THE DEWAR FORMS OF FURAN, THIOPHENE AND PYRROLE

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Low temperature Ar matrix photolysis of the parent aromatic form of the title compounds affords reactive intermediates which have been identified by FTIR spectroscopy and assigned to the Dewar form. All three Dewar heterocycles exhibit uv absorption up to ∿330 nm in analogy with bicyclopentane also prepared by the Ar matrix photolysis of cyclopentadiene and undergo photolysis on irradiation: the Dewar thiophene probably to the thiophene, the Dewar furan to cyclopropene-3-carboxaldehyde, and the Dewar pyrrole to pyrrole. In the case of thiophene, the Dewar form could be trapped in the liquid phase photolysis by furan as two isomeric Diels-Alder adducts and their structure established on the basis of MS, FTIR and high resolution ^{1}H and ^{13}C NMR spectroscopic data. These same adducts were also obtained when the trapping was done after photolysis of thiophene in a frozen glass at -170°C demonstrating that the trapping process intercepts an intermediate which can be stored at -170°C and not a short lived excited state of thiophene.

Attempts to trap Dewar furan or Dewar pyrrole were unsuccessful.

Additional primary products identified by FTIR spectroscopy in the Ar matrix photolysis of thiophene at 8K were thio-2,3-butadienal, vinyl thioketene and cyclopropenyl-3-carbothioaldehyde.

Irradiation of neat liquid furan at room temperature yielded four furan Diels-Alder adducts: two isomeric forms of furan + cyclopropene-3-carboxaldehyde and two isomeric forms of 2,3-butadienal. The analogous primary photolysis products as mentioned above were detected in the low temperature photolysis of thiophene by FTIR spectroscopy but could not be trapped with furan in liquid photolysis.

Trapping experiments with 2-deutero thiophene in the liquid phase using furan as above yielded Diels-Alder adducts in which the deuterium was fully scrambled between the C_2 and C_3 atoms (50:50) of the Dewar thiophene ring. Similarly, with 2,2-dideutero thiophene the scrambling is also complete, however, the four possible isotopomers have not yet been resolved.

Scrambling experiments with 2-deutero furan in ethereal solution indicated the occurrence of scrambling in the furan-cyclopropene-3-carboxaldehyde which, however was incomplete.

Ab initio molecular orbital calculations have been carried out using 6-31G basis set with polarization functions on the heteroatoms on furan, thiophene, pyrrole, benzene, their Dewar forms and their other valence isomers. The Dewar forms have been found to be the lowest of the valence isomers in every case and they were found to lie 71-84 kcal/mole above the aromatic forms. The isomerization processes are currently under investigation.