Synthesis of New Heterocycles via Unsaturated Azides

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Classical syntheses of N-heterocycles using organic azides include 1,3-dipolar cycloadditions to yield 1,2,3-triazoles and intramolecular insertion reactions via short-lived nitrenes to give cyclic products, e.g. indoles. However, other reactions of azides, particularly of vinyl azides also offer effective routes to heterocycles. Thus, allenyl azides 2, which are easily accessible from propargyl azides 1 via [3,3] sigmatropic shift of the azido group or by prototropic (base-catalyzed) rearrangement, electrocyclize rapidly to produce triazafulvenes 3. These intermediates can be trapped by nucleophiles NuH to afford functionalized triazoles 4.[1] On photolysis, 2 leads to methylene-2H-azirines 5 which prove to be the first heterocyclic triafulvenes.[2] Other highly strained azirines like 6[3] and 7 are also available from vinyl azides. The spiro compound 7 can be cleaved to give unknown isocyanocyclopentadienes 8. Presently, we study the transformation of 1,4-diazo-1,3-butadienes 9 into compounds of type 10, which are converted to aromatic pyridazines and pyrimidines.[4] The chemistry of the first azidocyclopentadienes 11 is also investigated.