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Der Pharma Chemica, 2013, 5(6):294-298
(http://derpharmachemica.com/archive.html)

ISSN 0975-413X
CODEN (USA): PCHHAX

A CaO catalyzed facile one pot synthesis of 2-aminothiophenes using Gewald reaction

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ABSTRACT

A simple and efficient protocol for the synthesis of 2-aminothiophenes via Gewald reaction from ketones with an active nitrile or ethyl ester and elemental sulphur using CaO, a cheapest catalyst ever reported in moderate to good yield in ethanol under reflux in 1 to 1.5 h.

Keywords: CaO catalyst, Gewald reaction, 2-aminothiophenes

INTRODUCTION

Gewald reaction leads to the product 2-aminothiophene or substituted thiophene and their derivatives have their contribution in the diverse field such as dyes, drug design, biodiagnostics, electronics and optoelectronics, sensors and self assembled super structures as well as in the preparation of biologically active molecules as a potent apoptosis inducer, a potential anti-inflammatory and anti-osteoporosis agent, an agonist of allosteric enhancers at the adenosine A_1 receptor were well established[1-14]. There is a continuous demand for the development of flexible synthetic method for this heterocyclic moiety. Many alterations have been incorporated to the conventional Gewald's[15-17] reaction by varying the components[18,19] and the conditions[20-35]. Synthesis of 2-aminothiophenes in one pot remains an attractive field because of the problem associated in terms of yield, reaction time, amount of catalyst required, cost effective and availability of the catalyst, careful preparation of the catalyst and reusability in most of the published procedures.

MATERIALS AND METHODS

All reagent and solvents available commercially were used without further purification. Reactions were followed by TLC analysis. Melting points were measured using open capillaries in a sulphuric acid bath. IR and ^{1}H NMR spectra in $CDCl_3$/DMSO-d_6 as a solvent were recorded on Perkin-Elmer and Varian 300 MHz spectrometer, respectively. Mass spectral datas were obtained using Thermo Scientific Corporation, DSQ II mass spectrometer.

General procedure for synthesis of 2-aminothiophenes *via* Gewald reaction
A mixture of ketone (1.0 mmol), nitrile (1.0 mmol), elemental sulphur (1.1 mmol) and CaO (1.0 mmol) in 12mL of ethanol were heated at reflux for the time showed in **Table 2.** When the reaction was completed (followed by TLC), the catalyst was filtered off and the ethanol was removed by evaporation and the dried reaction mixture was

dissolved in dichloromethane and washed with brine solution followed by water and the organic layer was dried with anhydrous Na_2SO_4. After evaporation of the solvent, the residue was subjected to column chromatography to isolate the desired product in its pure form. As shown in the Table 2 CaO catalysed Gewald reaction proceeded smoothly with a wide range of ketones. All the products were characterized by NMR, IR and Mass spectroscopic datas and comparison of their physical and spectroscopic data with authentic samples. Efficiency of CaO as a catalyst in Gewald reaction in comparison with other catalysts reported in the literature is given in the **Table 1**.

Ethyl 2-amino, 4, 5-dimethylthiophene-3-carboxylate *(entry 1):* mp 91-92 ^0C[17]. IR (KBr): υ 3433, 3336, 3218, 2918, 2855, 2190, 1716, 1609, 1520, 1305, 1047 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.2(t, 3H, J = 7.0 Hz), 2.0(s, 3H), 2.3(s, 3H), 4.5(q, 2H, J = 7.0 Hz), 6.5(br s, 2H) ^{13}C NMR ($CDCl_3$, 300 MHz): δ 21.8, 22.4, 23.5, 25.0, 99.0, 116.9, 121.3, 132.5, 160.0. HRMS calcd. for $C_9H_{13}NO_2S$: 199.0667. Found: 199.0632.

2-Amino-4, 5-dimethylthiophene-3-carbonitrile *(entry 2):* mp 141-142 ^0C[17]. IR (KBr): υ 3438, 3345, 3223, 2923, 2867, 2164, 1612, 1572, 1496, 1398, 1092 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 2.3(s, 3H), 2.4(s, 3H), 6.0(br s, 2H), ^{13}C NMR ($CDCl_3$, 300 MHz): δ 22.3, 22.4, 115.0, 121.9, 130.0, 153.5, and 160. HRMS calcd. for $C_7H_8N_2S$: 152.0408. Found: 152.0354.

Diethyl 2-amino-5-methyl-thiophene-3, 4-dicarboxylate *(entry 3):* mp107-108^0C[17]. IR (KBr): υ 3438, 3353, 3225, 2910, 2869, 2195, 1716, 1654, 1624, 1506, 1378, 1189 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.2(t, 6H, J = 7.0 Hz), 2.3(s, 3H) 4.5(q, J = 7.0 Hz, 4H), 6.8(br s, 2H), ^{13}C NMR ($CDCl_3$, 300 MHz): δ 13.5, 14.4, 60.6, 129.8, 142.3, 154.5, 159.7. HRMS calcd. for $C_{11}H_{15}NO_4S$: 257.0723. Found: 257.0704.

Ethyl 2-amino-3-cyano-5-methylthiophene-3-carboxylate *(entry 4):* mp 150-151 ^0C[30]. IR (KBr): υ 3440, 3335, 3243, 2965, 2886, 2164, 1608, 1570, 1506, 1377, 1030 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.6(t, J = 6.6Hz, 3H), 2.2(s, 3H), 2.5(q, J = 6.6 Hz, 2H) 6.0(br s, 2H), ^{13}C NMR ($CDCl_3$, 300 MHz): δ 22.3, 23.4, 23.9,60.2, 115.0, 121.9, 130.0, 153.5, 160.0. HRMS calcd. for $C_9H_{10}N_2O_2S$: 210.0463. Found: 210.0435.

Ethyl 2-amino-5-methylthiophene-3-carboxylate *(entry 5):* mp 46-47 ^0C[17]. IR (KBr): 3433, 3336, 3218, 2918, 2855, 2190, 1716, 1609, 1520, 1305, 1047 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.2 (t, 3H, J = 7.0Hz), 2.0(s, 3H), 4.5(q, 2H, J = 7.0 Hz), 6.1(s, 1H), 6.5(br s, 2H). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 21.8, 22.4, 23.5, 25.0, 99.0, 116.9, 121.3, 132.5, 160.0. HRMS calcd. for $C_8H_{11}NO_2S$: 185.0510. Found: 185.0487.

Ethyl 2-amino-4-phenylthiophene-3-carboxylate *(entry 6):* mp 97-98 ^0C[17]. IR (KBr): υ 3443, 3323, 3217, 2910, 2859, 2184, 1716, 1654, 1624, 1506, 1398, 1092 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.2(t, J = 7.05 Hz, 3H,), 4.7(q, J = 7.0 Hz, 2H), 5.4(br s, 2H), 6.5(s, 1H), 7.2-7.4(m, 5H). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 16.4, 62.6, 115.7, 126.9, 127.5, 129.3, 137.4, 138.5, 143.8, 153.5, 160.0. HRMS calcd for $C_{13}H_{13}NO_2S$: 247.0667. Found: 247.0641.

2-Amino-4-phenylthiophene-3-carbonitrile *(entry 7):* mp 141-142 ^0C[17]. IR (KBr): υ 3438, 3345, 3223, 2164, 1624, 1506, 1398, 1092 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 4.3(br s, 2H), 6.7(s, 1H), 7.4-7.9(m, 5H), ^{13}C NMR ($CDCl_3$, 300 MHz): δ 115.0, 126.4, 126.9, 128.3, 137.0, 137.5, 138.8, 144.3, 153.5, 160.0. HRMS calcd. for $C_{11}H_8N_2S$: 200.0408. Found: 200.0370.

Ethyl 2-amino-5, 6-dihydro-4H-cyclopenta[b]thiophene-3-carboxylate *(entry 8):* mp 90-91 ^0C[22]. IR (KBr): υ 3409, 3291, 2923, 2854, 1740, 1647, 1596, 1488, 1420, 1258, 1161, 1035, 782 cm^{-1}. ^{1}HNMR ($CDCl_3$, 300 MHz): δ 1.4 (t, J = 7.0 Hz, 3H), 2.6-2.8 (m, 4H), 2.2-2.4 (m, 2H), 4.25 (q, J = 7.0 Hz, 2H), 5.90 (br s, 1H); ^{13}C NMR ($CDCl_3$, 300 MHz): δ 14.5, 22.4, 24.6, 26.4, 58.6, 132.2, 160.8, 166.0, 106.0, and 116.8. HRMS calcd. for $C_{10}H_{13}NO_2S$: 211.0667. Found: 211.0634.

2-Amino-5, 6-dihydro-4H-cyclopenta[b]thiophene-3-carbonitrile *(entry 9):* mp 150-151 ^0C[30]. IR (KBr): υ 3446, 3324, 2932, 2910, 2836, 2209, 1615, 1523, 1392, 1121 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 2.3(q, 2H), 2.6-2.8(m, 4H), 5.8(br s, 2H). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 22.3, 23.8, 24.5, 106.8, 117, 132.1, 160.6. HRMS calcd. for $C_8H_8N_2S$: 164.0408. Found: 164.0382.

Ethyl 2-amino-4, 5, 6, 7-tetrahydrobenzo[b]thiophene-3-carboxylate *(entry 10):* mp 114-115 ^0C[22]. IR (KBr): υ 3423, 3298, 2938, 2854, 1697, 1684, 1587, 1456, 1420, 1258, 1160, 1030 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.4 (t, J = 7.0 Hz, 3H), 1.8 (m, 4H), 2.5 (m, 2H), 2.7 (m, 2H), 4.25 (q, J = 7.0Hz, 2H), 5.95 (br s, 1H). ^{13}C NMR

($CDCl_3$, 300 MHz): δ 14.2, 22.4, 22.6, 24.2, 26.4, 58.6, 132.2, 160.8, 166.0, 106.0, 116.8. HRMS calcd. for $C_{11}H_{15}NO_2S$: 225.0823. Found: 225.0804.

2-Amino-4, 5, 6, 7-tetrahydrobenzo [b] thiophene-3-carbonitrile *(entry 11)*: mp 146- 147 ^0C[22], IR (KBr): υ 3445, 3327, 2932, 2910, 2836, 2195, 1612, 1520, 1397, 1132, 501 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.8(m, 4H), 2.5(t, 4H), 4.7(br s, 2H), ^{13}C NMR ($CDCl_3$, 300 MHz): δ 21.4, 22.3, 23.7, 25.3, 89.0, 116.3, 123.2, 133.4, and 158.9. HRMS calcd. for $C_9H_{10}N_2S$: 178.0565. Found: 178.0532.

Ethyl 2-amino-5, 6, 7, 8-tetrahydro-4H-cyclohepta[b]thiophene-3-carobxylate *(entry 12)*: mp 88- 89 ^0C[6]. IR (KBr): υ 3446, 3287, 2965, 2857, 1707, 1694, 1589, 1486, 1465, 1258, 1160, 1030 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.4 (t, J = 7.0Hz, 3H), 1.42-1.45 (m, 2H), 2.2-2.4 (m, 4H), 2.6-2.8 (m, 4H), 4.25 (q, J = 7.0Hz, 2H), 5.9 (br s, 1H). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 17.7, 26.4, 27.6, 27.9, 28.2, 61.6, 87.2, 116.8, 124.0, 136.0, 159.8. HRMS calcd. for $C_{12}H_{17}NO_2S$: 239.0980. Found: 239.0965.

2-Amino-5, 6, 7, 8-tetrahydro-4H-cyclohepta[b]thiophene-3-carbonitrile *(entry 13):* mp 125-126 ^0C[6]. IR (KBr): υ 3443, 3330, 2935, 2891, 2836, 2195, 1619, 1523, 1335, 1095 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz): δ 1.6(m, 4H), 1.8(m, 2H), 2.5-2.7(m,4H), 4.5(br s, 2H). ^{13}C NMR ($CDCl_3$, 300 MHz): δ 25.8, 26.0, 26.7, 27.1, 28.0, 89.4, 116.3, 122.3, 133.6, 160.0. HRMS calcd. for $C_{10}H_{12}N_2S$: 192.0721. Found: 92.0702.

Scheme 1

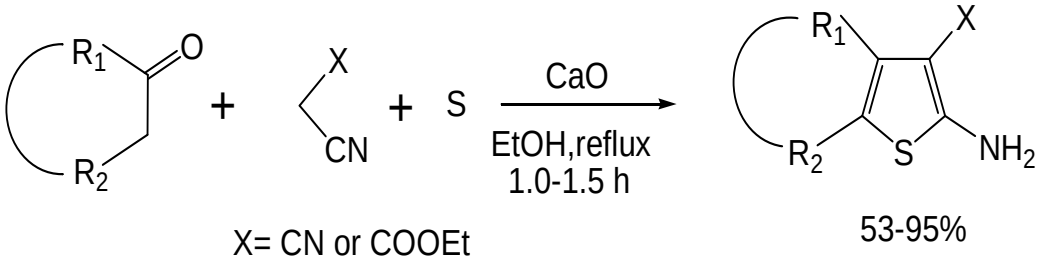

Table 1. CaO catalysed Gewald reaction in comparison with other catalysts reported in the literature

CATALYST	CONDITIONS	YIELD (%)
KF- immobilized on alumina	ethanol , reflux, 3.5-7 h and mw, 3.5-8min	48-91[30] and55-92
KG- 60-piperazine adsorbed on amorphous silica	ethanol, reflux 4h	37-89[40]
N-Methylpiperazine immobilized on polyacrylonitrile fiber	ethanol, 2-7 h	79-91[41]
Mg /La mixed oxides	mw, 4-8min and ethanol,reflux,1- 1.5h	80-91 and 85-92[42]
Ethylenediammonium diacetate	[Bmim][BF_4],50°C / [Bmim][PF_6], 50°C	59-89[22]
1,1,3,3tetramethylguanidine lactate- solvent cum catalyst	80°C,4-7h and mw,4-8min	57-90 and 60-92[43]
Ultrasonic aqueous conditions, diethylamine	5-8min	87-97[38]
Morpholine	rt, 14-25h	51-100[44]
Diethylamine	DMF,60°C,10h	43[45]
L-Proline	DMF,60°C,20h	74[45]
Triethyl phosphate	DMF,60°C,12h	Trace[45]
N-methylimidazole	DMF,60°C,12h	48[45]
NN-dimethylglycine	DMF,60°C,11h	57[45]
Isoquinoline	DMF,60°C,13h	49[45]
Imidazole	DMF,60°C,10h	75[45]
Mg-Al Hydrotalcite	ethanol, reflux, 8-14h	56-91[46]
Cs_2CO_3	Ethanol, reflux,3h	85-92[47]
CaO	Ethanol, reflux, 1-1.5h	53-95

RESULTS AND DISCUSSION

Gewald reaction was mediated first by excess amount of organic base like morpholine and later on several modifications using ionic liquid[20,22], solid support[36], soluble polymer support[29,37], microwave irradiation[27], ultrasonic aqueous conditions[38], electrochemical inducement[39] etc. have been deployed and are listed in the **Table 1**. Heterogeneous catalysts are considered as a potential alternative to homogeneous catalysts due to the advantages such as easy recovery, simple product isolation and reusability. In this respect many catalysts such as Na_2CO_3,

NaOH, $NaHCO_3$ and K_3PO_4 have been utilized to facilitate ylidene- sulphur intermediate formation and the ring closure in two step version[32]. In this row to find a cheapest catalyst falling in the alkaline and alkaline earth metal groups, we have opted Mg and Ca metal oxides and their efficiency towards Gewald reaction was analysed. It was identified that only CaO having the potential to catalyse one pot multicomponent reactions (**scheme 1**) of a ketone with an active nitrile or ethyl ester and elemental sulphur into substituted 2-aminothiophenes in good yields. List of the 2-aminothiophene derivatives synthesized with the time requirement and percentage of isolable yield are depicted in **Table 2**.

Table 2. Calcium oxide catalyzed synthesis of 2-aminothiophenes

Entry	Ketone		X	Yield %/ (Reaction time in h)
	R_1	R_2		
1	CH_3	CH_3	COOEt	60/1.0
2	CH_3	CH_3	CN	53/1.5
3	CH_3	COOEt	COOEt	61/1.0
4	CH_3	COOEt	CN	65/1.5
5	H	CH_3	COOEt	69 /1.0
6	Ph	H	COOEt	59/1.0
7	Ph	H	CN	58 /1.5
8	$(CH_2)_3$		COOEt	70 /1.0
9	$(CH_2)_3$		CN	61/1.5
10	$(CH_2)_4$		COOEt	95/1.0
11	$(CH_2)_4$		CN	90/1.0
12	$(CH_2)_5$		COOEt	80/1.5
13	$(CH_2)_5$		CN	77/1.0

In conclusion a simple protocol with an efficient heterogeneous catalyst CaO, under heating conditions in ethanol for the synthesis of 2-aminothiophenes *via* Gewald reaction have been reported. Advantages of this protocol can be listed as low cost material CaO as a catalyst with comparatively good yield, simple experimental and workup procedures and low catalyst loading.

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