Homoallenyl azines and proton sponges

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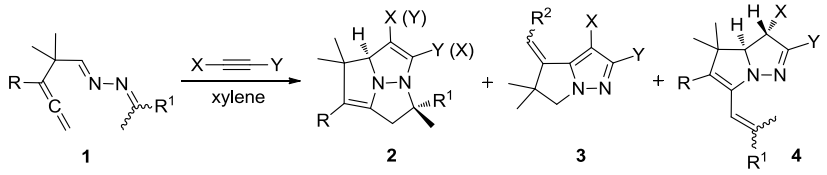
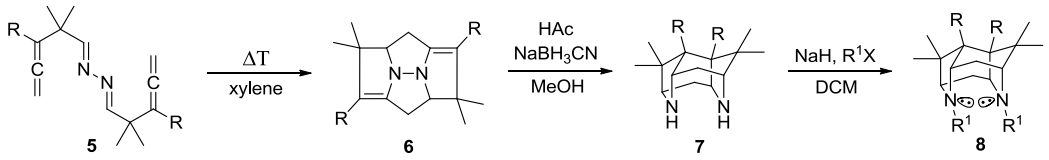
Allenyl synthon is nowadays used for the preparation of a large variety of organic compounds exhibiting various biological activities. Synthesis of non-symmetrical allenyl azines **1** and their chemical transformations are extensively studied at our laboratories. It was found that azines **1** reacted thermally with various dipolarophiles in combined intra-intermolecular criss-cross cycloaddition. The first project of my Thesis is based on the reactions of **1** with various alkynes in boiling xylene affording a mixture of three possible products. We isolated expected substituted 1,10-diazatricyclo[5.2.1^{4,7}.0^{1,10}]deca-2,6-dienes **2** but in some cases new pyrrolo[1,2-*b*]pyrazoles **3** and **4** were obtained as well. This reaction was found to be diastereoselective with high atom economy. The influence of dipolarophile nature as well as the substitution at **1** is discussed on the basis of the proposed mechanisms. It is worth noting that pyrrolo[1,2-*b*]pyrazoles might show interesting biological activity as their skeleton is very similar to that of *Withasomnine* alkaloid.



The second project deals with the preparation and basicity investigation of new structural types of proton sponges (PS). The general feature of all PS is the presence of two basic nitrogen centers in the molecule, which have an orientation that allows the uptake of one proton to yield a stabilized intramolecular hydrogen bond. Herein, we report a molecular framework design differing significantly from the traditional topology of proton sponges. We developed a suitable synthetic approach to the preparation of compounds **6** by intramolecular criss-cross cycloaddition reactions of symmetrical homoallenyl azines **5**. The acid-catalyzed rearrangement of cycloadducts **6** afforded bidentate caged secondary amines **7** in quantitative yields and following alkylation reactions led to air nonsensitive highly stable substituted diazatetracyclo[4.4.0.1^{3,10}.1^{5,8}]dodecanes **8** with rare alicyclic scaffolding. Their pK_{BH}+ values were determined by ^{1}H NMR transprotonation experiments as well as their sensitivity toward nucleophiles, acids and bases. The molecular structures of free base and monoprotonated form of **8** were proved by X-ray structure analysis.



References:

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