

Abstract

1,3-Dipolar cycloaddition reactions of N,N-cyclic azomethine imines and ynone, prepared from N-Boc L-alanine, were used in the synthesis of 5-oxo-6,7-dihydro-1*H*,5*H*-pyrazolo[1,2-*a*]pyrazoles with a combination of copper(I) iodide and Hünig's base as the catalyst. Reactions were regio- and stereoselective and gave the products in high yields. All products were obtained as pairs of diastereoisomers that were separated by preparative liquid chromatography. Structures of some products were determined by X-ray analysis and VCD spectroscopy. By comparing spectroscopic and optical properties of compounds, the structures of the rest of the products were determined as well. Reactions of other ynones with achiral N,N-cyclic azomethine imines were also performed with copper metal as a catalyst. Reactions were regioselective. Reaction rates were measured for different forms of copper(0). In one of the experiments, copper was removed from the reaction mixture by filtration and in the other, mercury was added to reaction mixture. From these experiments we concluded that copper metal acted as a source of a homotopic catalytic system. Our experiments were in line with formation of copper acetylide as the catalytic species in this reaction.

Ynones reacted with bicyclic azomethine imines at room temperature or at 80 °C to give diazacyclopenta[*cd*]indenes with moderate yields, representing the first examples of such a heterocyclic system. Reaction rates were measured for the reaction of azomethine imine **20a** with ynone **3d**. We concluded, that the reaction proceeds without any intermediates being formed (a concerted mechanism). Enthalpy, entropy and free energy of transition state were also calculated.

1,3-Dipolar cycloadditions of ynones were also performed with some other dipoles. Reaction proceeded with an azide, nitrile oxides and diazo esters. Thus, new five-membered heterocyclic compounds with amino acid residue were prepared. Nitrones and sydnones were less reactive towards ynones and no products of these reactions were isolated.

Reactions of N,N-cyclic azomethine imines with butenone gave products in the presence of strong acids. When TFA was used, mixtures of two diastereoisomers were isolated. *Para*-toluenesulfonic acid and (+)-10-camphorsulfonic acid only gave one isomer.

Keywords: ynones, azomethine imines, dipoles, 1,3-dipolar cycloadditions