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Synthesis of benzoxazole-2-ones, benzothiazole-2-ones and their 2-thione derivatives: Efficient conversion of 2-thione to 2-oxo derivatives

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A highly practical procedure for preparing benzoxazole-2-ones, benzothiazole-2-ones and its 2-thione derivatives using ethylchloroformate and carbon disulfide and the corresponding aminophenols and aminothiophenols as the starting materials in one-pot protocol is presented. The yields vary from good to excellent, the conditions are mild, and the use of toxic and harmful chemicals is avoided. An efficient conversion of benzoxazole-2-thione to 2-one derivative in high yield has also been carried out.

Keywords: Benzoxazole-2-ones, benzothiazole-2-ones, oxazolidin-2-ones, oxazolidin-2-thiones

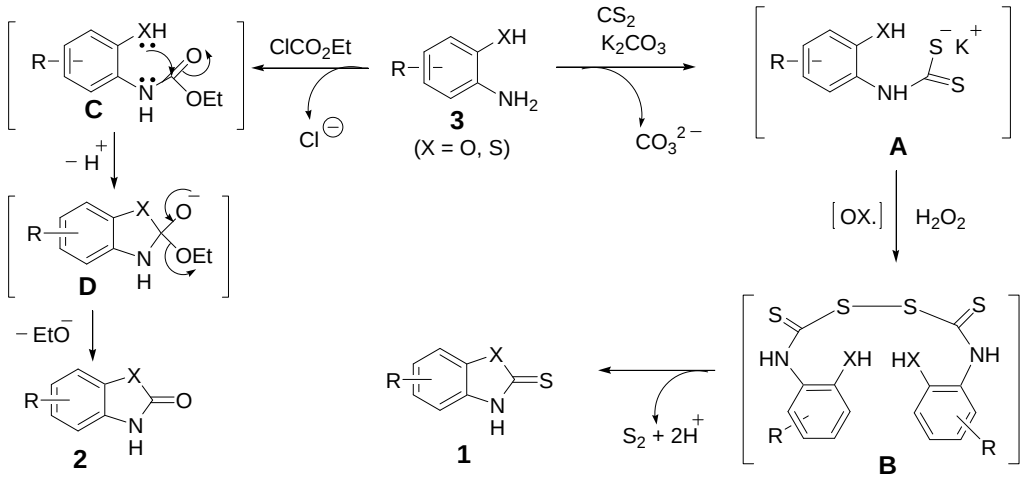
Oxazolidin-2-ones and 2-thiones are important compounds in both pharmaceutical and synthetic organic chemistry. They are widely used as chiral auxiliaries in asymmetric synthesis[1] of a number of natural and unnatural products and have a wide range of applications in pharmacology[2]. Numerous synthetic methods have been described in the literature for the preparation of oxazolidin-2-ones[3–5]. These classical syntheses are based on the direct or indirect use of toxic and hazardous reagents (phosgene, isocyanates *etc.*) as a source of carbon and lead to the formation of a vast amount of toxic wastes. To overcome this drawback, significant efforts have been undertaken for the use of non-toxic reagents and development of procedures with low environmental impact. Nowadays the use and design of environmental-friendly reagents and reactions has become an important research target which is mainly due to their useful properties like high versatility, easy treatment and work up, mild experimental conditions, high yield, selectivity, low cost and recyclability.

In this paper are reported simple, efficient and scaleable syntheses of a series of benzoxazol-2-ones, benzothiazol-2-ones and their 2-thione derivatives from easily available 2-aminophenols and thiophenols. An efficient conversion of 2-thione to 2-oxo derivatives with excellent yields has been described. All the compounds have been characterized using FT-IR, NMR and mass spectral studies. The plausible mechanistic details of these reactions are shown in **Scheme I**, **Scheme II** and **Table I**.

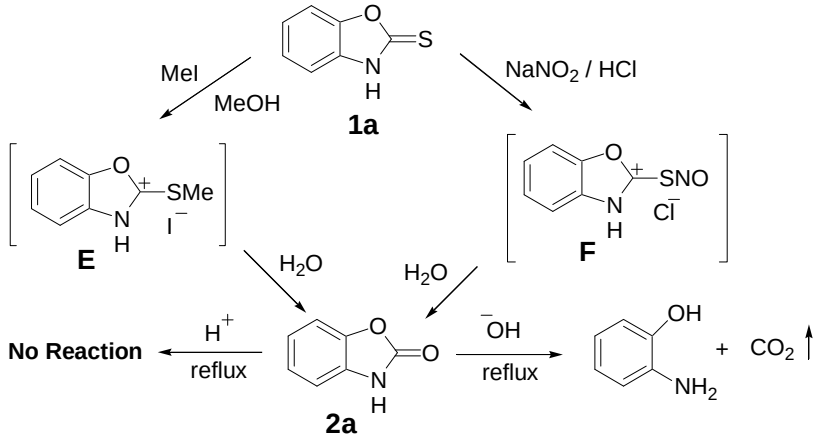
Results and Discussion

The current procedure (**Scheme I**) consists of three steps: N-protection by carbon disulfide *via* dithiocarbamate formation **A**, oxidation by 30% hydrogen peroxide to give **B**, and finally ring closing to give benzoxazole-2-thione **1**. In contrast, benzoxazole-2-ones **2** were synthesized by –OH protection by ethylchloroformate followed by nucleophilic addition-elimination mechanism. Most of the experiments were performed with **3** as the starting aminophenol because of its potential advantages. For economic and safety reasons ethanol was chosen as the solvent after a few preliminary test runs.

Formation of **1** from **3** is believed to involve two intermediates (**A** and **B**, **Scheme I**). Addition of CS_2 to the amino group of **3** generates the first intermediate **A**. This is followed by the thiol anion **A** being oxidized by H_2O_2 to afford the second intermediate **B**. Finally, **B** loses two protons and S_2 to yield two molecules of **1**. Although only an equimolar amount of CS_2 was needed according to the stoichiometry of the reaction, the presence of a slight excess of CS_2 (2 molar equiv.) led to higher yields, perhaps because some of the CS_2 escaped from the system during the reaction. Further increasing the amount of added CS_2, however, was not rewarding. The oxidation and the subsequent ring-closure proceeded very fast because sulfur precipitated out immediately after introduction of H_2O_2. Benzoxazole-2-ones **2** were also synthesized involving two intermediates (**C** and **D**, **Scheme I**). The XH group of



Scheme I



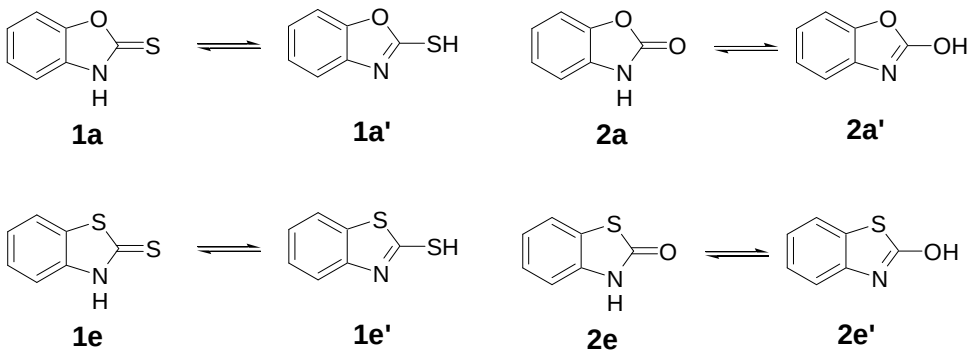
Scheme II

Table I — Synthesis of **1** and **2** from the corresponding aminophenol **3**

Compd	X	R
1a	O	H
1b	O	CH_3
1c	O	Cl
1d	O	NO_2
1e	S	H
2a	O	H
2b	O	CH_3
2c	O	Cl
2d	O	NO_2
2e	S	H

3 was protected by ethylchloroformate to give intermediate **C**, which undergoes intramolecular nucleophilic addition forming tetrahedral intermediate **D**. Finally, **D** loses chloride ion yielding **2**.

Conversion of cyclic carbonyl compounds to their corresponding thio analogues has been reported[6]. The interest of this research group in the synthesis of benzoxazole-2-ones and 2-thiones prompted the exploration of some methods for the reverse process. Herein are described two efficient and convenient approaches for the conversion of benzoxazole-2-thione into the corresponding 2-one derivative in good yield. The reaction of **1a** with methyl iodide in aqueous methanol at reflux temperature gave **2a** *via* methylmercaptoiodide intermediate **E** followed by hydrolysis (**Scheme II**). Alternatively **1a** on reaction with sodium nitrite and hydrochloric acid led to **2a** *via* a nitroso intermediate **F**, followed by hydrolysis. Attempts have also been made to perform the acidic and alkaline hydrolysis of **2a**. Under alkaline condition **2a** undergoes decomposition to yield *o*-amino-phenol but appears to be stable to acidic hydrolysis (**Scheme II**), as treatment with dil. H_2SO_4



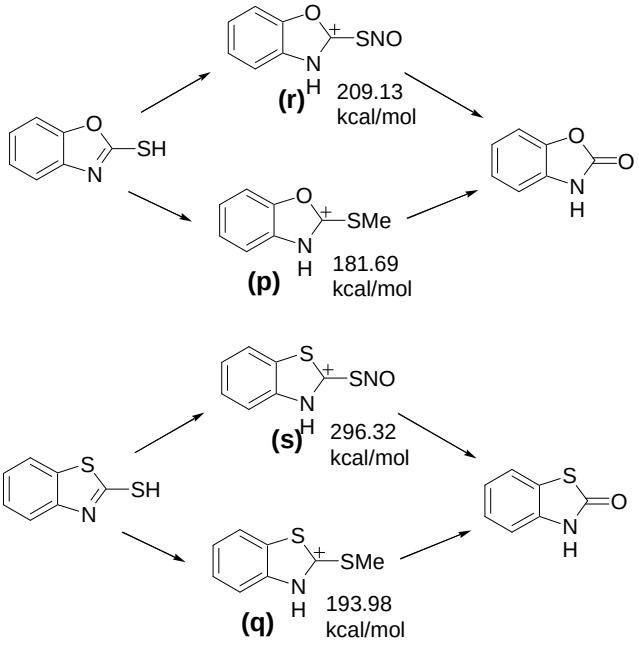
Scheme III

in methanol under reflux for 5 hr did not lead to any discernible changes at all. It is interesting to note that benzoxazole-2-one is stable towards acid.

Two tautomeric forms of the molecules **1** and **2** are possible as shown in **Scheme III**. Molecular mechanical calculations reveal that tautomer **2a** is more stable than its isomer **2a′** as the latter has 1.54 times higher steric energy. On the other hand, in case of molecule **1** the tautomer **1a′** is more stable. The ratios of steric energies are 1.23:1.00 for **a** and **a′**. Similarly, in the molecule **2e** and **1e** the relative steric energies of the **2e** and **2e′**, and **1e** and **1e′** tautomeric forms are 1.00:1.66 and 4.84: 1.00, respectively.

Heat of formation of the molecules was calculated by semi-empirical quantum mechanical (AM1) method (using MOPAC ver 6.0). For molecule **2a** the higher stability of form **a** is evinced by a higher negative ΔH_f value (-25.59 kcal/mol) as compared to **a′** form (–10.67 kcal/mol). Similarly, the form **2e** is more stable (–22.81 kcal/mol) than form **2e′** (–6.56 kcal/mol). In consistence with the results of molecular mechanical calculations the tautomer **1a′** has higher stability (38.05 kcal/mol) than the tautomer **1a** (54.11 kcal/mol). However, in contrast to the MM calculations the results of semiempirical quantum mechanical calculations reveal that the heat of formation of **1e** and **1e′** are almost identical (25.18 and 26.53 kcal/mol, respectively).

These results can be corroborated with the reported theoretical studies on formamides/thioformamides. Wiberg *et al.*[7] by *ab-initio* calculations using density difference maps have concluded that charge polarization in the C-S bond is much weaker than that in the C=O bond and hence the contribution of NH-C=X (X = O/S) is much reduced in thioformamide than in formamide. By NBO analysis Bharatam *et al.*[8] have recently shown that there is $n_N \longrightarrow \pi^*_{[ex]}$ electron delocalization in amides which increases



Scheme IV

with a decrease in the energy difference between the two interacting orbitals. This increases the contribution of N=C-SH tautomer in thioamides.

As already mentioned the molecule **1** was converted to **2** by two different routes. The transition states were optimized by AM1 calculations, which show that the paths (**p**) and (**q**) are more facile than the paths (**r**) and (**s**) as the former ones involve intermediate carbocations with comparatively lower energies (**Scheme IV**).

A new class of benzoxazole-2-ones, benzothiazole-2-ones and their 2-thione derivatives has been synthesized in one-pot protocol. The reaction scheme is straightforward and efficient. An efficient conversion of benzoxazole-2-thione to 2-one derivative has been achieved in high yield. An attempt to perform hydrolysis under acidic and basic

conditions has also been made. The efficient synthesis of these benzoxazole-2-ones and thiones are important for the preparation of biologically active pharmaceutical compounds. This synthesis also provides intermediates for synthesizing amino alcohol derivatives. In conclusion, a simple work-up, low consumption of solvent, fast reaction rates, mild reaction condition and good yields make this method an attractive and useful contribution to the preparation benzofused five membered heterocycles.

Experimental Section

All chemicals and reagents were obtained from Sigma-Aldrich, Lancaster, Spectrochem and Merck and were used as received. All reactions were carried out under a dry, oxygen-free nitrogen atmosphere. Reaction temperatures refer to external oil bath temperatures. All organic solvents were purified and dried according to established procedures[9] immediately prior to use. Progress of reaction was monitored by TLC on Merck silica gel plates (layer thickness 0.2 mm) using appropriate solvent systems and iodine vapour was used as visualizing reagent. Column chromatographic purifications were performed over silica gel (230-400 mesh). Infrared spectra were recorded on a Jasco FT-IR spectrometer and the frequencies (ν) of absorption maxima are reported in wave numbers (cm^{-1}). Melting points were measured on a melting point apparatus and are uncorrected. Elemental analyses were performed by Central Drug Research Institute, Lucknow. ^1H and ^{13}C NMR spectra were recorded on Jeol AL 300 FT-NMR spectrometer. The chemical shifts are reported in δ (ppm) downfield from tetramethylsilane. Mass spectra were recorded at 70 eV ionizing voltage on a Jeol-SX-102 instrument.

General synthetic procedure for benzoxazole-2-thiones and benzothiazole-2-thione, 1: To a stirred mixture of *o*-aminophenol/thiophenol (10 mmol) and powdered anhyd. K_2CO_3 (5 mmol, 0.690 g) in dry ethanol at RT was added very slowly carbon disulfide (20 mmol). After completion of the addition, the solution was stirred at 50°C (bath temp.) for 2 hr. Then H_2O_2 (15 mmol) was added dropwise over a period of 1 hr to the mixture. A yellow brown color appeared and then gradually faded away. A few minutes after completion of addition the insoluble materials were filtered off. The filtrate was diluted with ethyl acetate (70 mL) and washed with water (3×15 mL) and brine and dried over anhyd. Na_2SO_4. The drying agent was removed by filtration and the filtrate was concentrated almost to dryness on a rotary evaporator to give a product that was further purified with the help of column chromatography over silica gel using hexane/ethyl acetate (4:1) as eluent.

General synthetic procedure for benzoxazole-2-ones and benzothiazole-2-one, 2: To a stirred solution of *o*-aminophenol/thiophenol (10 mmol) in dioxane (20 mL) at RT, ethyl chloroformate (10 mmol) was added dropwise and the contents were further stirred for 4 hr. TLC confirmed the completion of the reaction. The solvent was evaporated *in vacuo* and the residue was extracted with ethyl acetate and then the organic layer was washed with brine. The ethyl acetate layer was then dried over anhyd. Na_2SO_4 and concentrated under reduced pressure on rotary evaporator to give the crude product which was further purified with the help of column chromatography over silica gel using hexane/ethyl acetate (10:1) as eluent.

Benzoxazolidine-2-thione, 1a: Following the general experimental procedure for **1**, the mixture of *o*-aminophenol (10 mmol, 1.09 g), powdered anhyd. K_2CO_3 (5 mmol, 0.690 g) and CS_2 (20 mmol, 1.21 mL) in dry ethanol (25 mL) was treated with H_2O_2 (15 mmol, 1.7 mL) to afford **1a,** yield 951 mg (63%), m.p. 193-95°C. Anal. Calcd. for C_7H_5NOS: C, 55.62; H, 3.33. Found: C, 55.84; H, 3.42%. IR (KBr): 3171, 1238, 1007 cm^{-1}; ^1H NMR ($CDCl_3$): δ 10.75 (s, 1H, NH, D_2O exchangeable), 7.06-7.54 (m, 4H, C_6H_4); ^{13}C NMR ($CDCl_3$): δ180.9, 133.3, 130.4, 129.3, 127.7, 125.4, 124.6, 122.3, 121.2, 118.9, 110.6, 109.4; MS (EI, 70 eV): *m/z* (%) 152 (M+1, 100), 108 (25), 107 (15), 102 (9).

(4-Methyl)-benzoxazolidine-2-thione, 1b: Following the general experimental procedure for **1**, the mixture of 2-amino-4-methylphenol (10 mmol, 1.23 g), powdered anhyd. K_2CO_3 (5 mmol, 0.690 g) and CS_2 (20 mmol, 1.21 mL) in dry ethanol (20 mL) was treated with H_2O_2 (15 mmol, 1.7 mL) to afford **1b**, yield 891 mg (54%), m.p. 92°C. Anal. Calcd. for C_8H_7NOS: C, 58.17; H, 4.27. Found: C, 58.54; H, 4.52%. IR (KBr): 3299, 1271, 1105 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.30 (s, 1H, NH, D_2O exchange-able), 7.00-7.25 (m, 3H, C_6H_3), 2.40 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$): δ 181.2, 147.9, 138.8, 132.5, 122.0, 112.5, 107.8, 21.3; MS (EI, 70 eV): *m/z* (%) 166 (M+1, 100), 151 (32), 122 (27), 107 (12).

(4-Chloro)-benzoxazolidine-2-thione, 1c: Following the general experimental procedure for **1**, the mixture of 2-amino-4-chlorophenol (10 mmol, 1.43 g), anhyd. K_2CO_3 (5 mmol, 0.690 g) and CS_2 (20 mmol, 1.21

mL) in anhydrous ethanol (20 mL) was treated with H_2O_2 (15 mmol, 1.7 mL) to afford **1c**, yield 1202 mg (65%), m.p. 280°C. Anal. Calcd. for C_7H_4NOSCl: C, 45.30; H, 2.17. Found: C, 45.54; H, 2.32%. IR (KBr): 3380, 1213, 1125, 1086 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.30 (s, 1H, NH, D_2O exchangeable), 7.20-6.50 (m, 3H, C_6H_3); ^{13}C NMR ($CDCl_3$): δ 180.9, 133.2, 129.3, 127.7, 124.6, 121.2, 118.9; MS (EI, 70 eV): *m/z* (%) 186 (M+1, 100), 188 (30), 152 (23), 140 (4).

(4-Nitro)-benzoxazolidine-2-thione, 1d: Following the general experimental procedure for **1**, the mixture of 2-amino-4-nitrophenol (10 mmol, 1.54 g), anhyd. K_2CO_3 (5 mmol, 0.690 g) and CS_2 (20 mmol, 1.21 mL) in anhydrous ethanol (20 mL) was treated with H_2O_2 (15 mmol, 1.7 mL) to give **1d**, yield 1047 mg (54%), m.p. 99°C. Anal. Calcd. for $C_7H_4N_2O_3S$: C, 42.86; H, 2.05. Found: C, 42.64; H, 2.23%. IR (KBr): 3356, 1595, 1350, 1122, 1042 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.40 (s, 1H, NH, D_2O exchangeable), 8.35-6.70 (m, 3H, C_6H_3); ^{13}C NMR ($CDCl_3$): δ 181.2, 133.2, 132.5, 122.1, 112.5, 106.8; MS (EI, 70 eV): *m/z* (%) 196 (M^+, 100), 150 (26), 106 (4), 102 (21).

Benzothiazolidine-2-thione, 1e: Following the general experimental procedure for **1**, the mixture of 2-aminothiophenol (10 mmol, 1.25 g), anhyd. K_2CO_3 (5 mmol, 0.690 g) and CS_2 (20 mmol, 1.21 mL) in anhyd. ethanol (20 mL) was treated with H_2O_2 (15 mmol, 1.7 mL) to afford **1e,** yield 968 mg (58%), m.p. 126-28°C. Anal. Calcd. for $C_7H_5NS_2$: C, 50.27; H, 3.01. Found: C, 50.44; H, 2.92%. IR (KBr): 3171, 1571, 1238, 930 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.30-7.32 (m, 5H, NH and C_6H_4); ^{13}C NMR ($CDCl_3$): δ 183.3, 142.1, 138.8, 129.2, 122.3, 107.2; MS (EI, 70 eV): *m/z* (%) 168 (M+1, 100), 124 (18), 123 (11).

Benzoxazolidine-2-one, 2a: Following the general experimental procedure for **2**, the mixture of 2-aminophenol (10 mmol, 1.09 g) in dioxane (20 mL) is stirred at RT for 30 min. Very slow addition of ethylchloroformate (10 mmol, 0.95 mL) affords **2a**, yield 929 mg (69%), m.p. 81°C. Anal. Calcd. for $C_7H_5NO_2$: C, 62.23; H, 3.73. Found: C, 62.54; H, 3.52%. IR (KBr): 3241, 1721, 1615, 1551, 1123 cm^{-1}; ^1H NMR ($CDCl_3$): δ 9.70 (s, 1H, NH, D_2O exchangeable), 8.25-6.75 (m, 4H, C_6H_4); ^{13}C NMR ($CDCl_3$): δ 146.7, 125.7, 125.42, 121.3, 120.8; MS (EI, 70 eV): *m/z* (%) 136 (M+1, 32), 108 (100), 107 (25), 102 (12).

(4-Methyl)-benzoxazolidine-2-one, 2b: Following the general experimental procedure for **2**, the mixture of 2-amino-4-methylphenol (10 mmol, 1.23 g) in dioxane (20 mL) is stirred at RT. Very slow addition of ethylchloroformate (10 mmol, 0.95 mL) affords **2b**, yield 1080 mg (72%), m.p. 81°C. Anal. Calcd. for $C_8H_7NO_2$: C, 64.43; H, 4.73. Found: C, 64.64; H, 4.48%. IR (KBr): 3426, 1703, 1605, 1548, 1451, 928 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.60 (s, 1H, NH, D_2O exchangeable), 7.25-6.75 (m, 3H, C_6H_3), 2.25 (s, 3H, CH_3); ^{13}C NMR ($CDCl_3$): δ 144.9, 130.5, 126.2, 121.8, 118.4, 20.5; MS (EI, 70 eV): *m/z* (%) 150 (M+1, 42), 121 (100), 106 (15).

(4-Chloro)-benzoxazolidine-2-one, 2c: Following the general experimental procedure for **2**, the 2-amino-4-chlorophenol (10 mmol, 1.43 g) when added to the solution of sodium (20 mmol, 460 mg) in dioxane (20 mL) followed by dropwise addition of ethylchloroformate (10 mmol, 0.95 mL) affords **2c**, yield 660 mg (78%), m.p. 96°C. Anal. Calcd. for $C_7H_4NO_2Cl$: C, 49.59; H, 2.38. Found: C, 49.74; H, 2.54%. IR (KBr): 3225, 1611, 1194, 1092 cm^{-1}; ^1H NMR ($CDCl_3$): δ 7.49-6.63 (m, 4H, NH and C_6H_3); ^{13}C NMR ($CDCl_3$): δ 147.9, 130.5, 127.2, 121.2, 120.9; MS (EI, 70 eV): *m/z* (%) 169 (M^+, 30), 141 (100), 134 (23), 102 (8).

(4-Nitro)-benzoxazolidine-2-one, 2d: Following the general experimental procedure for **2**, the 2-amino-4-nitrophenol (10 mmol, 1.54 g) when added to the solution of sodium (20 mmol, 460 mg) in dioxane (20 mL) followed by dropwise addition of ethylchloroformate (10 mmol, 0.95 mL) affords **2d**, yield 1300 mg (72%), m.p. 160°C. Anal. Calcd. for $C_7H_4N_2O_4$: C, 46.69; H, 2.24. Found: C, 46.96; H, 2.42%. IR (KBr): 3218, 1623, 1599, 1343 cm^{-1}; ^1H NMR ($CDCl_3$): δ 8.70 (s, 1H, NH, D_2O exchangeable), 8.68-6.80 (m, 3H, C_6H_3); ^{13}C NMR ($CDCl_3$): δ 146.2, 127.5, 125.6, 121.3, 118.8; MS (EI, 70 eV): *m/z* (%) 180 (M^+, 9), 177 (10), 149 (100), 121 (2), 102 (25), 87 (4).

Benzoxazolidine-2-one, 2e: Following the general experimental procedure for **2**, the 2-aminophenol (10 mmol, 1.25 g) when added to the solution of sodium (20 mmol, 460 mg) in dioxane (20 mL) followed by dropwise addition of ethylchloroformate (10 mmol, 0.95 mL) gives **2e**, yield 780 mg (52%), m.p. 63°C. Anal. Calcd. for C_7H_5NOS: C, 55.61; H, 3.33. Found: C, 55.87; H, 3.64%. IR (KBr): 3432, 1667, 1580, 1518 cm^{-1}; ^1H NMR ($CDCl_3$): δ 10.00 (s, 1H, NH, D_2O exchangeable), 7.40-7.12 (m, 4H, C_6H_4); ^{13}C NMR ($CDCl_3$): δ 146.9, 125.6, 121.2, 120.8, 117.9; MS (EI, 70 eV): *m/z* (%) 152 (M+1, 100), 124 (5).

Conclusion

In conclusion a simple one pot procedure with low consumption of solvent, fast reaction rates, mild reaction condition and good yield makes this protocol an attractive and useful contribution to the preparation of benzofused oxazolidin-2-ones, thiazolidin-2-ones and their thione derivatives.

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