SOME ANIONIC REACTIONS OF Δ^2-PYRAZOLINES

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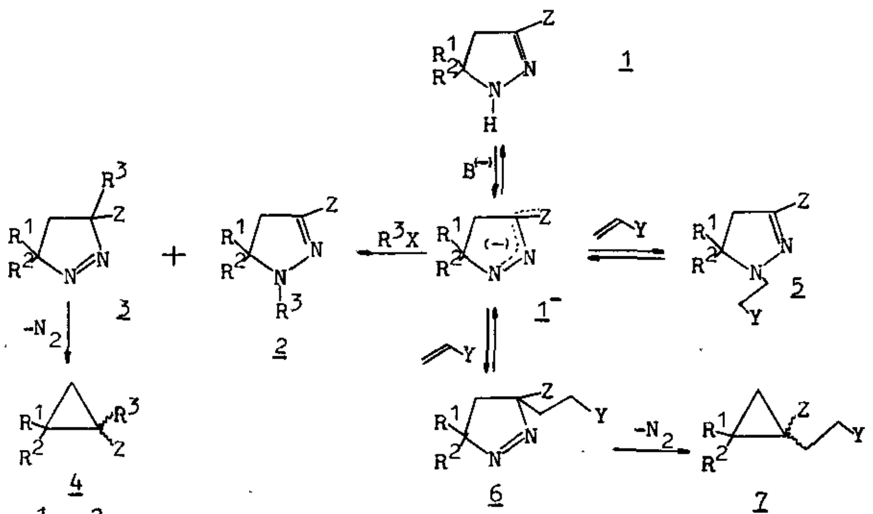
It has been found that Δ^2-pyrazolines 1 reacted in basic medium /typically in the presence of conc. aq. NaOH solution and a quaternary ammonium salt as a catalyst - so called catalytic two-phase, CTP, system/ with alkyl halides or electrophilic alkenes to give N-substituted Δ^2-pyrazolines 2, and cyclopropanes 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



R^1, R^2 = H, C_6H_5;
Z = CN, CO_2-t-Bu, $SO_2C_6H_5$;
Y = CN, CO_2-t-Bu;

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