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**SYNTHESIS OF NEW BIS ENAMINONE DERIVATIVE VIA THE 1,3
DIPOLAR CYCLOADDITION REACTION OF BIS AZIDE AND
FURANYL 4- NITRO ACETOPHENONE**

***Abstract:** The reaction of 1,3-dipolar cycloaddition of 1,4-bis(azidomethyl)benzene has been studied with furanyl 4- nitro acetophenone (chalcone) experimentally. the reaction of 1,4-bis(azidomethyl)benzene with chalcone using reflux for 73 hours in the toluene solvent and CuCl as catalyst has the result of forming bis-enaminone, and the reaction has been followed by thin-layer chromatography (TLC). The compound has been separated by column*

chromatography. The isolated and purified product was characterized by spectral methods FT-IR, $^1\text{H-NMR}$, $^{13}\text{C-NMR}$.

Keywords: Triazoline; 1,3-Dipolar Cycloaddition; enaminone; chalcone; bis azide.

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ПОЛУЧЕНИЕ АЗО ПОЛИМЕРА СВОБОДНОЙ РАДИКАЛЬНОЙ ПОЛИМЕРИЗАЦИЕЙ С ИСПОЛЬЗОВАНИЕМ (AIBN) В КАЧЕСТВЕ ИНИЦИАТОРА

Аннотация: Экспериментально изучена реакция 1,3-дипольного циклоприсоединения 1,4-бис (азидометил) бензола с фуранил-4-нитроацетофеноном (халконом). реакция 1,4-бис (азидометил) бензола с

халконом с использованием кипячения с обратным холодильником в течение 73 часов в толуольном растворителе и CuCl в качестве катализатора приводит к образованию бисенаминона, и реакция отслеживается с помощью тонкослойной хроматографии (ТСХ). Соединение разделяли колоночной хроматографией. Выделенный и очищенный продукт характеризовали спектральными методами FT-IR, ^1H -ЯМР, ^{13}C -ЯМР.

Ключевые слова: Триазолин; 1,3-диполярное циклоприсоединение; енаминон; халкон; бис азид.

1. Introduction:

Organic azides are considered very important dipoles due to their industrial and biological applications ^{[1] [2]}. It is also considered to be one of the energy-rich functional molecules. Also, the compounds of organic azides reaction by dipolar cycloaddition method (1,3-DC) with unsaturated compounds containing double and triple bonds to form five-membered heterocyclic rings are triazoline or triazole, some of these rings are characterized by chemical stability, while others disintegrate an absolute molecule of nitrogen, to give the three-ring aziridine compounds, which in most cases disintegrate to give enamine or amino compounds^[2-4]. One of these products is the enamionone, which is an important organic compound containing the functional group $\text{N}-\text{C}=\text{C}-\text{C}=\text{O}$ have two types: 1) open-chain enamionones: where the characteristic group is part of a chain. 2) ringed enamionones: where the characteristic group is part of a ring. ^{[5] [6]} Enaminones are characterized by biological activity, where the effectiveness of some of these compounds has been studied and they have antibacterial and anticonvulsant activities ^[7-9] and anti-inflammatory activity ^[10] and anti-oxidant ^[11]

2. Experimental section:

2.1. Apparatus and materials

NMR spectra were recorded on a Bruker AVANCE 400 MHz spectrometer and CDCl_3 was used as NMR solvent. - FT-IR spectra were recorded on a Jasco

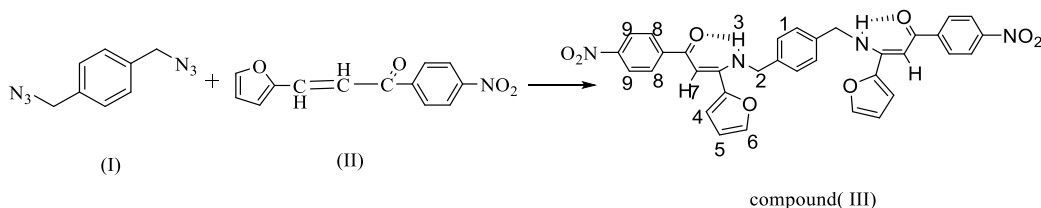
FT-IR 4100/tybe obtained by KBr disk method. All materials are commercial reagent grade and were obtained from Merck Co.

2.2. Synthesis of 1,4-bis(azidomethyl)benzene (I): 100 mL dimethylformamide is added to the 1,4-bis(chloromethyl)benzene (0,1 mole, 17.5g) and mixed with sodium azide solution (0,2mole, 13g) dissolved in 100 mL of water and the mixture is heated in a flask with reflux on a water bath for 21 hours and the temperature is 80 °C. The resulting diazide is separated by ether extraction and the ether layer is dried with anhydrous sodium sulfate. The bis azide (I) is separated by evaporating the solvent under vacuum and used as it is without purification (KBr, Cm^{-1}): $\text{C}_{\text{SP}^2}\text{-H}$ (3059), $\text{C}_{\text{SP}^3}\text{-H}$ (2915), $\text{C}=\text{C}_{\text{aromatic}}$ (1620), N_3 (2093).

2.3. Synthesis of furanyl 4- nitro acetophenone (chalcone) (II): A solution of 4-Nitroacetophenone (0.01 mol) in ethanol (10 ml) was added to a solution of furfural (0.01 mol) in ethanol (10 ml). To this mixture 40% NaOH solution was added drop wise as to make it just alkaline (pH 10 ~ 11). The reaction mass was stirred for 18 hrs at room temperature. The product was isolated by filtration and crystallized using appropriate solvent.(melting point = 150-152 °C). (KBr, Cm^{-1}): $\text{C}_{\text{SP}^2}\text{-H}$ (3086), $\text{C}=\text{O}$ (1685), $\text{C}=\text{C}_{\text{alekene}}$ (1588), $\text{C}=\text{C}_{\text{aromatic}}$ (1550), NO_2 (1522,1320), C-O-C (1017).

3. Results and Discussion:

the bis-enaminone derivative (III) was prepared from the reaction of 1,4-bis (azidomethyl) benzene with chalcone using reflux for 73 hours in the toluene solvent and CuCl as catalyst, and the reaction has been followed by thin-layer chromatography (TLC). The compound III has been separated by column chromatography with (Ethyl acetate/ n-Hexane) (v/v, 30/70) to give an orange precipitate product. (yield 86.9%, m.p= 265-266 °C).



Scheme 1: Reaction of of 1,4-bis (azidomethyl) benzene with chalcone.

(KBr, Cm^{-1}): N-H (3435), C-H sp^2 (3080), C-H sp^3 (2983), C=O (1735), C=C_{alkene} (1625), C=C_{aromatic} (1600), NO₂ (1517,1460), C-N (1190), C-O-C (1020). ¹H-NMR (400 MHz), (CDCl₃-d), (1) 7.27-7.33 (dt, $J_4=2\text{Hz}, J_3=2.3\text{Hz}, J_2=10.4\text{Hz}$, 4H). (2) 4.80-4.84 (d, $J=5.52\text{Hz}$, 4H). (3) 12.05-12.10 (t, $J=6\text{Hz}$, 2H). (4) 7.36-7.38 (dd, $J_3=2.24\text{Hz}, J_4=8.08\text{Hz}$, 2H). (5) 6.86-6.88 (t, $J=6.16\text{Hz}$, 2H). (6) 7.61-7.64 (dd, $J_3=1.16\text{Hz}, J_4=6\text{Hz}$, 2H). (7) 6.54 (s, 2H). (8) 8.23-8.27 (dt, $J_4=2.32\text{Hz}, J_3=3.16\text{Hz}, J_2=8.88\text{Hz}$, 4H). (9) 8.02-8.05 (dt, $J_4=2.24\text{Hz}, J_3=3.64\text{Hz}, J_2=8.84\text{Hz}$, 4H).

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