International Journal of Research and Applications

ISSN (online): 2349-0020 ISSN (print): 2394-4544 http://www.ijraonline.com/

Research Article

Phosphonium Ionic liquid catalyzed Decarboxylation of an assortment of substituted Coumarin-4-aceticacid

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ARTICLE INFO

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DOI:
http://dx.doi.org/
10.17812/IJRA.7.25(1)2020

Manuscript:
Received: 19th Jan, 2020
Accepted: 13th Feb, 2020
Published: 10th Mar, 2020

Publisher:
Global Science Publishing Group, USA
http://www.globalsciencepg.org/

ABSTRACT

Ionic liquids are good catalysts in various green organic modifications. Coumarins are pharmaceutically significant and medicinally potent. Herewith decarboxylation of substituted coumarin-4-carboxylicacids 1a-h into 4-methyl substituted coumarin derivatives 2a-h using [PhosIL-Cl] catalyst with recyclables herewith reported. This method is environmentally benign, under mild conditions, simple workup protocols to afford excellent yields when we compared to conventional method. The products 2a-h were reported in Scheme-1 and Table-1&2 and confirmed by measuring melting points and 1H and 13C NMR spectra under deuterated chloroform as the NMR solvent. Mass of the synthesized coumarin derivatives are recorded as ESI-MS.

Keywords: Coumarin-4-carboxylic acid, phosphonium ionic liquid, decarboxylation.

1. INTRODUCTION

Coumarins are among the key classes of compounds which occur naturally, and interest in their chemistry continues unabated attributable for their functionality as biologically active agents [1].The core structural unit of several pharmaceutical agents. A number of coumarin derivatives have been isolated from natural sources and their pharmacological and biochemical properties depend upon the archetype of substitutions [2]. Substitutions can occur at any of the six available sites of their basic molecular moiety of coumarin, hence these compounds are tremendously variable in structure and activity. Nitrogen and oxygen containing heterocycles are perhaps by far the most explored heterocyclic compounds because of their occurrence in a myriad of natural

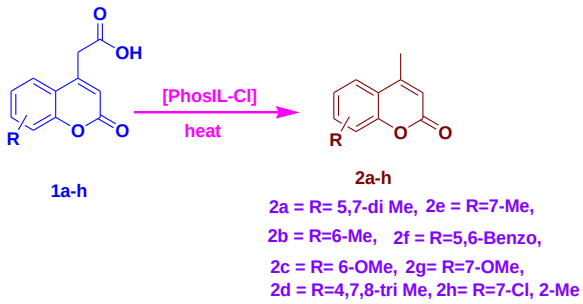
products and biologically active compounds. For this reason, synthetic chemists continue to be interested in the construction and functionalization of these heterocycles [3].

This structural diversity leads in coumarins exuding different biological properties that promote human health and help minimize disease risk. In the class of coumarins, 4-methylcoumarins have enjoyed a special status as they form the core of industrially important coumarins like 7-hydroxy-4- methylcoumarin [4]. Because of the utmost significance of this heterocyclic system and their diverse pharmacological properties, many strategies for the synthesis of substituted coumarins have been developed [5]. There are several other important groups of ring containing hetero atom with medicinal uses. coumarin ring carrying various constituents[6]. Classical routes to coumarins incorporate Pechmann, Knoevenagel, Perkin, Reformatsky and Wittig condensation reactions [7]. Most of these methods suffer from expensive catalyst, harsh reaction conditions, multi-step synthesis or low chemical yield. However, due to simple and relatively inexpensive starting materials, the Pechmann reaction was widely used for the synthesis of coumarins.

The synthesis of 4-methylcoumarin has been mainly reported via the Pechmann condensation using diverse catalyst like H2SO4-microwave [8], montmorillonite clay [9] and PPA [10]. In the present study we describe a protocol to synthesize 4-methyl-coumarin derivatives from substituted coumarin 4-acetic acid via decarboxylation. Herein coumarin 4-acetic acid is converted to 4-methyl-coumarins through decarboxylation in presence of DMF as solvent under reflux. The reactions were successfully by both conventional and microwave irradiation method. Subhash et .al. [11] reported the synthesis of 4-methyl coumarin, wherein ethyl acetoacetate was charged in toluene, later 2 equiv of zinc was added. Then substituted phenol was added followed by the addition of iodine.

Maria et.al [12] reported the synthesis of 4-methyl coumarin. Pedireddi et. al. [13] reported the synthesis of 4-methyl coumarins. when substituted cinnamate esters is reacted with substituted phenols in presence of FeCl3 in DCE solvent under stirring for 6hrs afforded 4-methyl coumarin derivatives. Vijayakumar et. al. [14] reported the synthesis of 4-methyl coumarins by using catalyst as PWA/mont-K10. Ionic liquids play a promising role for the quick synthesis of desired products with excellent yields [15].

Herewith describe the decarboxylation diverse coumarin-4- carboxylic acid into 4-methyl coumarin derivatives by ionic liquids to give promising yields.



Scheme-1 Decarboxylation of substituted coumarin-4-carboxylic acid to 4-Methyl coumarins by PIL's.

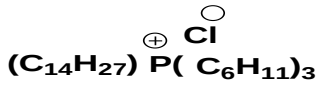


Fig. (1). Representation of tetradecyl-(trihexyl)-phosphonium chloride ionic liquid [PhosIL-Cl]

2. MATERIALS AND METHODS

To the 1 mmol of various coumarin 4-acetic acid is stirred with 2ml of [PhosIL-Cl] ionic liquid to afforded 4-methyl coumarin derivatives 2a-h under 75-80oC with promising yields (80-92%).The synthesis of the target compounds were described (shown Scheme-1, fig 1 and Table-1) with catalytic recyclables.(Table-2) The desired products are recovered by vacuum filtration. The products can be analyzed by melting point and characterized by IR, 1H, 13CNMR and ESI-MS spectra.

3. RESULTS AND DISCUSSION

Table1. Decarboxylation of various coumarin-4-carboxylicacids using Phosphonium Ionic Liquid[a]

Entry	Time (min)	Yield (%)[b]	M.P.(^{0}C)
2a	30	86	179-180
2b	25	90	120-121
2c	25	80	182-183
2d	35	85	147-148
2e	30	82	120-121
2f	25	92	181-182
2g	30	80	158-159
2h	25	85	145-146

a. Reaction Condition: Coumarin-4-carboxylic acid (1 mmol), in [PhosIL-Cl] 2ml was stirred at 75^{0}C temperatures.
b. Isolated and unoptimized yield.

Table 2. Recyclables of the Phosphonium Ionic Liquid

Entry	Yield (%) of [PhosIL-Cl]		
	Recycle1	Recycle2	Recycle3
2a	90	86	80
2b	88	85	78
2c	92	88	80

Spectral and Analytical data of synthesized various chalcones (2a-h)

4,5,7-trimethyl-2H-chromen-2-one(2a): light yellow solid; IR (KBr) (vmax/cm^{-1}): 1713 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$,δ ppm) δ2.36(s,3H, -CH_3), 2.58(s, 3H, - CH_3),2.66 (s, 3H, CH_3), 6.14 (s, 1H, Ar-H), 6.87 (s, 1H, Ar-H), 6.99 (s, 1H, Ar-H); ^{13}C NMR (100 MHz ,$CDCl_3$, δ ppm): 21.09, 24.19,25.03, 115.40, 116.10, 116.76, 129.50, 136.36, 141.78, 154.19, 155.15, 160.65;ESI-MS: 188 [M]+; Anal. calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43; Found: C, 76.51; H, 6.47%.

4,6-dimethyl-2H-chromen-2-one(2b): light yellow solid; IR (KBr) (vmax/cm^{-1}): 1717 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.05 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 6.20(s, 1H, Ar-H), 7.14-7.19 (m, 1H, Ar-H), 7.25 (d, 1H, J=1.6Hz, Ar-H), 7.30 (s, 1H, Ar-H); ^{13}C NMR (100 MHz, $CDCl_3$,) δ 21.73, 25.46, 113.68, 117.73, 121.25, 124.75, 125.51, 141.40, 151.75, 152.78,161.32; ESI-MS: 174 [M]+; Anal. calcd for $C_{11}H_{10}O_2$: C, 75.84; H, 5.79;Found: C, 75.81; H, 5.81%.

6-methoxy-4-methyl-2H-chromen-2-one(2c): Pale white solid; IR (KBr) (vmax/cm^{-1}): 1714 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.24 (s, 3H, C H_3), 3.72 (s,3H, CH_3), 6.27 (s, 1H, Ar-H), 7.22 (d, 1H, J=8.4Hz, Ar-H) 7.32-7.37 (m, 2H, Ar-H); ESI-MS: 190 [M]+; Anal. calcd for $C_{11}H_{10}O_3$:C, 69.46; H, 5.30; Found: C, 69.81; H, 5.28%.

4,7,8-trimethyl-2H-chromen-2-one(2d): light yellow solid; IR (KBr) (vmax/cm^{-1}): 1716 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.37 (s, 3H, CH_3), 2.39 (s, 3H, CH_3),2.41 (s, 3H, CH_3), 6.22 (s, 1H, Ar-H), 7.10(d, 1H, J=8Hz, Ar-H), 7.34 (d, 1H, J=8Hz, Ar-H), ESI-MS: 188 [M]+; Anal. calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.43; Found: C, 76.61; H, 6.39%.

4,7-dimethyl-2H-chromen-2-one(2e): light yellow solid; IR (KBr) (vmax/cm^{-1}): 1718 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.34 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 6.15 (s, 1H, Ar-H), 7.02-7.07 (m, 2H, Ar-H),7.40 (d, 1H, J=8Hz, Ar-H), ESI-MS: 174 [M]+; Anal. calcd for $C_{11}H_{10}O_2$: C, 75.84; H, 5.79; Found: C, 75.78; H, 5.74%.

1-methyl-3H-benzo[f]chromen-3-one(2f): light brown solid; IR (KBr) (vmax/cm^{-1}): 1710 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.93 (s, 3H, CH_3), 6.38 (s, 1H, Ar-H), 7.45-7.66 (m, 3H, Ar-H), 7.90-7.97 (m, 2H), 8.59 (d, 1H, J=8.4Hz, Ar-H), ESI-MS: 210 [M]+; Anal. calcd for $C_{14}H_{10}O_2$: C, 79.98; H, 4.79; Found: C, 80.11; H, 4.74%.

7-methoxy-4-methyl-2H-chromen-2-one(2g): yellow solid; IR (KBr) (vmax/cm^{-1}): 1712 (C=O); ^{1}H NMR (400 MHz,$CDCl_3$) δ 2.42 (s, 3H, CH_3), 3.86 (s,3H, OCH_3), 6.30 (s, 1H, Ar-H), 7.02 (d, 1H, J=3.2Hz, Ar-H) 7.09-7.12 (m, 2H, Ar-H), 7.27 (d, 1H, 9.2Hz, Ar-H); ESI-MS: 190 [M]+; Anal. calcd for $C_{11}H_{10}O_3$: C, 69.46; H, 5.30; Found: C, 69.53; H, 5.35%.

7-chloro-4-methyl-2H-chromen-2-one(2h): Pale yellow; IR (KBr) (vmax/cm^{-1}): 1713 (C=O); ^{1}H NMR (400 MHz, $CDCl_3$) δ 2.34 (s, 3H, CH_3), 6.15 (s, 1H, Ar- H), 7.02-7.06 (m, 2H, Ar-H), 7.40 (d,

1H, 8Hz, Ar- H); ESI-MS: 194 [M]+, 196[M+2]+; Anal. calcd for $C_{10}H_7ClO_2$: C, 61.72; H, 3.63; Found: C, 61.69; H, 3.57%.

4. CONCLUSION

We have noted green approaches to establishing decarboxylation of various coumarin-4-carboxylic acids to substitute high-purity coumarin with effective product yields. A simple and effective process using recyclable phosphonium ionic liquid has been reported herein. The selectivity of additional, attractive and useful reaction method. The products are medicinally shown in potent activity.

ACKNOWLEDGMENT

The authors are gratitude to the Chaitanya Deemed to be University of Chancellor and Vice Chancellor for their facilitation of laboratory and financial support.

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