



Reactive Intermediates in the Photolysis of Furan, Thiophene and Pyrrole:
The Dewar and the Ring Contraction Forms.

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Five member aromatic heterocycles have been known to undergo scrambling of the ring atoms upon photolysis. These reactions are characterized by their selectivity and several mechanisms have been proposed involving the intermediacy of a variety of isomeric structures, in particular, the Dewar () and the ring contracted () forms, however, evidence for their formation is scarce.

We have carried out a series of low temperature argon-matrix photolysis and solution-phase trapping experiments on the parent furan, thiophene and pyrrole in order to obtain evidence on the formation of these reaction intermediates.

Low temperature argon-matrix photolysis of furan, thiophene and pyrrole resulted in the isolation and FTIR detection of a series of primary photolysis products among which the Dewar and the ring contracted form could be identified. Subsequent longer wavelength photolysis causes the Dewar furan to isomerize to the ring contracted cyclopropene-3-carbaldehyde which was itself photostable under matrix conditions. In contrast both Dewar thiophene and cyclopropene-3-carbothialdehyde as well as the pyrrole isomers regenerated the parent thiophene and pyrrole on photolysis.

In liquid-phase photolysis irradiation of furan resulted in the isolation and IR, ^1H and ^{13}C NMR and mass spectral characterization of the Diels-Alder adducts of cyclopropene-3-carbaldehyde and 2,3-butadienal. No Dewar furan Diels-Alder adduct was formed under these conditions.

Irradiation of thiophene either in furan solution or in an ether glass at -170°C followed by addition of furan in the dark, afforded the two isomeric Diels-Alder

adducts of furan to Dewar thiophene which were also characterized by IR, ^1H and ^{13}C NMR and mass spectra.

Both, trapping and argon-matrix experiments on different deuterium-substituted thiophenes indicated complete scrambling of the deuterium in the Dewar thiophene.

Ab initio m.o. calculations have been carried out using a 6-31G basis set with polarization functions on the heteroatoms on furan, thiophene, pyrrole and benzene and their valence bond and ring contracted isomers. The computed order of stabilities will be presented.