Richter

Iminium and Pyridinium Photochemistry

7/13/05
Group Meeting

Leader in the Field: **Patrick Mariano**

Born: 1942
BS: Fairleigh Dickinson University (1964)
Ph.D.: University of Wisconsin (H. Zimmerman - 1969)
Postdoc: Yale (H. Wasserman - 1970)
University of Texas (Austin): 1971 - 1980
University of Maryland: 1980 - 1999
University of New Mexico: 2000 - present.

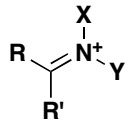
Disclaimers:

1. Most reactions were pulled either from reviews or journals like *Tetrahedron Letters* where reporting yields are not required therefore many yields are not given.
2. Most reactions had little mechanistic analysis associated with the report.

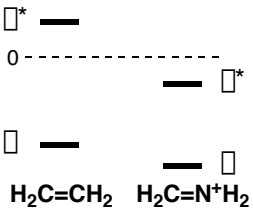
Essentials of Imminium Photochemistry:

Mariano, P. S. *Tetrahedron*. **1983**, *39*, 3845.

1. Exists in the structure with a full double bond and positive charge on nitrogen. Isoelectronic with simple olefins.



2. Static/planar structure with high rotational barriers. Can be lowered if conjugated to systems capable of stabilizing positive charges. Therefore little isomerization observed.
3. Only one photochemical transition possible: $\pi - \pi^*$. Occurs in the UV and visible regions (similar to olefins).
4. Pyridiniums and phenyl substituted iminiums have long-lived singlet excited states.
5. HOMO and LUMO π-orbitals much lower than the corresponding olefins.



6. Ground state reactions observed: nucleophilic attack or deprotonation adjacent to the nitrogen atom.
7. Excited state reactions observed: cis-trans isomerization (C=C not C=N), electrocyclizations, and cycloadditions. Note: Due to the increased electron density on carbon, nucleophilic additions should not be possible.
8. Low LUMO allows easy single-electron reduction to form α-amino radicals.
9. Great receptors in SET processes. Unique reactivity available for such excited states (depending on ionization energies and electron affinities:

$$A^* + B \longrightarrow A^{\bullet -}B^{\bullet +}$$

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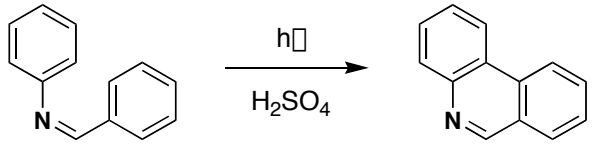
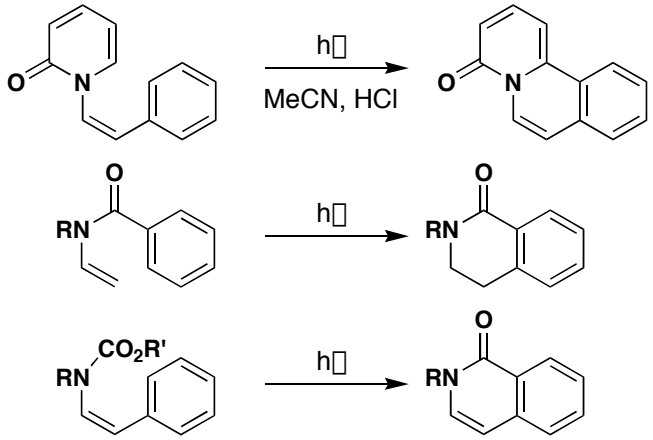
Cyclizations and Dimerizations:

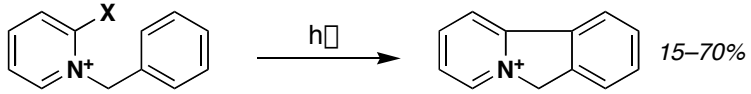
1. Mariano, P. S. *Tetrahedron.* **1983**, *39*, 3845.



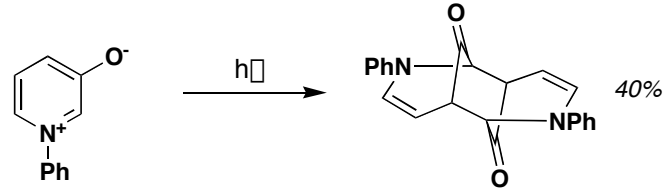
2. Mariano, P. S. *J. Org. Chem.* **1977**, *42*, 1122.



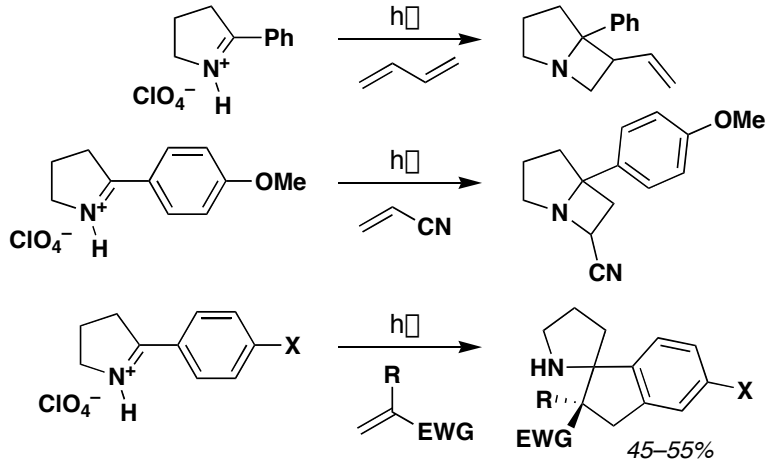
3. Bradsher, C. K. *Tetrahedron Lett.* **1966**, 3341.; Lyle, R. E. *J. Org. Chem.* **1973**, *38*, 2351.; Katritzky, A. R. *Heterocycles.* **1987**, *26*, 2963. Park, Y.-T. *J. Heterocyclic Chem.* **1991**, *28*, 1083.



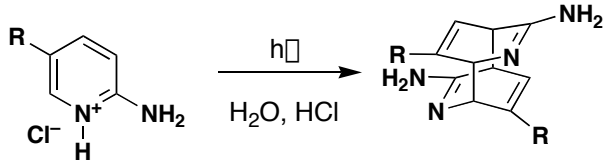
4. Katritzky, A. R. *J. Chem. Soc. Perkin Trans. 1.* **1979**, 2535.



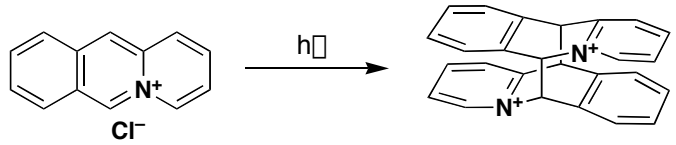
5. Mariano, P. S. *Tetrahedron.* **1983**, *39*, 3845. *(Sole Example)*



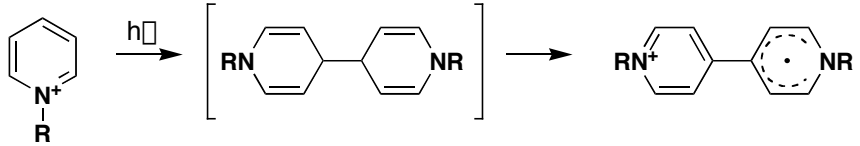
6. Taylor, E. C. *J. Am. Chem. Soc.* **1961**, *83*, 4484
Taylor, E. C. *J. Am. Chem. Soc.* **1963**, *85*, 776.



7. Beavers, L. E. *J. Org. Chem.* **1957**, *22*, 1740.



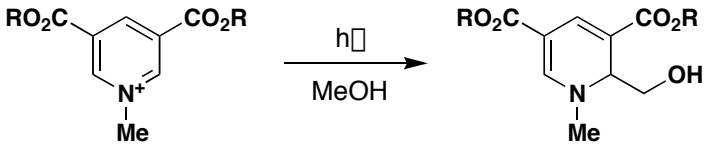
8. Mariano, P. S. *Tetrahedron.* **1983**, *39*, 3845.



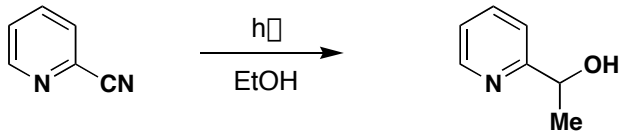
Iminium and Pyridinium Photochemistry

Additions of Alcochols and Ethers:

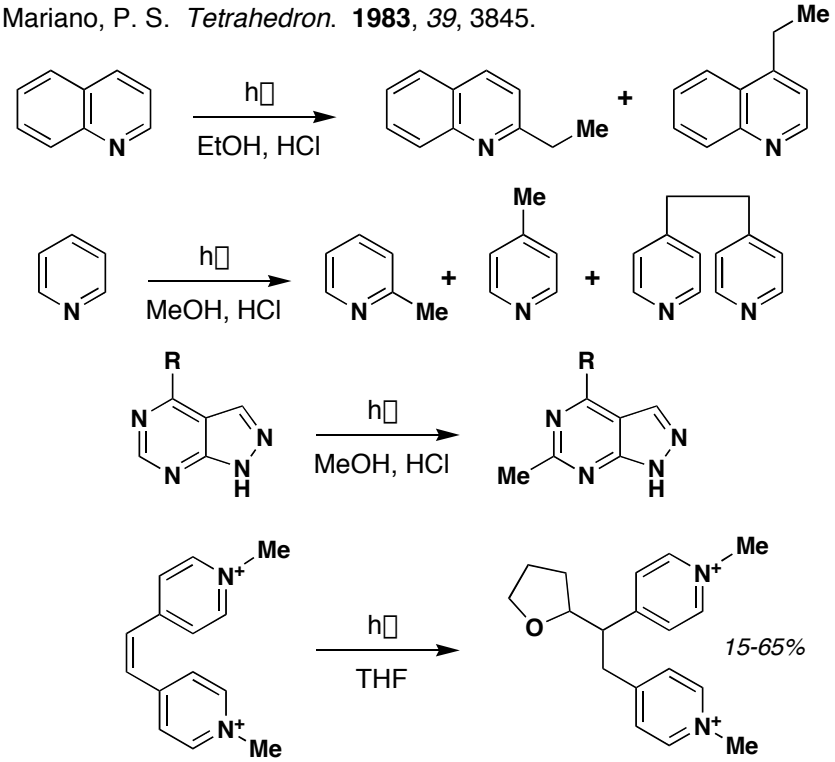
1. Mariano, P. S. *Tetrahedron*. **1983**, *39*, 3845
   Katritzky, A. R. *Heterocycles*. **1987**, *26*, 2963.



2. Mariano, P. S. *Tetrahedron*. **1983**, *39*, 3845.

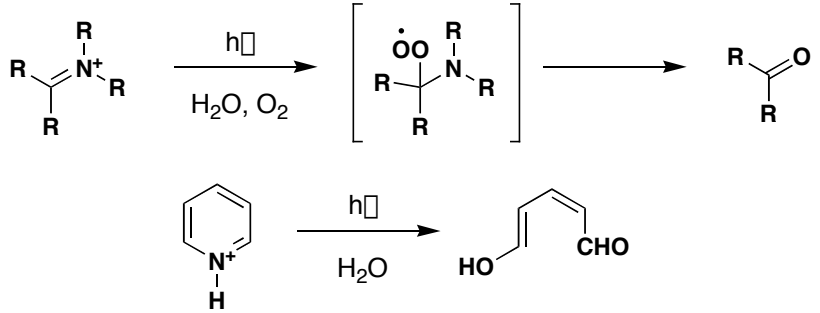


3. Mariano, P. S. *Tetrahedron*. **1983**, *39*, 3845.



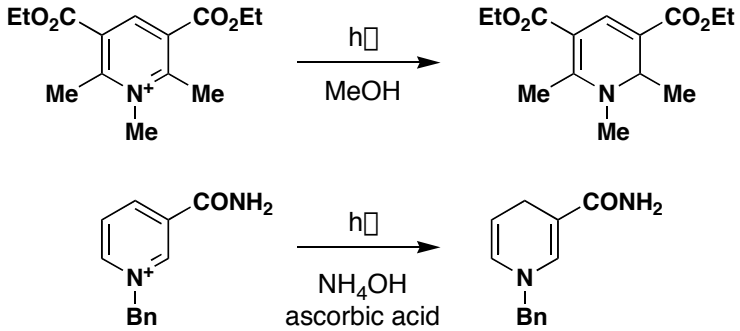
Hydrolyses:

1. Mariano, P. S. *Tetrahedron*. **1983**, *83*, 3845.

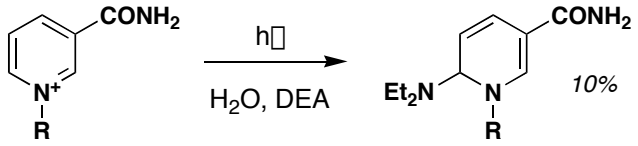


Reductions:

1. Mariano, P. S. *Tetrahedron*. **1983**, *83*, 3845.



2. Matsuo, T. *Tetrahedron Lett.* **1975**, *16*, 1389.



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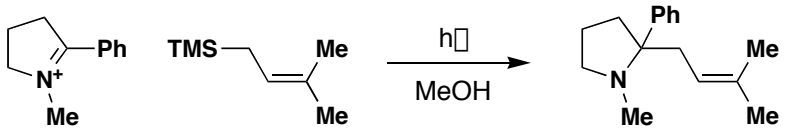
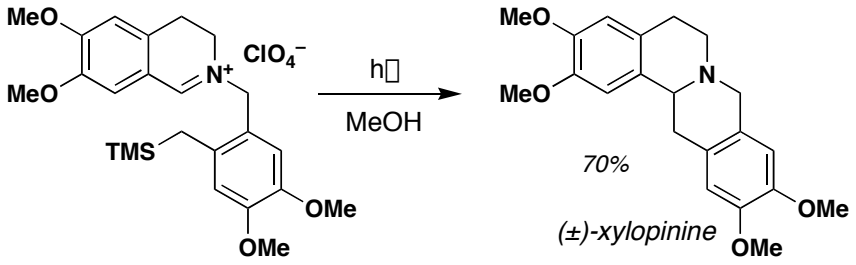
Cyclizations with Allylic Silanes:

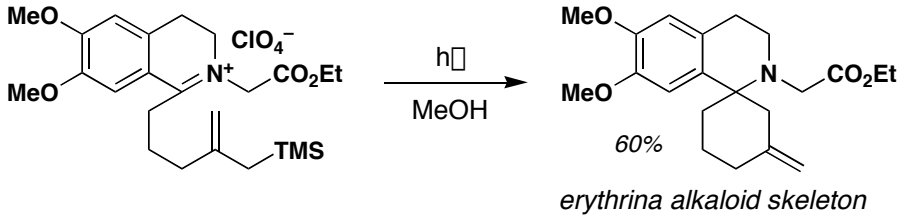
1. Mariano, P. S. *J. Org. Chem.* **1984**, *49*, 213.



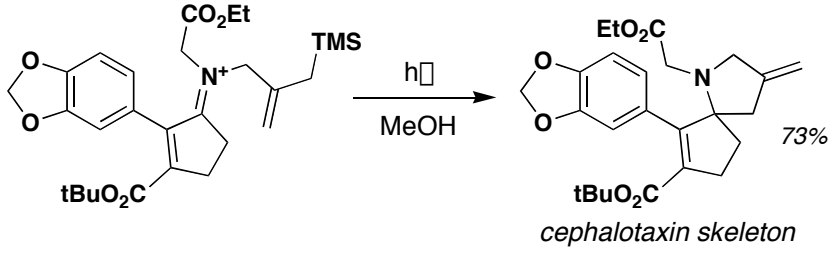
2. Mariano, P. S. *J. Org. Chem.* **1987**, *52*, 704.



3. Mariano, P. S. *J. Org. Chem.* **1987**, *52*, 1478
   Mariano, P. S. *Tetrahedron Lett.* **1985**, *26*, 5867.

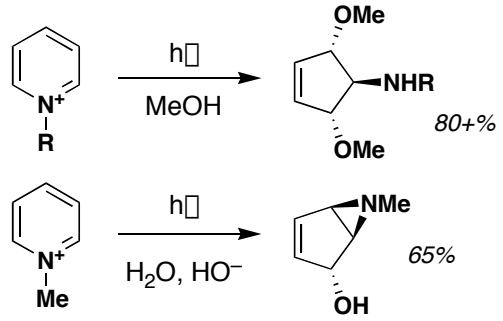


4. Mariano, P. S. *J. Org. Chem.* **1984**, *49*, 228.

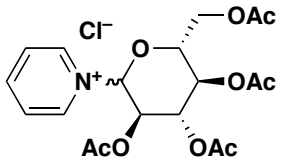


Pyridinium Photoadditions:

1. Mariano, P. S. *Acc. Chem. Res.* **1983**, *16*, 130
   Mariano, P. S. *Tetrahedron*. **1983**, *39*, 3845.



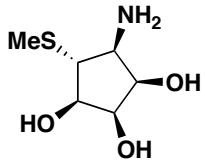
2. Burger, U. *Tetrahedron*. **2000**, *56*, 43111.



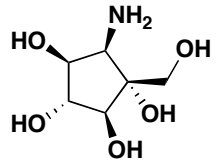
Makes 2 diastereomers which are separable by crystallization. *85%*

3. Syntheses utilizing reaction (Mariano)

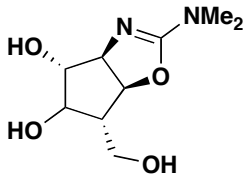
– Mannostatin A
(*J. Org. Chem.* **1998**, *63*, 6072)



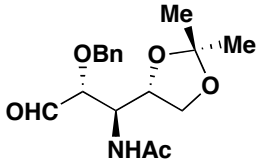
– Trehazolamine
(*J. Org. Chem.* **2005**, *70*, 5618)



– Allosamizoline
(*Tetrahedron Lett.* **2001**, *42*, 4755)



– Protected Pentoses
(*J. Org. Chem.* **2002**, *67*, 3525).



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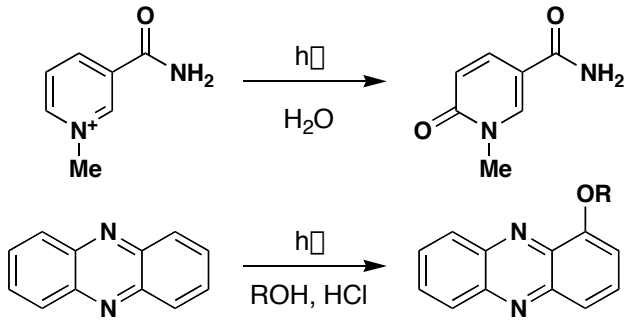
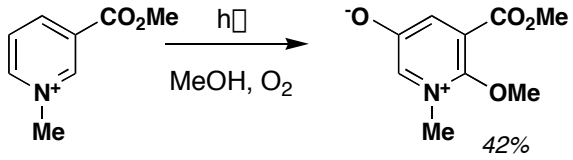
Oxidations:

1. Mariano, P. S. *Tetrahedron.* **1983**, *39*, 3845.

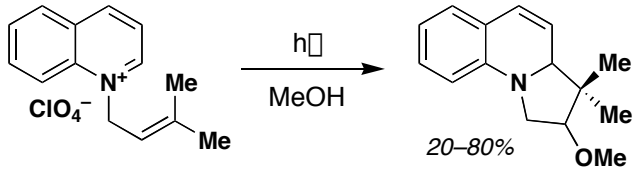


2. Sugimori, A. *Chem. Lett.* **1992**, 715.

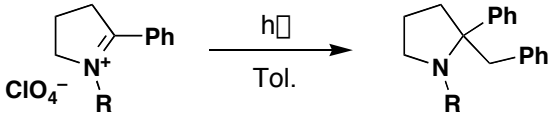


Miscellaneous Reactions:

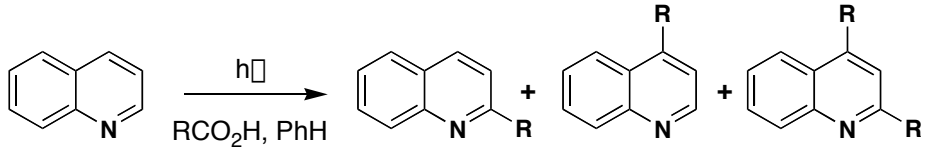
1. Mariano, P. S. *Tetrahedron Lett.* **1982**, *23*, 919.



2. Mariano, P. S. *Acc. Chem. Res.* **1983**, *16*, 130.

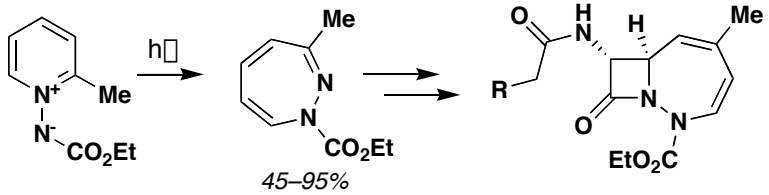


3. Mariano, P. S. *Tetrahedron.* **1983**, *39*, 3845.

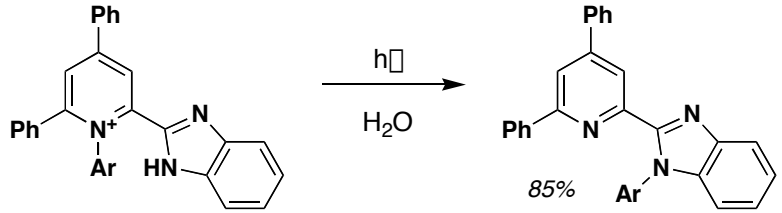


R			
Me	40%	20%	5%
Et	40%	–	10%
iPr	35%	27%	9%

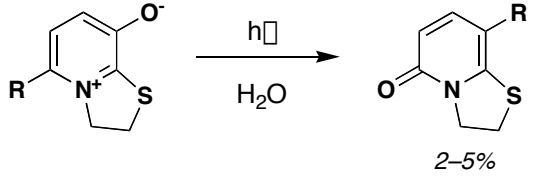
4. Streith, J. *Heterocycles.* **1977**, *6*, 1513
   Streith, J. *Heterocycles.* **1977**, *6*, 2021.



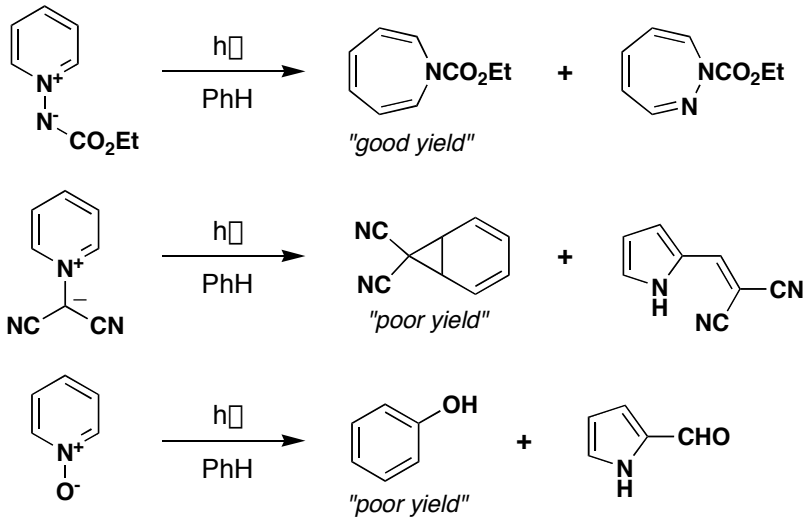
5. Katritzky, A. R. *Tetrahedron Lett.* **1982**, *23*, 1241.



6. Undheim, K. *J. Chem. Soc. Perkin Trans. 1.* **1979**, 1150.



7. Streith, J. *Chem. Ber.* **1987**, *120*, 355.



8. Katritzky, A. R. *Heterocycles*. **1976**, *5*, 71.