

SOME ANIONIC REACTIONS OF Δ^2 -PYRAZOLINES

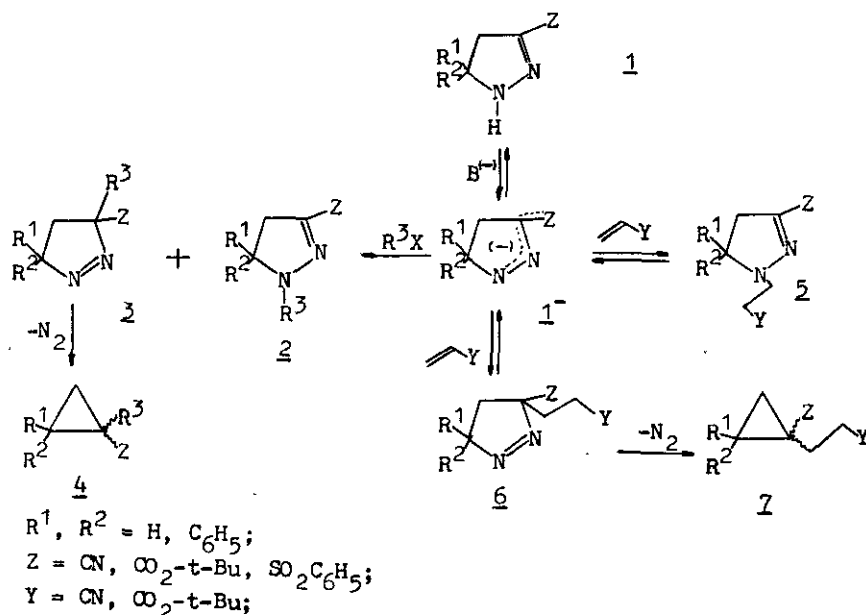
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It has been found that Δ^2 -pyrazolines **1** reacted in basic medium /typically in the presence of conc. aq. NaOH solution and a quaternary ammonium salt as a catalyst - so called catalytic two-phase, CTP, system/ with alkyl halides or electrophilic alkenes to give N-substituted Δ^2 -pyrazolines **2**, and cyclopropanes **4** or cyclopropanes **7** respectively. The normal alkyl bromides or allyl halides formed the N-substituted pyrazolines **2** /yields 30-96%/, while benzyl halides the mixture of the products **2** and **4** /yields ca.80%, **2**/**4** ca.0.8/. On the other hand the electrophilic alkenes gave exclusively the cyclopropanes **7** in good yields.

The key intermediate in these transformations is the ambident anion **1**⁻ that reacts irreversibly with alkyl halides either at nitrogen to give **2** or at carbon atom to give **4** via the unstable Δ^1 -pyrazolines **3**. Similarly the anion **1**⁻ can form with the electrophilic alkenes the compounds **5** and **6**. However the reversible nature of these reactions, and irreversible decomposition of the Δ^1 -pyrazolines **6** shifted the equilibrium toward the formation of the cyclopropanes **7** /Scheme/.

Scheme



These reactions present a new approach to the preparation of some functionalized cyclopropanes via anionic reactions of the Δ^2 -pyrazolines.