

SYNTHESIS OF THE POLAR DOUBLE BONDED COMPOUNDS

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Abstract. By Knoevenagel condensation of some aromatic and heteroaromatic aldehydes with 3-oxo-3-tiophen-2-yl-propannitrile and also cinn- and α -bromocinnamaldehydes with malononitrile at room temperature the corresponding adducts were synthesized with good yield. Structures of all synthesized compounds confirmed by NMR spectroscopy.

Keywords: cinnamaldehyde, α -bromocinnamaldehyde, malononitrile, 3-oxo-3-tiophen-2-yl-propannitrile, NMR.

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1. Introduction

Arylmethylenemalononitriles are important synthones for synthesis of biologically active pyrimidine, pyridine and 4H-pyran derivatives and various new heterocycles. Benzylidenemalononitrile was investigated as cell activators (Turpaev *et al.*, 2011) and stimulator (Turpaev & Drapier, 2009). By researchers have been carried out Knoevenagel condensations of malononitrile with aromatic aldehydes in short reaction time, non-catalyst conditions and room temperature and arylmethylenemalononitriles were separated in pure as reactions products (Wang *et al.*, 2005; Trotzki *et al.*, 2008).

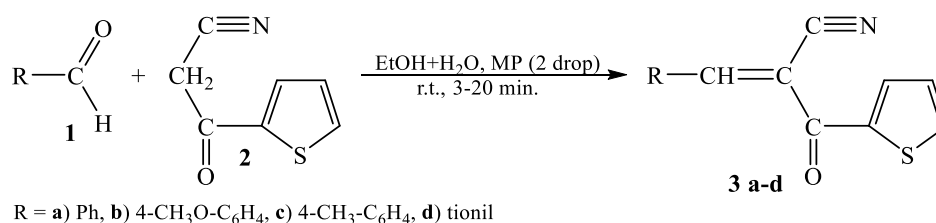
In the next paper, Knoevenagel condensation was carried out in the presence of NH₄OAc or silica gel and MW, without solvent for aromatic ketones and malononitrile. This reaction also was investigated in the presence of a catalyst and hot water (Wang & Cheng, 2004).

Liangce Rong and colleagues presented Knoevenagel condensation of methyleneactive compounds with aromatic aldehydes without solvent, room temperature, at the presence of TEBA and arylidene compounds were synthesized (Rong *et al.*, 2006). In the next article, a high yield of arylidene compounds was synthesized in MW and non-solvent conditions by using NaF and LiCl catalyst (Mogilaiah *et al.*, 2003).

Many catalysts, such as 1,4-diazabicyclo[2.2.2]octane (DABCO) (Yu & Wang, 2013), DABCO-based ion liquid (Xu *et al.*, 2010; Ying *et al.*, 2014), also Gallium chloride (Muralidhar & Girija, 2014) are effective in Knoevenagel condensations of various types of aromatic, aliphatic, heterocyclic, α,β -unsaturated aldehydes and ketones with methyleneactive compounds. In presented works from 3-nitrobenzaldehyde and acetylacetone polar double-bonded compounds were synthesized (Abiyeva *et al.*, 2018).

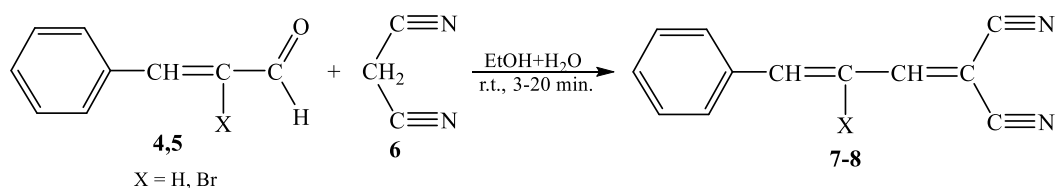
2. Results and discussions

Knoevenagel products are very important at a synthesis of polyfunctional substituted heterocyclic systems. According to the concise literature survey above, the different sulfur, nitrogen, bromine contents Knoevenagel adducts were obtained in high yields by condensation of some aromatic and heteroaromatic aldehydes with 3-oxo-3-tiophen-2-yl-propannitrile in ethanol-water medium and at room temperature.



In these reactions conditions 2 drops of methylpiperazine were used as catalyst.

The corresponding condensations products were obtained at the same reaction condition and by the Knoevenagel condensation of the cinn- and α -bromocinnamaldehydes with the malononitrile, but without any catalysts.



Obtained crystals were filtered by the paper and recrystallized from ethanol-water mixture.

In the ¹H NMR spectra of obtained compounds the CH protons of double bonds at 8.2-8.6 ppm., in the ¹³C NMR spectra their carbons at 150.16-155.55 ppm. were observed and the another indicated signals according to described above given compounds.

3. Experimental part. General remarks

All commercially available chemicals were obtained from Merck and Fluka (sigmaaldrich) companies and used without further purification. Melting points were measured on an Stuart SMP30 apparatus without correction. ¹H/¹³C NMR spectra were recorded on BrukerAvance 300-MHz spectrometer at 300 and 75 MHz, respectively. Thin-layer chromatography (TLC) on commercial aluminum-backed plates of silica gel (60 F254) was used to monitor the progress of reactions.

Experimental procedure

3-Phenyl-2-(thiophene-2-carbonyl)acrylonitrile (3a): Benzaldehyde (7.64 mmol) was solved by stirring in ethanol-water (80:20) and 3-oxo-3-tiophen-2-yl-propannitrile (7.7 mmol) was solved in 35 ml of ethanol by heating. Then benzaldehyde solution mixed with 3-oxo-3-tiophen-2-yl-propannitrile and 2 drops of methylpiperazine

was added. Obtained reaction mixture was stirred at room temperature for 5-7 minutes. Reaction progress was controlled by TLC (EtOAc/n-hexane, 3:1) when the reaction mixture was cooling, needle-type crystals are obtained. Crystals were filtered by the paper and recrystallized from ethanol-water mixture. Yield: 1.5 g, 81.82%.

Light green powder; mp.104°C; ^1H NMR (300 MHz, DMSO-*d*6): 7.27-8.11 (m, 8H, 5CH_{arom}+3CH_{thiophen.}); 8.30 (s, 1H, CH=). ^{13}C NMR (75 MHz, DMSO-*d*6): 109.34 (=C_{quat}), 117.19 (CN), 129.29 (CH_{arom}), 129.58 (2CH_{arom}), 131.25 (2CH_{arom}), 132.17 (C_{ar}), 133.60 (CH_{thioph}), 135.64 (CH_{thioph}), 137.22 (CH_{thioph}), 141.30 (C_{thioph}), 155.31 (CH=), 179.55 (C=O).

3-(4-Methoxyphenyl)-2-(thiophene-2-carbonyl)acrylonitrile (3b): Was synthesized by the same methods. Crystals were filtered by the paper and recrystallized from ethanol-water mixture. Yield: 1.62 g, 79.67%.

Yellow powder; mp.85°C; ^1H NMR (300 MHz, DMSO-*d*6): 3.87 (s, 3H, CH₃O); 7.14-8.15 (m, 7H, 4CH_{arom}+3CH_{thiophenyl.}); 8.29 (s, 1H, CH=). ^{13}C NMR (75 MHz, DMSO-*d*6): 56.23 (CH₃O), 105.74 (=C_{quat}), 115.40 (2CH_{arom}), 118.14 (CN), 124.85 (C_{thio}), 129.45 (CH_{thioph}), 134.13 (2CH_{arom}), 135.51 (CH_{thioph}), 136.95 (CH_{thioph}), 141.54 (C_{ar}), 155.21 (CH=), 164.03 (O-C_{ar}), 180.13 (C=O).

2-(Thiophene-2-carbonyl)-3-(p-tolyl)acrylonitrile (3c): Was synthesized by the same methods. Crystals were filtered by the paper and recrystallized from ethanol-water mixture. Yield: 1.66 g, 86.46%.

White powder; mp.78°C; ^1H NMR (300 MHz, DMSO-*d*6): 2.40 (s, 3H, CH₃-Ar); 7.32-8.19 (m, 7H, 4CH_{arom}+3CH_{thiophenyl.}); 8.31 (s, 1H, CH=). ^{13}C NMR (75 MHz, DMSO-*d*6): 21.84 (CH₃-Ar), 108.23 (=C_{quat}), 117.59 (CN), 129.53 (CH_{thioph}), 129.62 (C_{ar}), 130.38 (2CH_{arom}), 131.49 (2CH_{arom}), 135.97 (CH_{thioph}), 137.34 (CH_{thioph}), 141.29 (C_{thioph}), 144.74 (C_{ar}), 155.45 (CH=), 180.21 (C=O).

3-(Thiophen-2-yl)-2-(thiophene-2-carbonyl)acrylonitrile (3d): Was synthesized by the same methods. Crystals were filtered by the paper and recrystallized from ethanol-water mixture. Yield: 1.58 g, 90.28%.

White powder; mp.153°C; ^1H NMR (300 MHz, DMSO-*d*6): 7.31-8.25 (m, 6H, 6CH_{thio.}); 8.65 (s, 1H, CH=). ^{13}C NMR (75 MHz, DMSO-*d*6): 104.53 (=C_{quat}), 117.90 (CN), 129.37 (CH_{thio}), 129.49 (CH_{thio}), 135.38 (CH_{thio}), 136.49 (C_{thio}), 136.99 (CH_{thio}), 137.86 (CH_{thio}), 141.20 (CH_{thio}), 141.58 (C_{thio}), 148.54 (CH=), 179.29 (C=O).

2-(3-Phenylallylidene)malononitrile (7): Cinn- or α -bromocinnamaldehydes (7.6 mmol) were solved in 45 ml of ethanol-water mixture (4:1) and stirred, and then malononitrile (7.7 mmol) was added. The reaction progress was controlled by TLC (EtOAc/n-hexane, 3:1). After several minutes white crystals were obtained. Yield: 1.25 g, 91.24%.

Light yellow powder; mp.128°C; ^1H NMR (300 MHz, DMSO-*d*6): 7.22 (dd, 1H, CH=, 11.4 Hz); 7.48-7.73 (m, 6H, 5CH_{arom}+CH=); 8.23 (d, 1H, CH=, $^3J_{\text{H-H}} = 11.7$ Hz). ^{13}C NMR (75 MHz, DMSO-*d*6): 81.44 (=C_{quat}), 112.62 (CN), 114.59 (CN), 122.93 (CH=), 129.59 (2CH_{arom}), 129.68 (2CH_{arom}), 132.26 (CH_{arom}), 134.54 (C_{ar}), 151.55 (CH=), 162.46 (CH=).

2-(2-Bromo-3-phenylallylidene)malononitrile (8): Was synthesized by the same methods. Crystals were filtered by the paper and recrystallized from ethanol-water mixture. Yield: 1.74 g, 88.32%.

White powder; mp.156°C; ^1H NMR (300 MHz, DMSO-*d*6): 7.53-7.92 (m, 5H, 5CH_{arom}); 8.13 (CH=), 8.36 (CH=). ^{13}C NMR (75 MHz, DMSO-*d*6): 83.12 (=C_{quat}),

112.37 (=C_{quat}), 114.89 (CN), 114.98 (CN), 129.39 (2CH_{arom}), 131.36 (2CH_{arom}), 132.35 (CH_{arom}), 133.71 (C_{ar}), 150.16 (CH=), 160.37 (CH=).

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