The investigation of alkylation of benzylidene malononitrile with benzoylacetone and acetoacetanilide

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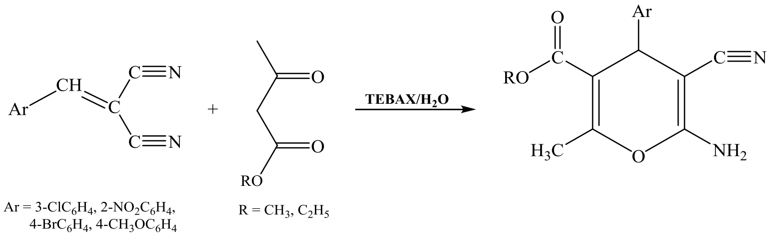
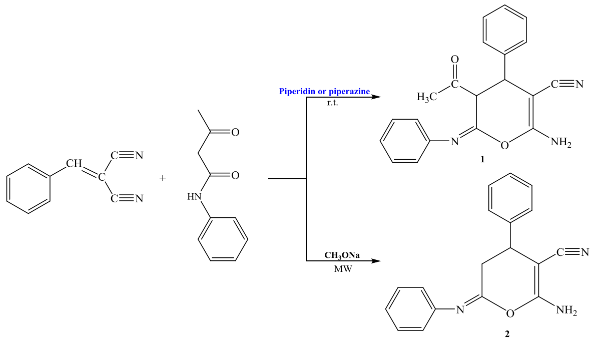
Abstract

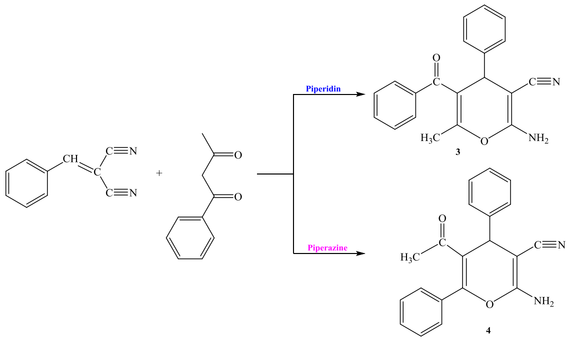
Many pyran derivatives exhibit a wide spectrum of pharmacological activities and biological activities at melanocortin receptors and are being used in the design of peptidomimetics relating to a tripeptide structure, such as fungicidal, insecticidal and acaricidal activity, antiviral activity, miticidal activity, stimulant activity and anticonvulsant activity. Because of the toxic and volatile nature of many organic solvents, ionic liquids and aqueous media are emerging as effective solvents for 'green' processes. Water is cheap, not dangerous and very digressive for environment, so it is used as solvent in Diels-Alder's, Klayzen rearrangement, Reformatski and pinakol-interaction reactions. Due to this reason, China scientist Xiang-Shan Wang used aceto-acetic with arylmethylidene-malonnitriles in water solution and in the presence of catalyst triethylbenzylammonium chloride (TEBAX) obtained 6-amino-5-ciano-4-aryl-2-methyl-4H-pyran-3-carboxylate derivatives with high yield.



Egyptian scientists F M Abdelrazek and others presented the same reaction with ammonia acetate in ethanol media and they obtained pyran which was subjected to substitution reaction and its products were reacted in the presence of TEA and ethanol with thiocarbamide and got pirimidine derivatives which contained pyran ring. When we carried out the alkylation of benzylidene malononitrile and acetoacetanilide in the ethanol media, in the presence of piperidine (piperazine), formation of product 1 was observed the. During NMR studies of the compound 1 in DMSO-d6 has been identified the keto-enol tautomerism. When we used sodium methylate as base, the different product 2 was obtained. From all these observation, we propose that, in this case also the formation of product 1 took place, but then it underwent the attack of methoxide anion which resulted in the splitting of methyl acetate to give product 2.



We established that in benzene media in the presence of piperidine by interaction of benzilidene malononitrile with benzoylacetone product 3 were obtained. We propose that in these conditions the enolization of benzoylacetone can take place in carbonyl group near the methyl group. When we changed the reaction condition, which means using piperazine as base and methanol as solvent, the formation of product 4 took place. Probably in the second case, the enolization took place in carbonyl group near the phenyl group. The reaction scheme is presented as:



The reactions were monitored by thin-layer chromatography method. Structures of synthesized compounds were confirmed by IR, ^{1}H and ^{13}C NMR spectroscopy.

Biography

F N Naghiyev has completed his PhD from Baku State University, Azerbaijan. Currently, he is a Post-doctoral Researcher and Specialist in the NMR laboratory at the same university. He has published more than 14 papers, also one patent in local and international literature.

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