9 (1 H), 2.8 (1 H), 2.5 (2 H), 1.2 (3 H); IR (neat) 3347, 3057, 2957, 2870, 1584, 1468, 1437, 1385 cm^{-1}; for **21** and **22**, MS m/z 164.1065 ((M + H)$^+$, calcd for $C_{10}H_{14}NO$, 164.1075).

E. 2-(2,2-Dimethylpropionyl)pyridine (10e). A solution of **10e** (16.5 mg, 0.1 mmol in 4 mL) was irradiated for 2.5 h. Analysis of the photolysate indicated a >90% yield of **20** along with <3% of an unidentified product.

(48) Kögl, F.; Salemink, C. A. *Recl. Trav. Chim. Pays-Bas* **1952**, *71*, 779. Kanojia, R. M.; Wachter, M. P.; Levine, S. D.; Adams, R. E.; Chen, R.; Chin, E.; Cotter, M. L.; Hirsch, A. F.; Huettmann, R.; Kane, V. V.; Ostrowski, P.; Shaw, C. J.; Mateos, J. L.; Noriega, L.; Guzman, A.; Mijarez, A.; Tovar, L.; Shefter, E. *J. Org. Chem.* **1982**, *47*, 1310.

F. 2-(3,3-Dimethylbutyryl)pyridine (10f). Irradiation of a solution **10f** (17.5 mg, 0.1 mmol in 4 mL) for 2 h yielded a 4.5% yield of **10a** as the only product.

G. 2-Acetylpyrazine (11a). **11a** was isolated unchanged after 24-h irradiation.

H. 2-Propionylpyrazine (11b). A solution of **11b** (13.6 mg, 0.1 mmol in 4 mL) was irradiated 4 h to give 10.8 mg (80%) of **27**, mp 53–55 °C, after flash chromatography. For **27**: ^{1}H NMR ($CDCl_3$) δ 8.7 (1 H), 8.4 (2 H), 3.6 (1 H), 1.4 (4 H); IR (CCl_4) 3593, 3360, 3054, 3004, 2970, 1573, 1531, 1470, 1325 cm^{-1}; MS m/z 137.0685 ($(M + H)^+$; calcd for $C_7H_9N_2O$, 137.0715). Irradiation of **11b** (13.6 mg, 0.01 mol) in hexane (4 mL) led to the slow destruction of **11b**.

I. 2-Butyrylpyrazine (11c). GCMS analysis of the photolysate from **11c** (0.05 M) after 4 h indicated the presence of **11a** (~1%) and a 1:1 isomeric mixture of the diastereomers of cyclopropanol **28** (~95%). For **28**: ^{1}H NMR ($CDCl_3$) δ 8.8 (1 H), 8.4 (2 H), 3.5–3.3 (1 H), 1.6–0.90 (6 H); IR (KBr) 3145, 3017, 2981, 2954, 2925, 1590, 1567, 1477, 1290 cm^{-1}; MS m/z 151.0842 ($(M + H)^+$; calcd for $C_8H_{11}N_2O$, 151.0871).

J. 2-(3-Methylbutyryl)pyrazine (11d). GCMS analysis of the photolysate from **11d** (0.05 M) after 4 h indicated the formation of **11a** (~2%) and the cyclopropanol **29** (~90%). The isolated yield of **29** was 86%. For **29**: ^{1}H NMR ($CDCl_3$) δ 8.7 (1 H), 8.4 (2 H), 3.4 (1 H), 1.6 (1 H), 1.4 (3 H), 0.98 (1 H), 0.89 (3 H); IR ($CDCl_3$) 3580, 3385, 2954, 2860, 1590 cm^{-1}; MS m/z 164.0954 (M^+; calcd for $C_9H_{12}N_2O$, 164.0950). Irradiation of 0.04 M solution of **11d** in hexane led to the slow destruction of **11d**.

K. 2-(3,3-Dimethylbutyryl)pyrazine (11f). Irradiation of 0.02 M solution of **11f** for 20 h led to the near-quantitative formation of **11a**. Irradiation of 0.04 M solution of **11f** in hexane for 20 h gave **11a** in a 15% yield.

L. 3-Propionylpyridazine (12b). **12b** was isolated unchanged after 24–90-h irradiation in hexane, *tert*-butanyl alcohol, or acetone at $\lambda > 313$ nm and at $\lambda > 280$ nm.

M. 3-(3-Methylbutyryl)pyridazine (12d). **12d** was recovered unchanged after irradiating for 90 h in hexane or *tert*-butyl alcohol at $\lambda > 280$ nm. Irradiation at $\lambda > 200$ nm led to the slow destruction of **12d** to nonvolatile materials. Acetone-sensitized irradiation of **12d** (0.02 M in acetone as solvent) at $\lambda > 280$ nm gave the cyclopropanol **30** (~10%) along with unchanged **12d** (~15%). For **30**: ^{1}H NMR ($CDCl_3$) δ 9.0 (1 H), 7.7 (1 H), 7.5 (1 H), 1.7 (1 H), 1.4 (3 H), 1.0 (1 H), 0.88 (3 H); IR (CCl_4) 3584, 3370, 3001, 2954, 2872, 1583, 1438, 1370 cm^{-1}; MS m/z 165.0983 ($(M + H)^+$; calcd for $C_9H_{13}N_2O$, 165.1028).

N. 3-(3,3-Dimethylbutyryl)pyridazine (12f). **12f** was recovered unchanged after 36–48-h irradiation at (a) $\lambda > 280$ nm in *tert*-butyl alcohol (0.05 M) or (b) $\lambda > 280$ nm in acetone (0.02 M).

O. 3-(3-Methylbutyl)pyridazine (16). **16** was recovered unchanged under the conditions employed for **12f**.

P. 3-Acetyl-6-(3-methylbutyl)pyridazine (18). **18** was recovered unchanged under the conditions employed for **12f** and **16**.

Quantum Yield Measurements. All measurements were made at λ ~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. 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 9. A. Samples of **9** in *tert*-butyl alcohol (0.004 M, 4 mL) and acetone (0.004 M, 4 mL) were irradiated at λ ~313 nm in a merry-go-round for 8 h. GLC analysis of the photolysate indicated the formation of **8** in a ratio of 1:1.4 (*tert*-butyl alcohol to acetone).

B. Samples of **9** (0.05 M in a mixture (9:1) of *tert*-butyl alcohol and benzene) in the presence of (a) indanone (0.8 M), (b) propiophenone (0.8 M), (c) 3-methoxyacetophenone (0.08 M), and (d) no sensitizer were irradiated under conditions analogous to those reported above. GLC analysis of the photolysate indicated the formation of **8** in a ratio of 0.8:0:0:1 (a:b:c:d).

2-Acetylpyridine-Sensitized Irradiation of 3-Propionylpyridazine (12b). A solution of **10a** (24 mg, 0.2 mmol) and **12b** (7 mg, 0.05 mmol) in *tert*-butyl alcohol (4 mL) was irradiated at 313 nm for 48 h. GLC analysis of the photolysate indicated total recovery of unreacted **12b**.

Quenching Experiments. A. Attempted Quenching of Valerophenone Triplet by 6-Methyl-4-pyrimidinecarbonitrile (8). Solutions of valerophenone (0.8 M) containing varying amounts of **8** (0–0.0064 M) in benzene (4 mL) were irradiated on a merry-go-round for 2.25 h. The amount of acetophenone formed was determined quantitatively on an analytical GC and was shown to be independent of the concentration of **8**.

B. 2-(3-Methylbutyryl)pyridine (10d) Triplet by Piperylene. Solutions of **10d** (0.05 M) in a mixture (9:1) of *tert*-butyl alcohol and benzene (4 mL) containing varying amounts of piperylene (0–0.000 35 M) were irradiated in a merry-go-round at $\lambda > 340$ nm for 1.5 h. Quantitative determinations of **10a** and **20** were made on an analytical GC. A Stern–Volmer plot of the data gave slopes 32.5 and 32.6 M^{-1} for **10a** and **20**, respectively.

C. 2-(3,3-Dimethylbutyryl)pyridine (10f) Triplet by 3-(3-Methylbutyryl)pyridazine (12f). Solutions of **10f** (0.1 M) in *tert*-butyl alcohol (4 mL) were irradiated in the presence of **12d** (0–0.007 M). The amount of **10a** formed was determined by GC. Stern–Volmer analysis of the data gave slope 26.7 M^{-1}.

D. Attempted Isomerization of *cis*-Piperylene by 3-(3-Methylbutyryl)pyridazine (12d). A solution of **12d** (0.03 M) in *tert*-butyl alcohol (4 mL) was irradiated in the presence of isomerically pure *cis*-piperylene (0.05 M) at $\lambda > 340$ nm. GC analysis of the photolysate on column c indicated no isomerization of *cis*-piperylene.

Rearrangement of Cyclopropanol 20 to 10e. Treatment of **20** (16.5 mg, 0.1 mmol) with methanolic sodium hydroxide at room temperature for 40 h gave the ketone **10e** (11 mg, 67%) as the only isolable product. The same product was formed when **20** was heated in benzene solution.

Air Oxidation of 20. Cyclopropanol **20** was passed through a silica column under a positive pressure of air. Under these conditions a near-quantitative conversion of **20** to the peroxy hemiacetal **26** was observed, mp 84–85 °C, after flash chromatography. For **26**: ^{1}H NMR ($CDCl_3$): δ 8.5 (1 H), 7.8 (1 H), 7.7 (1 H), 7.4 (1 H), 6.5 (1 H), 2.9 (2 H), 1.6 (6 H); ^{13}C NMR ($CDCl_3$) δ 154.8, 147.6, 137.6, 124.1, 120.0, 105.7, 84.3, 59.2, 27.3, 25.0; IR (KBr) 3397, 2971, 1587, 1439, 1381, 1084 cm^{-1}; MS m/z 195 (M^+). Anal. ($C_{10}H_{13}NO_3$) C, H, N.

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