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Synthesis of a Highly Reactive Heterocyclic Reactant and Its Unusual Photochemistry; Mechanistic and Exploratory Organic Photochemistry[1,2]

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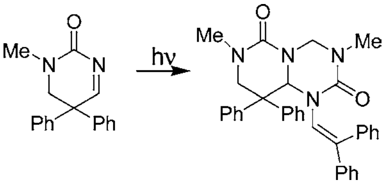
ABSTRACT



A unique new set of reactions has been observed in heterocyclic photochemistry. 2-Methyl-4,4-diphenyl-3,4-dihydropyrimidin-1(2*H*)-one has been synthesized and its photochemistry investigated. This compound has been found to lead to a rearranged, dimeric product arising from a unique bond-scission process.

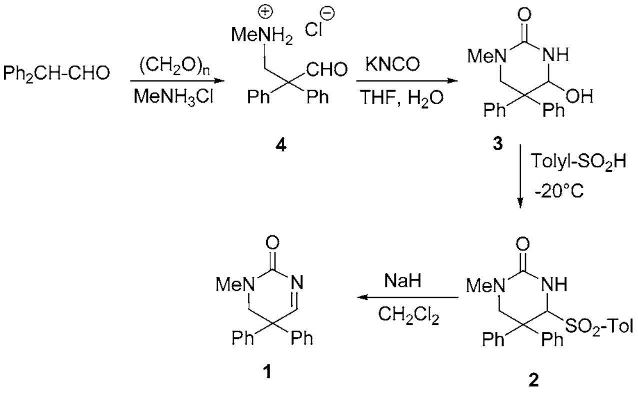
We recently began a study of heterocyclic analogues of carbocyclic photochemical reactants. The aim was to determine whether parallel reactivity was observed, and also the use of heterocycles promised to provide better substrates for host−guest chemistry as a consequence of enhanced hydrogen bonding.

The first heterocycle selected was the dihydropyrimidin-one **1**. The precursor sulfone **2** was obtained as outlined in Scheme 1. Treatment with sodium hydride then afforded the desired nitrogen enone analogue **1**.

However, this compound proved to be remarkably reactive toward even weak nucleophiles. For example, with water, or exposure to the atmosphere, it rapidly formed hydroxy compound **3** and, additionally, dimeric ether **5**.[3] This is depicted in eq 1. The evidence is that there is initial formation of the hydroxy heterocycle **3**, which then undergoes Michael addition to highly reactive aza-enone **1**.

Hence, our study of the photochemistry of aza-enone **1** was carried out with thorough purging with nitrogen in a semimicro immersion apparatus and with a copper sulfate filter. This photolysis (benzene, 10 h) led to a single

Scheme 1. Synthesis of Dihydropyrimidin-one **1**



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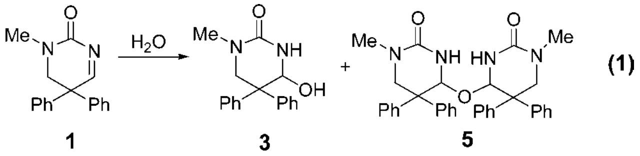
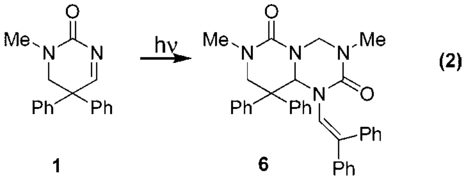
(1) This is publication number 273 of our General Series.

(2) For publication number 272, see: Zimmerman, H. E. The Quantitative Cavity Concept in Crystal Lattice Organic Photochemistry; Mechanistic and Exploratory Organic Photochemistry. In *CRC Handbook of Photochemistry and Photobiology*; Horspool, W., Ed.; CRC, Inc.: Boca Raton, FL, 2004, Chapter 75.

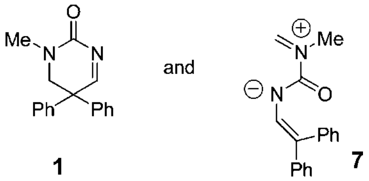
10.1021/ol048438h CCC: $27.50



photoproduct whose structure was established by NMR and X-ray analyses to be that of compound **6**. Note eq 2.



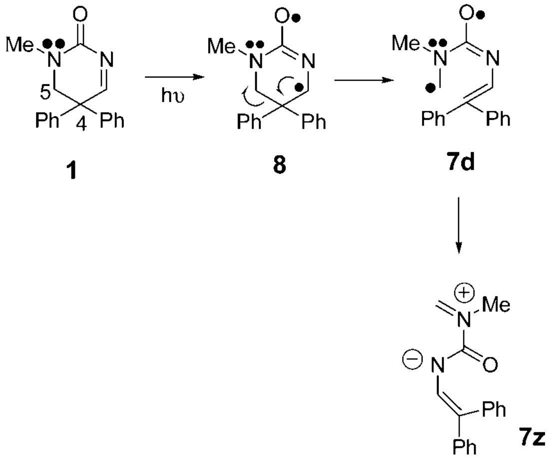
Consideration of the photoproduct structure, together with the known electrophilic reactivity of aza-enone **1**, suggested that this product arises from two fragments: reactant **1** and zwitterion **7**. Hence, the photochemistry must initially lead to this zwitterion. Further insight came from unpublished heterocyclic photochemistry in our hands,[4] which suggests a general tendency for fission of bond 4−5 in heterocycles of this type.



The mechanism for formation of **7** is thus suggested in Scheme 2. The reaction is characteristic of a singlet process.[4] Thus, species **7z** and **7d** are both singlets. However, the reaction begins on the singlet (i.e., S_1) hypersurface. Radiationless decay to S_0 seems likely to occur via a conical intersection or avoided crossing at this point, and this is being explored computationally.

At this point, our computations[5] utilizing CASSCF and natural orbital analysis suggest that S_1 species **7d** is best described as a singlet diradical, while **7z** is an S_0 zwitterion.

Scheme 2. Photochemical Mechanism



A further point is that this type of photochemical reactivity arises as a consequence of stabilization of the valence at C-5 by the adjacent nitrogen lone pair. This has analogy where C-5 is substituted by other stabilizing substituents.[6]

Acknowledgment. Support of this research by the National Science Foundation is gratefully acknowledged with special appreciation for its support of basic research. Additionally, we acknowledge initial efforts by Dr. Vladimir Tyurin. Finally, we dedicate this paper to Prof. Nikolai Zefirov on the occasion of his 70th birthday.

Supporting Information Available: Experimental details, X-ray data, and computational details. This material is available free of charge via the Internet at http://pubs.acs.org.

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[3] Compounds **3** and **5** were characterized by NMR and high-resolution MS. The sulfone **2** was characterized by NMR and elemental analysis.

[4] Studies with Dr. Oleg Mitkin to be published.

[5] Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Zakrzewski, V. G.; Montgomery, J. A., Jr.; Stratmann, R. E.; Burant, J. C.; Dapprich, S.; Millam, J. M.; Daniels, A. D.; Kudin, K. N.; Strain, M. C.; Farkas, O.; Tomasi, J.; Barone, V.; Cossi, M.; Cammi, R.; Mennucci, B.; Pomelli, C.; Adamo, C.; Clifford, S.; Ochterski, J.; Petersson, G. A.; Ayala, P. Y.; Cui, Q.; Morokuma, K.; Malick, D. K.; Rabuck, A. D.; Raghavachari, K.; Foresman, J. B.; Cioslowski, J.; Ortiz, J. V.; Stefanov, B. B.; Liu, G.; Liashenko, A.; Piskorz, P.; Komaromi, I.; Gomperts, R.; Martin, R. L.; Fox, D. J.; Keith, T.; Al-Laham, M. A.; Peng, C. Y.; Nanayakkara, A.; Gonzalez, C.; Challacombe, M.; Gill, P. M. W.; Johnson, B. G.; Chen, W.; Wong, M. W.; Andres, J. L.; Head-Gordon, M.; Replogle, E. S.; Pople, J. A. *Gaussian 98*, revision A.9; Gaussian, Inc.: Pittsburgh, PA, 1998.

[6] (a) Zimmerman, H. E.; Solomon, R. D. *J. Am. Chem. Soc.* **1986**, *108*, 6276−6289. (b) Note also ref 7.

[7] Canovas, A.; Fonrodona, J.; Bonet, J.-J.; Brianso, M. C.; Brianso, J. L. *Helv. Chim. Acta* **1980**, *63*, 2380−2389.