Zirconium Dodecylphosphonate: Selective and Constructive Catalyst for Preparation of 2-Alkyl Benzoxazoles from Aliphatic Carboxylic Acids

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ABSTRACT: *In this study, zirconium dodecylphosphonate was synthesized by the reported method in scientific literature. 2-Alkylbenzoxazoles were prepared from aliphatic carboxylic acids and 2-aminophenol in the presence of this catalyst under solvent-free conditions at 100°C. Their structures were recognized by IR, ^{1}H NMR, and ^{13}C NMR. Then, we used aromatic carboxylic acids in the similar reaction. But, the results show aromatic carboxylic acids don't react with 2-aminophenol. So, this method introduces a selective and constructive method for synthesis of 2-alkyl benzoxazoles without salt formation. On the other hand, this research offers several advantages such as high yields, good reaction times, easy work-up and use of a safe catalyst.*

KEYWORDS: *Zirconium dodecylphosphonate; 2-Alkyl benzoxazoles; Aliphatic carboxylic acids; 2-Aminophenol; Solvent-free.*

INTRODUCTION

Benzoxazoles are an important class of compounds and have exhibited a variety of biological activities such as melatonin receptor agonist [1], anticancer [2], anti-micro bacterial [3], elastase inhibitory [4], photochromic agents [5] and laser dyes [6]. There are several known strategies for the synthesis of 2-substituted benzoxazoles includes: coupling of carboxylic acids [7], acid chlorides [8], nitriles [9], aldehydes and orthoesters [10], 2-halophenols [11] and aryl methanols with 2-aminophenol [12]. The use of carboxylic acids is more appropriate than using their derivatives because carboxylic acids are more stable than their derivatives and commercially available. This method can occur under strongly acidic conditions using boric acid [13] and polyphosphoric acid [14]. But these conditions are not appropriate for sensitive reagents. On the other hand, they have been just used for preparation of 2-aryl benzoxazoles. Polyphosphoric anhydride [15] and combination reagent PS-PPh_3/CCl_3CN [16] are the other reagents that used for this conversion. These methods have many advantages but suffer from harsh conditions such as use of high temperatures (MW and 160 °C), use of excess amount of

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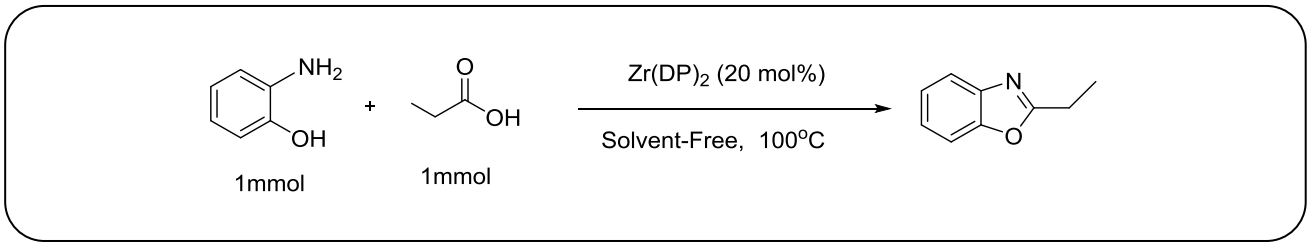


Fig. 1: Reaction between 2-ethylbenzoxazol and 2-aminophenol as a model reaction.

The reagents and use of the solvent. So, introduce a new method for this conversion is necessary. As part of our current studies on development of new heterocyclic systems [17], we have shown that zirconium dodecylphosphonat is an effective catalyst for conversion of aliphatic carboxylic acids into their corresponding 2-alkyl benzoxazoles.

EXPERIMENTAL SECTION

2-Aminophenol and aliphatic carboxylic acids were bought from Merck Company and were used without further purification. Zirconium dodecylphosphonate were prepared by known methods [18]. Melting points (uncorrected) were measured on an Electrothermal 9100 apparatus. ^{1}H and ^{13}C-NMR spectra sere measured with a Bruker DRX-FT 250 Avance spectrometer. IR spectra were obtained by using a 470-Shimadzu IR spectrophotometer. CHNS were recorded on a Vario EL authomated analyzed, model 11086109.

General Procedure for Preparation of benzoxazole derivatives by using $Zr(DP)_2$ as catalyst

Zirconium dodecylphosphonate (0.2 mmol) was added to a mixture of 2-aminophenol (1mmol) and aliphatic carboxylic acid (1 mmol) at 100 °C and was stirred for 2 hours. The progress of the reaction was monitored by TLC. After completion of the reaction, dichloromethane (10 mmol) was added to the reaction mixture and then was quenched with aqueous solution of $NaHCO_3$ (2×10 mL). The organic layer was separated, washed with water and dried over $CaCl_2$. Evaporation of the solvent gave an almost pure product which was purified by column chromatography with petroleum ether to give the pure product.

RESULTS AND DISCUSSION

The study of dodecyl phosphonic acid and its salt applications in order to synthesis heterocyclic compounds is one of the fields that our research group is willing to do [17]. In recent years many studies have been done on dodecyl sulphonic acid and its salts [19], but similar phosphonic acids have not been noticed considerably. Our purpose in this research is, introducing another application of zirconium dodecylphosphonate to prepare 2-alkyl benzoxazoles.

In the first step, the synthesis of 2-ethylbenzoxazole was studied as a model reaction. For this purpose, a reaction carried out between 1 mol of 2-aminophenol and 1 mol of propionic acid in the presence of 20 mol % of zirconium dodecylphosphonate under solvent-free conditions at 100 °C (Fig. 1). The reaction completed in 2 hours. The formation of 2-ethylbenzoxazole was confirmed by ^{1}H and ^{13}C-NMR spectra.

In the next step, in order to optimize the reaction conditions, the effect of temperature, solvent and amount of catalyst investigated. The results are summarized in Table 1.

No production was produced under solvent-free conditions, without using catalyst at 100 °C (Table 1, Entry 1) and under solvent-free conditions in the presence of 20 mol % of $Zr(DP)_2$ at 50 °C (Table 1, Entry 5) after 24 hours. The reaction stopped at the amide step in toluene, DMSO and water solvents under reflux conditions (Table 1, Entries 8, 9 and 10).

According to Table 1, the best conditions were under solvent-free conditions in the presence of 20 mol % of $Zr(DP)_2$ at 100 °C (Entry 4).

The optimized conditions were used to produce other products. As shown in Table 2, all the aliphatic carboxylic acids expect cyclohexyl carboxylic acid (Table 2, Entry 6) completed after 2 hours. Cyclohexyl carboxylic acid did not even complete after passing 24 hours.

In continued, in order to study the effect of catalyst in formation of 2-aryl benzoxazoles, benzoic acid and

4-chloro benzoic acid was selected. But, no products were formed after 24 hours.

Table 1: Optimization of Reaction Conditions for Preparation of 2-Ethylbenzoxazole.

Entry	Solvent	Amount of $Zr(DP)_2$ (mol%)	Time (h)	Temp.(˚C)	Yield (%)
1	Solvent-free	-	24	100	-
2	Solvent-free	5	2	100	50
3	Solvent-free	10	2	100	75
4	Solvent-free	20	2	100	98
5	Solvent-free	20	24	50	-
6	Solvent-free	20	2	150	75
7	Ethanol	20	24	Reflux	Trace
8	Toluene	20	24	Reflux	a
9	DMSO	20	24	Reflux	a
10	Water	20	24	Reflux	a

The reaction stopped at the amide step

Supplementary Materials Available: Spectral data

2-Methyl-1,3-benzoxazole (Table 2, Entry 1)

Yellow Oil; FT-IR (KBr, cm^{-1}): 3025, 2825, 1660, 1473, 1456, 1376; ^{1}H-NMR (250 MHz, $CDCl_3$): δ=2.56 (s, 3H, CH_3), 7.26-7.31 (m, 2H, arom.), 7.43-7.49 (m, 1H, arom.), 7.63-7.67 (m, 1H, arom.). ^{13}C-NMR (63 MHz, $CDCl_3$): δ= 21.68, 110.17, 119.40, 124.06, 124.41, 142.88, 149.81, 163.79.

2-Ethyl-1,3-benzoxazole (Table 2, Entry 2)

Yellow Oil; FT-IR (KBr, cm^{-1}): 3043, 1629, 1479, 1375, 1225, 773, 695. ^{1}H-NMR (250 MHz, $CDCl_3$): δ=1.26-1.33 (m, 3H, CH_3), 2.48-2.55 (m, 2H, CH_2), 7.26-7.30 (m, 2H, arom.), 7.44-7.48 (m, 1H, arom.), 7.65-8.01 (m, 1H, arom.). ^{13}C-NMR (63 MHz, $CDCl_3$): δ=14.0, 23.2, 110.5, 119.9, 124.0, 124.4, 144.3, 147.1, 168.2.

2-Propyl-1,3-benzoxazole (Table 2, Entry 3)

Yellow Oil, FT-IR (KBr, cm^{-1}): 2961, 2927, 1651, 1460, 855. ^{1}H-NMR (250 MHz, $CDCl_3$): δ=0.90-0.95 (m, 3H, CH_3), 2.47-2.59 (m, 2H, CH_2), 2.73-2.79 (m, 2H, CH_2), 7.28-7.39 (m, 2H, arom.), 7.47-7.48 (m, 1H, arom.), 7.65-7.68 (m, 1H, arom.). ^{13}C-NMR (63 MHz, $CDCl_3$): δ=14.0, 23.6, 31.3, 110.1, 119.3, 123.9, 124.3, 142.3, 150.0, 166.3.

2-(2-Phenylethyl)-1,3-benzoxazole (Table 2, Entry 4)

Yellow Oil, FT-IR (KBr, cm^{-1}): 2983, 1654, 1456, 1370. ^{1}H-NMR (250 MHz, $CDCl_3$): δ=2.73-2.79 (t, *J*=7.5 Hz, 2H, CH_2), 2.92-2.93 (t, *J*=7.5 Hz, 2H, CH_2), 7.21-7.37 (m, 7H, arom.), 7.75-7.76 (m, 1H, arom.), 7.71-7.88 (m, 1H, arom.). ^{13}C-NMR (63 MHz, $CDCl_3$): 32.4, 37.2, 110.6, 119.1, 123.9, 124.7, 125.9, 127.7, 129.6, 139.2, 142.1, 149.6, 166.0.

2-(3-Phenylpropyl)-1,3- benzoxazole (Table 2, Entry 5)

Yellow Oil, FT-IR (KBr, cm^{-1}): 2973, 1655, 1479, 1370. ^{1}H-NMR (250 MHz, $CDCl_3$): δ=2.17-2.29 (m, 2H, CH_2), 2.73-2.79 (m, 2H, CH_2), 2.92-2.98 (m, 2H, CH_2), 7.19-7.31 (m, 7H, arom.), 7.45-7.47 (m, 1H, arom.), 7.65-7.68 (m, 1H, arom.). ^{13}C-NMR (63 MHz, $CDCl_3$): δ=27.96, 28.24, 35.09, 110.26, 119.54, 124.07, 124.46, 126.04, 128.42, 128.50, 141.22, 142.35, 149.27, 165.57. Anal. Calc. For $C_{16}H_{15}NO$ (237.30): C, 80.98; H, 6.37; N, 5.90%. Found: C, 80.90; H, 6.35; N, 5.90%.

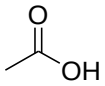
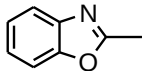
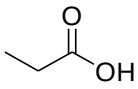
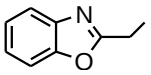
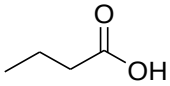
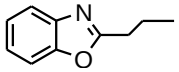
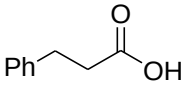
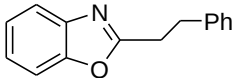
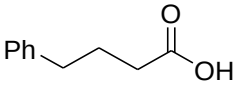
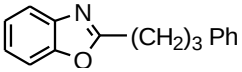
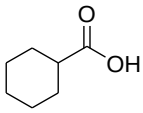
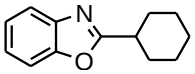
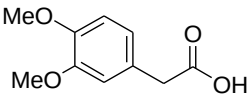
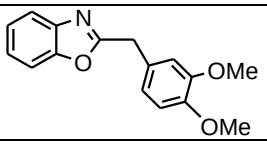
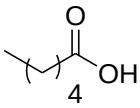
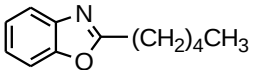
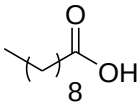
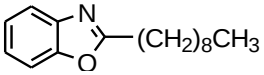
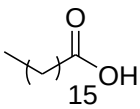
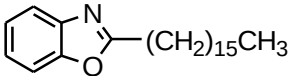
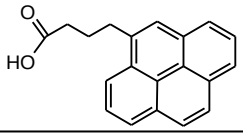
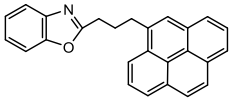
2-Cyclohexyl-1,3- benzoxazole (Table 2, Entry 6)

Yellow Solid, M. P. 164 °C [163-165 °C, Lit.]; FT-IR (KBr, cm^{-1}): 2980, 1665, 1463, 1375. ^{1}H-NMR (250 MHz, $CDCl_3$): δ=1.69-2.19 (m, 7H, cylohexyl-), 2.91-2.95 (m, 3H, cyclohexyl-), 2.97 (m, 1H, CH-), 7.25-7.31 (m, 2H, arom.), 7.45-7.48 (m, 1H, arom.), 7.68-7.70 (m, 1H, arom.). ^{13}C-NMR (63 MHz, $CDCl_3$): δ=25.61, 25.75, 29.65, 30.46, 110.25, 119.59, 123.94, 124.30, 129.0, 131.21, 142.31, 149.23, 161.49.

2-(3,4-Dimethoxybenzyl)-1,3-benzoxazole (Table 2, Entry 7)

Yellow Solid, M. P. 216 °C; FT-IR (KBr, cm^{-1}): 2978, 1650, 1476, 1375, 1110, 857. ^{1}H-NMR (250 MHz, $CDCl_3$): δ=1.25-1.33 (m, 6H, CH_3), 1.37 (s, 2H, CH_2),

Table 2: Reaction between 2-aminophenol and aliphatic carboxylic acids in the presence of zirconium dodecylphosphonate as catalyst.

Entry	Carboxylic acid	Product	Isolated Yield (%)	Time (h)	M.P. (B. P.)/°C [Lit.]
1			95	2	(178) [10e, 21]
2			98	2	(640) [10e, 21]
3			90	2	Oil
4			83	2	(354.5)
5			95	2	Oil
6			70	24	164 163-165 [20]
7			87	2	216
8			82	2	Oil
9			90	2	256
10			85	2	274
11			90	120	110

7.11-7.15 (d, *J*=8.5 HZ, 2H, arom.), 7.26 (s, 2H, arom.), 7.52-7.55 (d, *J*=8.5 Hz, 2H, arom.). ^{13}C-NMR (63 MHz, $CDCl_3$): δ=31.4, 56.0, 110.2, 115.4, 119.5, 122.0, 123.3, 126.0, 129.4, 141.2, 145.3, 149.2, 149.4, 161.4. Anal. Calc. For $C_{16}H_{15}NO_3$ (269.30): C, 71.36; H, 5.61; N, 5.20%. Found: C, 71.38; H, 5.64; N, 5.20%.

2-Pentyl-1,3-benzoxazole (Table 2, Entry 8)

Yellow Oil, FT-IR (KBr, cm^{-1}): 3131, 2915, 1637, 1554, 1425, 812, 770. ^{1}H-NMR (250 MHz, $CDCl_3$): δ=0.88-0.95 (m, 3H, CH_3), 1.37-1.44 (m, 4H, $CH_3(C\underline{H}_2)_2CH_2CH_2$-), 1.89-1.91 (m, 2H, $CH_3(CH_2)_2C\underline{H}_2CH_2$-), 2.88-2.95 (m, 2H, $CH_3(CH_2)_2CH_2C\underline{H}_2$-), 7.25-7.31 (m, 2H, arom.), 7.44-7.46 (m, 1H, arom.), 7.65-7.72 (t, *J*=9.25 Hz, 1H, arom.). ^{13}CNMR (63 MHz, $CDCl_3$): δ=14.09, 22.67, 26.44, 28.58, 30.34, 110.19, 119.48, 123.97, 124.32, 141.38, 150.75, 167.32.

2-Nonyl-1,3-benzoxazole (Table 2, Entry 9)

Yellow Solid, M. P. 256 °C; FT-IR (KBr, cm^{-1}): 3020, 1625, 1470, 755, 698. ^{1}H-NMR (250 MHz, $CDCl_3$): δ=0.84-0.92 (m, 3H, CH_3), 1.26-1.44 (m, 12H, CH_2), 1.82-1.94 (m, 2H), 2.88-2.94 (m, 2H), 7.26-7.31 (m, 2H, arom.), 7.44-7.48 (m, 1H, arom.), 7.68 (m, 1H, arom.). ^{13}C-NMR (63 MHz, $CDCl_3$): δ=14.10, 22.66, 26.76, 28.63, 29.16, 29.25, 29.39, 31.85, 110.21, 119.49, 123.99, 125.27, 141.38, 150.75, 167.35. Anal. Calc. For $C_{16}H_{23}NO$ (245.37): C, 78.32; H, 9.45; N, 5.71%. Found: C, 78.36; H, 9.41; N, 5.70%.

2-Hexadecyl-1,3-benzoxazole (Table 2, Entry 10)

Yellow Solid, M. P. 274 °C; FT-IR (KBr, cm^{-1}): 3124, 1615, 1455, 843, 720. ^{1}H-NMR (250 MHz, $CDCl_3$): δ=0.85-0.87 (m, 3H, CH_3), 0.94-1.25 (m, 26H, CH_2), 1.83-1.92 (m, 2H, CH_2), 2.85-2.91 (m, 2H, CH_2), 7.12-7.25 (m, 4H, arom.). ^{13}C-NMR (63 MHz, $CDCl_3$): δ=26.83, 28.69, 29.78, 32.03, 110.25, 119.59, 124.39, 125.35, 141.52, 150.86, 167.38. Anal. Calc. For $C_{23}H_{37}NO$ (343.56): C, 80.41; H, 10.86; N, 4.08%. Found: C, 80.38; H, 10.90; N, 4.08%.

2-(3-(Pyrene-4-yl)propyl)-1,3-benzoxazole (Table 2, Entry 11)

Pale-Yellow Solid, M. P. 110 °C. FT-IR (KBr, cm^{-1}): 3111, 1620, 1476, 1325, 834. ^{1}H-NMR (250 MHz, $CDCl_3$): δ=2.13-2.48 (m, 2H, CH_2-), 3.01-3.07 (m, 2H, CH_2-), 3.43-3.49 (m, 2H, CH_2-), 7.26-7.30 (m, 2H, arom.), 7.41 (m, 1H), 7.56 (m, 1H), 7.87 (m, 1H), 7.96-8.23 (m, 8H, arom.). ^{13}C-NMR (63 MHz, $CDCl_3$): δ=28.30, 28.44, 32.67, 110.27, 119.59, 123.22, 124.11, 124.51, 124.78, 124.81, 124.94, 125.10, 125.83, 126.73, 127.35, 127.41, 127.47, 128.71, 130.02, 130.87, 131.40, 135.35, 150.80, 166.79. Anal. Calc. For $C_{26}H_{19}NO$ (361.44): C, 86.40; H, 5.30; N, 3.88%. Found: C, 86.45; H, 5.36; N, 3.86%.

CONCLUSIONS

Consequently, we have presented a simple method for preparation of 2-alkyl benzoxazoles from aliphatic carboxylic acids without formation the acid salt. On the other hand, our research offers several advantages such as high yields, good reaction times, easy work-up and use of a safe catalyst.

The literature survey shows that the preparation of 2-aryl benzoxazole derivatives has noticed more than 2-alkyl benzoxazoles. Since this paper includes synthesis of 2-alkyl derivatives, we believe the available report can complete previous researches done in this field so far.

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