Synthesis of Unusual Molecules by Flash Vacuum Pyrolysis of Heterocyclic Compounds

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The generation of several unstable molecules and reactive intermediates using a combination of flash vacuum pyrolysis and low temperature or matrix isolation of the products will be described.

Thus, diazacycloheptatetraenes are obtained via pyridylnitrenes by pyrolysis of tetrazolopyridines. Isoxazol-5(4H)-ones substituted in position 4 are useful starting materials for the preparation of acetylenes, isonitriles, fulminates, fulminic acid, isocyanoamines, ketenimines, and other compounds.

In contrast to the isoxazolones, furan-2(3H)-ones undergo extrusion of CO only, with the formation of acylallenes. In certain cases, 3-ethynylcoumarins are also formed.

Furan-2,3-diones extrude CO to give diacylketenes. The same type of reaction is observed with thiophen-2,3-diones, but the major product is now a thiet-2-one. Extensions of this reaction and the first isolation of a stable thietone will also be described.