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# Pseudo-Michael Reaction of 2-hydrazinoimidazolines: New Synthetic Approach to Imidazo[2,1-c][1,2,4]triazepine System

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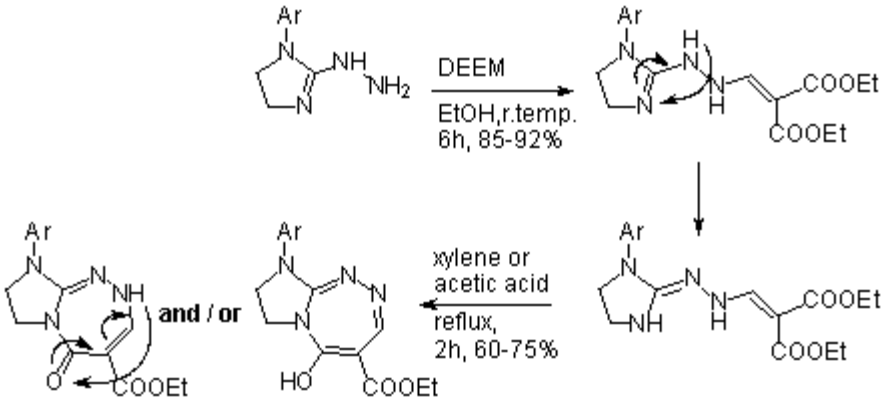
In a two-step reaction (pseudo-Michael/acylation) of 1-aryl-2-hydrazinoimidazolines with DEEM (diethyl ethoxymethylenemalonate) formation of 2,3-dihydroimidazo[2,1--c][1,2,4]triazepine system was observed. This type of reaction usually lead to formation of 5:6 or 6:6 membered fused hetero-cyclic systems whereas reaction of hydrazine derivatives (alkyl or aryl) or hydrazides and DEEM give pyrazoline carboxylates. In the literature formation of fused 1,2,4-tri-azepines in reaction of a-hydrazinoazoheterocycles is not mentioned. In first step of reaction of 1-aryl-2-hydrazinoimidazolines with Michael reagents chain enamine is formed. Special feature of its structure is location of double C=N bond outside of the imidazolidine ring. That location not only makes the structer more rigid but slows mutarotation on N-6 nitrogen atom ($sp^2$ hybrydization) so much that in $^1H$ NMR spectra signals of every hydrogen located on the side chain is duplicated (J = 8-12 Hz). The same feature cause transfer of hydrogen atom between N-6 and N-5 nitrogens. This transfer allows second step of reaction (acylation) to occure. Besides cyclization, 1,5-sigmatropic effect is observed in newly formed triazepine ring. Depending on used solvent (xylene or acetic acid) product of reaction is a mixture (1:4 - 1:3) of ethyl 1-aryl-5(1H,8H)oxo-2,3-dihydroimidazo[2,1-c][1,2,4]triaze-pine-6-carboxylate and ethyl 1-aryl-5-hydroxy-2,3-dihydroimidazo[2,1-c][1,2,4]triaze-pine-6-carboxylate or only 5-hydroxy isomer.




This reaction mechanism as shown in the scheme is strongly supported by spectral and crystallographic data.

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