



### 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:

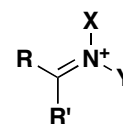
1. Most reactions were pulled either from reviews or journals like *Tetrahedron Letters* where reporting yields are not required therefore many yields are not given.

2. Most reactions had little mechanistic analysis associated with the report.

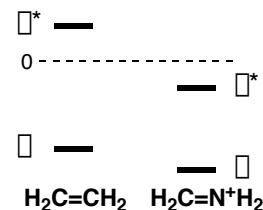
#### Essentials of Iminium Photochemistry:

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

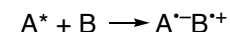
1. Exists in the structure with a full double bond and positive charge on nitrogen. Isoelectronic with simple olefins.



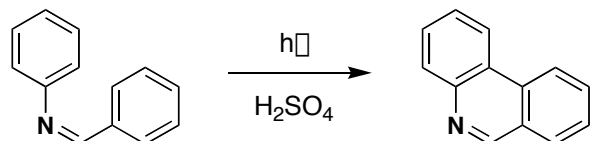
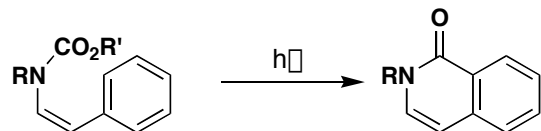
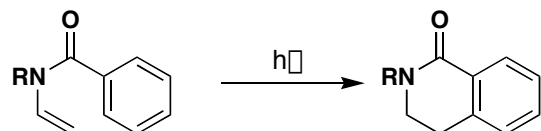
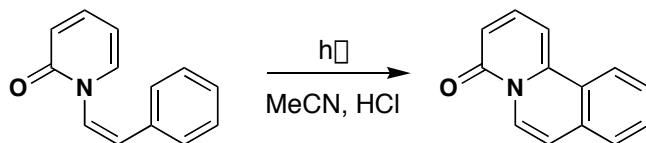
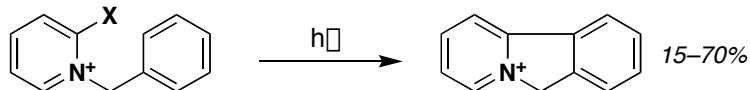
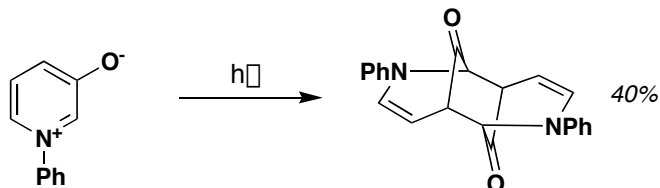
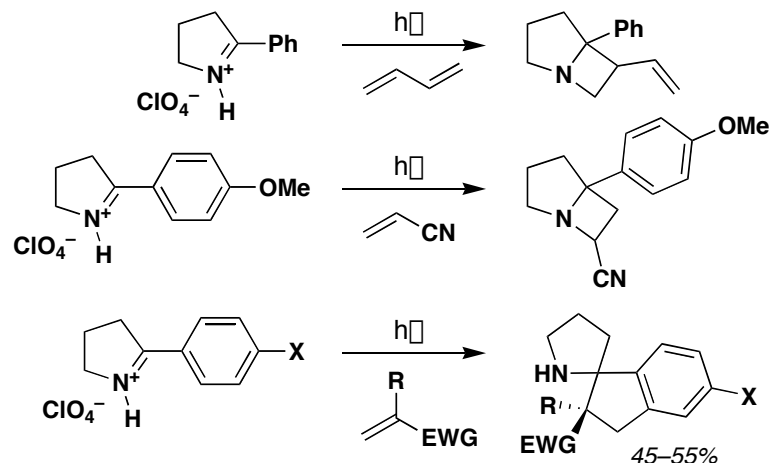
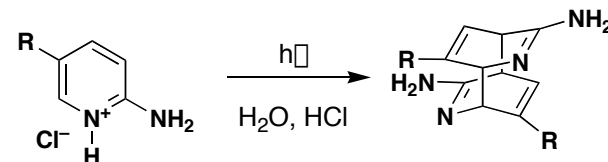
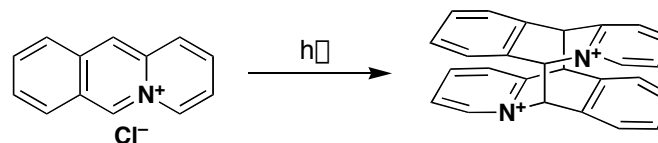
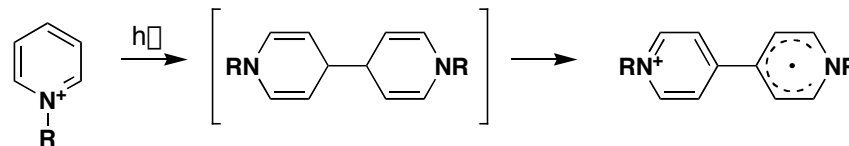
2. Static/planar structure with high rotational barriers. Can be lowered if conjugated to systems capable of stabilizing positive charges. Therefore little isomerization observed.
3. Only one photochemical transition possible:  $\pi \rightarrow \pi^*$ . Occurs in the UV and visible regions (similar to olefins).
4. Pyridiniums and phenyl substituted iminiums have long-lived singlet excited states.
5. HOMO and LUMO  $\pi$ -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  $\pi$ -amino radicals.
9. Great receptors in SET processes. Unique reactivity available for such excited states (depending on ionization energies and electron affinities:

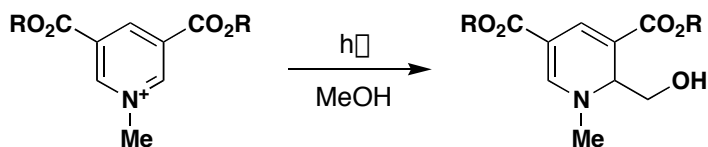


## Cyclizations and Dimerizations:

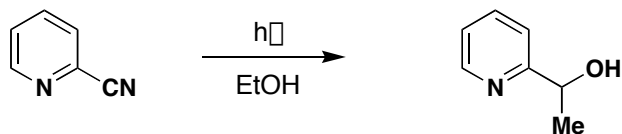
1. Mariano, P. S. *Tetrahedron*. **1983**, *39*, 3845.2. Mariano, P. S. *J. Org. Chem.* **1977**, *42*, 1122.3. Bradsher, C. K. *Tetrahedron Lett.* **1966**, 3341.; Lyle, R. E. *J. Org. Chem.* **1973**, *38*, 2351.; Katritzky, A. R. *Heterocycles*. **1987**, *26*, 2963.  
Park, Y.-T. *J. Heterocyclic 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.

**Additions of Alcohols and Ethers:**

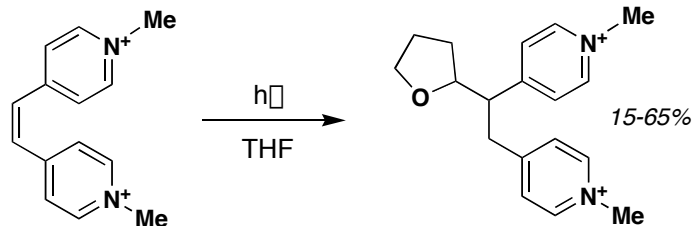
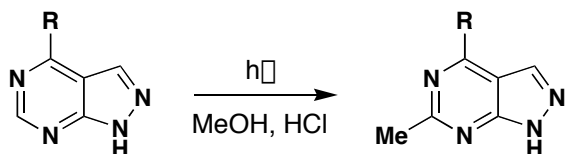
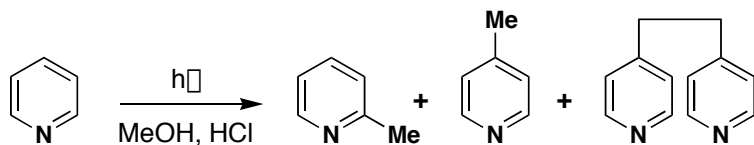
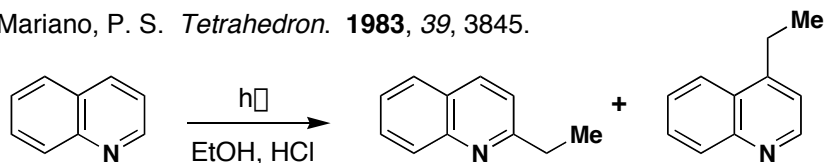
1. Mariano, P. S. *Tetrahedron*. **1983**, *39*, 3845  
Katritzky, A. R. *Heterocycles*. **1987**, *26*, 2963.



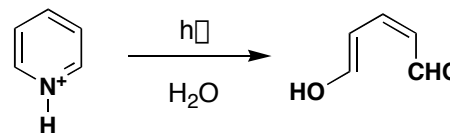
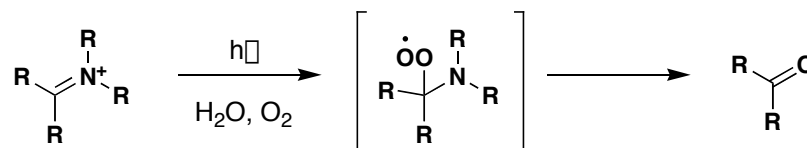
2. Mariano, P. S. *Tetrahedron*. **1983**, *39*, 3845.



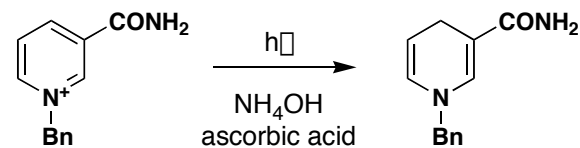
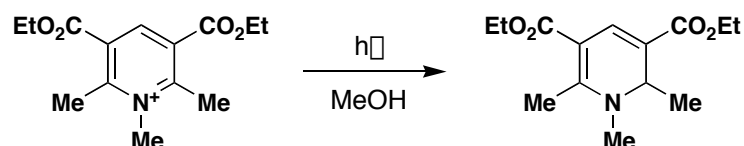
3. Mariano, P. S. *Tetrahedron*. **1983**, *39*, 3845.

**Hydrolyses:**

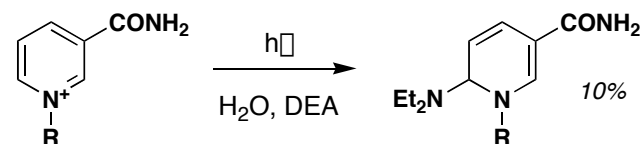
1. Mariano, P. S. *Tetrahedron*. **1983**, *83*, 3845.

**Reductions:**

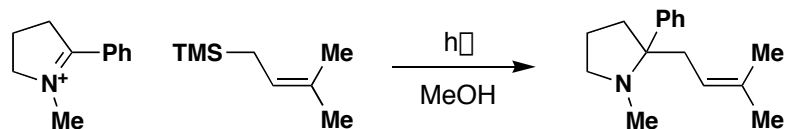
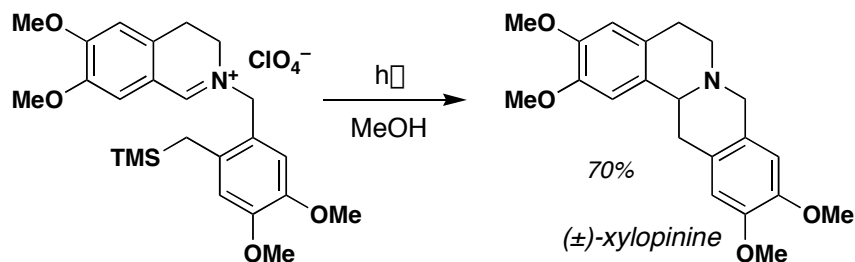
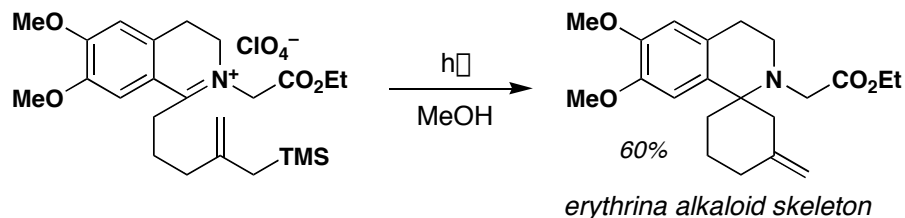
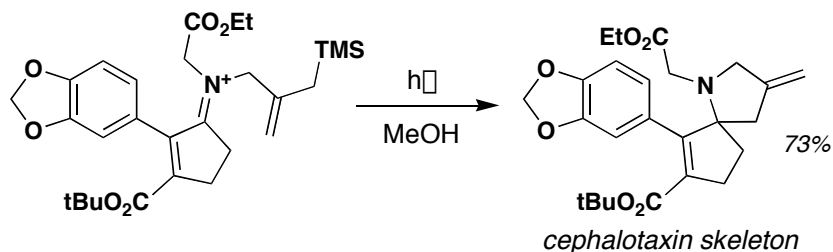
1. Mariano, P. S. *Tetrahedron*. **1983**, *83*, 3845.



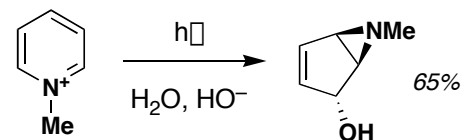
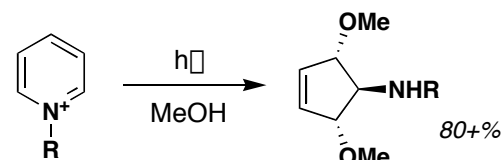
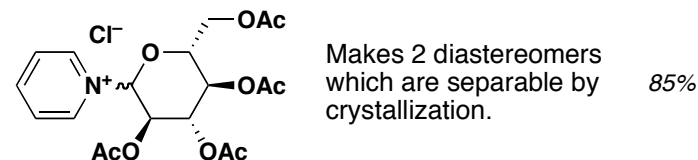
2. Matsuo, T. *Tetrahedron Lett.* **1975**, *16*, 1389.



## Cyclizations with Allylic Silanes:

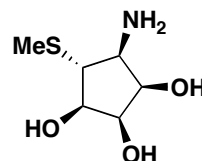
1. Mariano, P. S. *J. Org. Chem.* **1984**, *49*, 213.2. Mariano, P. S. *J. Org. Chem.* **1987**, *52*, 704.3. Mariano, P. S. *J. Org. Chem.* **1987**, *52*, 1478Mariano, P. S. *Tetrahedron Lett.* **1985**, *26*, 5867.4. Mariano, P. S. *J. Org. Chem.* **1984**, *49*, 228.

## Pyridinium Photoadditions:

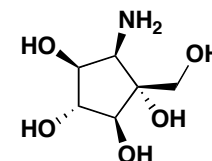
1. Mariano, P. S. *Acc. Chem. Res.* **1983**, *16*, 130Mariano, P. S. *Tetrahedron.* **1983**, *39*, 3845.2. Burger, U. *Tetrahedron.* **2000**, *56*, 43111.

3. Syntheses utilizing reaction (Mariano)

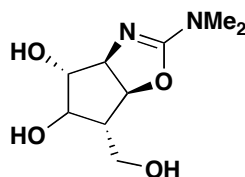
– Mannostatin A

*(J. Org. Chem.* **1998**, *63*, 6072)

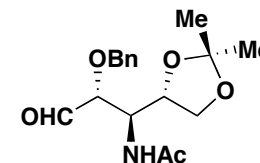
– Trehazolamine

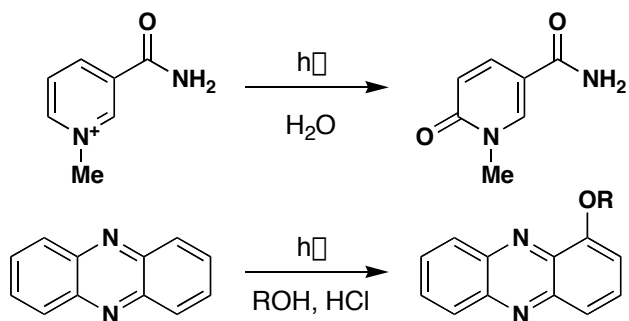
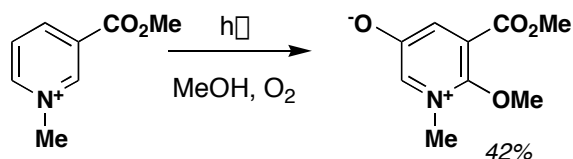
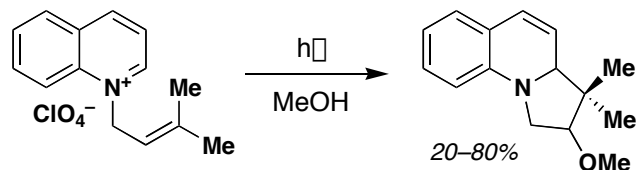
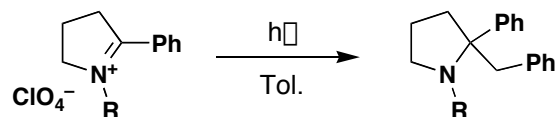
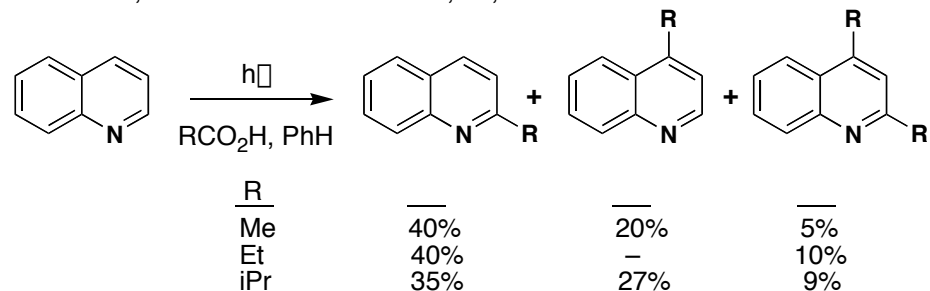
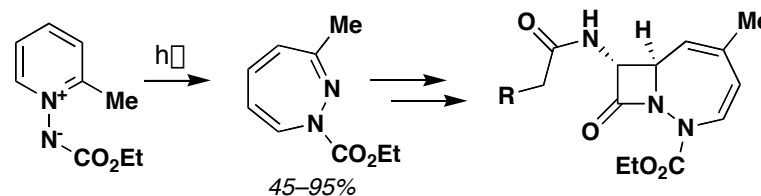
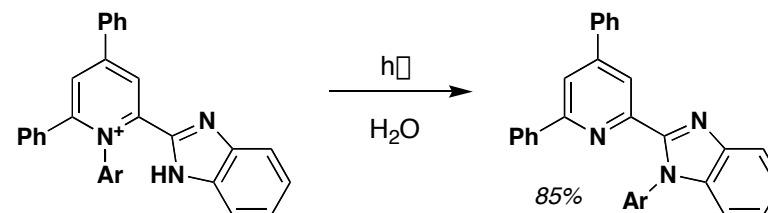
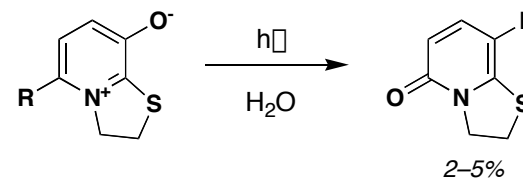
*(J. Org. Chem.* **2005**, *70*, 5618)

– Allosamizoline

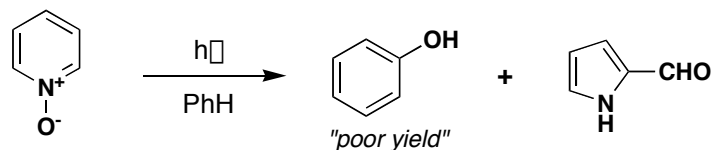
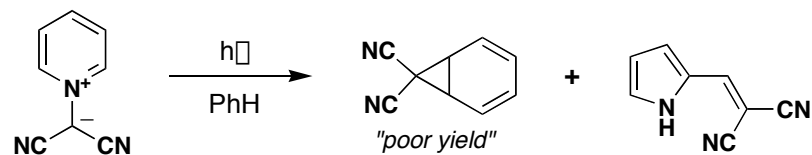
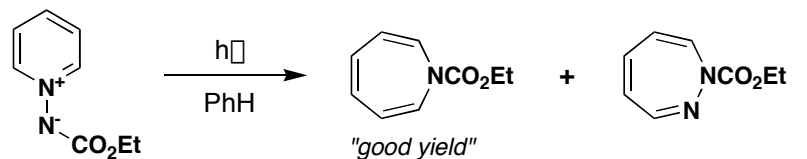
*(Tetrahedron Lett.* **2001**, *42*, 4755)

– Protected Pentoses

*(J. Org. Chem.* **2002**, *67*, 3525).

**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*, 3845.4. 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.

