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SYNTHESIS OF NOVEL SUBSTITUTED 4-HYDROXY-3-OXO-3,4-DIHYDRO-2*H*-1,4-BENZOXAZINE-6,7-DICARBONITRILES

Sergey I. Filimonov,^{a*} Zhanna V. Chirkova,^a Igor G. Abramov,^a Sergey I. Firgang,^b Galina A. Stashina,^b and Kyrill Yu. Suponitsky^c

^a Yaroslavl State Technical University, 150023 Yaroslavl, Russian Federation
Fax: +7 4852 44 0729, e-mail: filimonovsi@ystu.ru

^b N. D. Zelinsky Institute of Organic Chemistry, Russian Academy of Sciences,
119991 Moscow, Russian Federation
Fax: +7 499 135 5328, e-mail: galina_stashina@chemical-block.com

^c A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy
of Sciences, 119991 Moscow, Russian Federation
e-mail: kirshik@yahoo.com

Abstract – New method has been elaborated for synthesis of novel substituted 4-hydroxy-3-oxo-3,4-dihydro-2*H*-1,4-benzoxazine-6,7-dicarbonitriles by means of activated nucleophilic substitution of the bromine atom in 4-bromo-5-nitrophthalonitrile by treatment of the latter with sodium salts of substituted 3-cyano-2-hydroxy-3-phenyl acrylates followed by reductive cyclisation. The structure of the resulting substituted 4-hydroxy-3-oxo-3,4-dihydro-2*H*-1,4-benzoxazine-6,7-dicarbonitriles has been determined by single crystal X-ray diffraction analysis.

INTRODUCTION

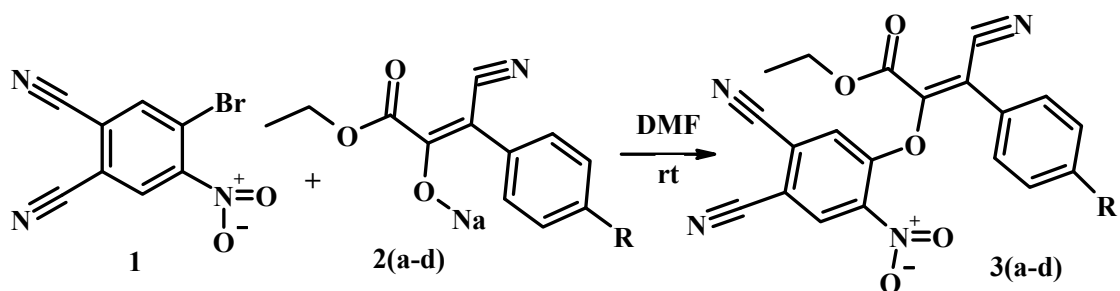
4-Hydroxy-1,4-benzoxazin-3-ones are among the most interesting representatives of six-membered heterocyclic systems. This structural moiety is found in glycosides of key gramineous plants;¹ furthermore, it determines the antibacterial, antifungal² and herbicide^{3,4} properties of these compounds. Derivatives of 4-hydroxy-1,4-benzoxazinone are being intensely studied; over 500 studies concerning various aspects of chemistry and biology of this class of compounds have already been published over the past 50 years. One of the main methods for synthesizing the 1,4-benzoxazin-3-one ring involves

alkylation of nitrophenols with α -haloacid derivatives followed by reductive cyclization.^{5,6} Other method involves acylation of corresponding chlorine anhydride with *ortho*-aminophenols followed by reductive alkylating cyclization.^{5,6} One more widely used method involves condensation of *ortho*-aminophenols with derivatives of α -ketoacid. Dimethyl acetylenedicarboxylate⁷ uses here as condensing reagent with formation of corresponding 1,4-benzoxazine-2-one.⁸⁻¹⁰ Nucleophilic substitution is described only getting of phenoxazines derivatives.¹¹ There are some alternative ways for synthesis of heterocyclic phthalonitriles, but usually they based on high-temperature substitution of bromine (iodine) on cyanogroup (Rosenmund von Braun Synthesis) with cyanide copper (I) with low yield,¹²⁻¹⁴ or more effective method with use of cyanide zinc and various palladium derivatives.^{15,16}

However, the literature lacks information on the synthesis of substituted 4-hydroxy-3-oxo-3,4-dihydro-2*H*-1,4-benzoxazine-6,7-dicarbonitriles by activated aromatic nucleophilic substitution. It should also be noted that substituted *ortho*-dicarbonitriles are promising compounds for synthesising various macrocycles^{12,17,18} and a number of other compounds incorporating carbonyl, anhydride, imide, isoindoline and tetrazole moieties.¹⁹

RESULTS AND DISCUSSION

This study aims at development of a new two-stage synthesis of substituted 4-hydroxy-3-oxo-3,4-dihydro-2*H*-1,4-benzoxazine-6,7-dicarbonitriles based on reductive cyclisation of addition products of sodium salts of substituted 3-cyano-2-hydroxy-3-phenyl acrylates **2(a-d)** to 4-bromo-5-nitrophthalonitrile **1** (BNPN). The characteristic features of BNPN that behaves as a highly activated substrate in S_NAr reactions were considered in a number of papers.²⁰⁻²² It is the most convenient substrate for synthesis of various heterocyclic systems fused with phthalonitrile. It is necessary to notice that there are almost no information about using of substituted 3-cyano-2-hydroxy-3-phenylacrylate as nucleophilic reagents,²³ however it is known, that they are condensed with carbonyl derivatives with formation of corresponding 4-Oxo-3,4-dihydro-2*H*-[1,3]oxazine-6-carboxylic acid ethyl ester.^{24,25}



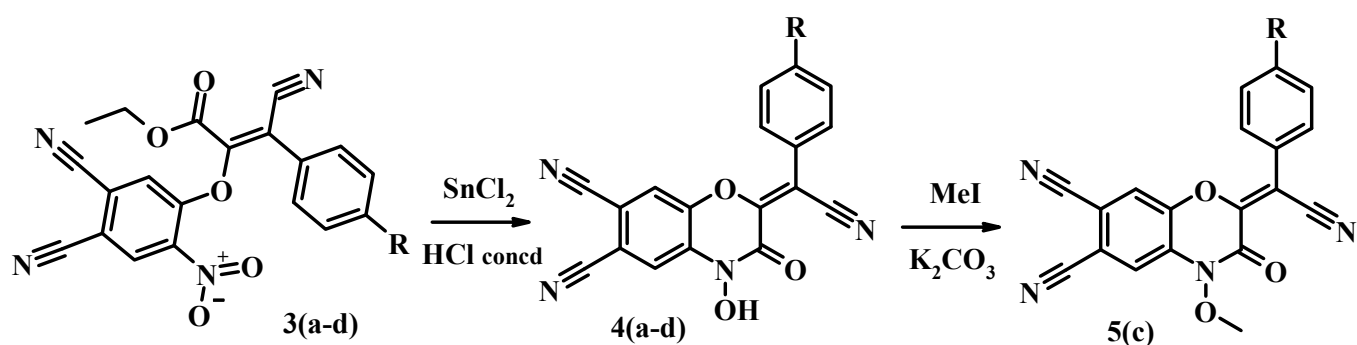
2, 3 a-R=H, b- R=Me, c- R= OMe, d- R=Cl

Scheme 1. Synthesis of compounds **3(a-d)**

The first stage, *i.e.* reaction of BNPN with an excess of salts **2(a-d)**, was carried out for 24-48 h in a DMF solution at room temperature (Scheme 1). Increasing the reaction temperature favoured side reactions and thus decreased the yield of the target product.

It was found that an increase in the amount of salt **2(a-d)** in the reaction mixture increased the yield of ester **3(a-d)**, which reached a maximum with a two-fold excess of the reagent. Conversely, addition of potassium carbonate or sodium methoxide to the reaction mixture decreased the yield. Notwithstanding the ambident nature of nucleophile **2(a-d)**, O-nucleophilic substitution was the dominating process under the conditions used, to give esters **3(a-d)** as the main reaction products (white crystals; yield 38-64%). Furthermore, esters with electron-donating substituents (Me, OMe) at the phenyl ring are formed more quickly. Salts containing substituents R = H or Cl react much more slowly, especially for R = Cl (complete conversion of BNPN took about 150 hours). Synthesized substituted enol ethers **3** are unstable in solutions, containing bases, because they can be exposed cleavage (similar mechanism is described for 1,3-diketones)^{26,27} with formation of 4-hydroxy-5-nitrophthalonitrile, therefore target product with low-activity substrate have received with a low yield, and nitrophenol is isolated as sodium salts with 15-20% yields.

At the second stage, esters **3(a-d)** were reduced with tin(II) in hydrochloric acid at 40-50 °C to give bright yellow high-melting target products **4(a-d)**, poorly soluble in the majority of organic solvents, in 60-75% yields (Scheme 2). It is known that reduction of the nitro group in nitroesters with similar structures in the presence of tin (II),²⁸ zinc,²⁹ indium³⁰ or palladium on carbon^{31,32} under mild conditions initially gave a hydroxylamine, which then underwent spontaneous cyclisation to give the corresponding N-hydroxy compounds. In some cases, formation of crystal hydrates was detected.³¹



3, 4 a-R=H, b- R=Me, c- R= OMe, d- R=Cl

Scheme 2. Synthesis of substituted 4-hydroxy-3-oxo-3,4-dihydro-2H-1,4-benzoxazine-6,7-dicarbonitriles

It appeared rather difficult to determine unambiguously the structure of the resulting compounds **3(a-d)** and **4(a-d)** by NMR spectroscopy, but all compounds is represented by homogeneous products. Electron impact did not always allow the molecular ion to be detected for these compounds, but only low-molecular fragments could be observed. The assumption that compound **4c***¹ belongs to derivatives of N-hydroxy substituted oxazines was made upon hydroxyl group methylation with methyl iodide. ¹H NMR revealed an additional methoxy group signal at δ 4.06 in reaction product **5c** at N₁.

An information on the structure of the compounds synthesized in the present study **4(a-d)** was obtained by the single crystal X-ray study of **4c**.^{*} The single crystals were obtained from THF solution in the form of yellow prisms. An independent unit cell consists of **4c** and water molecule in the 1:1 ratio. General view of **4c**•H₂O is depicted in Figure 1. The **4c** molecule adopts planar geometry and orientation of substituents at C1=C11 double bond corresponds to *E*-isomer. This probably is defined by an orientation of substituents in the initial ester **3c**. The C14-H14A...O1 intramolecular H-bond is observed in the structure of **4c**. However the planar molecular geometry is probably governed by π -conjugation between π -donor and π -acceptor substituents rather than weak C-H...O interaction which should be considered as a forced interaction.

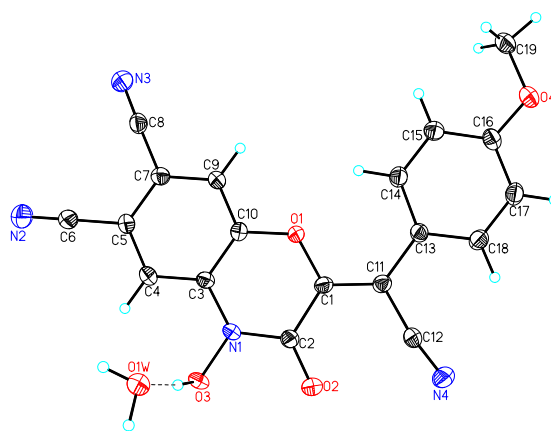
The presence of π -conjugation is supported by elongation of C1=C11 and shortening of C11-C13 bonds (normally observed X-ray values are 1.339 и 1.488Å,³³ respectively) as well as bond lengths distribution in C13...C18 and C3...C10 phenyl cycles which adopt to a some extent quinoid geometry. The C14-C15 and C7-C18 bonds in aryl substituent at methoxy-group (C13...C18) are somewhat shorter than others while simultaneous influence of two cyano-groups in phtalonitrile cycle (C3...C10) and π -donor properties of O1 and N1 atoms of oxazine cycle lead to shortening of C7-C9, C9-C10, C3-C4, C4-C5 bonds (Table 1).

¹ *¹ Reflection for compound **4c** were collected at SMART 1000 diffractometer ($\lambda(\text{Mo-K}\alpha)=0.71073$ Å, graphite monochromator, ω -scans) at 120K. The structure solved by the direct methods and refined by the full-matrix least-squares procedure against F^2 in anisotropic approximation. Hydrogen atoms of OH group and water molecule were found in the difference Fourier synthesis and refined in isotropic approximation. All the other hydrogen atoms were placed in geometrically calculated positions and refined within riding model.

4c: C₁₉H₁₂N₄O₅: monoclinic, space group $P2_1/c$: $a = 11.786(3)$ Å, $b = 17.643(4)$ Å, $c = 8.329(2)$ Å, $\beta = 105.348(5)$, $V = 1670.2(6)$ Å³, $Z=4$, $M=376.33$, $d_{\text{calc}}= 1.497$ g·cm⁻³, $\mu=0.112$ mm⁻¹, $F(000)=776$, $R_2=0.1403$, $GOF=1.017$ for 4430 independent reflections with $2\theta < 58^\circ$, $R_1= 0.0570$ for 2964 reflections with $I > 2\sigma(I)$

Table 1. Selected geometry characteristics of **4c**•H₂O

Bond	Distance, Å	Bond	Distance, Å
C3-C4	1.392(3)	C11-C13	1.482(2)
C4-C5	1.391(3)	C13-C14	1.397(3)
C5-C7	1.405(3)	C14-C15	1.384(3)
C7-C9	1.392(3)	C15-C16	1.389(3)
C9-C10	1.378(3)	C16-C17	1.395(3)
C3-C10	1.396(2)	C17-C18	1.381(3)
C1-C11	1.364(3)	C13-C18	1.406(3)

**Figure 1.** ORTEP view of **4c**•H₂O (thermal ellipsoids are drawn at 50% probability level)

Intensive fluorescent at $\lambda_{\text{max}} = 560 - 580$ nm was observed for synthesized benzoxazines **4(a-d)** upon UV irradiation ($\lambda = 265$ nm) which makes them to be promising compounds for an application as elements of new fiber-optic, fluorescent and other modern optical materials.³⁴

EXPERIMENTAL

IR spectra were measured on a Perkin-Elmer RX-1 spectrometer in the range of 700–4000 cm⁻¹

NMR spectra were recorded on a Bruker DRX-500 instrument at 30 °C, residual solvent proton signals in ¹H NMR spectra (δ_{H} 2.50) or the signal of DMSO-*d*₆ in ¹³C spectra (δ_{C} 39.5) were used as references for chemical shift measurements.

The starting BNPN **1** was synthesised using the procedure reported elsewhere.³⁵

The starting sodium salts **2(a-d)** were synthesised using the procedure reported elsewhere.³⁶

General procedure for the synthesis of compounds 2(a-d) – Ethyl (2*E*)-3-cyano-2-hydroxy-3-(aryl)acrylates sodium salts.

Hexane (300 mL) and sodium hydride (0.11 mol) are added to a solution of benzyl cyanide (0.1 mol) and

diethyl oxalate (0.11 mol) in 50 mL of anhydrous dioxane and the suspension is stirred without heating until hydrogen evolution ceases completely and a yellow precipitate is formed (2-4 h); the latter is filtered off, washed with dry hexane and used in reactions without further purification.

General procedure for the synthesis of compounds 3(a-d)

Compound **2(3)** (0.0044 mol) is added to a solution of BNPN (0.002 mol) in 3 mL of DMF; the mixture is stirred for 24-48 h at room temperature and poured into 10 mL of cold 1% hydrochloric acid solution. The resulting resinous precipitate is extracted with CH_2Cl_2 , thoroughly washed with water, and chromatographed on silica gel using hexane: CH_2Cl_2 (1:2) as the eluent. The eluent is evaporated, and the resulting precipitate is filtered off and recrystallised from EtOH.

General procedure for the synthesis of compounds 4(a-d)

A solution of compound **2** in EtOH (3 mL) is added to a solution of tin dichloride (0.007 mol) in concentrated hydrochloric acid (2 mL). The reaction mixture is stirred for 1 h at 50 °C; the resulting yellow precipitate is filtered off and recrystallized from a DMF: EtOH (1:2) mixture.

General procedure for the synthesis of compounds 5

Compound **4** (0.001 mol) is dissolved in DMF (3 mL); potassium carbonate (0.0012 mol) and methyl iodide (0.0012 mol) are added in succession. The reaction mixture is stirred at room temperature for 24 h and then diluted with water (3 mL); the resulting precipitate is filtered off and recrystallised from a DMF: EtOH mixture (1:2).

Ethyl (2E)-3-cyano-2-(4,5-dicyano-2-nitrophenoxy)-3-phenylacrylate (3a)

yield 44%, mp 143-145 °C (EtOH); IR (KBr) ν 2240 ($\text{C}\equiv\text{N}$), 1742 ($\text{C}=\text{O}$), 1539 (NO_2), 1261 ($\text{C}-\text{O}-\text{C}$), 1141 ($\text{C}-\text{O}-\text{C}$) cm^{-1} ; ^1H NMR ($\text{DMSO}-d_6$): δ 1.15 (t, $J=7.1$ Hz, 3H, CH_3), 4.25 (q, $J=7.1$ Hz, 2H, CH_2), 7.51 (m, 3H, aryl), 7.64 (m, 2H, aryl), 8.60 (s, 1H, 6-H), 8.93 (s, 1H, 3-H). ^{13}C NMR ($\text{DMSO}-d_6$): δ 13.50, 63.37, 111.07, 114.18, 114.29, 114.87, 115.61, 120.60, 124.11, 128.87, 129.17, 129.24, 131.18, 131.37, 141.12, 147.32, 150.81, 158.41; Anal. Calcd for $\text{C}_{19}\text{H}_{18}\text{N}_8\text{O}_5$: C, 61.86; H, 3.11; N, 14.43. Found: C, 61.95; H, 2.94; N, 14.47.

Ethyl (2E)-3-cyano-2-(4,5-dicyano-2-nitrophenoxy)-3-(4-methylphenyl)acrylate (3b)

yield 64%, mp 154-156 °C (EtOH); IR (KBr) ν 2240 ($\text{C}\equiv\text{N}$), 1714 ($\text{C}=\text{O}$), 1538 (NO_2), 1297 ($\text{C}-\text{O}-\text{C}$), 1157 ($\text{C}-\text{O}-\text{C}$) cm^{-1} ; ^1H NMR ($\text{DMSO}-d_6$): δ 1.22 (t, $J=7.0$ Hz, 3H, CH_3), 2.36 (s, 3H, CH_3'), 4.28 (q, $J=7.0$ Hz, 2H, CH_2), 7.28 (d, $J=8.1$ Hz, 2H, aryl), 7.55 (d, $J=8.1$ Hz, 2H, aryl), 8.55 (s, 1H, 6-H), 8.87 (s, 1H, 3-H); Anal. Calcd for $\text{C}_{21}\text{H}_{14}\text{N}_4\text{O}_5$: C, 62.69; H, 3.51; N, 13.92. Found: C, 62.82; H, 3.32; N, 13.98.

Ethyl (2E)-3-cyano-2-(4,5-dicyano-2-nitrophenoxy)-3-(4-methoxyphenyl)acrylate (3c)

yield 58%, mp 152-154 °C (EtOH); IR (KBr) ν 2238 ($\text{C}\equiv\text{N}$), 1717 ($\text{C}=\text{O}$), 1542 (NO_2), 1295 ($\text{C}-\text{O}-\text{C}$), 1159 ($\text{C}-\text{O}-\text{C}$) cm^{-1} ; ^1H NMR ($\text{DMSO}-d_6$): δ 1.19 (t, $J=7.3$ Hz, 3H, CH_3), 3.80 (s, 3H, OCH_3), 4.25 (q, $J=7.3$ Hz, 2H, CH_2), 7.02 (d, $J=8.8$ Hz, 2H, aryl), 7.65 (d, $J=8.8$ Hz, 2H, aryl), 8.53 (s, 1H, 6-H), 8.90 (s,

1H, 3-H); ^{13}C NMR (DMSO- d_6): δ 13.51, 55.57, 63.15, 110.93, 114.18, 114.32, 114.70, 114.88, 115.64, 120.60, 121.23, 123.95, 130.92, 131.39, 141.11, 145.52, 150.92, 158.65, 161.44; Anal. Calcd for $\text{C}_{21}\text{H}_{14}\text{N}_4\text{O}_6$: C, 60.29; H, 3.37; N, 13.39. Found: C, 60.44; H, 3.24; N, 13.42.

Ethyl (2E)-3-(4-chlorophenyl)-3-cyano-2-(4,5-dicyano-2-nitrophenoxy)acrylate (3d)

yield 38%, mp 161-162 °C (EtOH); IR (KBr) ν 2239 ($\text{C}\equiv\text{N}$), 1737 ($\text{C}=\text{O}$), 1540 (NO_2), 1292 ($\text{C}-\text{O}-\text{C}$), 1152 ($\text{C}-\text{O}-\text{C}$) cm^{-1} ; ^1H NMR (DMSO- d_6): δ 1.22 (t, $J=7.0$ Hz, 3H, CH_3), 4.28 (q, $J=7.0$ Hz, 2H, CH_2), 7.51 (d, $J=8.5$ Hz, 2H, aryl), 7.67 (d, $J=8.5$ Hz, 2H, aryl), 8.56 (s, 1H, 6-H), 8.88 (s, 1H, 3-H); Anal. Calcd for $\text{C}_{20}\text{H}_{11}\text{ClN}_4\text{O}_5$: C, 56.82; H, 2.62; N, 13.25. Found: C, 56.42; H, 2.32; N, 13.08.

(2E)-2-[Cyano(phenyl)methylene]-4-hydroxy-3-oxo-3,4-dihydro-2H-1,4-benzoxazine-6,7-dicarbonitrile (4a)

yield 64%, mp 228-229 °C; IR (KBr) ν 3350 (OH), 2235 ($\text{C}\equiv\text{N}$), 2213 ($\text{C}\equiv\text{N}$), 1686 ($\text{C}=\text{O}$), 1610 (Ar), 1260 ($\text{C}-\text{O}-\text{C}$) cm^{-1} ; ^1H NMR (DMSO- d_6): δ 7.50(t, $J=7.2$ Hz, 1H, aryl), 7.55(t, $J=7.2$ Hz, 2H, aryl), 7.76 (d, $J=7.2$ Hz, 2H, aryl), 8.01 (s, 1H, 5-H), 8.11 (s, 1H, 8-H), 12.28 (br.s, 1H, OH); ^{13}C NMR (DMSO- d_6): δ 97.39, 109.49, 110.65, 115.18, 115.29, 116.98, 117.37, 120.89, 128.81, 129.53, 130.44, 132.35, 142.17, 150.47, 150.58; Anal. Calcd for $\text{C}_{18}\text{H}_8\text{N}_4\text{O}_3\cdot\text{H}_2\text{O}$: C, 62.43; H, 2.91; N, 16.18. Found: C, 62.58; H, 2.98; N, 16.10.

(2E)-2-[Cyano(4-methylphenyl)methylene]-4-hydroxy-3-oxo-3,4-dihydro-2H-1,4-benzoxazine-6,7-dicarbonitrile (4b)

yield 75%, mp 279-280 °C; IR (KBr) ν 3462 (OH), 2242 ($\text{C}\equiv\text{N}$), 2220 ($\text{C}\equiv\text{N}$), 1680 ($\text{C}=\text{O}$), 1613 (Ar), 1260 ($\text{C}-\text{O}-\text{C}$) cm^{-1} ; ^1H NMR (DMSO- d_6): δ 2.42 (s, 3H, CH_3), 7.32 (d, $J=8.5$ Hz, 2H, aryl), 7.67 (d, $J=8.5$ Hz, 2H, aryl), 7.88 (s, 1H, 5-H), 7.95 (s, 1H, 8-H), 12.18 (br.s, 1H, O-H); ^{13}C NMR (DMSO- d_6): δ 20.98, 97.82, 109.62, 110.76, 115.32, 115.43, 117.06, 117.46, 121.01, 127.71, 128.87, 129.50, 132.51, 139.55, 142.35, 150.13, 150.65; Anal. Calcd for $\text{C}_{19}\text{H}_{10}\text{N}_4\text{O}_3\cdot\text{H}_2\text{O}$: C, 63.33; H, 3.36; N, 15.55. Found: C, 63.08; H, 3.46; N, 15.32.

(2E)-2-[Cyano(4-methoxyphenyl)methylene]-4-hydroxy-3-oxo-3,4-dihydro-2H-1,4-benzoxazine-6,7-dicarbonitrile (4c)

yield 68%, mp 290-291 °C; IR (KBr) ν 3424 (OH), 2235 ($\text{C}\equiv\text{N}$), 2217 ($\text{C}\equiv\text{N}$), 1687 ($\text{C}=\text{O}$), 1611 (Ar), 1259 ($\text{C}-\text{O}-\text{C}$) cm^{-1} ; ^1H NMR (DMSO- d_6): δ 3.84 (s, 3H, O CH_3), 7.09 (d, $J=8.5$ Hz, 2H, aryl), 7.75 (d, $J=8.5$ Hz, 2H, aryl), 7.97 (s, 1H, 5-H), 8.11 (s, 1H, 8-H), 12.17 (br.s, 1H, OH); ^{13}C NMR (DMSO- d_6): δ 55.29, 92.26, 107.23, 110.48, 114.04, 114.14, 115.89, 118.27, 119.24, 119.71, 123.83, 130.18, 135.15, 143.13, 150.22, 151.19, 159.29; Anal. Calcd for $\text{C}_{19}\text{H}_{10}\text{N}_4\text{O}_4\cdot\text{H}_2\text{O}$: C, 60.64; H, 3.21; N, 14.89. Found: C, 60.32; H, 3.32; N, 14.78.

(2E)-2-[Cyano(4-chlorophenyl)methylene]-4-hydroxy-3-oxo-3,4-dihydro-2H-1,4-benzoxazine-6,7-dicarbonitrile (4d)

yield 61%, mp 288-289 °C; IR (KBr) ν 3456 (OH), 2236 (C $\equiv$ N), 2217 (C $\equiv$ N), 1692 (C=O), 1612 (Ar), 1256 (C-O-C) cm^{-1} ; ^1H NMR (DMSO- d_6): δ 7.54 (d, $J=8.5$ Hz, 2H, aryl), 7.78 (d, $J=8.5$ Hz, 2H, aryl), 8.03 (s, 1H, 5-H), 8.14 (s, 1H, 8-H), 12.27 (br.s, 1H, O-H); Anal. Calcd for $\text{C}_{18}\text{H}_7\text{ClN}_4\text{O}_3 \cdot \text{H}_2\text{O}$: C, 56.78; H, 2.38; N, 14.71. Found: C, 56.32; H, 2.12; N, 14.46.

(2E)-2-[Cyano(4-methoxyphenyl)methylene]-4-methoxy-3-oxo-3,4-dihydro-2H-1,4-benzo-xazine-6,7-dicarbonitrile (5c)

yield 78%, mp 269-270 °C; IR (KBr) ν 2235 (C $\equiv$ N), 2217 (C $\equiv$ N), 1699 (C=O), 1611 (Ar), 1259 (C-O-C), 1190 (C-O-C) cm^{-1} ; ^1H NMR (DMSO- d_6): δ 3.87 (s, 3H, OCH₃), 4.06 (s, 3H, OCH₃), 7.07 (d, $J=8.8$ Hz, 2H, aryl), 7.76 (d, $J=8.8$ Hz, 2H, aryl), 8.09 (s, 1H, 5-H), 8.14 (s, 1H, 8-H); Anal. Calcd for $\text{C}_{20}\text{H}_{12}\text{N}_4\text{O}_4$: C, 64.52; H, 3.25; N, 15.05. Found: C, 64.32; H, 3.15; N, 14.96.

REFERENCES

1. T. Ishizaki, Y. Hashimoto, K. Shudo, and T. Okamoto, *Tetrahedron Lett.*, 1982, **23**, 4055.
2. S. Oeztuerk, A. M. Ozturk, G. Hakan, and A. Nurten, *Farmaco*, 2000, **55**, 715.
3. H. M. Niemeryer, *J. Agric. Food Chem.*, 2009, **57**, 1677.
4. F. A. Mac'as, N. Chinchilla, R. M. Varela, J. M. G. Molinillo, D. Marn, and J. M. De Siqueira, *J. Agric. Food Chem.*, 2008, **56**, 9941.
5. J. Ilas, S. Petra, T. Anderluh, M. Sollner, and D. Kikelj, *Tetrahedron*, 2005, **61**, 7325.
6. J. Teller, 'Houben-Weyl Methods of Organic Chemistry, Hetarenes IV: 1,4-(Benz)Oxazines', ed by E. Schaumann, Georg Thieme: Stuttgart, 1997, E 9a, pp. 134-177.
7. X. Li, N. Liu, H. Zhang, S. E. Knudson, R. A. Slayden, and P. J. Tonge, *Bioorg. Med. Chem. Lett.*, 2010, **20**, 6306.
8. D. G. Orphanos and A. Taurins, *Can. J. Chem.*, 1966, **44**, 1795.
9. Z. G. Aliev, O. P. Krasnykh, A. N. Maslivets, and L. O. Atovmyan, *Russ. Chem. Bull.*, 2000, **49**, 2045.
10. V. L. Gein, N. A. Rassudikhina, and E. V. Voronina, *Pharm. Chem. J.*, 2006, **40**, 554.
11. St. Radl, 'Advances in Heterocyclic Chemistry: Aromatic nucleophilic denitrocyclization reaction', Vol. 83, ed. by A. R. Katritzky, Academic Press, Inc., London, 2002, pp. 189-257.
12. S. A. Mikhaleiko, V. M. Derkacheva, and E. A. Luk'yanets, *Russ. J. Gen. Chem.*, 1981, **51**, 1405.
13. C. Pardo, M. Yuste, J. Elguero, and J. Porphyrins, *Phthalocyanines*, 2000, **4**, 505.
14. W. J. Youngblood, *J. Org. Chem.*, 2006, **71**, 3345.
15. G. M. Barrett, G. R. Hanson, J. P. White, D. J. Williams, and A. S. Micallef, *Tetrahedron*, 2007, **63**, 5244.
16. Z. Iqbal, A. Lyubimtsev, and M. Hanack, *Synlett*, 2008, **15**, 2287.

17. V. E. Maizlish, A. E. Balakirev, O.V. Shishkina, and G. P. Shaposhnikov, *Russ. J. Gen. Chem.*, 2001, **71**, 246.
18. O. V. Shishkina, V. E. Maizlish, and G. P. Shaposhnikov, *Russ. J. Gen. Chem.*, 1998, **68**, 813.
19. R. J. Herr, *Bioorg. Med. Chem.*, 2002, **10**, 3379.
20. I. G. Abramov, A. V. Smirnov, S. A. Ivanovskii, M. B. Abramova, V. V. Plachtinsky, and M. S. Belysheva, *Mendeleev Commun.*, 2001, **11**, 80.
21. I. G. Abramov, A. V. Smirnov, S. A. Ivanovskii, M. B. Abramova, and V. V. Plachtinsky, *Heterocycles*, 2001, **55**, 1161.
22. S. I. Filimonov, Zh. V. Chirkova, I. G. Abramov, A. S. Shashkov, S. I. Firgang, and G. A. Stashina, *Mendeleev Com.*, 2009, **19**, 332.
23. R. Gompper and H. H. Vogt, *Chemische Berichte*, 1981, **114**, 2866.
24. J. F. Stambach, L. Jung, and R. Hug, *Heterocycles*, 1994, **38**, 297.
25. D. K. Pyun, W. J. Jeong, H. J. Jung, J. H. Kim, J. S. Lee, C. H. Lee, and B. J. Kim, *Synlett*, 2001, 1950.
26. R. G. Pearson and E. A. Mayerle, *J. Am. Chem. Soc.*, 1951, **73**, 926.
27. D. J. Bray, K. A. Jolliffe, L. F. Lindoy, and J. C. McMurtrie, *Tetrahedron*, 2007, **63**, 1953.
28. H. P. Buchstaller and U. Anlauf, *Synthesis*, 2005, 639.
29. D. Sicker, B. Pratorius, G. Mann, and L. Meyer, *Synthesis*, 1989, 211.
30. B. K. Banik, I. Banik, S. Samajdar, and M. Wilson, *Heterocycles*, 2004, **63**, 283.
31. M. Belley, E. Sauer, D. Beaudoin, P. Duspara, L. A. Trimble, and P. Dubé, *Tetrahedron Lett.*, 2006, **47**, 159.
32. J. Atkinson, P. Morand, and T. Arnason, *J. Org. Chem.*, 1991, **56**, 1788.
33. F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, and R. J. Taylor, *Chem. Soc., Perkin Trans. 2*, 1987, 1.
34. O. S. Wolfbeis, 'Springer Series on Fluorescence. Springer'-Verlag Berlin Heidelberg, 2008.
35. S. A. Ivanovskii, M. V. Dorogov, I. G. Abramov, and A. V. Smirnov, Russian Patent, 2167855, 2001.
36. C. Maurin, F. Bailly, and Ph. Cotelle, *Tetrahedron*, 2004, **60**, 6479.