

THE SYNTHESIS OF AZATROPOLONES AND THEIR CHEMICAL PROPERTIES

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The synthetic utility of dioxopyrrolines as versatile synthons has been demonstrated by the syntheses of various heterocyclic compounds. Our study is now extended to the synthesis of an azatropolone, a nitrogen analog of α -tropolone.

Irradiation of a mixture of 2-phenyl-3-ethoxycarbonyl- Δ^2 -pyrroline-4,5-dione and phenylacetylene in dimethoxyethane with high pressure lamp (100 W, pyrex filter) at 0° C for 30 min yielded the cyclobutene (1). Pyrolysis of 2 afforded the azatropolone (2) as a yellow needles in 60% yield. The isomeric azatropolone (3) as a yellow needles was formed by further irradiation of 1 in 10% yield.

The azatropolone (2) and (3) were easily attacked by protic solvent such as methanol and water, to give pyridine-2-carboxylate derivatives (4) and (5) in quantitative yields, respectively. The formation of the pyridine-2-carboxylate derivative was explained by a benzylic acid type rearrangement.

The acidic character of the azatropolone was demonstrated by the rapid consumption of diazomethane. Thus, 2 gave the methyl ether (6) as a sole product and 3 afforded two isomeric methyl ethers (7) and (8).

The azatropolone is possibly equilibrated in one NH-form and two OH-forms. The presence of their forms was demonstrated by the above diazomethane experiment and by the benzylic acid rearrangement.

The chemical reactivity of the azatropolone seems to be attributable to the non-coplanarity of the 7-membered ring of which conformation was rigidly established by the X-ray analysis of 9.

