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SYNTHESIS OF NEW PYRANE AND CYCLOHEXANONE DERIVATIVES ON THE BASE OF SOME KNOEVENAGEL ADDUCTS

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The formation of cyclohexanone and 3,4-dihydro-2H-pyran derivatives by using of Michael addition reaction between the 3-(4-tolyl)-, 3-(4-methoxyphenyl)-, 3-phenyl-, 3-pyridinyl-2-(thiophene-2-carbonyl)acrylonitriles or 3-(4-tolyl)-, 3-(thiophen-2-yl), and 2-(4-bromobenzoyl)-3-(4-fluorophenyl)acrylonitriles to the acetoacetanilide were observed. Structures of all synthesized compounds confirmed by nuclear magnetic resonance spectroscopy and X-Ray analysis.

Keywords: thiophene, acrylonitriles, acetoacetanilide, cyclohexanone, dihydropyran, nuclear magnetic resonance.

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Dihydropyran, cyclohexanone derivatives have high biologically activity and widely extended in nature. In the literatures there are a lot of information on synthesis and various transformation of this type compounds [1–15]. Also, the Michael addition is the fundamental reaction of formation of C–C bond in organic synthesis and we discussed it in early investigations [16–29].

In article [8] was presented Michael addition of acetoacetanilide to Knoevenagel adducts. So, it was established that by Michael interaction of 2-(thiophene-2-carbonyl)-3-(p-to-

lyl)-acrylonitrile and 3-(4-methoxyphenyl)-2-(thiophene-2-carbonyl)acrylonitrile with acetoacetanilide in methanol at room temperature as dihydropyran so cyclohexanone [8] derivatives were formed. Reaction schemes presented in below. As seen from the scheme, for obtaining of cyclohexanone derivatives, the methylene-active compound (3) transferred to anion (4) by the action of base at first stage and at next stage obtained anion attacks to carbonyl group and occurs closing cycle by formation of cyclohexanone derivatives (5 a,b).

Also, it was established, that for obtaining pyrane derivative by the same reaction, formed methyleneactive compound (or corresponding Michael adduct) (3) transferred to

enol-form (6). Further, as result of interaction of electron pair of oxygen of hydroxyl to carbon of keton group taken place cycle formation by formation of dihydropyran derivatives (7 *a,b*).

By the Michael addition of 3-phenyl-2-(thiophene-2-carbonyl)acrylonitrile and 3-(pyridine-4-yl)-2-(thiophene-2-carbonyl)acrylonitrile with acetoacetanilide at the same conditions (by the same mechanism) the dihydropyran deriva-

tives with high yield and cyclohexanone derivatives with low yield are synthesized. The X-Ray molecular structure of dihydropyran derivative (9b) is given in below (Figure).

X-Ray structure of 5-cyano-2-hydroxy-2-methyl-N-phenyl-4-(pyridin-4-yl)-6-(thiophen-2-yl)-3,4-dihydro-2H-pyran-3-carboxamide (**9b**).

By the Michael addition of 2-(4-bromobenzoyl)-3-(4-fluorophenyl)acrylonitrile, 2-(4-bromobenzoyl)-3-(thiophene-2-yl)acrylonitrile and

2-(4-bromobenzoyl)-3-(p-tolyl)acrylonitrile with acetoacetanilide the similar products (**12** *a,b,c* and **13** *a,b,c*) were synthesized.

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. X-Ray analyses were performed on Bruker APEX X-Ray equipment. Thin-layer chromatography (TLC) on commercial aluminum-backed plates of silica gel (60

F254) was used to monitor the progress of reactions.

General experimental procedure

3-Cyano-4-hydroxy-6-oxo-N-phenyl-4-(thiophen-2-yl)-2-(p-tolyl)cyclohexane-1-carboxamide (5a). Mixture of 2-(thiophene-2-carbonyl)-3-(p-tolyl)acrylonitrile (2.9 mmol) and acetoacetanilide (3 mmol) dissolved in 35 ml of methanol was stirred 5–7 minutes and 2–3 drop methylpiperazine was added and stirring was continued. Reaction progress was tracked by TLC (EtOAc/n-hexane, 2:1). Reaction mixture was kept quietly for 24–48 hours. By

evaporating of solvent crystals were precipitated. Crystals were separated by filter paper and recrystallized from ethanol (95%) – water mixture. Yield – 0.89 g, 71.77%. $T_{\text{melt.}}=210^{\circ}\text{C}$.

^1H NMR (300 MHz, DMSO- d_6), δ , m.h.: 2.23 (s, 3H, CH₃); 2.79 (d, 1H, CH, $^3J_{\text{H-H}} = 14.1$); 3.50 (d, 1H, CH, $^3J_{\text{H-H}} = 13.8$); 4.01 (s, 1H, OH); 4.06 (s, 2H, CH₂); 4.28 (d, 1H, CH, $^3J_{\text{H-H}} = 9.9$); 6.97–7.48 (m, 12H, 9Ar–H+3CH_{thioph.}); 9.94 (s, 1H, NH). ^{13}C NMR spektr (DMSO- d_6), δ , m.h.: 21.14 (CH₃–Ar), 44.26 (CH), 47.40 (CH), 54.07 (CH₂), 62.64 (CH), 75.29 (C_{quat.}), 119.02 (CN), 119.49 (2CH_{arom.}), 123.87 (CH_{thioph.}), 124.45 (CH_{arom.}), 125.71 (CH_{thioph.}), 127.63 (CH_{thioph.}), 128.75 (2CH_{arom.}), 129.14 (2CH_{arom.}), 129.54 (2CH_{arom.}), 137.06 (C_{ar.}), 137.17 (C_{ar.}), 139.14 (C_{ar.}), 150.57 (C_{thioph.}), 165.85 (O=C–NH), 203.12 (C=O).

Found, %: 69.71 C, 5.07 H, 6.56 N. C₂₅H₂₂N₂O₃S. Calculated, %: 69.77 C, 5.12 H, 6.51 N.

3-Cyano-4-hydroxy-2-(4-methoxyphenyl)-6-oxo-N-phenyl-4-(thiophen-2-yl)-cyclohexane-1-carboxamide (5b) was synthesized in the same conditions by using of 3-(4-methoxyphenyl)-2-(thiophene-2-carbonyl)acrylonitrile (yield 1.1 g, 85.27%). $T_{\text{melt.}}=200^{\circ}\text{C}$.

^1H NMR (300 MHz, DMSO- d_6), δ , m.h.: 2.77 (d, 1H, CH, $^3J_{\text{H-H}} = 14.1$); 3.48 (d, 1H, CH, $^3J_{\text{H-H}} = 14$); 3.56 (s, 1H, OH); 3.69 (s, 3H, CH₃O); 4.00 (s, 1H, OH); 4.03 (s, 2H, CH₂); 4.27 (d, 1H, CH, $^3J_{\text{H-H}} = 9.6$); 6.89–7.47 (m, 12H, 9Ar–H+3CH_{thioph.}); 9.93 (s, 1H, NH). ^{13}C NMR spektr (DMSO- d_6), δ , m.h.: 43.88 (CH), 47.51 (CH), 54.06 (CH₂), 55.37 (CH₃O), 62.79 (CH), 75.22 (C_{quat.}), 114.23 (2CH_{arom.}), 119.07 (CN), 119.52 (2CH_{arom.}), 123.87 (CH_{thioph.}), 124.42 (CH_{arom.}), 125.70 (CH_{thioph.}), 127.62 (CH_{thioph.}), 129.14 (2CH_{arom.}), 129.98 (2CH_{arom.}), 131.96 (C_{ar.}), 139.13 (C_{ar.}), 150.59 (C_{thioph.}), 158.90 (O–C_{ar.}), 165.90 (O=C–NH), 203.14 (C=O).

Found, %: 67.31 C, 4.99 H, 6.23 N. C₂₅H₂₂N₂O₄S. Calculated, %: 67.26 C, 4.93 H, 6.28 N.

5-Cyano-2-hydroxy-2-methyl-N-phenyl-6-(thiophen-2-yl)-4-(p-tolyl)-3,4-dihydro-2H-pyran-3-carboxamide (7a) was synthesized in the same conditions by using of 2-

(thiophene-2-carbonyl)-3-(p-tolyl)acrylonitrile (yield 0.25 g, 20.16%). $T_{\text{melt.}}=188^{\circ}\text{C}$.

^1H NMR (300 MHz, DMSO- d_6), δ , m.h.: 1.76 (s, 3H, CH₃); 2.26 (s, 3H, CH₃); 3.03 (d, 1H, CH, $^3J_{\text{H-H}} = 11.5$); 3.46 (s, 1H, OH); 4.39 (d, 1H, CH, $^3J_{\text{H-H}} = 11.5$); 6.94–7.51 (m, 12H, 9Ar–H + 3CH_{thioph.}); 9.84 (s, 1H, NH). ^{13}C NMR spektr (DMSO- d_6), δ , m.h.: 21.00 (CH₃), 26.26 (CH₃), 39.67 (CH), 54.96 (CH), 84.14 (=C_{quat.}), 95.28 (O–C_{quat.}), 119.62 (2CH_{arom.}), 120.12 (CN), 124.11 (CH_{arom.}), 124.67 (2CH_{arom.}), 127.72 (CH_{thioph.}), 128.78 (CH_{thioph.}), 129.39 (2CH_{arom.}), 129.86 (2CH_{arom.}), 129.54 (CH_{thioph.}), 138.31 (CH₃–C_{ar.}), 139.23 (C_{ar.}), 140.16 (C_{ar.}), 141.85 (C_{thioph.}), 165.98 (O–C_{quat.}=), 166.64 (CONH).

Found, %: 69.82 C; 5.18 H; 6.46 N. C₂₅H₂₂N₂O₃S. Calculated, %: 69.77 C; 5.12 H; 6.51 N.

5-Cyano-2-hydroxy-4-(4-methoxyphenyl)-2-methyl-N-phenyl-6-(thiophen-2-yl)-3,4-dihydro-2H-pyran-3-carboxamide (7b) was synthesized in the same conditions by using of 3-(4-methoxyphenyl)-2-(thiophene-2-carbonyl)acrylonitrile (yield 0.16 g, 12.40%). $T_{\text{melt.}}=181^{\circ}\text{C}$.

^1H NMR (300 MHz, DMSO- d_6), δ , m.h.: 1.79 (s, 3H, CH₃); 3.05 (d, 1H, CH, $^3J_{\text{H-H}} = 11.3$); 3.42 (s, 1H, OH); 4.41 (d, 1H, CH, $^3J_{\text{H-H}} = 11.3$); 6.98–7.59 (m, 12H, 9Ar–H + 3CH_{thioph.}); 9.87 (s, 1H, NH). ^{13}C NMR spektr (DMSO- d_6), δ , m.h.: 26.32 (CH₃), 39.81 (CH), 55.05 (CH), 55.93 (OCH₃), 84.85 (=C_{quat.}), 96.02 (O–C_{quat.}), 115.77 (2CH_{arom.}), 121.58 (2CH_{arom.}), 119.86 (CN), 124.92 (CH_{arom.}), 127.80 (CH_{thioph.}), 128.82 (CH_{thioph.}), 129.71 (CH_{thioph.}), 130.05 (2CH_{arom.}), 131.17 (2CH_{arom.}), 137.34 (C_{ar.}), 140.08 (C_{ar.}), 142.26 (C_{thioph.}), 159.71 (O–C_{ar.}), 165.62 (O–C_{quat.}=), 166.68 (CONH).

Found, %: 67.32 C, 4.98 H, 6.24 N. C₂₅H₂₂N₂O₄S. Calculated, %: 67.26 C, 4.93 H, 6.28 N.

5-Cyano-2-hydroxy-2-methyl-N,4-diphenyl-6-(thiophen-2-yl)-3,4-dihydro-2H-pyran-3-carboxamide (9a). Mixture of 3-phenyl-2-(thiophene-2-carbonyl)acrylonitrile (2.9 mmol) and acetoacetanilide (3 mmol) dissolved in 35 ml of methanol was stirred 5–7 min and 2–3

drop methylpiperazine was added and stirring was continued. Reaction progress was tracked by TLC (EtOAc/*n*-hexane, 2:1). Reaction mixture was kept quietly for 24–48 hours. By evaporating of solvent crystals were precipitated. Crystals were separated by filter paper and recrystallized from ethanol (95%) – water mixture. Yield – 0.9 g, 75%. $T_{\text{melt.}}=186^{\circ}\text{C}$.

^1H NMR (300 MHz, DMSO- d_6), δ , m.h.: 1.72 (s, 3H, CH_3); 3.07 (d, 1H, CH, $^3J_{\text{H-H}} = 11.7$); 3.57 (s, 1H, OH); 4.38 (d, 1H, CH, $^3J_{\text{H-H}} = 11.7$); 7.00–7.89 (m, 13H, 10Ar-H+3CH_{thioph.}); 9.86 (s, 1H, NH). ^{13}C NMR spektr (DMSO- d_6), δ , m.h.: 26.38 (CH_3), 40.62 (CH), 55.87 (CH), 86.25 ($=\text{C}_{\text{quat.}}$), 99.73 (O- $\text{C}_{\text{quat.}}$), 119.58 (CN), 119.66 (2CH_{arom.}), 124.15 (CH_{arom.}), 128.03 (CH_{arom.}), 128.47 (CH_{thioph.}), 128.60 (CH_{arom.}), 128.87 (2CH_{arom.}), 129.05 (3CH_{arom.}), 129.78 (CH_{thioph.}), 130.63 (CH_{thioph.}), 135.99 (C_{ar.}), 138.87 (C_{thioph.}), 140.12 (C_{ar.}), 166.77 (O- $\text{C}_{\text{quat.}}$), 167.63 (O=C-NH).

Found, %: 69.28 C, 4.75 H, 6.78 N. $\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_3\text{S}$. Calculated, %: 69.23 C, 4.81 H, 6.73 N.

5-Cyano-2-hydroxy-2-methyl-N-phenyl-4-(pyridin-4-yl)-6-(thiophen-2-yl)-3,4-dihydro-2H-pyran-3-carboxamide (9b). Mixture 4-pyridinecarboxaldehyde or (2.9 mmol) and 2-thenoylacetonitrile (3 mmol) dissolved in 50 ml of ethanol-water (4:1) was stirred 5 minutes, reaction mixture was kept quietly for 36 hours. Then, added acetoacetanilide (3 mmol) to reaction mixture, stirring for 5 min and 2–3 drop methylpiperazine was added. Reaction mixture was kept quietly for 24 hours. Reaction progress was tracked by TLC (EtOAc/*n*-hexane, 2:1). By evaporating of solvent crystals were precipitated. Crystals were separated by filter paper and recrystallized from ethanol (95%) – water mixture. Yield 0.97 g, 79.51%. $T_{\text{melt.}}=165^{\circ}\text{C}$.

^1H NMR (300 MHz, DMSO- d_6), δ , m.h.: 1.70 (s, 3H, CH_3); 3.05 (d, 1H, CH, $^3J_{\text{H-H}} = 11.4$); 3.88 (s, 1H, OH); 4.39 (d, 1H, CH, $^3J_{\text{H-H}} = 11.4$); 7.03–8.56 (m, 12H, 9Ar-H+3CH_{thioph.}); 9.88 (s, 1H, NH). ^{13}C NMR spektr (DMSO- d_6), δ , m.h.: 26.31 (CH_3), 40.21 (CH), 55.04 (CH), 84.45 ($=\text{C}_{\text{quat.}}$), 99.72 (O- $\text{C}_{\text{quat.}}$), 119.71 (CN),

120.02 (2CH_{arom.}), 124.29 (CH_{arom.}), 124.44 (CH_{arom.}), 128.52 (CH_{thioph.}), 129.21 (3CH_{arom.}), 130.11 (CH_{thioph.}), 130.97 (CH_{thioph.}), 135.67 (C_{ar.}), 138.68 (C_{thioph.}), 149.17 (C_{ar.}), 150.38 (2CH_{arom.}), 166.68 (O- $\text{C}_{\text{quat.}}$), 167.23 (O=C-NH).

Found, %: 66.14 C; 4.51 H; 10.13 N. $\text{C}_{23}\text{H}_{19}\text{N}_3\text{O}_3\text{S}$. Calculated, %: 66.19 C; 4.56 H; 10.07 N.

3-Cyano-4-hydroxy-6-oxo-N,2-diphenyl-4-(thiophen-2-yl)cyclohexane-1-carboxamide (10a) was synthesized in the same conditions by using of 3-phenyl-2-(thiophene-2-carbonyl)acrylonitrile (yield 0.22 g, 18.33%). $T_{\text{melt.}}=206^{\circ}\text{C}$.

^1H NMR (300 MHz, DMSO- d_6), δ , m.h.: ^1H NMR spektr (DMSO- d_6), δ , m.h.: 2.72 (d, 1H, CH, $^3J_{\text{H-H}} = 14$); 3.47 (d, 1H, CH, $^3J_{\text{H-H}} = 13.5$); 3.97 (s, 1H, OH); 4.01 (s, 2H, CH_2); 4.25 (d, 1H, CH, $^3J_{\text{H-H}} = 9.4$); 7.05–7.85 (m, 13H, 10Ar-H+3CH_{thioph.}); 9.91 (s, 1H, NH). ^{13}C NMR spektr (DMSO- d_6), δ , m.h.: 44.46 (CH), 47.65 (CH), 54.18 (CH_2), 62.83 (CH), 75.28 (O- $\text{C}_{\text{quat.}}$), 116.27 (2CH_{arom.}), 119.10 (CN), 123.11 (CH_{thioph.}), 124.55 (CH_{arom.}), 125.77 (CH_{thioph.}), 127.68 (CH_{arom.}), 127.82 (CH_{thioph.}), 128.91 (2CH_{arom.}), 129.33 (2CH_{arom.}), 129.79 (2CH_{arom.}), 137.68 (C_{ar.}), 139.30 (C_{ar.}), 150.52 (C_{thioph.}), 165.72 (O=C-NH), 203.08 (C=O).

Found, %: 69.17 C; 4.86 H; 6.68 N. $\text{C}_{24}\text{H}_{20}\text{N}_2\text{O}_3\text{S}$. Calculated, %: 69.23 C; 4.81 H; 6.73 N.

3-Cyano-4-hydroxy-6-oxo-N-phenyl-2-(pyridin-4-yl)-4-(thiophen-2-yl)cyclohexane-1-carboxamide (10b) was synthesized in the same conditions by using of 3-(pyridin-4-yl)-2-(thiophene-2-carbonyl)acrylonitrile (yield 0.19 g, 15.70%). $T_{\text{melt.}}=194^{\circ}\text{C}$.

^1H NMR (300 MHz, DMSO- d_6), δ , m.h.: ^1H NMR spektr (DMSO- d_6), δ , m.h.: 2.76 (d, 1H, CH, $^3J_{\text{H-H}} = 14$); 3.50 (d, 1H, CH, $^3J_{\text{H-H}} = 13.5$); 3.99 (s, 1H, OH); 4.05 (s, 2H, CH_2); 4.29 (d, 1H, CH, $^3J_{\text{H-H}} = 9.4$); 7.07–8.62 (m, 12H, 9Ar-H+3CH_{thioph.}); 9.96 (s, 1H, NH). ^{13}C NMR spektr (DMSO- d_6), δ , m.h.: 43.79 (CH), 47.48 (CH), 53.99 (CH_2), 62.76 (CH), 75.32 (O- $\text{C}_{\text{quat.}}$), 118.24 (2CH_{arom.}), 119.15 (CN), 123.24 (CH_{thioph.}), 124.59 (CH_{arom.}), 125.81 (CH_{thioph.}), 126.14 (2CH_{arom.}), 127.87 (CH_{thioph.}), 129.86

(2CH_{arom.}), 139.36 (C_{ar.}), 149.31 (C_{ar.}), 149.78 (2CH_{arom.}), 150.56 (C_{thioph.}), 165.88 (O=C–NH), 203.12 (C=O).

Found, %: 66.24 C; 4.62 H; 10.02 N. C₂₃H₁₉N₃O₃S. Calculated, %: 66.19 C; 4.56 H; 10.07 N.

6-(4-Bromophenyl)-5-cyano-4-(4-fluorophenyl)-2-hydroxy-2-methyl-N-phenyl-3,4-dihydro-2H-pyran-3-carboxamide (12a). Mixture of 2-(4-bromobenzoyl)-3-(4-fluorophenyl)acrylonitrile (2.9 mmol) and acetoacetanilide (3 mmol) dissolved in 35 ml of methanol was stirred 5–7 min and 2–3 drop methylpiperazine was added and stirring was continued. Reaction progress was tracked by TLC (EtOAc/n-hexane, 2:1). Reaction mixture was kept quietly for 24–48 hours. By evaporating of solvent crystals were precipitated. Crystals were separated by filter paper and recrystallized from ethanol (95%) – water mixture. Yield 1.08 g, 73.47%. *T*_{melt}=135°C.

¹H NMR (300 MHz, DMSO-*d*₆), δ, m.h.: 1.71 (s, 3H, CH₃); 3.02 (d, 1H, CH, ³*J*_{H-H} = 11.7); 3.52 (s, 1H, OH); 4.35 (d, 1H, CH, ³*J*_{H-H} = 11.7); 7.00–7.97 (m, 13H, 13Ar–H); 9.85 (s, 1H, NH). ¹³C NMR spektr (DMSO-*d*₆), δ, m.h.: 26.37 (CH₃), 39.88 (CH), 55.94 (CH), 89.19 (=C_{quat.}), 99.65 (O–C_{quat.}), 115.79–116.07 (CH_{arom.}), 119.70 (CN), 120.00 (2CH_{arom.}), 124.19–124.87 (CH_{arom.}), 129.17 (3CH_{arom.}), 130.70 (3CH_{arom.}), 131.08 (CH_{arom.}), 131.99 (2CH_{arom.}), 132.85 (Br–C_{ar.}), 136.13–136.16 (C_{ar.}), 138.81 (2C_{ar.}), 160.32–167.71 (F–C_{ar.}), 161.51 (=C_{quat.}–O), 166.75 (HN–C=O).

Found, %: 61.60 C; 3.99 H; 5.47 N. C₂₆H₂₀N₂O₃FBr. Calculated, %: 61.54 C; 3.94 H; 5.52 N.

6-(4-Bromophenyl)-5-cyano-2-hydroxy-2-methyl-N-phenyl-4-(thiophen-2-yl)-3,4-dihydro-2H-pyran-3-carboxamide (12b) was synthesized in the same conditions by using of 2-(4-bromobenzoyl)-3-(thiophen-2-yl)acrylonitrile (yield 0.95 g, 79.17%). *T*_{melt}=117°C.

¹H NMR (300 MHz, DMSO-*d*₆), δ, m.h.: 1.70 (s, 3H, CH₃); 3.06 (d, 1H, CH, ³*J*_{H-H} = 11.7); 3.58 (s, 1H, OH); 4.63 (d, 1H, CH, ³*J*_{H-H} = 11.7); 6.99–7.88 (m, 12H, 9Ar–H+3CH_{thioph.}); 10.01 (s, 1H, NH). ¹³C NMR

spektr (DMSO-*d*₆), δ, m.h.: 26.27 (CH₃), 35.95 (CH), 56.42 (CH), 89.56 (=C_{quat.}), 99.85 (O–C_{quat.}), 119.69 (CN), 119.90 (2CH_{arom.}), 124.24 (Br–C_{ar.}), 126.06 (CH_{thioph.}), 127.34 (CH_{thioph.}), 127.51 (CH_{thioph.}), 129.23 (2CH_{arom.}), 130.68 (3CH_{arom.}), 132.09 (2CH_{arom.}), 132.14 (C_{ar.}), 138.86 (C_{thioph.}), 142.63 (C_{ar.}), 161.02 (=C_{quat.}–O), 166.56 (HN–C=O).

Found, %: 69.35 C; 4.64 H; 6.70 N. C₂₄H₁₉N₂O₃S. Calculated, %: 69.40 C; 4.58 H; 6.75 N.

6-(4-Bromophenyl)-5-cyano-2-hydroxy-2-methyl-N-phenyl-4-(p-tolyl)-3,4-dihydro-2H-pyran-3-carboxamide (12c) was synthesized in the same conditions by using of 2-(4-bromobenzoyl)-3-(p-tolyl)acrylonitrile (yield 0.21 g, 14.48%). *T*_{melt}=207°C.

¹H NMR (300 MHz, DMSO-*d*₆), δ, m.h.: 1.74 (s, 3H, CH₃); 2.30 (s, 3H, Ar–CH₃); 3.03 (d, 1H, CH, ³*J*_{H-H} = 11.7); 3.57 (s, 1H, OH); 4.45 (d, 1H, CH, ³*J*_{H-H} = 11.7); 7.05–7.92 (m, 13H, 13Ar–H); 9.90 (s, 1H, NH). ¹³C NMR spektr (DMSO-*d*₆), δ, m.h.: 21.14 (CH₃–Ar), 26.32 (CH₃), 40.47 (CH), 55.57 (CH), 86.36 (=C_{quat.}), 99.33 (O–C_{quat.}), 119.61 (CN), 119.73 (2CH_{arom.}), 124.18 (CH_{arom.}), 125.06 (2CH_{arom.}), 125.13 (Br–C_{ar.}), 128.49 (2CH_{arom.}), 130.51 (2CH_{arom.}), 130.87 (2CH_{arom.}), 133.15 (2CH_{arom.}), 135.28 (C_{ar.}), 139.78 (C_{ar.}), 140.65 (C_{ar.}), 141.27 (C_{ar.}), 161.35 (O–C_{quat.}), 166.64 (O=C–NH).

Found, %: 64.46 C; 4.63 H; 5.52 N. C₂₇H₂₃N₂O₃Br. Calculated, %: 64.41 C; 4.57 H; 5.57 N.

4-(4-Bromophenyl)-3-cyano-2-(4-fluorophenyl)-4-hydroxy-6-oxo-N-phenylcyclohexane-1-carboxamide (13a) was synthesized in the same conditions by using of 2-(4-bromobenzoyl)-3-(4-fluorophenyl)acrylonitrile (yield 0.28 g, 17.69%). *T*_{melt}=164°C.

¹H NMR (300 MHz, DMSO-*d*₆), δ, m.h.: 2.84 (d, 1H, CH, ³*J*_{H-H} = 14.1); 3.58 (d, 1H, CH, ³*J*_{H-H} = 13.8); 4.08 (s, 1H, OH); 4.11 (s, 2H, CH₂); 4.35 (d, 1H, CH, ³*J*_{H-H} = 9.9); 7.03–7.62 (m, 12H, 9Ar–H+3CH_{thioph.}); 9.97 (s, 1H, NH). ¹³C NMR spektr (DMSO-*d*₆), δ, m.h.: 45.18 (CH), 47.89 (CH), 54.21 (CH₂), 62.72 (CH), 75.31 (O–C_{quat.}), 115.92–116.20 (CH_{arom.}), 119.12 (CN), 119.34 (2CH_{arom.}), 123.21–123.49

(CH_{arom}), 125.56 (CH_{arom}), 129.23 (3CH_{arom}), 130.45 (2CH_{arom}), 130.98 (CH_{arom}), 131.82 (2CH_{arom}), 132.85 (Br-C_{ar}), 135.92-135.95 (C_{ar}), 138.22 (C_{ar}), 138.26 (C_{ar}), 160.46-166.96 (C_{ar}), 165.93 (O=C-NH), 203.05 (C=O).

Found, %: 61.49 C; 3.88 H; 5.57 N.
C₂₆H₂₀N₂O₃FBr. Calculated, %: 61.54 C; 3.94 H; 5.52 N

4-(4-Bromophenyl)-3-cyano-4-hydroxy-6-oxo-N-phenyl-2-(thiophen-2-yl)cyclohexane-1-carboxamide (13b) was synthesized in the same conditions by using of 2-(4-bromobenzoyl)-3-(thiophen-2-yl)acrylonitrile (yield 0.18 g, 15%). *T*_{melt}=143⁰C.

¹H NMR (300 MHz, DMSO-*d*₆), δ, m.h.: 2.74 (d, 1H, CH, ³*J*_{H-H} = 14.2); 3.55 (d, 1H, CH, ³*J*_{H-H} = 13.8); 3.96 (s, 1H, OH); 4.09 (s, 2H, CH₂); 4.24 (d, 1H, CH, ³*J*_{H-H} = 9.9); 7.02-7.54 (m, 12H, 9Ar-H+3CH_{thioph}); 9.91 (s, 1H, NH). ¹³C NMR spektr (DMSO-*d*₆), δ, m.h.: 44.18 (CH), 47.36 (CH), 54.11 (CH₂), 62.57 (CH), 75.42 (O-C_{quat}), 119.08 (CN), 119.38 (2CH_{arom}), 123.07 (Br-C_{ar}), 125.14 (CH_{arom}), 125.39 (CH_{thioph}), 128.08 (CH_{thioph}), 128.48 (2CH_{arom}), 128.62 (CH_{thioph}), 129.44 (2CH_{arom}), 131.28 (2CH_{arom}), 136.67 (C_{ar}), 139.14 (C_{ar}), 149.98 (C_{thioph}), 165.69 (O=C-NH), 203.02 (C=O).

Found, %: 69.45 C; 4.53 H; 6.81 N.
C₂₄H₁₉N₂O₃S. Calculated, %: 69.40 C; 4.58 H; 6.75 N.

4-(4-Bromophenyl)-3-cyano-4-hydroxy-6-oxo-N-phenyl-2-(p-tolyl)cyclohexane-1-carboxamide (13c) was synthesized in the same conditions by using of 2-(4-bromobenzoyl)-3-(p-tolyl)acrylonitrile (yield 1.10 g, 75.86%). *T*_{melt}=238⁰C.

¹H NMR (300 MHz, DMSO-*d*₆), δ, m.h.: 2.28 (s, 3H, CH₃); 2.85 (d, 1H, CH, ³*J*_{H-H} = 13.7); 3.54 (s, 1H, OH); 3.67 (d, 1H, CH, ³*J*_{H-H} = 13.7); 4.12 (s, 2H, CH₂); 4.30 (d, 1H, CH, ³*J*_{H-H} = 10.0); 7.14-7.65 (m, 13H, 13Ar-H); 9.97 (s, 1H, NH). ¹³C NMR spektr (DMSO-*d*₆), δ, m.h.: 21.18 (CH₃-Ar), 44.36 (CH), 47.51 (CH), 54.19 (CH₂), 62.71 (CH), 76.04 (O-C_{quat}), 119.15 (CN), 119.44 (2CH_{arom}), 123.14 (Br-C_{ar}), 125.37 (CH_{arom}), 128.45 (2CH_{arom}), 129.17 (2CH_{arom}), 129.26 (2CH_{arom}), 130.23 (2CH_{arom}), 131.97

(2CH_{arom}), 137.46 (C_{ar}), 137.77 (C_{ar}), 139.70 (C_{ar}), 142.11 (C_{ar}), 165.92 (O=C-NH), 202.92 (C=O).

Found, %: 64.35 C; 4.52 H; 5.62 N.
C₂₇H₂₃N₂O₃Br. Calculated, %: 64.41 C; 4.57 H; 5.57 N.

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**BƏZİ KNOEVENAGEL ADDUKTLARI ƏSASINDA YENİ PİRAN VƏ TSİKLOHEKSANON
TÖRƏMƏLƏRİNİN SİNTEZİ****F.N.Nağıyev**

3-(4-Tolil)-, 3-(4-metoksifenil)-, 3-fenil-, 3-piridinil-2-(tiofen-2-karbonil)akrilonitrillərin, eləcə də 3-(4-Tolil)-, 3-(thiophen-2-yl) və 2-(4-brombenzoil)-3-(4-flüorfenil)akrilonitrilin asetoasetanilid ilə Mixael birləşmə reaksiyasından həm əvəzlənmiş tsikloheksanon, həm də 3,4-dihidro-2H-piran törəmələri alınmışdır. Sintez edilmiş birləşmələrin quruluşları nüvə maqnit rezonansı spektroskopiyası və X-Ray analizinin köməyi ilə təsdiq edilmişdir.

Açar sözlər: *tiofen, akrilonitrillər, asetoasetanilid, tsikloheksanon, dihidropiran, nüvə maqnit rezonansı spektroskopiyası.*

**СИНТЕЗ НОВЫХ ПРОИЗВОДНЫХ ПИРАНА И ЦИКЛОГЕКСАНОНА НА ОСНОВЕ НЕКОТОРЫХ
АДДУКТОВ КНОВЕНАГЕЛЯ****Ф.Н.Нагиев**

Присоединением по Михаэлю ацетоацетанилида к 3-(4-толил)-, 3-(4-метоксифенил)-, 3-фенил-, 3-пиридирил-2-(тиофен-2-карбонил)акрилонитрилам или 3-(4-толил)-, 3-(тиофен-2-ил) и 2-(4-бромбензоил)-3-(4-фторфенил)акрилонитрилам получены производные циклогексанона и 3,4-дигидро-2H-пирана. Структуры всех синтезированных соединений подтверждены данными спектроскопией ядерно-магнитного резонанса и рентгенографии.

Ключевые слова: *тиофен, акрилонитрилы, ацетоацетанилид, циклогексанон, дигидропиран, спектроскопия ядерно-магнитного резонанса.*