

[Heterocycles, 43, 1185-1188 (1996)]

[Lab. of General Chemistry]

**Dye-Sensitized Photooxidation of 2,4-Disubstituted Imidazoles:  
The Formation of Isomeric Imidazolinones.**

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Irradiation of 2,4-disubstituted imidazoles in MeOH with a 100 W high-pressure mercury lamp through a Pyrex filter under oxygen using hematoporphyrin as a sensitizer resulted in the formation of isomeric 3-imidazolin-5-ones **1** and 2-imidazolin-4-ones **2**. The uv and <sup>1</sup>H-nmr spectral data can be used to distinguish clearly between isomeric **1** and **2**.

[Spectrochim. Acta, 52A, 297-303 (1996)]

[Lab. of Instrumental Center]

**X-Ray and Vibrational Studies of Methyl (N-Benzoylaminoxy)acetate.**

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The crystal and molecular structures of methyl (N-benzoylaminoxy)acetate (MBAOA) have been determined by X-ray diffraction. In the crystal the amide C=O of one molecule is hydrogen-bonded to the amide NH of an adjacent molecule. The ester C=O bond is cis-oriented to the C-O(aminoxy) bond. The IR and Raman spectra of MBAOA and its deuterated analogs have been measured in the solid state and in solution. In polar solvents the ester  $\nu$ C=O was observed as a doublet in the IR spectra, suggesting the existence of the two conformers. The X-ray analysis and the IR and Raman data indicate that the conformer with the higher frequency of the ester  $\nu$ C=O in solution has the ester C=O bond cis-oriented to the C-O(aminoxy) bond.

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[Lab. of Manufacturing Pharmacy]

**Novel Cycloaddition of 2-Alkyl-3-benzoyl-2-thianaphthalenes.**

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Deprotonation of 2-alkyl-3-aryoyl-2-thiochromenium tetrafluoroborates **1** with 2 equiv. of triethylamine in ethanol afforded the unexpected benzothiopyran derivatives **2** along with ethyl benzoate derivatives **3**. The structure of compounds **2** is confirmed by X-ray crystallography of the benzoyl derivative **2a**. The X-ray structure of compound **2a** shows that the S-methyl group is located just above the benzene ring of the benzoyl group and causes an upfield shift of the S-methyl signal in the <sup>1</sup>H NMR spectrum compared to an ordinary S-methyl group. The relevant bond distances between the S-methyl hydrogens and the Csp<sup>2</sup> carbons of the benzene ring suggest the presence of some attractive force such as CH- $\pi$  interaction between the benzene ring and the methyl hydrogens. On the basis of several experimental evidence, a possible mechanism for the formation of products **2** and **3** is proposed.