Photochemical Fragmentation of 4-Alkylpyrimidines

and 2-Alkylquinolines

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Abstract: Hydrogen abstraction and fragmentation occur on acetone-sensitized photolysis of 4alkylpyrimidines 1a-c with formation of 4-methylpyrimidine (2); the selectivity for primary, secondary, and tertiary hydrogen transfer is considerably greater in 1a-c than in 2-alkylquinolines 7a-c.

We have found that hydrogen transfer and fragmentation occur on acetone-sensitized population of the first triplet state ($n\pi$ *) of the 4-alkylpyrimidines 1a-c (eq 1). Direct irradiation of pyrimidines 1a-c, which were prepared following a known procedure,^{1,2} in benzene or *tert*-butyl alcohol as solvent, using a medium-pressure mercury arc lamp and either a potassium chromate solution ($\lambda \sim 313$ nm) or Pyrex glass ($\lambda > 280$ nm) as a filter, led to no reaction and recovery of starting pyrimidine. Irradiation in acetone ($E_T \sim 79-82$ kcal/mol³) as solvent through Pyrex, however, led to slow destruction of starting material and



formation of 4-methylpyrimidine (2), which was isolated and identified by comparison with authentic commercially available material. The first triplet of 4-alkylpyrimidines is an $\pi\pi$ state at -84 kcal/mol that is expected to be mixed with a nearby $\pi\pi$ second triplet;⁴ our observations indicate that this first triplet is accessible on sensitization with acetone and that it mediates hydrogen abstraction by N(3) as shown in eq 1. These results are noteworthy in comparison with the photochemistry of 4-acyl-6-alkylpyrimidines such as 3 and 4.² Substituents such as acetyl and cyano modify the properties of both $\pi\pi$ and $\pi\pi$ triplets in other nitrogen aromatics,⁵ and in 3 and 4 and similar ketones there are *two* $\pi\pi$ triplets that can activate hydrogen abstraction by nitrogen, one at 70-71 kcal/mol mediating reaction at N(3), and one at 79-84 kcal/mol leading to reaction at N(1).^{2,6} The present study indicates that the first triplet in 1 and the upper nitrogen $\pi\pi$ triplet in 3, two $\pi\pi$ triplets having similar energies, mediate comparable chemical behavior. This observation is helpful in understanding the more complex photochemical behavior of 3 and 4. The hydrogen transfer reaction of 1a-c is also of interest in light of EPR evidence⁷ for formation of 5 upon direct irradiation of 4-methylpyrimidine (2) in methanol at 113 K; this process is believed to involve an $\pi\pi$ triplet,^{7,8} and on the basis of its spectroscopic properties the radical was specifically assigned structure 5 rather than 6.⁷

For comparison with the behavior of **1a-c** we examined the photochemistry of quinolines **7a-c**, which were prepared by a previously described route.⁹ These compounds underwent hydrogen transfer and fragmentation (eq 2) on direct irradiation in a reaction known⁹ to occur from a singlet m^* state. Relative quantum yields for formation of **8** (rel. ϕ_8) from **7a-c** in benzene and relative quantum yields for formation of **8** (rel. ϕ_8) from **7a-c** in benzene and relative quantum yields for formation of **2** (rel. ϕ_2) from **1a-c** in acetone- d_6 are gathered in Table I. Relative quantum yields per hydrogen available for transfer (rel. ϕ/H) are also shown. The rel. ϕ_2 's reported are for 0.04 M solutions. Determinations on **1a-b** at 0.02 M gave essentially the same results, indicating that concentration effects^{2,10} in energy transfer from acetone do not significantly influence rel. ϕ_2 . Values of rel. ϕ_8 in *tert*-butyl alcohol were little different from those in benzene, in keeping with the conclusion that abstractions in **7a-c** involve direct hydrogen atom transfer rather than initial electron transfer.¹¹ This finding also



indicates that protic solvents do not enhance quantum yields for products in these quinolines, unlike their effect on type II abstractions by the carbonyl group.¹² The results in Table I reveal little discrimination among primary, secondary, and tertiary hydrogens in fragmentation of the quinolines, but greater selectivity in the pyrimidines. Since the data refer to the overall reactions of eq 1 and 2, they cannot be interpreted as simply reflecting selectivity in the initial hydrogen transfer. They reveal, however, considerable variation in these reactions as a function of specific heteroaromatic system, and work is now in progress to clarify the source of this variation.

Substitution pattern	Pyrimidines ¹			Quinolines ²		
	Compound	Rel. ϕ_2	Rel. ϕ_2/H	Compound	Rel. ϕ_8	Rel. ϕ_8/H
Tertiary		2.6	7.7	7a	0.55	1.7
Secondary	1b	2.0	2.9	7b	1.4	2.1
Primary	1c	1.0	1.0	7c	1.0	1.0

Table I. Relative quantum yields for fragmentation of 1a-c and 7a-c

¹ In acetone. ² In benzene.

Acknowledgment. We thank the National Science Foundation for support of this research and the Norman and Rosita Winston Foundation for a fellowship to S. P.

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(Received in USA 9 September 1988)