APPLICATION OF KLOPMAN'S POLYELECTRONIC PERTURBATION APPROACH TO ELECTROPHILIC SUBSTITUTION ON PYRIDINES AND THEIR N-OXIDES

Gerritt P. Bean

Chemistry Dept., Western Illinois Univ., Macomb, IL 61455.
Work done at WIU.

The application of Klopman's "polyelectronic *perturbation" method (J. Am. Chem. Soc.*, 90, *222 (1968)*) to the predication of orientation of electrophilic substitution on aromatic compounds considers the orbital energy difference between the electrophile and the occupied pi electron orbitals of the aromatic system. When this difference is large (the electrophile is "hard" according to Pearson's HSAB theory) the reaction is "charge-controlled" and orientation depends upon the total pi electron charge density. If the difference is small (a "soft" electrophile), the electron density of the HOMO is dominant and the reaction is "frontier-controlled". The necessary orbital energies and coefficients of the wave functions were obtained by the INDO method for a series of pyridines, their N-oxides and the corresponding conjugate acids. The function

$$\sum_{i=1}^{n} 2 (c_{ij})^2 / (E_i - E_E)$$

for position *i* was calculated over the *n* occupied pi orbitals for the values of E_E ranging from 1 to 8 e.v.; corresponding to a range from soft to hard for the HSAB behavior of the electrophile. The results are in good agreement with the known substitution pattern of these compounds.

FUSED RING 3-(3-PYRIDYL)SYDNONES

Steven J. Hodson, Kenneth Turnbull and Geoffrey Waldo

Chemistry Department, Wright State University, Dayton, Ohio 45435

3-(3-Pyridyl)sydnone, the first 3-heteroaryl sydnone (J.M.Tien and I.M.Hunsberger, J.Am.Chem.Soc.,77,6604(1955)), is photochromic in the solid state; turning from colourless to blue on exposure to direct sunlight. Storage overnight in the dark or brief heating regenerate the colourless form. The structural requirements for this property have not been elucidated. One suggestion is that coplanarity, in the crystal, between the aryl and sydnone rings is a requirement for pyridyl sydnone photochromism.

The present study was initiated to examine the validity, if any, of this premise *via* the synthesis of fused ring 3-(3-pyridyl)sydnones. Routes to such compounds, along with model studies conducted on their 3-phenyl analogues, will be presented.

FACILE SYNTHESIS OF N^4-MONO AND N^4,N^4-DISUBSTITUTED 2-ACETYLPYRIDINE THIOSEMICARBAZONES VIA TRANSAMINATION

D. L. Klayman and A. J. Lin

Division of Experimental Therapeutics, Walter Reed Army Institute of Research, Washington D.C. 20012

The broad spectrum and profound biological activities of α-(N)-heterocyclic carboxaldehyde thiosemicarbazones have led medicinal chemists to search for more potent agents of this class. Many members of a new series of N^4-mono and N^4,N^4-disubstituted 2-acetylpyridine