Tetrahedron 69 (2013) 3082–3087

Contents lists available at SciVerse ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Ultrasound-promoted synthesis of novel 2-imino-3-aryl-2,3-dihydrobenzo[*d*]oxazol-5-ol 2-iminooxazolidines derivatives

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ARTICLE INFO

Article history:
Received 22 November 2012
Received in revised form 6 January 2013
Accepted 22 January 2013
Available online 31 January 2013

Keywords:
p-Benzoquinone
Arylcyanamide
2-Iminooxazolidines
Chemoselective tosylation
Ultrasound irradiation
Room temperature

ABSTRACT

A synthesis of novel 2-iminooxazolidineswas developed by the reaction between arylcyanamides with *p*-benzoquinone at room temperature under ultrasound irradiation in excellent yields. Also, the chemoselective tosylation of the products were performed at room temperature under ultrasound irradiation in good yields.

1. Introduction

In recent years, cycloaddition reactions have emerged as a valuable tool for the construction of heterocyclic compounds.[1a] Amongst these, 1,4-cycloaddition provides a unique and efficient route for the synthesis of various five-membered heterocycles. A diverse array of heterocyclic compounds occurs naturally and their functions are often of fundamental importance to living systems. Amongst them, nitrogen-containing heterocycles are important compounds from a biological and pharmacological point of view.[1]

It is known that *p*-benzoquinone can act as a precursor to a variety of organic compounds via conjugate addition of nitrogen-, sulfur-, oxygen- and carbon-nucleophiles and also of electron-accepting components for the synthesis of charge-transfer complexes and radical-ion salts.[2,3]

Reactivities of *p*-benzoquinones[4–6] in cyc1oaddition reactions depend on the electronic and steric character of the substituents. Nucleophilic addition may proceed beyond the initial 2-substituted mono-adducts up to tri- or even tetra-substituted products. New heterocycles can be prepared if the adduct contains electrophilic as well as the nucleophile groups.[7,8] In this respect cyanamides are useful, since they have both nucleophilic (amino) and electrophilic (cyano) canters. In some cases the cyano group participates in a specific fashion to give addition, cycloaddition, cyclotrimerization reactions and complex formation.[7,8] Many of these reactions require relatively forcing conditions, which might be overcome by using ultrasound (US) energy, which is being increasingly applied in synthetic organic chemistry.[9] Ultrasound irradiation involves high energies and pressures on an extremely short time scale. In liquid irradiated with high-intensity ultrasound, the collapse of bubbles caused by cavitation produces intense local heating and high pressures, with very short lifetimes; these transient, localized hot spots drive high energy chemical reactions. The hot spot has an equivalent temperature of roughly 5000 °C (9000 °F), a pressure of about 2000 atm, a lifetime considerably less than a microsecond and heating and cooling rates above 10 billion °C per second.[9]

To the best of our knowledge, ultrasound irradiation has not so far been used in the reactions of arylcyanamides, and as part of our ongoing interest in heterocyclic chemistry,[10] we now wish to report the synthesis of novel 2-imino-3-aryl-2,3-dihydrobenzo[*d*]oxazol-5-ol derivatives by the reaction of arylcyanamides with *p*-benzoquinone at room temperature under ultrasound irradiation (Scheme 1).

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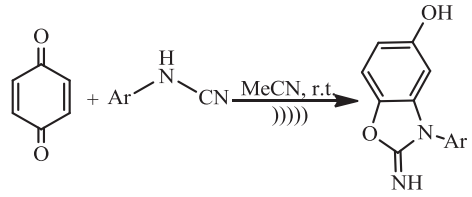
0040-4020/$ – see front matter © 2013 Elsevier Ltd. All rights reserved.
http://dx.doi.org/10.1016/j.tet.2013.01.069



Scheme 1. Synthesis of novel 2-imino-3-aryl-2,3-dihydrobenzo[*d*]oxazol-5-ol derivatives.

2. Result and discussion

Initially, the reaction of 2,5-dichlorophenylcyanamide and *p*-benzoquinone was studied as a model. Conventional conditions were used with different solvents under reflux reaction conditions with 50% excess of *p*-benzoquinone (Table 1, entries 1–3). Polar protic solvents such as ethanol, methanol, and water attacked the *p*-benzoquinone and the desired products were obtained in low yield due to formation of side products.[11] When acetonitrile was used, the reaction yield was about 25% of the product after 48 h under reflux condition (Table 1, entry 3). Much better results were achievable under ultrasound irradiation (Table 1, entry 4). The higher yield and lower reaction time during the ultrasonic irradiation can be attributed to the implosive collapse of the cavitation period of the sound waves. The optimum conditions were found to be 1.0 mmol of *p*-benzoquinone and 1.0 mmol of cyanamide in acetonitrile (5.0 mL). Increasing the amount of *p*-benzoquinone to more than 1.0 mmol showed no substantial improvement in the yield.

Table 1
The model reaction in the synthesis of 3-(2,5-dichlorophenyl)-2-imino-2,3-dihydrobenzo[*d*]oxazol-5-ol under thermal and ultrasound irradiation conditions[a]

Entry	Method	*p*-BQ[d] [mmol]	Solvent [mL]	Time [h]	Yield[g] [%]
1	Without US[b]	1.5	MeOH (12)	48	10
2	Without US[b]	1.5	EtOH (12)	48	11
3	Without US[b]	1.5	MeCN (12)	48	25
4	With US[c]	1.0	MeCN (5)	10[e]	81
5	With US[c]	1.0	MeCN (5)	10[f]	35

[a] 2,5-Dichlorophenylcyanamide (1 mmol).
[b] Reaction under reflux conditions.
[c] The ultrasonic power 50 W, irradiation frequency 28 kHz.
[d] *p*-Benzoquinone.
[e] Room temperature.
[f] At 50 °C.
[g] Isolated yield.

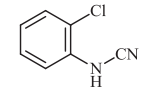
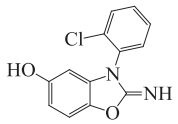
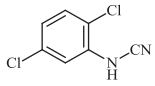
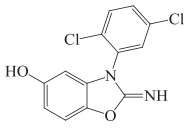
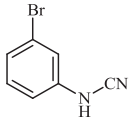
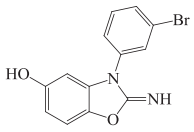
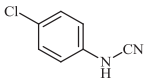
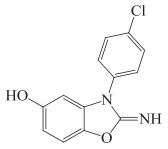
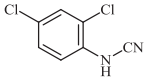
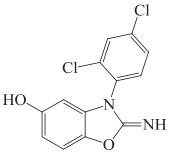
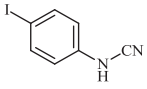
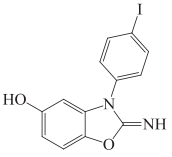
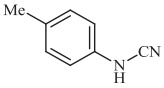
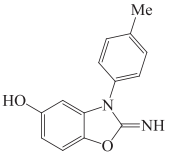
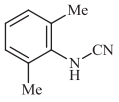
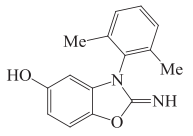
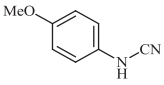
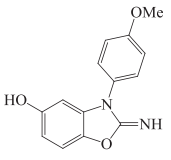
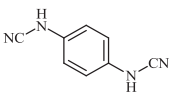
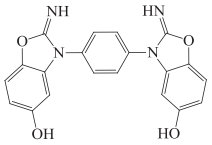
Using equimolar amounts of the reactants and getting high yields, means no starting material will remain as residue in the reaction mixture, minimizing waste streams, which is in accordance with the first principle of green chemistry.[12]

In order to further improve the yield of reaction, a higher temperature we used under ultrasound irradiation (Table 1, entry 5), but the yields decreased. Increasing temperature usually increases the formation of side products and cyanamide residue in the reaction mixture.

The reactions of several aromatic cyanamides were tested in the synthesis of novel 2-iminooxazolidines under ultrasound irradiation at room temperature and the results are indicated in Table 2. In all cases, reaction times are reduced and the yields increased.

To study the effects of the nature of the substituent groups on the benzene ring of cyanamide, various 2-imino-3-aryl-2,3-dihydrobenzo[*d*]oxazol-5-ol derivatives were obtained in high yields under ultrasound irradiation from different aromatic cyanamides containing both electron-donating and electron-withdrawing groups (Table 2). Cyanamides having methyl or methoxy as an electron-donating group (entries 7–9) reacted completely at room temperature after 30–90 min, while the

Table 2
Formation of 2-imino-3-aryl-2,3-dihydrobenzo[*d*]oxazol-5-ol derivatives via secondary arylcyanamides

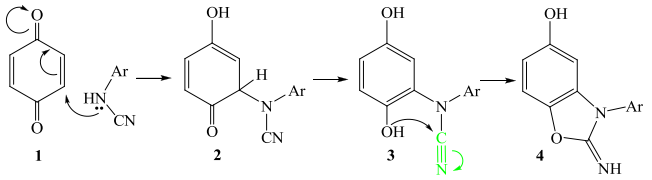
Entry	Cyanamide	Product	Time [min]	Yield[a] [%]
1			150	88
2			600	81
3			145	82
4			300	92
5			180	80
6			300	92
7			90	83
8			30	85
9			120	84
10			45	80

[a] Isolated yields.

species bearing the electron-withdrawing groups such as Cl and Br (entries 1–5) required higher reaction times, which indicates that the nature of the substituent has an effect on the reaction time.

The presence of the two NH and CN groups in 1,4-phenylenecyanamide (Table 2, entry 10) interestingly afforded the double-addition product.

The possible mechanism for the synthesis of 2-imino-3-aryl-2,3-dihydrobenzo[*d*]oxazol-5-ol derivatives under ultrasound irradiation is shown in Scheme 2. The reaction of *p*-benzoquinone with cyanamides occurs through the conjugate addition mechanism followed by the intramolecular cycloaddition reaction of phenolic OH. In the other words, the process does not stop at the stage of (2,5-dihydroxyphenyl)arylcyanamide (**3**) formation. Intramolecular addition of the hydroxyl group to the cyano group leads to ring closure, yielding 2-imino-3-aryl-2,3-dihydrobenzo[*d*]oxazol-5-ol derivatives. The driving force for these reactions is presumed to be the thermodynamically favored formation of novel aromatic compounds and a very reactive electrophile species (**3**).



Scheme 2. The possible mechanism for the synthesis of 2-imino-3-aryl-2,3-dihydrobenzo-[*d*]oxazol-5-ol derivatives.

The products were characterized by IR, ^{1}H NMR and ^{13}C NMR spectroscopy, melting points, and elemental analysis. Formation of the products was confirmed by IR spectra, which showed two characteristic NH and OH peaks.

The reactivity of several 2-imino-3-aryl-2,3-dihydrobenzo-[*d*]oxazol-5-ols was also tested in the reaction with tosyl chloride and K_2CO_3under ultrasound irradiation at room temperature in ethanol and the results are indicated in Table 3. With those molecules containing both the hydroxyl and imino groups, only the *O*-tosylated products were formed, which showed a good chemoselectivity. Apparently, the steric hindrance of the aryl ring on the nitrogen prohibits the N-tosylation (Scheme 3 and Table 3).

The structures of the *O*-tosylated products were in agreement with their IR and NMR spectra. In the IR spectra of the products, the OH peak had disappeared and two strong absorptions bands were detected. New absorption bands at ~1130–1135 cm^{-1} and 1355–1372 cm^{-1} in the FT-IR spectra of the *O*-tosylated products were attributed to theSO_2 of the tosyl group.

3. Conclusions

In conclusion, we have developed an efficient and simple procedure for the synthesis of2-imino-3-aryl-2,3-dihydrobenzo[*d*]oxazol-5-ol derivatives under ultrasound irradiation. This method has the advantages of excellent yields and reaction rates, simple methodology, mild reaction conditions, excellent chemoselectivity and easy work-up.

4. Experimental

4.1. General

All reagents were purchased from the Merck and Aldrich chemical companies and used without further purification. The NMR spectra were recorded in DMSO or $CDCl_3$. ^{1}H NMR spectra were recorded on a Bruker Avance DRX 400 and 300 MHz instruments. The chemical shifts (δ) are reported in parts per million relative to TMS as an internal standard and *J* values are given in hertz. ^{13}C NMR spectra were recorded at 100and 75 MHz. FT-IR (KBr) spectra were recorded on a Perkin–Elmer 781 spectrophotometer. Melting points were taken in open capillary tubes with a BUCHI 510 melting point apparatus and are uncorrected. Elemental analysis was performed using Heraeus CHN–O-Rapid analyzer. TLC was performed on silica gel polygram SIL G/UV 254 plates.

4.2. Preparation of the arylcyanamides

Cyanamides were prepared according to the lit.[10a]

4.3. General experimental procedure for the synthesis of 2-imino-3-aryl-2,3-dihydrobenzo[*d*]oxazol-5-ol derivatives

A mixture of *p*-benzoquinone (1.0 mmol) and cyanamide (1 mmol) in MeCN (5 mL) was irradiated with ultrasound for the appropriate time at room temperature. After completion (as monitored by TLC), the solid residue was filtered from the reaction mixture and then was washed with acetone to afford the pure product. The desired pure products were characterized by ^{1}H NMR, ^{13}C NMR, FT-IR, elemental analysis (CHN), and melting points.

4.3.1. 3-(2-Chlorophenyl)-2-imino-2,3-dihydrobenzo[d]oxazol-5-ol (Table 2, entry 1). Yield 88%; mp 199–202 °C; FT-IR (KBr, cm^{-1}): 3329, 3068, 1687, 1620, 1589, 1497, 1477, 1439, 1406, 1306, 1189, 1108, 1066, 1010, 838, 818, 768, 721, 703, 658, 620; ^{1}H NMR (300 MHz, DMSO-d_6): δ_H 9.26 (br s, 1H), 7.92–7.54 (m, 4H), 7.03 (d, *J*=8.4 Hz, 1H), 6.40 (d, *J*=8.4 Hz, 1H), 5.95 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ_C 155.2, 154.5, 137.5, 134.1, 132.7, 132.2, 131.6, 131.4, 131.2, 129.3, 109.6, 107.6, 96.4; CHN: Anal. Calcd for $C_{13}H_9ClN_2O_2$: C, 59.90; H, 3.48; N, 10.75. Found: C, 59.86; H, 3.08; N, 10.75.

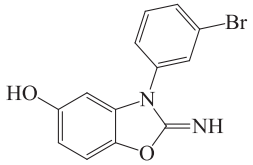
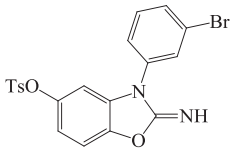
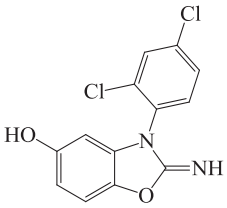
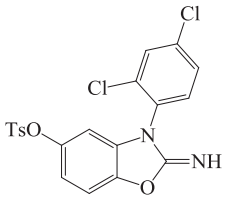
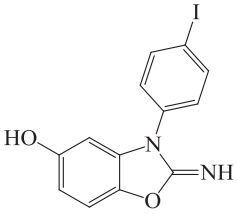
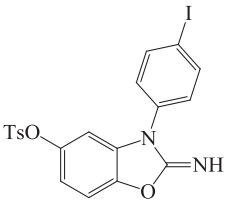
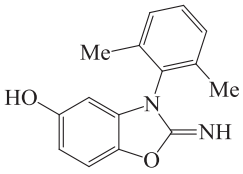
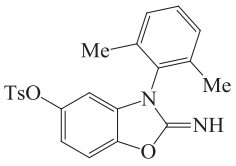
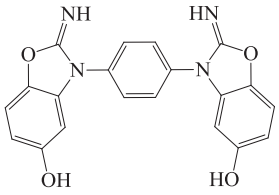
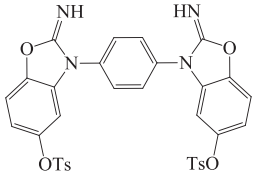
4.3.2. 3-(2,5-Dichlorophenyl)-2-imino-2,3-dihydrobenzo[d]ox-azol-5-ol (Table 2, entry 2). Yield 81%; mp 231–234 °C; FT-IR (KBr, cm^{-1}): 3332, 3096, 2683, 1681, 1621, 1601, 1560, 1490, 1476, 1426, 1401, 1306, 1194, 1099, 1014, 848, 826, 784, 712, 661, 613, 582, 438; ^{1}H NMR (300 MHz, DMSO-d_6): δ_H 8.00–7.40 (m, 3H), 7.25 (br s, 1H), 6.97 (d, *J*=8.1 Hz, 1H), 6.72 (br s, 1H), 6.35 (d, *J*=8.1 Hz, 1H), 5.96 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ_C 154.6, 154.4, 137.4, 133.6, 133.0, 132.4, 131.5, 131.3, 129.4, 127.6, 109.6, 107.7, 96.5; CHN: Anal. Calcd for $C_{13}H_8Cl_2N_2O_2$: C, 52.91; H, 2.73; N, 9.49. Found: C, 52.80; H, 2.65; N, 9.62.

4.3.3. 3-(3-Bromophenyl)-2-imino-2,3-dihydrobenzo[d]oxazol-5-ol (Table 2, entry 3). Yield 82%; mp 164–167 °C; FT-IR (KBr, cm^{-1}): 3330, 3065, 1674, 1618, 1590, 1488, 1478, 1438, 1394, 1307, 1199, 1168, 1116, 1073, 1014, 780, 744, 724, 713, 699, 653, 624; ^{1}H NMR (300 MHz, DMSO-d_6): δ_H 9.40 (br s, 1H), 7.85 (s, 1H), 7.48–7.64 (m, 3H), 7.00 (d, *J*=8.5 Hz, 1H), 6.80 (br s, 1H), 6.41 (d, *J*=8.2 Hz, 2H); ^{13}C NMR (75 MHz, DMSO-d_6): δ_C 154.7, 154.4, 137.3, 136.9, 133.2, 131.7, 130.5, 128.9, 124.9, 122.2, 109.6, 107.9, 96.6; CHN: Anal. Calcd for $C_{13}H_9BrN_2O_2$: C, 51.17; H, 2.97; N, 10.49. Found: C, 51.29; H, 2.85; N, 10.31.

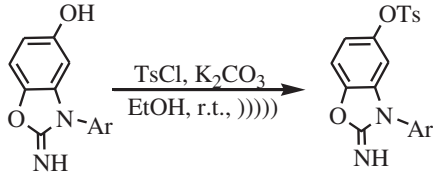
4.3.4. 3-(4-Chlorophenyl)-2-imino-2,3-dihydrobenzo[d]oxazol-5-ol(Table 2, entry 4). Yield 92%; mp 210–212 °C; FT-IR (KBr, cm^{-1}): 3361, 3088, 1674, 1620, 1499, 1466, 1382, 1275, 1188, 1159, 1087, 1003, 970, 811, 713, 628; ^{1}H NMR (300 MHz, DMSO-d_6): δ_H 9.35 (br s, 1H), 7.63 (d, *J*=8.6 Hz, 2H), 7.58 (d, *J*=8.6 Hz, 2H), 7.00 (d, *J*=8.4 Hz, 1H), 6.60 (br s, 1H), 6.45 (d, *J*=8.4 Hz, 1H), 6.37 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ_C 154.4, 155.2, 137.3, 134.2, 133.4, 132.0, 129.9, 127.9, 109.5, 107.8, 96.6; CHN: Anal. Calcd for $C_{13}H_9ClN_2O_2$: C, 59.90; H, 3.48; N, 10.75. Found: C, 60.03; H, 3.32; N, 10.89.

4.3.5. 3-(2,4-Dichlorophenyl)-2-imino-2,3-dihydrobenzo[d]ox-azol-5-ol(Table 2, entry 5). Yield 80%; mp 216–218 °C; FT-IR (KBr, cm^{-1}): 3333, 3100, 2875, 2683, 1678, 1618, 1587, 1561, 1487, 1473, 1306,

Table 3
Formation of *O*-tosylated products

Entry	2-Iminooxazolidines	Product	Time [h]	Yield[a] [%]
1			1.5	87
2			3	85
3			2.5	84
4			1	86
5			4	85

[a] Yields are after work-up.



Scheme 3. The N-tosylation of several 2-imino-3-aryl-2,3-dihydrobenzo[*d*]oxazol-5-ols.

1251, 1216, 1192, 1163, 1029, 1017, 898, 818, 778, 711, 677, 616, 563, 541, 441, 408; ^{1}H NMR (300 MHz, DMSO-d_6): δ_H 7.93 (s, 1H), 7.80–7.76 (m, 1H), 7.62 (s, 1H), 7.30 (s, 1H), 7.00 (d, J=8.4 Hz, 1H), 6.90 (br s, 1H), 6.40 (d, J=8.4 Hz, 2H); ^{13}C NMR (75 MHz, DMSO-d_6): δ_C 154.6, 154.3, 137.1, 135.5, 132.8, 131.6, 129.7, 129.4, 127.9, 125.9, 109.6, 108.1, 96.8; CHN: Anal. Calcd for $C_{13}H_8Cl_2N_2O_2$: C, 52.91; H, 2.73; N, 9.49. Found: C, 52.74; H, 2.58; N, 8.37.

4.3.6. 3-(4-Iodophenyl)-2-imino-2,3-dihydrobenzo[d]oxazol-5-ol (Table 2, entry 6). Yield 92%; mp 248–251 °C; FT-IR (KBr, cm^{-1}): 3358, 3059, 1666, 1627, 1617, 1583, 1566, 1499, 1404, 1381, 1273, 1190, 1158, 1058, 1001, 969, 820, 711, 684, 634, 622, 501; ^{1}H NMR (300 MHz, DMSO-d_6): δ_H 9.33 (br s, 1H), 7.88 (d, J=8.1 Hz, 2H), 7.41 (d, J=8.1 Hz, 2H), 6.99 (d, J=8.4 Hz, 1H), 6.70 (br s, 1H), 6.41 (d, J=8.4 Hz, 1H), 6.36 (s, 1H); ^{13}C NMR (75 MHz, DMSO-d_6): δ_C 155.1, 154.3, 138.8, 137.3, 135.2, 133.3, 128.2, 109.5, 107.9, 96.63, 93.09; CHN: Anal. Calcd for $C_{13}H_9IN_2O_2$: C, 44.34; H, 2.58; N, 7.96. Found: C, 44.64; H, 2.40; N, 8.22.

4.3.7. 3-(4-Methylphenyl)-2-imino-2,3-dihydrobenzo[d]oxazol-5-ol (Table 2, entry 7). Yield 83%; mp 207–209 °C; FT-IR (KBr, cm^{-1}): 3360, 3064, 1675, 1618, 1580, 1516, 1494, 1475, 1442, 1408, 1382, 1272, 1225, 100, 998, 970, 821, 811, 793, 713, 689, 646, 619, 608; ^{1}H NMR (300 MHz, DMSO-d_6): δ_H 9.35 (br s, 1H), 7.37 (d, J=7.6 Hz, 2H), 7.34 (d, J=7.6 Hz, 2H), 6.99 (d, J=8.4 Hz, 1H), 6.40 (d, J=8.4 Hz, 1H), 6.30 (s, 1H), 2.35 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6): δ_C 155.9, 154.5, 137.7, 137.3, 134.1, 132.6, 130.5, 126.1, 109.4, 107.6, 96.4, 21.1;

CHN: Anal. Calcd for $C_{14}H_{12}N_2O_2$: C, 69.99; H, 5.03; N, 11.66. Found: C, 69.82; H, 4.84; N, 11.49.

4.3.8. 3-(2,6-Dimethylphenyl)-2-imino-2,3-dihydrobenzo[d]ox-azol-5-ol (Table 2, entry 8). Yield 85%; mp 204–207 °C; FT-IR (KBr, cm^{-1}): 3347, 3315, 2954, 1862, 2688, 1679, 1616, 1475, 1379, 1296, 1178, 1101, 1003, 837, 798, 778, 728, 709, 634, 446; ^1H NMR (300 MHz, DMSO-d_6): δ_H 9.30 (br s, 1H), 7.30–7.27 (m, 3H), 7.02 (d, J=8.2 Hz, 1H), 6.43 (br s, 1H), 6.36 (d, J=7.6 Hz, 1H), 5.79 (d, J=2.3 Hz, 1H), 2.07 (s, 6H); ^{13}C NMR (75 MHz, DMSO-d_6): δ_C 154.7, 154.2, 137.7137.3, 133.9, 132.2, 129.5, 129.1, 109.5, 107.1, 95.6, 17.7; CHN: Anal. Calcd for $C_{15}H_{14}N_2O_2$: C, 70.85; H, 5.55; N, 11.02. Found: C, 70.34; H, 5.46; N, 10.87.

4.3.9. 3-(4-Methoxyphenyl)-2-imino-2,3-dihydrobenzo[d]oxaz-ol-5-ol (Table 2, entry 9). Yield 84%; mp 177–180 °C; FT-IR (KBr, cm^{-1}): 3336, 3089, 1673, 1617, 1579, 1499, 1479, 1414, 1294, 1196, 1161, 1090, 1011, 969, 833, 811, 744, 706, 625, 501; ^1H NMR (300 MHz, DMSO-d_6): δ_H 9.30 (br s, 1H), 7.45 (d, J=8.1 Hz, 2H), 7.90 (d, J=8.1 Hz, 2H), 6.98 (d, J=8.3 Hz, 1H), 6.55 (br s, 1H), 6.34 (d, J=8.3 Hz, 1H), 6.18 (s, 1H), 3.80 (s, 3H); ^{13}C NMR (75 MHz, DMSO-d_6): δ_C 158.9, 155.5, 154.3, 137.2, 134.4, 127.9, 115.2, 109.3, 107.2, 96.1, 55.8; CHN: Anal. Calcd for $C_{14}H_{12}N_2O_3$: C, 65.62; H, 4.72; N, 10.93. Found: C, 65.36; H, 4.61; N, 11.11.

4.3.10. 3,3′-(1,4-Phenylene)bis-(2-imino-2,3-dihydrobenzo[d]-ox-azol-5-ol) (Table 2, entry 10). Yield 80%; mp 231–234 °C; FT-IR (KBr, cm^{-1}): 3329, 3069, 1674, 1618, 1521, 1480, 1396, 1292, 1190, 1161, 1110, 1007, 971, 810, 715, 640, 521; ^1H NMR (300 MHz, DMSO-d_6): δ_H 9.35 (br s, 2H), 7.77 (s, 4H), 6.50–7.15 (m, 4H), 6.40 (d, J=8.1 Hz, 4H); ^{13}C NMR (75 MHz, DMSO-d_6): δ_C 154.9, 154.4, 137.3, 134.0, 133.5, 127.1, 109.5, 107.7, 96.5; CHN: Anal. Calcd for $C_{20}H_{14}N_4O_4$: C, 64.17; H, 3.77; N, 14.97. Found: C, 63.94; H, 3.59; N, 14.78.

4.4. General experimental procedure for the synthesis of 2-imino-3-aryl-2,3-dihydrobenzo[*d*]oxazol-5-yl 4-methylbenzenesulfonate derivatives

A mixture of 2-imino-3-aryl-2,3-dihydrobenzo[*d*]oxazol-5-ol (1 mmol), *p*-toluenesulfonyl chloride (1 mmol) and K_2CO_3 (1 mmol) in EtOH (5 mL) was irradiated with ultrasound for the appropriate time at room temperature. After completion (as monitored by TLC), the solvent was concentrated and the solid residue was washed with water to give the crude solid product. Then, a crystallization step was performed using aqueous ethanol to afford the pure product. The desired pure products were characterized by ^1H NMR, ^{13}C NMR, FT-IR, elemental analysis (CHN), and melting points.

4.4.1. 3-(3-Bromophenyl)-2-imino-2,3-dihydrobenzo[d]oxazol-5-yl 4-methylbenzenesulfonate (Table 3, entry 1). Yield 87%; mp 189–190 °C; FT-IR (KBr, cm^{-1}): 3334, 3086, 1702, 1590, 1495, 1478, 1430, 1388, 1363, 1221, 1192, 1171, 1135, 1092, 1071, 996, 888, 868, 850, 818, 784, 742, 722, 700, 684, 665, 653, 617, 594, 554, 520; ^1H NMR (400 MHz, DMSO-d_6): δ_H 7.72 (d, J=8.4 Hz, 2H), 7.64–7.61 (m, 2H), 7.45–7.44 (m, 2H), 7.37 (d, J=8.4 Hz, 3H), 7.09 (d, J=8.8 Hz, 1H), 6.69 (d, J=8.8 Hz, 1H), 6.59 (d, J=2.4 Hz, 1H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ_C 156.2, 145.7, 145.6, 142.9, 135.3, 133.2, 131.9, 131.6, 131.3, 129.9, 128.7, 128.6, 124.2, 123.3, 116.1, 109.4, 103.5, 21.8; CHN: Anal. Calcd for $C_{20}H_{15}BrN_2O_4S$: C, 52.30; H, 3.29; N, 6.10. Found: C, 52.42; H, 3.37; N, 6.21.

4.4.2. 3-(2,4-Dichlorophenyl)-2-imino-2,3-dihydrobenzo[d]ox-azol-5-yl 4-methylbenzenesulfonate (Table 3, entry 2). Yield 85%; mp 164–166 °C; FT-IR (KBr, cm^{-1}): 3339, 3038, 1711, 1693, 1597, 1491, 1476, 1369, 1221, 1194, 1171, 1130, 1093, 1078, 1163, 999, 900, 853, 812, 797, 748, 723, 666, 649, 632, 598, 553; ^1H NMR (400 MHz, DMSO-d_6): δ_H 7.72 (d, J=8.0 Hz, 2H), 7.67 (d, J=8.4 Hz, 2H), 7.44–7.41 (dd, J=2.4, 2.0 Hz, 1H), 7.37 (d, J=8.0 Hz, 3H), 7.19 (d, J=8.8 Hz, 1H), 6.77–6.75 (d, J=8.8 Hz, 1H), 6.61 (d, J=2.4 Hz, 1H), 2.49 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ_C 156.4, 145.9, 145.8, 142.8, 134.1, 133.2, 132.6, 132.4, 131.9, 131.8, 129.9, 128.6, 127.7, 125.2, 117.0, 110.1, 104.0, 21.8; CHN: Anal. Calcd for $C_{20}H_{14}Cl_2N_2O_4S$: C, 53.46; H, 3.14; N, 6.23. Found: C, 53.81; H, 3.21; N, 6.32.

4.4.3. 3-(4-Iodophenyl)-2-imino-2,3-dihydrobenzo[d]oxazol-5-yl 4-methylbenzenesulfonate (Table 3, entry 3). Yield 84%; mp 199–201 °C; FT-IR (KBr, cm^{-1}): 3344, 3043, 1704, 1496, 1480, 1355, 1170, 1132, 1092, 893, 857, 819, 753, 592, 553; ^1H NMR (400 MHz, DMSO-d_6): δ_H 7.89 (d, J=8.4 Hz, 2H), 7.72 (d, J=8.0 Hz, 2H), 7.36 (d, J=8.0 Hz, 3H), 7.24 (d, J=8.4 Hz, 2H), 7.09 (d, J=8.8 Hz, 1H), 6.66 (d, J=8.8 Hz, 1H), 6.58 (d, J=2.4 Hz, 1H), 2.50 (s, 3H); ^{13}C NMR (100 MHz, DMSO-d_6): δ_C 156.2, 145.7, 145.6, 142.9, 139.2, 133.7, 133.2, 131.9, 129.9, 128.7, 127.2, 116.0, 109.4, 103.6, 93.4, 21.8; CHN: Anal. Calcd for $C_{20}H_{15}IN_2O_4S$: C, 47.44; H, 2.99; N, 5.53. Found: C, 47.52; H, 3.10; N, 5.64.

4.4.4. 3-(2,6-Dimethylphenyl)-2-imino-2,3-dihydrobenzo[d]ox-azol-5-yl 4-methylbenzenesulfonate (Table 3, entry 4). Yield 86%; mp 121–123 °C; FT-IR (KBr, cm^{-1}): 3329, 3052, 1699, 1609, 1490, 1369, 1212, 1191, 1172, 1091, 988, 956, 864, 840, 822, 722, 745, 665, 652, 630, 599, 556, 525; ^1H NMR (400 MHz, DMSO-d_6): δ_H 7.68 (d, J=8.4 Hz, 2H), 7.36 (t, J=7.6 Hz, 1H), 7.31 (d, J=8.4 Hz, 2H), 7.25 (d, J=7.6 Hz, 2H), 7.16 (d, J=8.8 Hz, 3H), 6.73 (d, J=8.8 Hz, 1H), 6.17 (d, J=2.4 Hz, 1H), 2.46 (s, 3H), 2.09 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6): δ_C 156.8, 145.9, 145.6, 143.0, 137.2, 133.2, 131.8, 130.3, 129.8, 129.6, 129.4, 128.6, 115.9, 109.8, 103.2, 21.7, 17.7; CHN: Anal. Calcd for $C_{22}H_{20}N_2O_4S$: C, 64.69; H, 4.94; N, 6.86. Found: C, 64.78; H, 4.86; N, 6.94.

4.4.5. 3,3′-(1,4-Phenylene)bis(2-imino-2,3-dihydrobenzo[d]ox-azole-5,3-diyl)bis(4-methylbenzenesulfonate) (Table 3, entry 5). Yield 85%; mp 115 °C dec; FT-IR (KBr, cm^{-1}): 3338, 3067, 1705, 1617, 1598, 1519, 1485, 1454, 1381, 1292, 1257, 1219, 1193, 1180, 1132, 1091, 991, 956, 895, 862, 835, 814, 742, 664, 594, 552, 529; ^1H NMR (400 MHz, DMSO-d_6): δ_H 7.76 (d, J=8.4 Hz, 4H), 7.66 (s, 4H), 7.39 (d, J=8.4 Hz, 6H), 7.04 (d, J=8.8 Hz, 2H), 6.72 (s, 2H), 6.67 (d, J=8.8 Hz, 2H), 2.50 (s, 6H); ^{13}C NMR (100 MHz, DMSO-d_6): δ_C 156.2, 145.7, 145.5, 142.9, 133.7, 133.2, 132.0, 129.9, 128.7, 126.7, 116.1, 109.4, 103.7, 21.8; CHN: Anal. Calcd for $C_{34}H_{26}N_4O_8S_2$: C, 59.81; H, 3.84; N, 8.21. Found: C, 59.90; H, 3.87; N, 8.27.

Acknowledgements

The authors are thankful to the Bu-Ali Sina University, Hamedan Iran for the support of this work.

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