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Study on the Synthesis and Transformations of some Substituted 4-methylquinolin-2(1*H*)-ones

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Abstract: Some different substituted 4-methylquinolin-2(1H)-ones have been synthesized by closing corresponding (un)substituted acetoacetanilides in the presence of ionic liquid [Bmim]OH. Obtained quinolines were converted to its 2-chloro derivatives by reaction with $POCl_3$. Some compounds of substituted tetrazolo[1,5-a]quinolines were synthesized by reacting these 2-chloro derivatives with sodium azide in DMF as solvent. The structures of obtained compounds have been confirmed using spectroscopic methods (IR, NMR and MS).

Keywords: Knorr synthesis, 4-methylquinolin-2(1H)-ones, ionic liquid, sodium azido.

1. Introduction

Quinolones present in molecular skeleton of quinolone antibiotics, which are currently used in disease treatments [1], and is the most consumed antibacterial quinolone worldwide [2]. Of the quinolones, quinolin-2(1*H*)-ones have been synthesized [3], but its 2-chloro derivatives have not been studied much. On the other hand, the ionic liquids have been recently prepared and studied to use in many different chemical processes [4]. Herein, we report some study results about the synthesis and transformations of substituted 4-methylquinolin-2(1H)-ones from corresponding (un)substituted anilines and ethyl acetoacetate.

2. Experimental Section

Melting points were determined by open capillary method on STUART SMP3 instrument (BIBBY STERILIN, UK) and are uncorrected. IR spectra (KBr disc) were recorded on an Impact 410 FT-IR Spectrometer (Nicolet, USA), ^{1}H and ^{13}C NMR spectra were recorded on Avance Spectrometer AV500 (Bruker, Germany) at 500 MHz and 125.8 MHz, respectively, using DMSO-d_6 as solvent and TMS as internal standard. Analytical thin-layer chromatography (TLC) was performed on silica gel 60 $WF_{254}S$ (Merck, Germany), 1-Butyl-3-methylimidazolium hydroxide, [Bmim]OH, was prepared by our method [5].

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*2.1. General procedure for synthesis of substituted 4-methylquinolin-2(1H)-ones (**3a-h**)*

To a mixture of appropriate (un)substituted anilines (**1b-d**, 0.1 mol), ethyl acetoacetate (15.1 ml, 0.12 mol) in 100-ml one-necked round-bottomed flask 0.2 ml of [Bmim]OH was added. After that, xylene (15 ml) was added to the reaction mixture while shaking well. A single distillation apparatus was set up and the distillation was carried out slowly and carefully for about 120 minutes to remove ethanol that was created in reaction. Then, the solvent xylene was removed by rotating distillation under reduced pressure. The residue, namely crude acetoacetanilides **2a-d**, was used directly to ring close to quinoline-2(1*H*)-ones **3a-d**.

To the above obtained residue in a 100-ml one-necked round-bottomed flask, 30 ml of 70−72% H_2SO_4 (d=1.72 g/cm^3) was added while stirring well. Then, the reaction mixture was heated carefully on the water bath at 90°C. The smoke formed at this temperature indicated that the reaction began. After the release of smoke was diminished and the reaction mixture was no longer bubbling gas anymore, the mixture was heated at 95°C for about 30 minutes. The mixture was cooled to about 60° C and poured carefully into 300 g of crushed ice, then filtered the precipitate, washed well with cold water to pH 7 acid, and crystallized from 96% ethanol to efford the products **3a-d**.

3a, **R=H:** White solid, yield 78%, mp 221−223°C. IR (KBr), ν (cm^{-1}): 3105, 2914, 2815, 2723, 1659, 1544, 1503, 1431, 1388. ^{1}H NMR (500.13 MHz, DMSO-d_6), δ (ppm): 11.58 (s, 1H, NH lactam), 7.71 (dd, 1H, *J* = 1.0, 8.0 Hz. H-8), 7.50 (td. 1H. *J* = 1.0, 8.0 Hz, H-7), 7.31 (dd, 1H, *J* = 1.0, 8.0 Hz, H-5), 7.20 (td, *J* = 1.0, 8.0 Hz, 1H, H-6), 2.42 (d, 1H, *J* = 1.5 Hz, 4-Me), ^{13}C NMR (125.75 MHz, DMSO-d_6), δ (ppm): 162.11 (C-2), 148.42 (C-4), 139.10 (C-8a), 130.75 (C-7), 125.19 (C-5), 122.13 (C-6), 121.29 (C-3), 120.06 (C-4a), 115.88 (C-8), 18.91 (4-Me).

3b, **R=6-Me:** White solid, yield 71.9%, mp 188−190°C. IR (KBr) ν (cm^{-1}): 3429, 3150, 2843, 1654, 1554, 1496, 1424, 1377.

3c, **R=7-Me:** White solid, yield 87.9%, mp 175−177°C. IR (KBr) ν (cm^{-1}): 3280, 3155, 2999, 2866, 1663, 1560, 1497, 1420, 1374.

3d, **R=8-Me:** White solid, yield 75.1%, mp 178−180°C. IR (KBr) ν (cm^{-1}): 3414, 3279, 3073, 2893, 1661, 1546, 1490, 1406, 1390. ^{1}H NMR (500.13 MHz, DMSO-d_6) δ (ppm): 11.50 (s, 1H, NH), 7.59 (d, 1H, *J* = 8.0 Hz, H-5), 7.10 (s, 1H, H-3), 7.03 (dd, 1H, *J* = 1.0, 8.0 Hz, H-6), 6.31 (d, 1H, *J* = 1.0 Hz, H-8), 2.39 (d, 3H, *J* = 1.0 Hz, 4-Me), 2.37 (s, 3H, 7-Me), ^{13}C NMR (125.75 MHz, DMSO-d_6) δ (ppm): 162.26 (C-2), 148.26 (C-4), 140.73 (C-8a), 139.25 (C-7), 125.05 (C-6), 123.49 (C-5), 120.29 (C-3), 118.96 (C-4a), 115.63 (C-8), 21.68 (7-Me), 18.87 (4-Me),

3e, **R=6,8-diMe:** White solid, yield 48.8%, mp 188−190°C. IR (KBr) ν (cm^{-1}): 3285, 3150, 2890, 2866, 1665, 1560, 1497, 1420, 1374. ^{1}H NMR (500.13 MHz, DMSO-d_6), δ (ppm): *Amide tautomer:* 8.07 (s, 1H, OH), 7.62 (s, 1H, H-5), 7.52 (s, 1H, H-7), 7.43 (d, 1H, *J* = 0.5 Hz, H-3), 2.65 (d, 3H, *J* = 0.5 Hz, 4-Me), 2.62 (s, 3H, 6-Me), 2.51 (s, 3H, 8-Me); *Iminol tautomer:* 12,17 (s br, 1H, NH), 7.72 (s, 1H, H-5), 7.64 (s, 1H, H-7), 7.00 (s, 1H, H-3), 2.49 (s, 3H, 4-Me), 2.23 (s, 3H, 6-Me), 2.22 (s, 3H, 8-Me). ^{13}C NMR (125.75 MHz, DMSO-d_6), δ (ppm): *Amide tautomer:* 148.7 (C-2), 136.6 (C-4), 135.4 (C-8a), 128.4 (C-6), 127.2 (C-8), 122.5 (C-3), 122.2 (C-5 & C-7), 20.8 (6-Me), 18.7 (8-Me),18.4 (4-Me), *Iminol tautomer:* 153.6 (C-2), 148.2 (C-8a), 136.1 (C-4), 133.2 (C-8), 132.0 (C-7), 131.2 (C-5), 127.0 (C-6 & C-7), 121.7 (C-3), 21.8 (6-Me), 18.4 (4-Me), 18.1 (8-Me),

3f, **R=6-OMe:** White solid, yield 59.8%, mp 257−259°C. IR (KBr) ν (cm^{-1}): 3155, 2991, 2855, 1658,1619, 1550, 1497, 1420, 1373.

3g, **R=7-OMe:** White solid, yield 75.1%, mp 263−265°C. IR (KBr) ν (cm^{-1}): 3247, 2953, 2827, 1655, 1610, 1549, 1500, 1490, 1413, 1390.

3h, **R=6-OEt:** White solid, yield 57.7%, mp 259−261°C. IR (KBr) ν (cm^{-1}): 3155, 2991, 2855, 1670,1619, 1550, 1497, 1390. ^{1}H NMR (500.13 MHz, DMSO-d_6), δ (ppm): *Amide tautomer*: 11,46 (s, 1H, NH), 7,85 (d, 2H, *J* = 9,0, H-8), 7,44 (dd, 2H, *J* = 2,75, 9,25 Hz, H-7), 7,42 (s, 2H, H-3), 7,33 (d, 2H, *J* = 2,5 Hz, H-5), 4,42 (q, 4H, *J* = 7,0 Hz, 2×6-O**CH$_2$**CH$_3$), 2,65 (s, 6H, 4-Me×2), 1,42 (t, 6H, *J* = 7,0 Hz, 2×6-OCH$_2$**CH$_3$**), *Iminol tautomer*: (δ_{OH} absent due to trace of water in solvent DMSO-d_6), 7.25 (d, 1H, *J* =9.0 Hz, H-8), 7.16 (dd, 1H, *J* = 2.5, 9.0 Hz, H-7), 7.12 (d, 1H, *J* = 2.0 Hz, H-5), 6.38 (s, 1H, H-3), 4.08 (q, 2H, *J* = 7.0 Hz, 6-O**CH$_2$**CH$_3$), 2.40 (s, 3H, 4-Me), 1.35 (t, 3H, *J* = 7.0 Hz, 6-OCH$_2$**CH$_3$**). ^{13}C NMR (125.75 MHz, DMSO-d_6), δ (ppm): *Amide tautomer*: 157.4 (C-2 & C-6), 147.9 (C-4), 130.3 (C-4a & C-8a), 123.0 (C-8), 122.7 (C-3), 119.8 (C-7), 104.2 (C-5), 64.1 (2×6-O**CH$_2$**CH$_3$), 18.6 (4-Me), 15.0 (6-OCH$_2$**CH$_3$**), *Iminol tautomer*: 161.6 (C-2), 153.8 (C-6), 147.4 (C-4), 143.1 (C-8a), 133.5 (C-8), 128.3 (C-7), 121.7 (C-4a), 120.7 (C-7), 117.1 (C-3), 108.1 (C-5), 64.0 (6-O**CH$_2$**CH$_3$), 19.0 (4-Me), 15.1 (6-OCH$_2$**CH$_3$**).

*2.2. General procedure for synthesis of substituted 2-chloro-4-methylquinolines (**4a-d**)*

To the appropriate (un)substituted 4-methylquinolin-2(1*H*)-one (**3a** or **3b-d**, 0.02 mol), in 50-ml one-necked flask was added freshly distilled phosphoryl chloride (8 ml) and shaked the mixture well. Heated the reaction mixture on water at 70° C until the solid dissolved completely, and then 1 h more. Cooled the reaction mixture to room temperature, and poured slowly and carefully into 300 g of crushed ice while stirring well (noted that crushed ice remained in the mixture to ensure the temperature was not over 20°C in this process), then neutralised the solution with 4M sodium hydroxide to pH 7, and allowed to stand overnight. Checked the pH of the solution, if the pH decreased, then NaOH solution was added until neutral pH is reached. Filtered the precipitate separated, carefully rinsed with cold water until neutral pH. Crystallized from 96% ethanol to yield products **4a-d** as white powder.

4a, **R=H:** Opaque white solid, yield 89.2%, mp 51−52°C. IR (KBr) ν (cm^{-1}): 3286, 3057, 2933, 2871, 1581, 1552, 1500, 1439, 1390. ^{1}H NMR (500.13 MHz, DMSO-d_6), δ (ppm): 8.01 (d, 1H, *J* = 8.25 Hz, H-8), 7.96 (d, 1H, *J* = 7.25 Hz, H-5), 7.72 (td, 1H, *J* = 1.0, 7.25 Hz, H-6), 7.58 (td, 1H, *J* = 1.0, 8.25 Hz, H-7), 7.25 (s, 1H, H-3), 2.69 (s, 3H, 4-Me). ^{13}C NMR (125.75 MHz, DMSO-d_6), δ (ppm): 150.6 (C-2), 147.7 (C-4), 147.6 (C-8a), 130.3 (C-7), 129.2 (C-8), 127.0 (C-4a), 126.7 (C-6), 123.8 (C-5), 122.5 (C-3), 18.6 (4-Me). ESI-MS, *m/z* (%): 180([M+2+H]$^+$, 31), 178([M+H]$^+$, 100), 183(5), 157(15), 142(15), 120(20), 106(10), 79(20).

4b, **R=6-Me:** Pale brown solid, yield 96.1%, mp 98−100°C. IR (KBr) ν (cm^{-1}): 3153, 3059, 2915, 2852, 1558, 1501, 1435, 1376. ^{1}H NMR (500.13 MHz, $CDCl_3$), δ (ppm): 7.90 (d, 1H, *J* = 8.5 Hz, H-8), 7.71 (pseudo-singlet, 1H, H-5), 7.55 (dd, 1H, *J* = 1.5, 8.5 Hz, H-7), 7.21 (s, 1H, H-3), 2.66 (s, 3H, 6-Me), 2.56 (s, 3H, 4-Me), ^{13}C NMR (125.75 MHz, $CDCl_3$), δ (ppm): 149.6 (C-2), 147.0 (C-4), 146.1 (C-8a), 136.7 (C-6), 132.4 (C-7), 128.8 (C-8), 126.9 (C-4a), 122.9 (C-5), 122.4 (C-3), 21.8 (6-Me), 18.6 (4-Me). ESI-MS, *m/z* (%): 194 ([M+2+H]$^+$, 30), 192([M+H]$^+$, 100), 179(5), 174(10), 163(10), 157(15), 142(5), 120(5).

4c, **R=8-Me:** Pale brown solid, yield 86.1%, mp 92−93°C. IR (KBr) ν (cm^{-1}): 3107, 3013, 2956, 2837, 1591, 1426,1488, 1393.

4d, **R=6-OMe:** Grey-brown solid, yield 96.2%, mp 130−132°C. IR (KBr) ν (cm^{-1}): 3026, 2930, 2836, 1591, 1563, 1490, 1429, 1390.

*2.3. General procedure for synthesis of substituted 5-methyltetrazolo[1,5-a]quinolines (**5a**,**b**,**f**)*

To the mixture consisting of (un)substituted 2-chloro-4-methylquinolin (**4a**, **4b** or **4f**, 1 mmol) and sodium azide (1,5 mmol) in 50 ml of anhydrous DMF, a few crystals of KI was added. Shaked the reaction mixture well and

then heated on water bath at 75−80°C for 12 hours. The solvent was removed by distillation under reduced pressure. Water (about 50 ml) was added to the residue in order to dissolve inorganic salts. Precipitate was filtered, washed well with water, and crystallized from 96% ethanol with activated charcoal to obtain corresponding 5-methyltetrazolo[1,5-*a*]quinolines **5a**, **5b** or **5f**.

5a, **R=H:** Pale beige solid, yield 71.9%, mp 199−200°C. IR (KBr) ν (cm^{-1}): 1620, 1564, 1500, 1449, 1373. ^{1}H NMR (500.13 MHz, DMSO-d_6) δ (ppm): 8.84 (d, 1H, J = 7.5 Hz, H-9), 8.63 (d, 1H, J = 8.0 Hz, H-6), 7.99−7.98 (m, 1H, H-8), 7.96 (s, 1H, H-4), 7.85 (t, 1H, J = 7.25 Hz, H-7), 2.75 (s, 3H, 5-Me). ^{13}C NMR (125.75 MHz, DMSO-d_6) δ (ppm): 147.3 (C-3), 142.7 (C-1), 131.8 (C-5), 130.2 (C-8), 128.5 (C-7), 126.9 (C-6), 124.4 (C-10), 116.9 (C-9) và 111.5 (C-4), 19.5 (5-Me).

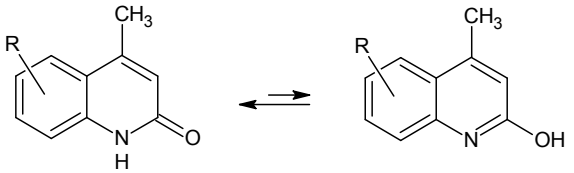
5b, **R=7-Me:** White crystal, yield 58.6%, mp 98−99°C. IR (KBr) ν (cm^{-1}): 1635, 1565, 1510, 1450, 1373. ^{1}H NMR (500.13 MHz, DMSO-d_6) δ (ppm): 7.80 (d, 1H, J = 8.5 Hz, H-9), 7.84 (s, 1H, H-4), 7.62 (dd, 1H, J = 1.75, 8.5 Hz, H-8), 7.38 (d, 1H, J = 1.75 Hz, H-6), 2.63 (d, 3H, J = 1.0 Hz, 5-Me), 2.51 (s, 3H, 7-Me). ^{13}C NMR (125.75 MHz, DMSO-d_6) δ (ppm): 149.1 (C-3), 148.5 (C-1), 145.9 (C-4), 137.1 (C-7), 133.0 (C-8), 128.5 (C-9), 127.0 (C-10), 123.8 (C-6), 122.5 (C-4), 18.4 (5-Me), 21.7 (7-Me),

5f, **R=6-OMe:** White solid, yield 90%, mp 150−151°C. IR (KBr) ν (cm^{-1}): 1630, 1574, 1503, 1460, 1377. ^{1}H NMR (500.13 MHz, DMSO-d_6) δ (ppm): 7.84 (d, 1H, J = 9.0 Hz, H-9), 7.44 (dd, 1H, J =9.0, 3.0 Hz, H-8), 7,41 (d, 1H, J = 0.5 Hz, H-4), 7.33 (d, 1H, J = 3.0 Hz, H-6), 3.94 (s, 3H, 7-OMe), 2.65 (d, 3H, J = 0.5 Hz, 5-Me). ^{13}C NMR (125.75 MHz, DMSO-d_6) δ (ppm): 158.1 (C-7), 147.9 (C-3), 147.4 (C-1), 143.2 (C-5), 130.3 (C-9), 128.2 (C-10), 122.9 (C-8), 122.7 (C-4), 103.5 (C-6), 56.1 (7-Me), 18.7 (5-Me).

3. Results and discussion

The conversion reaction of ethyl acetoacetate with (un)substituted anilines 1 into corresponding acetoacetanilides 2 considered completely when ethanol formed was no longer distilled. Then, the solvent was removed entirely, and the residue consists mostly of acetoacetanilide was used to direct ring-closure into 4-methylquinolin-2(1*H*)-ones 3 without isolation. We found that the use of concentrated (98%) sulfuric acid was not suitable for this cyclizing reaction due to no product was obtained or the reaction yields were very low. The concentration of sulfuric acid was >80% also show that the results are not satisfactory. Through a survey about the influence of the concentrations of sulfuric acid to obtain the satisfied yields of 4-methylquinolin-2(1*H*)-one, we found that concentrations of sulfuric acid around 70−72% to be the most appropriate for the above conversion of acetoacetanilides to corresponding 4-methylquinolin-2(1*H*)-ones. The lower concentrations of sulfuric acid did not promote this reaction (*Scheme 1*).

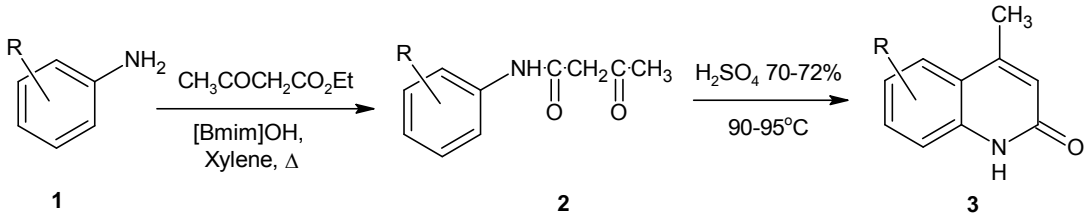
IR spectra of these quinolines 3 had some characteristic absoption bands, such as 3454−3341 cm^{-1} (ν_{NH_lactam}), 1537 cm^{-1} (δ_{NH_lactam}), 1657 cm^{-1} ($\nu_{C=O\_lactam}$). In ^{1}H NMR spectra, chemical shift was in region of 11.60−11.40 ppm belonging to NH bond in lactam. Carbon atom in carbonyl had resonance signals at δ=160−150 ppm. We found that some of substituted 4-methylquinolin-2(1*H*)-ones (3e and 3h) showed the existence of amide-iminol tautomerism below:



Amide tautomer was characterized by ^{1}H NMR signals of the NH(lactam) bond at δ=8.07 ppm, and C=O(lactam) at δ=153.6 ppm,

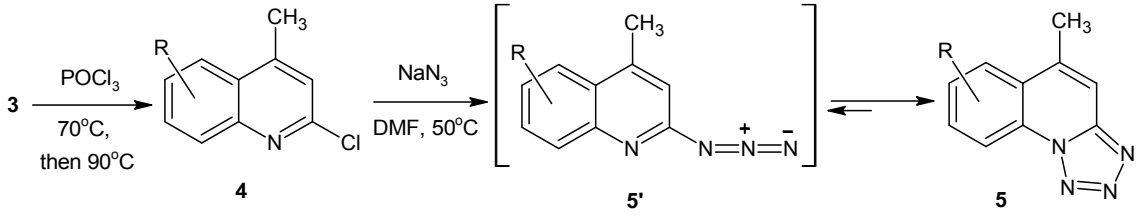
meanwhile, iminol tautomer had chemical shift at δ=12.17 ppm (OH phenol type), and the signal of C-2 carbon atom moved about more upfield, δ = 148.7 ppm.

In order to convert 4-methyl-quinoline-2(1*H*)-ones 3 to the chloro derivatives 4a-d, respectively, the former was allowed to react with $POCl_3$ at temperatures of 70−90°C (*Scheme 2*). The reaction yields were 86−90%. IR spectra of 2-chloro-4-methylquinolines 4 had some characteristic absoption bands, such as 3057−3120 cm^{-1} ($\nu_{C-H\_quinoline}$), 763 cm^{-1} (ν_{C-Cl}), 1530−1660 cm^{-1} ($\nu_{C=C\_aromatic}$). ^1H NMR spectra of 2-chloro-4-methylquinolines 4 had two regions of signals: aromatic (δ = 8.0–7.0 ppm) and aliphatic (δ =~2.7 ppm). ESI-MS of 4a, for example, had two peaks which had *m/z* 178 and *m/z* 180, with relative intensities at 31% and 100%, relative to the two pseudo-maloecular ions $[M+H]^+$ and $[M+H+2]^+$, respectively. This event was according to the presence of one chlorine atom in molecule 4a.



Scheme 1. Synthesis of substituted 4-methylquinolin-2(1*H*)-ones, where, R=H (**a**), 6-CH_3 (**b**), 7-CH_3 (**c**), 8-CH_3 (**d**), 6,8-diCH_3 (**e**), 6-OCH_3 (**f**), 7-OCH_3 (**g**), 6-O C_2H_5 (**h**).

Next, substituted 2-chloro-4-methylquinolines **4** was allowed to react with sodium azide in DMF. Reaction proceeded at 70°C. We found that reactions of the 4-chloro-2-methylquinolines with sodium azide gave general the corresponding 4-azido-2-methylquinolines [6], whereas the reaction of 2-chloro-4-methylquinolines with sodium azide did not normally lead to the corresponding azido derivatives, but azido intermediates **5′** ring-closured intramolecularly into fused-ring system of tetrazolo [1,5-*a*]quinoline **5** (*Scheme 2*).



Scheme 2. Conversion of substituted 4-methylquinolin-2(1*H*)-ones to corresponding (un)substituted 5-methyltetrazolo[1,5-*a*]quinolines, where, R=H (**a**), 6-CH_3 (**b**), 7-CH_3 (**c**), 8-CH_3 (**d**), 6,8-diCH_3 (**e**), 6-OCH_3 (**f**).

The conversion of 2-chloro-4-methylquinolines to tetrazolo[1,5-*a*]quinolines through corresponding 2-azido-4-methylquinolines was performed with DMF as solvent. This solvent helps dissolved the compound 2-chloroquinolines as well as sodium azide to facilitate the reaction. After the reaction, the tetrazolo[1,5-*a*]quinolines were deep yellow solid, have high melting temperature, soluble in DMF and DMSO, and slightly soluble in ethanol and methanol.

The IR spectra of all tetrazolo[1,5-*a*]quinolines 5 showed no absorption band in the region of 2200−2100 cm^{-1} of azido group.

This indicated that the 2-azido compounds did not exist, but instead of the fused heterocycle, namely tetrazolo[1,5-*a*]quinoline. The typical signal for all protons of the compound 5 appeared in ^{1}H NMR spectra. Methyl group in the position 5 on the quinoline ring component had chemical shift in the upfield region at δ =~2.75 ppm (as singlet). The signals located in the downfield region at δ=8.7−7.4 ppm belonged to four protons of tetrazolo[1,5-*a*]quinoline. Proton H-4 had a chemical shift at δ=7.96 ppm in singlet in 5a. Resonance signal of proton H-6 was downfield at δ=8.63 ppm as doublet with the coupling constant of *J*=8.0 Hz. Chemical shift at δ=8.84 ppm belonged to proton H-9 as doublet with *J*=7.5 Hz. Multiplet signal in region at δ=7.99−7.98 ppm belonged to the proton H-8; Meanwhile, proton H-7 had resonance at δ=7.85 ppm as triplet with *J*=7.25 Hz. Amongst the protons in benzene component of quinoline ring, this proton had a resonance in the strongest field.

4. Conclusion

The Knorr cyclization of (un)substituted acetoacetanides have been performed through acetoacetanilides in a one-pot reaction by using ionic liquid [Bmim]OH as catalyst from substituted anilines and ethyl acetoactate. Some obtained substituted 4-methylquinolin-2(1*H*)-ones have been converted to tetrazolo[1,5-*a*]quinoline via chloro derivatives. Their structures were confirmed by IR, NMR and MS methods.

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Nghiên cứu tổng hợp và chuyển hoá một số các 4-methylquinolin-2(1*H*)-on thế

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Tóm tắt: Một số hợp chất 4-methylquinolin-2(1*H*)-on thế khác nhau đã được tổng hợp bằng cách vòng hóa các acetoacetanilide thế tương ứng khi có mặt của chất lỏng ion [Bmim]OH. Các quinoline đã tổng hợp được chuyển hoá tiếp thành dẫn xuất chloro tương ứng bằng phản ứng với $POCl_3$. Một số hợp chất tetrazolo[1,5-*a*]quinolin thế đã nhận được bằng phản ứng của dẫn xuất chloro này với natri azide trong DMF. Cấu trúc của các hợp chất đã tổng hợp được xác nhận bằng các phương pháp phổ (IR, NMR và MS).

Từ khóa: Tổng hợp Knorr, 4-methylquinolin-2(1*H*)-on, chất lỏng ion, natri azide.