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Trimethyl phosphate mediated synthesis of 2-arylbenzothiazole derivatives

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ABSTRACT

Synthesis of 2-aryl benzothiazoles mediated by trimehtyl phosphate at room temperature with short reaction time by simple and alternative method, high yield of the product and simple recovery by present method. The obtained were characterized by H^1NMR, IR, Mass spectra

Keywords:-2-aryl-benzothiazole derivatives, trimehtylphosphate, 2-aminothiophenols, aromatic aldehydes.

INTRODUCTION

Synthesized compounds of 2-benzothizoles in various methods are known, the oldest method being the Jacobson synthesis. Owing to the wide range of biological activities and various medicinal applications, the synthesis of substituted benzothiazoles is emerging importance in recent times. The benzo thiozoles having importance as photo sensensitizers, doping in light emitting organic electro luminescent devices vulcanization accelerators,antioxidants.[1-12]

The reported method for the synthesis of 2-substituted bemzpthiazole involves condensation of 2-aminothiophenol with aldehydes in presence of trimethylphosphate in water and the methanol. However so many methods are developed to clean approaches for the synthesis of 2-substituted benzothiazoles [13-14]. As a common catalyst for Phase transfer, trimethylphosphate is able to expedite the reaction between anion or nucleophile and neutral substrate via transferring one phase to another, making collided with each other frequently[17-18].

MATERIALS AND METHODS

Experimental Section

All the chemicals are purchased from sigma-Aldrich. The liquid aldehydes were purified by distillation. The products were identified by recording their melting point by open capillary method and are corrected. The IR spectra were recorded on a FT-IR in KBr disc, The 1H NMR spectra were recorded on Joel60MHz and Joel GSX-300 spectrometer using $CDCl_3$ as solvent and TMS as an internal reference. The chemical shift expressed in δ values. The purity of the compounds is checked by TLC on silica gel glass plates in n-hexane95% and ethylacetate5% as a solvent mixture. The compounds are purified by column chromatography using silica gel (60-120 mesh) and as a adsorbent and n-hexane and ethyl acetate as eluents and solid products are recovered by evaporation of solvents.

Scheme-1

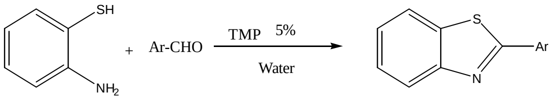
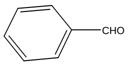
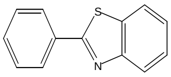
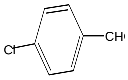
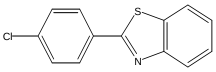
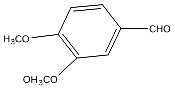
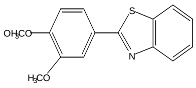
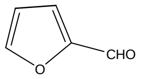
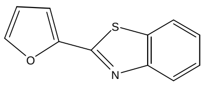
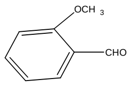
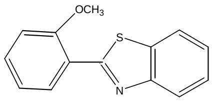
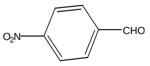
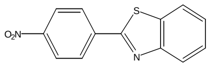
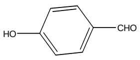
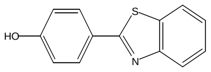


Table-1: The reactions of 2-aminothiophenol and aromatic aldehydes in water & trimethylphosphate (5%) as a catalyst

Entry	ArCHO	Product	Time/h	yields
1			1	98%
2			1.5	94%
3			1	96%
4			2.5	86%
5			2	88%
6			7	70%
7			1	94%

General procedure for the synthesis of 2-aryl-substituted benzothiazoles using trimethylphosphate as catalyst

A mixture of 2-aminothiophenol (1mmol) and aromatic aldehydes (1mmol) were added to 5% trimethylphosphate in a round bottomed flask and stirred under laboratory temperature. The progress of the reaction monitored by TLC.After completion of the reaction, the mixture was stirred with (3×10ml) ethyl acetate and the organic layer was washed with brine solution. The catalyst easily soluble in water and can be easily removed. The crude product purified column chromatography and the solid product was obtained by removal of solvent at reduced pressure and characterized.

2-phenylbenzothiazole:

white solid,mp 111-112^{0}C**,** ^{1}**HNMR** (300MHz,CDCl$_3$) δ8 -8.12(m,3H.ArH), 7.91(d,j7.7Hz,ArH) 7.48-7.53(m,4H,ArH). 7.40(d,j7.7Hz,ArH) ^{13}**CNMR** (75MHz,CDCl$_3$) δ168.1, 154.1, 135.0, 133.6, 131.0, 129.1, 126.3, 125.2, 123.2, 121.6. **IR**(KBr):3078,3053,1586,1561 cm^{-1}

2-(4-Chlorophenyl)benzothiazole:

yellow crystal; M.p 112-114^{0}C, ^{1}**H NMR** (300MHz,CDCl$_3$) δ7.8-78.06(m,4H,ArH),7 .5-7.51(m,4H,ArH). ^{13}**CNMR** (75MHz,CDCl$_3$) δ166.8, 154.3,137.2,135.3,129.5,128.7,125.6,123.5,121.8.2. **IR** (KBr): 3078, 3053, 1599, 1593 cm^{-1}.

2-(3,4-Dimethoxyphenyl)1,3-benzothiazole:

White crystal; M.p 166-167^{0}C; 1HNMR(CDCl3): δ8.05(dJ=6Hz,1H); 7.94(d,j=6H,1H); 7.74(s,1H), 7.59 (d,j=6.3Hz,1H), 7.47(t,j=5.46Hz,1H), 7.35(t,j=5.7,5.4Hz,1H), 6.93(d,j=6.3Hz,1H), 4.01(s,3H,OCH$_3$), 3.94(s,3H,-OCH$_3$), 3.94(s,3H,OCH$_3$); ^{13}**CMR**(CDCl$_3$): δ167.92, 154.03,151.53, 149.29, 134.8, 126.57, 126.21, 124.85, 122.77, 121.47, 121.12,110.96,109.72; **IR**(KBr):3078, 3053, 2965, 2839, 1593,1593 cm^{-1}

2-(Furan-2-yl)-1,3-benzothiazole:

Yellow crystal; M.p 99-101^{0}C; ^{1}HNMR(CDCl$_3$):δ8.09(d,j=8.4Hz,1H),7.9(d,4-7.48(m,1H),7.6(d,j=1.2Hz,1H),7.54-7.48(m,1H)7.43-7.32(m,1H),7.31-7.16 (m,1H),7.31-7.16(m,1H),7.57-6.55(m, 1H); ^{13}**CNMR**(CDCl$_3$): δ157.3,152.8, 148.6,144.6, 134.15, 126.4, 125.1, 123.4, 112.4 **IR(KBr)**:3123, 3055, 1584,1562cm^{-1}

2-(2-Methoxyphenyl)-1,3-benzothiazole:

White crystal; M.p 85-86^{0}C; ^{1}**HNMR**(CDCl$_3$):δ8.55(d,j=7.9Hz,1H),8.15(d,j=8.1Hz,1H),7.93(d,j=8.1Hz,1H),7.53-7.45(m,2H),7.41-7.36(m,1H),7.18-7.01(m,2H),4.074(s,3H); **IR**(KBr):3063,3015,1597,1584 cm^{-1}

2-(4-Nitrophenyl)-1, 3-benzothiazole:

Brown crystal; M.p 229-232^{0}C; ^{1}**HNMR**(CDCl$_3$):δ8.84(s,1H),8.44(d,J=8.0 Hz,1H),8.41(d,j=8Hz,1H),8.24(d,j=8 Hz, 1H), 8.16(d,j=8Hz,H), 7.88(t,j=8Hz,1H), 7.60(t,j=8 Hz,1H),7.54(t,j=8 Hz,1H); ^{13}**CNMR**(CDCl$_3$): δ161.9,157.5, 149.4,142.8,133.3, 130.7, 130.2, 126.6,126.5,122.5,120.3,119.5,111.8; **IR (KBr)**:3086, 3043, 1598, 1563cm^{-1}

2-(4-Hydroxyphenyl)benzothiazole: white solid; M.p 229-231 ^{0}C ^{1}**H NMR;**δ 7.89-8.08(m,4H.ArH), 7.36-7.50(m,2H,ArH), 6.906.95(m,2H,ArH), 3.64(s,1OH); ^{13}**CNMR:** δ167.9, 170.1, 154.1,134.5, 129.5, 126.8,125.3, 124.4, 122.5,122.7,11

RESULTS AND DISCUSSION

Initially, we compare with various conditions in the model reaction using 2-aminophenol with aromatic aldehyde the results are summarised. The results established that trimethyl phoshphate is also one of the alternative catalyst among all the catalyst screened in this transformation. Then we investigated with different amount of TMP (trimethyl phosphate) in water. The results were summarized in Table-1. It was found that aldehydes can react well with 2-aminophenol in good yields without using extra oxidants. It is noteworthy that present protocol is support to the previous method for the synthesis.

CONCLUSION

A facile synthesis of 2-arylbenzothiazole has been achieved with trimethylphosphate. Reaction condition is simple and the transformation could be performed at room temperature. Simple recovery of the target molecules and high yields

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