ISSN 1070-3632, Russian Journal of General Chemistry, 2018, Vol. 88, No. 5, pp. 892–897. © Pleiades Publishing, Ltd., 2018.
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Single-Pot Synthesis of Alkyl-Substituted Quinolines and Indoles via Photoinduced Oxidation of Primary Alcohols

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Received December 28, 2017

Abstract—Single-pot synthesis of alkyl-substituted quinolines and indoles has been performed via photoinduced oxidation of primary aliphatic alcohols (C_2–C_5) and condensation of the aldehydes (products of the alcohols oxidation) with aniline under the action of iron-containing catalysts and inorganic oxidants. The synthesis was the most efficient in the presence of $FeCl_3 \cdot 6H_2O$ as catalyst and 10% aqueous solution of NaOCl as oxidant with irradiation by Hg lamp. The synthesis mechanism through photoinduced oxidation of primary aliphatic alcohol has been suggested.

Keywords: alkylquinolines, alkylindoles, aliphatic alcohols, hypochlorites, photoinduced oxidation

DOI: 10.1134/S1070363218050080

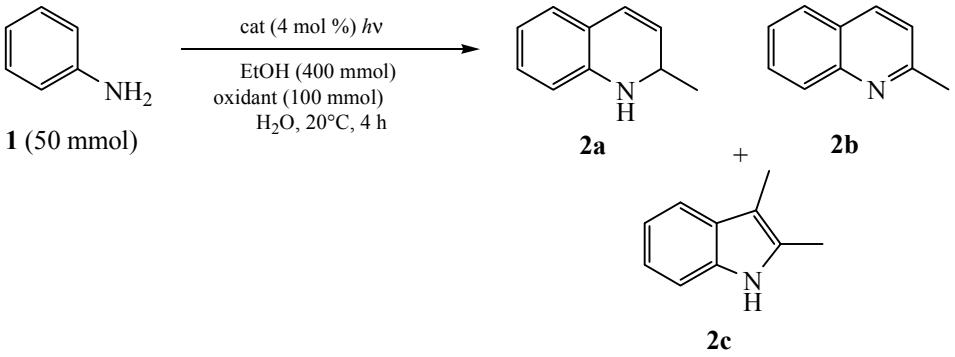
The approaches based on activation with UV or visible light as alternative to heat-induced (thermal) reactions have become important methods of catalytic synthesis of organic compounds [1–5]. This peculiar method has been used in the synthesis of nitrogen-containing heterocyclic compounds. For example, regioselective synthesis of indole derivatives induced by visible light has been described [6]. The reaction between arylamines, terminal alkyne, and quinones occurs in the presence of copper(I) chloride as catalyst. The reaction of *o*-ethenylaryl isocyanides with organic disulfides [$(PhTe)_2$ catalyst] photoinduced by visible light leads to sulfur-containing indole derivatives [7]. Photoinduced synthesis of quinoline bases from diazonium tetrafluoroborate and alkenes or alkynes in the presence of $NaBH_4$ in acetonitrile with different photocatalysts has been studied [8]. The highest efficiency was observed in the case of 10-methyl-9,10-dihydroacridine catalyst.

It is known that indole and quinoline derivatives are found in various alkaloids, many of which exhibit high biological activity. In view of this, derivatives of indole and quinoline have been widely applied in the synthesis of novel drugs [9–14]. Moreover, quinolines and tetrahydroquinolines are ligand of chiral catalysts [15] and are used in the production of organic light-emitting diodes (OLED) [16]. Polyquinolines prepared from quinolines can be used in the synthesis of nano- and mesostructured compounds, interesting materials for organic electronics and nonlinear optics [17].

Several thermal methods of synthesis of derivatives of indoles [18] and quinolines [19–21] have been described, yet the photocatalytic and photoinduced synthesis of these nitrogen-containing heterocycles are advantageous since they use simpler and better available reactants. At the same time, this process has been scarcely studied so far. Herein, we present the data on the single-pot synthesis of alkyl-substituted quinolines and indoles via photoinduced oxidation of primary aliphatic alcohols and dark catalytic condensation of the formed aldehydes with aniline under the action of iron-containing catalysts and inorganic oxidants.

Modeling of single-pot synthesis of alkyl-substituted quinolines and indoles. The single-pot synthesis of alkyl-substituted quinolines and indoles was studied in ethanol using a model system shown in Scheme 1. The conditions optimization was targeted at the choice of the most efficient catalyst and oxidizer and investigation of the photoactivation effect. In the model system, the products (2-methyl-1,2-dihydroquinoline **2a**, 2-methylquinoline **2b**, and 2,3-dimethylindol **2c**) were formed in the 1 : 1 : 1 molar ratio. In contrast to the known catalytic condensation

Scheme 1.



of aniline with aliphatic aldehyde [22], *N*-alkylanilines were not formed. The studied model system was elaborated basing on the two-stage catalytic synthesis of 2,3-dialkylquinolines via condensation of the products of alcohols photooxidation with aniline in the presence of $FeCl_3 \cdot 6H_2O$ [23].

The effects of the nature of catalyst and oxidation as well as photoactivation on the conversion of starting aniline **1** (used as the merit of the overall process efficiency) are summarized in Table 1. The following catalysts were tested: $FeCl_3 \cdot 6H_2O$, $Fe_2(SO_4)_3 \cdot 9H_2O$, $Fe(NO_3)_3 \cdot 6H_2O$, $K_3[Fe(CN)_6]$, $Fe(acac)_3$, and $Fe(OAc)_2$. The highest catalytic efficiency was observed for $FeCl_3 \cdot 6H_2O$ (Table 1, Exp. 1). $Fe_2(SO_4)_3 \cdot 9H_2O$, $Fe(NO_3)_3 \cdot 6H_2O$, and $Fe(OAc)_2$ were somewhat less active (Table 1, Exp. 4–6). The $K_3[Fe(CN)_6]$ and $Fe(acac)_3$ complexes did not reveal catalytic activity (Table 1, Exp. 7, 8).

Known selective oxidants transforming alcohols into the corresponding aldehydes: DMSO, CrO_3, and $K_2Cr_2O_7$ [24], I_2 [25], NaOCl, KOCl, and $Ca(OCl)_2$ [26–29] were also tested in the model system. DMSO did not reveal the oxidation activity (Table 1, Exp. 11). $K_2Cr_2O_7$ (Exp. 12) and CrO_3 (Exp. 13) were converted into the chromite $Fe(CrO_2)_2$ in an aqueous-alcoholic solution of iron(III) chloride. The iodoform reaction occurred in the experiment with I_2 (Table 1, Exp. 14).

Only aqueous solutions of hypochlorites NaOCl (Table 1, Exp. 1–6) and KOCl (Exp. 9) with mass fraction of the active compound 10% revealed acceptable oxidation activity. Aqueous suspension of $Ca(OCl)_2$ was less active (Table 1, Exp. 10).

Photoactivation of the model active was selective. It was targeted exclusively on the acceleration of the oxidation of ethanol into acetaldehyde with aqueous solution of NaOCl catalyzed by $FeCl_3 \cdot 6H_2O$. Further condensation of acetaldehyde with aniline occurred in the same reactor but without irradiation. The highest efficiency of the stage of EtOH oxidation and, hence, the overall process, was observed under irradiation with Hg lamp (Table 1, Exp. 1), whereas irradiation with Xe lamp was less efficient (Table 1, Exp. 2). However, acceptable result could be achieved with prolonged (24 h) irradiation with visible light. Without any photoactivation (in the dark chamber), the stage of EtOH was very slow, and the resulting conversion of compound **1** during 4 h was as low as 5% (Table 1, Exp. 3).

Thermal activation (up to 100°C) of EtOH oxidation with aqueous solution of NaOCl catalyzed by $FeCl_3 \cdot 6H_2O$ led to poor selectivity of the alcohol oxidation, yielding a mixture of acetaldehyde, acetic acid, acetal, ethyl acetate, and the chlorination products, similarly to the known haloform reaction [30]. Hence, the selectivity of the alcohol oxidation was reduced on heating, and further condensation stage will become nonselective as well.

Possible mechanism of synthesis of alkyl-substituted quinolines and indoles via photoinduced oxidation of primary aliphatic alcohols in the model system. UV irradiation is known to improve the efficiency of the Fenton process, due to the generation of hydroxyl radicals: $Fe(H_2O)^{3+} + h\nu \rightarrow Fe^{2+} + {}^{\cdot}OH + H^+$ [31, 32]. The maximum in the absorption spectrum (λ_{max}) of the hydrate complex $Fe(H_2O)^{3+}$ is at 240 nm. Hence, photoactivation with a medium-pressure Hg lamp (spectral range 222–1368 nm) could produce the ${}^{\cdot}OH$ radicals in the model system. The photogenerated ${}^{\cdot}OH$ could induce the radical oxidation of alcohols into aldehydes under a Hg lamp irradiation in the $FeCl_3 \cdot 6H_2O$–ROH system [33]. Basing on that, we suggested the following mechanism of synthesis of compounds **2a**–**2c** in the model system (Scheme 2).

Table 1. Effect of the catalyst and oxidant nature and photoactivation on conversion of aniline in model reaction

Exp. no.	Catalyst	Oxidant	Photoactivation	Conversion, %	Exp. no.	Catalyst	Oxidant	Photoactivation	Conversion, %
1	$FeCl_3 \cdot 6H_2O$	NaOCl	UV (λ<400 nm)	>99	8	$Fe(acac)_3$	NaOCl	UV (λ<400 nm)	–
2	$FeCl_3 \cdot 6H_2O$	NaOCl	Visible light (λ>400 nm)	33	9	$FeCl_3 \cdot 6H_2O$	KOCl	UV (λ<400 nm)	91
3	$FeCl_3 \cdot 6H_2O$	NaOCl	Dark chamber	5	10	$FeCl_3 \cdot 6H_2O$	$Ca(OCl)_2$	UV (λ<400 nm)	84
4	$Fe_2(SO_4)_3 \cdot 9H_2O$	NaOCl	UV (λ<400 nm)	95	11	$FeCl_3 \cdot 6H_2O$	DMSO	UV (λ<400 nm)	–
5	$Fe(NO_3)_3 \cdot 6H_2O$	NaOCl	UV (λ<400 nm)	98	12	$FeCl_3 \cdot 6H_2O$	$K_2Cr_2O_7$	UV (λ<400 nm)	27
6	$Fe(OAc)_2$	NaOCl	UV (λ<400 nm)	72	13	$FeCl_3 \cdot 6H_2O$	CrO_3	UV (λ<400 nm)	34
7	$K_3[Fe(CN)_6]$	NaOCl	UV (λ<400 nm)	–	14	$FeCl_3 \cdot 6H_2O$	I_2	UV (λ<400 nm)	Iodoform reaction

$Fe(H_2O)^{3+}$ ions absorbed quants of a Hg lamp irradiation and oxidized the coordinated water molecules with the formation of hydroxyl radicals and hydroxonium ions. Reduced Fe^{2+} ions were converted back into the hydrated $Fe(H_2O)^{3+}$ ions under the action of the oxidizer hypochlorite in acidic medium. Hence, a cyclic photoredox process generating hydroxyl radical was induced in the system. The alcohol molecules were oxidized by the hydroxyl radicals in an aqueous medium into acetaldehyde. Acetaldehyde was accumulated in the system only at the photoactivation stage.

The second stage of the single-pot synthesis, catalytic condensation, occurred upon addition of aniline without irradiation. The condensation led to the formation of the Schiff's bases (azomethines) in two forms: aldimine **2A** and enamine **2B**. Fe^{3+} ions induced the intermolecular cyclization of the azomethines **2A**, **2B** (pathway *a*) into 1,2-dihydroquinoline **2a**. That process was accompanied by elimination of aniline [34, 35]. Product **2b** was formed via oxidation of compound **2a** with NaOCl.

The formation of 2,3-dimethylindole **2c** from azomethine likely occurred via the pathway *b* under the catalytic action of Fe^{2+} ions, since the product **2c** appeared only in the deficiency of the oxidant in the system (no more than 100 mmol of hypochlorite), when Fe^{2+} were relatively stable.

Effect of the alcohol nature on the synthesis of alkyl-substituted quinolines and indoles. Slight influence of the nature of the primary alcohol (C_2–C_5) on the conversion of aniline **1** and the products composition (Table 2). Synthesis of alkyl-substituted quinolines and indoles in shown in Scheme 3.

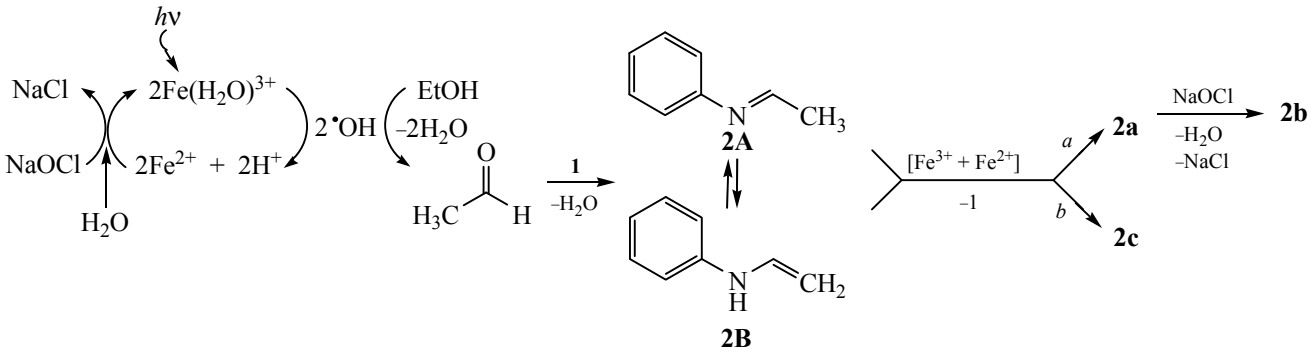
The reaction products contained substituted hydroquinolines **2a–5a**, quinolines **2b–5b**, and 2,3-dialkylindoles **2c–5c**. The yield of quinolines **2b–5b** was somewhat increased with the increase in the length of the hydrocarbon part of the alcohol, but the conversion of aniline was down to 87% (Table 2, Exp. 4).

In summary, we developed a single-pot method of synthesis of alkyl-substituted quinolines and indoles, via photoinduced oxidation of primary alcohol C_2–C_5 with a Hg lamp irradiation, followed by condensation of the formed aldehydes with anilines in dark with $FeCl_3 \cdot 6H_2O$ as catalyst and 10% aqueous solution of NaOCl as oxidant. The synthesis occurs at room temperature and atmospheric pressure in an aqueous medium within 4 h. The mechanism of the process was suggested.

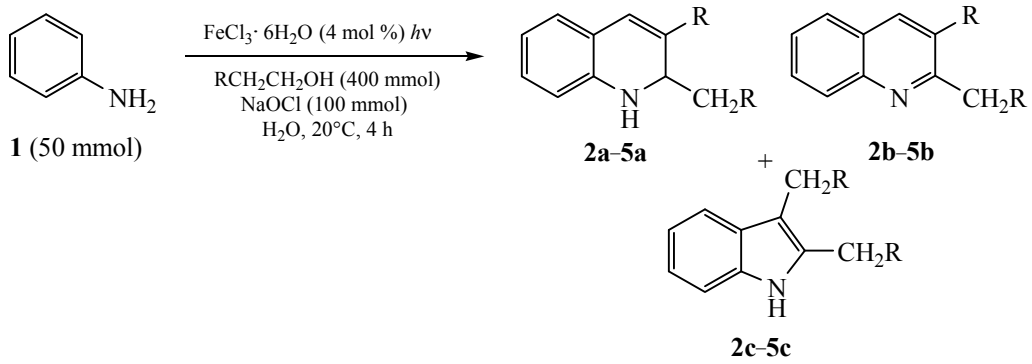
EXPERIMENTAL

The starting chemicals ("chemical pure" grade, EKOS-1, Russia): ethanol, propanol-1, butanol-1, pentanol-1, diethyl ether, and aniline were purified by distillation [36]. The catalysts: $FeCl_3 \cdot 6H_2O$, $Fe_2(SO_4)_3 \cdot 9H_2O$, $Fe(NO_3)_3 \cdot 6H_2O$ ("pure" grade, Brom, Russia), $Fe(acac)_3$, $Fe(OAc)_2$ (Acros Organics), $K_3[Fe(CN)_6]$ ("pure" grade, Reakhim, Russia) were used as

Scheme 2.



Scheme 3.



R = H, CH_3, C_2H_5, C_3H_7.

received. Aqueous solutions of hypochlorites NaOCl and KOCl (10 wt%) were prepared from chlorinated lime (A grade, Vekton, Russia) as described elsewhere [37].

The products were identified using a GCMS-QP2010S Ultra SHIMADZU chromato–mass spectrometer (column Restek Rtx-5MS, 30 m × 0.25 mm ID, 0.25 μm). Quantitative analysis of the products was performed using a hardware-software complex based on Khromatek-Kristall 5000.1 and 5000.2 chromatographs (columns Agilent Technologies 19091F-413 HP-FFAP, 30 m × 0.32 mm, 0.25 Micron; Analytical Science 30 m × 0.32 mm ID-BPS, 0.5 μm).

^{1}H and ^{13}C NMR spectra were recorded on equipment at the Center for the Collective Use "Chemistry" of the Institute of Organic Chemistry at the Ufa Scientific Centre of the Russian Academy of Sciences: Bruker Avance III spectrometer operating at 500.13 (^{1}H) and 125.47 MHz (^{13}C) with TMS as internal reference.

Single-pot synthesis of alkyl-substituted quinolines and indoles via photoinduced oxidation of primary aliphatic alcohols *(general procedure).* The synthesis was performed using a Photo Catalytic Reactor Lelesil Innovative Systems photocatalytic setup with a 250 mL photoreactor equipped with a magnetic stirrer. 74.5 mL of 10 wt% aqueous solution of NaOCl

Table 2. Effect of alcohol nature on conversion of aniline and composition of products of single-pot synthesis of alkyl-substituted quinolines and indoles

Exp. no.	Alcohol	Conversion, %	Products composition, %		
1	Ethanol	>99	**2a** (31)	**2b** (37)	**2c** (32)
2	Propanol-1	92	**3a** (32)	**3b** (38)	**3c** (30)
3	Butanol-1	89	**4a** (32)	**4b** (39)	**4c** (29)
4	Propanol-1	87	**5a** (34)	**5b** (41)	**5c** (25)

(100 mmol) were added at continuous stirring to a mixture of 2.0 mmol (4 mol% with respect to aniline) of a catalyst and 400 mmol of the corresponding alcohol. A 250 W medium-pressure Hg lamp was used as the irradiation source (spectral composition: 48% UV, 43% visible, 9% IR, 222–1368 nm). The light flux reached the reaction mixture after passing through an aqueous layer at 20°C, irradiation time 4 h. After the irradiation, 4.6 mL (50 mmol) of aniline was added to the mixture; it was stirred during 5 min and extracted with diethyl ether. The organic layer was separated and dried over anhydrous magnesium sulfate. Diethyl ether was distilled off, and the residue was analyzed and distilled under reduced pressure. Physico-chemical parameters of the reaction products coincided with the reference data [18–21].

2-Methylquinoline (2b). Yield 37%, yellow oil, bp 80–81°C (2 mmHg). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.78 s (3H, CH_3), 7.22 d (1H, C^3H, J = 8.0 Hz), 7.46 t (1H, C^6H, J = 7.5 Hz), 7.68 t (1H, C^7H, J = 7.5 Hz), 7.73 d (1H, C^5H, J = 9.2 Hz), 7.97 d (1H, C^8H, J = 8.0 Hz), 8.03 d (1H, C^4H, J = 7.5 Hz). ^{13}C NMR spectrum, δ_C, ppm: 25.12 (CH_3), 121.74 (C^3), 125.45 (C^6), 126.32 (C^{4a}), 127.37 (C^5), 128.80 (C^8), 129.19 (C^7), 135.84 (C^4), 147.76 (C^{8a}), 158.67 (C^2). Mass spectrum, m/z: 143 $[M]^+$.

2-Ethyl-3-methylquinoline (3b). Yield 38%, yellow oil, bp 97–99°C (2 mmHg). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.38 t (3H, $CH_2C\underline{H}_3$, J = 7.2 Hz), 2.38 s (3H, CH_3), 2.96 q (2H, CH_2, J = 7.6 Hz), 7.40 t (1H, C^7H, J = 8.0 Hz), 7.58 t (1H, C^6H, J = 8.0 Hz), 7.62 d (1H, C^5H, J = 8.0 Hz), 7.70 s (1H, C^4H), 8.06 d (1H, C^8H, J = 8.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 12.84 ($CH_2\underline{C}H_3$), 18.61 (CH_3), 29.44 ($\underline{C}H_2CH_3$), 125.61 (C^7), 126.72 (C^6), 127.38 (C^5), 128.23 (C^{4a}), 128.51 (C^8), 129.37 (C^3), 135.64 (C^4), 146.76 (C^{8a}), 163.21 (C^2). Mass spectrum, m/z: 171 $[M]^+$.

2-Propyl-3-ethylquinoline (4b). Yield 39%, yellow oil, bp 118°C (1 mmHg). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.97 t (3H, $CH_2CH_2C\underline{H}_3$, J = 7.2 Hz), 1.11 t (3H, $CH_2C\underline{H}_3$, J = 7.2 Hz), 1.80–1.90 m (2H, $CH_2C\underline{H}_2CH_3$), 2.82 q (2H, $C\underline{H}_2CH_3$, J = 7.2 Hz), 2.99 t (2H, $C\underline{H}_2CH_2CH_3$, J = 8.0 Hz), 7.44 t (1H, C^7H, J = 8.0 Hz), 7.62 t (1H, C^6H, J = 7.2 Hz), 7.72 d (1H, C^5H, J = 7.6 Hz), 7.84 s (1H, C^4H), 8.08 d (1H, C^8H, J = 8.0 Hz). ^{13}C NMR spectrum, δ_C, ppm: 14.41 ($CH_2CH_2\underline{C}H_3$), 14.53 ($CH_2\underline{C}H_3$), 22.96 ($CH_2\underline{C}H_2CH_3$), 25.23 ($\underline{C}H_2CH_3$), 37.85 ($\underline{C}H_2CH_2CH_3$), 125.68 (C^7), 126.96 (C^5), 127.08 (C^6), 127.55 (C^{4a}), 128.41 (C^8), 129.22 (C^3), 133.93 (C^4), 146.41 (C^{8a}), 162.11 (C^2). Mass spectrum, m/z: 199 $[M]^+$.

2-Butyl-3-propylquinoline (5b). Yield 41%, yellow oil, bp 143°C (1 mmHg). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.13 t [3H, $(CH_2)_2CH_2C\underline{H}_3$, J = 7.2 Hz], 1.25 t (3H, $CH_2CH_2C\underline{H}_3$, J = 7.2 Hz), 1.38 m [2H, $(CH_2)_2C\underline{H}_2CH_3$], 1.71 m (2H, $CH_2C\underline{H}_2CH_3$), 1.75 m (2H, $CH_2C\underline{H}_2CH_2CH_3$), 2.72 t [2H, $C\underline{H}_2(CH_2)_2CH_3$, J = 7.5 Hz], 2.81 t (2H, $C\underline{H}_2CH_2CH_3$, J = 7.2 Hz), 7.53 t (1H, C^6H, J = 7.8 Hz), 7.62 t (1H, C^7H, J = 7.8 Hz), 7.65 s (1H, C^4H), 7.78 d (1H, C^5H, J = 7.8 Hz), 8.01 d (1H, C^8H, J = 7.9 Hz). ^{13}C NMR spectrum, δ_C, ppm: 13.42 [$(CH_2)_2CH_2\underline{C}H_3$], 13.99 ($CH_2CH_2\underline{C}H_3$), 22.81 [$(CH_2)_2\underline{C}H_2CH_3$], 23.26 ($CH_2\underline{C}H_2CH_3$), 31.92 ($CH_2\underline{C}H_2CH_2CH_3$), 34.43 [$\underline{C}H_2(CH_2)_2CH_3$], 35.76 ($\underline{C}H_2CH_2CH_3$), 125.55 ($C^7$), 126.92 ($C^5$), 127.29 ($C^6$), 128.36 ($C^8$), 128.54 ($C^{4a}$), 130.21 ($C^3$), 134.23 ($C^4$), 146.85 ($C^{8a}$), 161.17 ($C^2$). Mass spectrum, m/z: 227 $[M]^+$.

2,3-Dimethylindole (2c). Yield 32%, white crystals, mp 98–100°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 2.21 s (3H, CH_3), 2.31 s (3H, CH_3), 6.95–7.05 m (2H, C^5H, C^6H), 7.19 d (2H, C^7H, J = 7.9 Hz), 7.48 d (2H, C^4H, J = 8.0 Hz), 7.66 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 8.43 (CH_3), 11.55 (CH_3), 107.35 (C^3), 110.28 (C^7), 117.83 (C^4), 118.87 (C^5), 120.77 (C^6), 129.39 (C^{3a}), 130.64 (C^2), 135.18 (C^{7a}). Mass spectrum, m/z: 145 $[M]^+$.

2,3-Diethylindole (3c). Yield 30%, colorless crystals, mp 29–30°C. ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 1.16 t (3H, CH_3, J = 7.4 Hz), 1.17 t (3H, CH_3, J = 7.4 Hz), 2.76 q (2H, CH_2, J = 7.4 Hz), 3.03 q (2H, CH_2, J = 7.4 Hz), 7.01–7.05 m (2H, C^5H, C^6H), 7.11 d (2H, C^7H, J = 7.9 Hz), 7.51 d (2H, C^4H, J = 8.0 Hz), 7.69 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 13.39 (CH_3), 13.69 (CH_3), 21.84 (CH_2), 22.21 (CH_2), 110.83 (C^3), 111.36 (C^7), 117.88 (C^4), 120.20 (C^5), 122.27 (C^6), 127.62 (C^{3a}), 136.33 (C^{7a}), 141.59 (C^2). Mass spectrum, m/z: 173 $[M]^+$.

2,3-Dipropylindole (4c). Yield 29%, pale yellow oil, bp 144°C (1 mmHg). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.95 t (3H, CH_3, J = 6.5 Hz), 0.98 t (3H, CH_3, J = 6.6 Hz), 1.71–1.73 m (4H, $CH_2C\underline{H}_2CH_3$), 2.73–2.92 m (4H, $C\underline{H}_2CH_2CH_3$), 6.96–7.05 m (2H, C^5H, C^6H), 7.21 d (2H, C^7H, J = 7.9 Hz), 7.49 d (2H, C^4H, J = 8.0 Hz), 7.61 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 13.35 (CH_3), 13.48 (CH_3), 22.08 ($CH_2\underline{C}H_2CH_3$), 22.30 ($CH_2\underline{C}H_2CH_3$), 25.58 ($\underline{C}H_2CH_2CH_3$), 30.05 ($\underline{C}H_2CH_2CH_3$), 111.02 (C^3), 111.26 (C^7), 118.47 (C^4), 120.24 (C^5), 122.33 (C^6),

128.05 (C^{3a}), 135.68 (C^{7a}), 137.16 (C^2). Mass spectrum, *m*/*z*: 201 $[M]^+$.

2,3-Dibutylindole (5c). Yield 25%, pale yellow oil, bp 162°C (1 mmHg). ^{1}H NMR spectrum ($CDCl_3$), δ, ppm: 0.88 t (3H, CH_3, J = 6.5 Hz), 0.92 t (3H, CH_3, J = 6.5 Hz), 1.36–1.42 m [4H, $(CH_2)_2C\underline{H}_2CH_3$], 1.62–1.67 m (4H, $CH_2C\underline{H}_2CH_2CH_3$), 2.75–2.94 m [4H, $C\underline{H}_2(CH_2)_2CH_3$], 6.96–7.08 m (2H, C^5H, C^6H), 7.26 d (2H, C^7H, J = 8.0 Hz), 7.52 d (2H, C^4H, J = 8.0 Hz), 7.68 br.s (1H, NH). ^{13}C NMR spectrum, δ_C, ppm: 13.76 (CH_3), 13.82 (CH_3), 22.06 [$(CH_2)_2\underline{C}H_2CH_3$], 22.38 [$(CH_2)_2\underline{C}H_2CH_3$], 30.54 ($CH_2\underline{C}H_2CH_2CH_3$), 33.03 ($CH_2\underline{C}H_2CH_2CH_3$), 24.36 [$\underline{C}H_2(CH_2)_2CH_3$], 27.94 [$\underline{C}H_2(CH_2)_2CH_3$], 109.12 ($C^3$), 111.01 ($C^7$), 117.09 ($C^4$), 119.58 ($C^5$), 121.79 ($C^6$), 127.83 ($C^{3a}$), 136.02 ($C^{7a}$), 136.75 ($C^2$). Mass spectrum, *m*/*z*: 229 $[M]^+$.

REFERENCES

1. Prier, C.K., Rankic, D.A., and MacMillan, D.W.C., *Chem. Rev*., 2013, vol. 113, p. 5322. doi 10.1021/cr300503r
2. Schultz, D.M. and Yoon, T.P., *Science*, 2014, vol. 343, p. 985. doi 10.1126/science.1239176
3. Narayanam, J.M.R. and Stephenson, C.R.J., *Chem. Soc. Rev*., 2011, vol. 40, p. 102. doi 10.1039/b913880n
4. Yoon, T.P., Ischay, M.A., and Du, J., *Nat. Chem*., 2010, vol. 2, p. 527. doi 10.1038/nchem.687
5. Nicewicz, D.A. and Nguyen, T.M., *ACS Catal*., 2014, vol. 4, p. 355. doi 10.1021/cs400956a
6. Sagadevan, A., Ragupathi, A., and Hwang, K.C., *Angew. Chem. Int. Ed*., 2015, vol. 54, p. 13896. doi 10.1002/ange.201506579
7. Mitamura, T., Iwata, K., and Ogawa, A., *J. Org. Chem*., 2011, vol. 76, p. 3880. doi 10.1021/jo200299d
8. Zhou, X.F., Sun, Y.Y., Dai, J.J., Xu, J., and Xu, H.J., *J. Photochem. Photobiol. (A)*, 2018, vol. 355, p. 186. doi 10.1016/j.jphotochem.2017.09.037
9. Eicher, T. and Hauptmann, S., *The Chemistry of Heterocycles: Structure, Reactions, Syntheses, and Applications*, Weinheim: Wiley-VCH, 2003.
10. Humphrey, G.R. and Kuethe, J.T., *Chem. Rev*., 2006, vol. 106, p. 2875. doi 10.1021/cr0505270
11. Joucla, L. and Djakovitch, L., *Adv. Synth. Catal*., 2009, vol. 351, p. 673. doi 10.1002/adsc.200900059
12. Alvarez-Builla, J., Vaquero, J.J., and Barluenga, J., *Modern Heterocyclic Chemistry*, Weinheim: Wiley-VCH, 2011.
13. Somei, M. and Yamada, F., *Nat. Prod. Rep*., 2004, vol. 21, p. 278. doi 10.1039/B212257J
14. Shiri, M., *Chem. Rev*., 2012, vol. 112, p. 3508. doi 10.1021/cr2003954
15. Biddle, M.M., Lin, M., and Scheidt, K.A., *J. Am. Chem. Soc*., 2007, vol. 129, p. 3830. doi 10.1021/ja070394v
16. Bhalla, V., Vij, V., Kumar, M., Sharma, P.R., and Kaur, T., *Org. Lett*., 2012, vol. 14, p. 1012. doi 10.1021/ol203339c
17. Makhmutov, A.R., Mustafin, A.G., and Usmanov, S.M., *Int. J. Environ. Sci. Educ*., 2016, vol. 11, p. 11831.
18. Tursky, M., Lorentz-Petersen, L.L.R., Olsen, L.B., and Madsen, R., *Org. Biomol. Chem*., 2010, vol. 8, p. 5576. doi 10.1039/c0ob00106f
19. Khusnutdinov, R.I., Bayguzina, A.R., and Aminov, R.I., *Russ. Chem. Bull*., 2013, vol. 62, p. 133. doi 10.1007/s11172-013-0019-z
20. Khusnutdinov, R.I., Bayguzina, A.R., and Aminov, R.I., *Russ. J. Gen. Chem*., 2015, vol. 85, no. 12, p. 2725. doi 10.1134/S1070363215120105
21. Khusnutdinov, R.I., Bayguzina, A.R., and Aminov, R.I., *Russ. J. Gen. Chem*., 2016, vol. 86, no. 7, p. 1613. doi 10.1134/S1070363216070136
22. Bulgakov, R.G., Kuleshov, S.P., Vafin, R.R., and Dzhemilev, U.M., *Russ. J. Org. Chem*., 2009, vol. 45, no. 6, p. 944. doi 10.1134/S1070428009060268
23. Makhmutov, A.R., *J. Sib. Federal Univ., Chem*., 2017, vol. 10, no. 2, p. 154. doi 10.17516/1998-2836-0014
24. Tojo, G. and Fernandez, M., *Oxidation of Alcohols to Aldehydes and Ketones*, New York: Springer, 2006, p. 375.
25. Gogoi, P. and Konwar, D., *Org. Biomol. Chem*., 2005, vol. 3, p. 3473. doi 10.1039/b509527a
26. Meyers, C.Y., *J. Org. Chem*., 1961, vol. 26, no. 4, p. 1046. doi 10.1021/jo01063a018
27. Stevens, R.V., Chapman, K.T., and Weller, H.N., *J. Org. Chem*., 1980, vol. 45, no. 10, p. 2030. doi 10.1021/jo01298a066
28. Nwaukwa, S.O. and Keehn, P.M., *Tetrahedron Letts*., 1982, vol. 23, p. 35. doi 10.1016/S0040-4039(00)97525-7
29. Anelli, P.L., Biffi, C., Montanari, F., and Quici, S., *J. Org. Chem*., 1987, vol. 52, no. 12, p. 2559. doi 10.1021/jo00388a038
30. Vollhardt, P and, Schore, N., *Organic Chemistry: Structure and Function*, New York: W.E. Freeman and Company, 2007, p. 882.
31. Feng, W. and Nansheng, D., *Chemosphere*, 2000, vol. 41, p. 1137. doi 10.1016/S0045-6535(00)00024-2
32. Ruppert, G. and Bauer, R., *J. Photochem. Photobiol. (A)*, 1993, vol. 73, p. 75. doi 10.1016/1010-6030(93)80035-8
33. Makhmutov, A.R. and Usmanov, S.M., *Bashkir Chem. J*., 2017, vol. 24, no. 4, p. 33.
34. Bulgakov, R.G., Kuleshov, S.P., Makhmutov, A.R., and Dzhemilev, U.M., *Kinet. Catal*., 2010, vol. 51, no. 4, p. 534. doi 10.1134/S0023158410040129
35. Bulgakov, R.G., Kuleshov, S.P., and Makhmutov, A.R., *Russ. Chem. Bull*., 2007, vol. 56, no. 3, p. 443. doi 10.1007/s11172-007-0071-7
36. Weissberger, A., Proskauer, E.S., Riddick, J.A., and Toops, E.E., *Technique of Organic Chemistry*, New York: Wiley, 1955, vol. 7.
37. Karyakin, Yu.V. and Angelov, I.I., *Chistye khimicheskie veshchestva* (Pure Chemical Dubstances), Moscow: Khimiya, 1974, p. 285.