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THE SYNTHESES OF AZATROPOLONES

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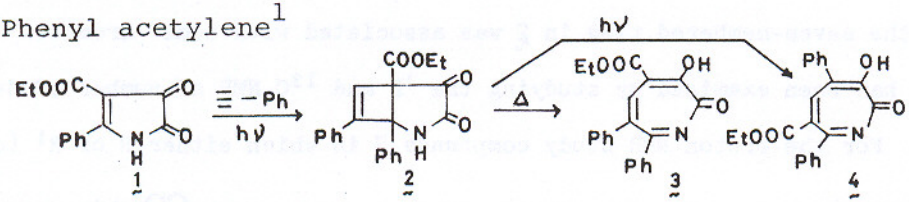
The syntheses of azatropolones, the monocyclic 6π-equivalent heterocyclic congeners of tropolone and their chemical property are reported. We have explored two synthetic pathways starting from a Δ^2-pyrroline-4,5-dione.

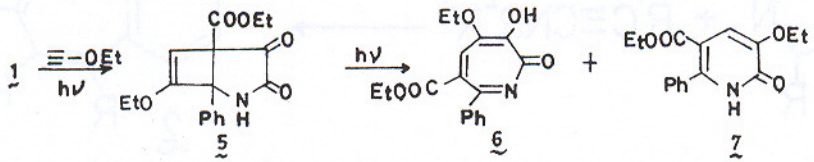
Synthesis

i) Photo- and thermal rearrangement of the cycloadduct of 2-phenyl-Δ^2-pyrroline-4,5-dione with acetylene derivative.

a) Phenyl acetylene[1]

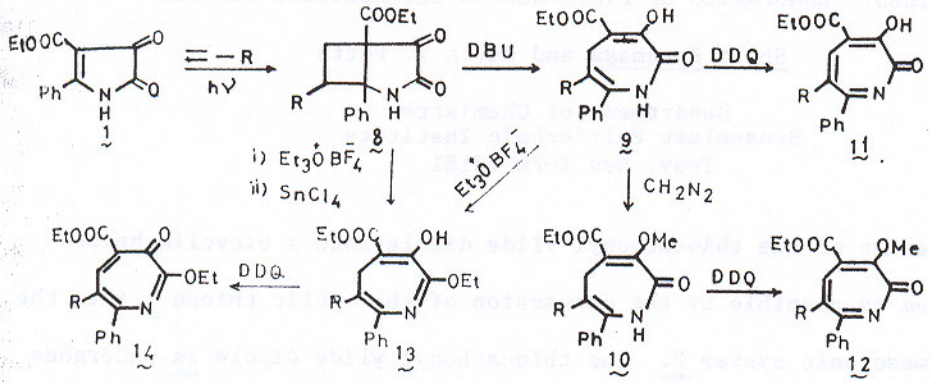


b) Ethoxy acetylene



In this case, the cycloadduct (5) could not be isolated. This fact indicated that the method has a serious limitation for preparing the azatropolones with different substitution patterns.

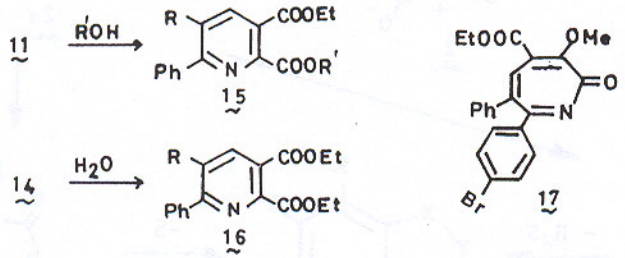
ii) Ring expansion of the 1,2-cycloadducts of 2-phenyl-Δ^2-pyrroline-4,5-dione with ethylene derivatives, followed by DDQ oxidation.



R = Ph, Et, OEt, OAc, SPh, H

Chemical Property

The azatropolone (11), and the imidic ester (14) are very labil for protic solvents and rearranged to pyridine-2-carboxylate derivatives in quantitative yield.



The reactivity may be attributable to the nonplanarity, therefore nonaromaticity of the azatropolone nucleus, whose conformation was determined by the *X*-ray analysis of the methyl ether (17).

REFERENCE

1. T. Sano, Y. Horiguchi and Y. Tsuda, Heterocycles, 9, 731 (1978).