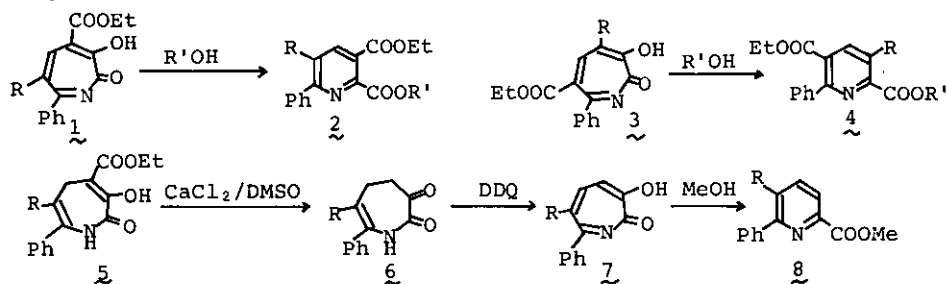


THE SYNTHESIS OF AZATROPOLONES AND AZATROPONES AND THEIR
CHEMICAL PROPERTIES

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Previously we reported the synthesis of a new heteroaromatic, azatropolones 1 and 2, which in protic solvents readily underwent skeletal rearrangement to afford pyridine-2-carboxylates 3 and 4. In connection with the chemical reactivity of azatropolone nucleus, we are interested in the synthesis of azatropolone which lacks of the ethoxycarbonyl group. New mono- and di-substituted azatropolones 7 are now synthesized by deethoxycarbonylation of dihydroazatropolone 5 by the use of CaCl_2 in DMSO and subsequent DDQ dehydrogenation of deethoxycarbonyl derivatives 6. In methanol, 7 undergoes a skeletal rearrangement to give methyl pyridine-2-carboxylate 8, suggesting that the reaction is characteristic of the azatropolone nucleus.



Next, we have synthesized 2-azatropone 12. Base catalyzed eliminative ring expansion of 4-acetoxy (or mesyloxy)-2-azabicyclo[3.2.0]heptan-3-ones 10 yielded the dihydroazatropone 11 in good yield. DDQ oxidation of 11 afforded 2-azatropone 12. In contrast to azatropolones, azatropones were stable to protic solvents. However, irreversible solvolytic changes in both acidic and basic media were observed.

