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# Ionic liquid catalyzed Green and One-Pot Synthesis of Chalcone through Claisen - Schmidt Condensation

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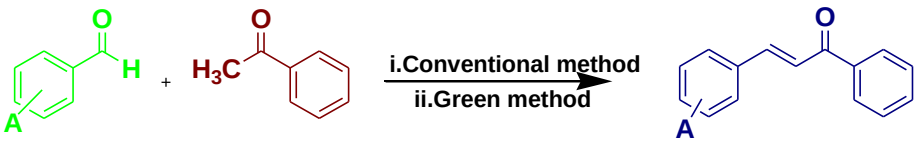
***Abstract:*** *Ionic liquids are good catalysts in various green organic transformations. Chalcones and their modifications are medicinally potent. Concrete and effective synthesis of chalcones from substituted benzaldehyde and acetophenone using [PhosIL-Cl] catalyst with recyclables herewith reported. This method is environmentally benign, under mild conditions, simple workup protocols to afford excellent yields when we compared to conventional method. The products **3a-i** were reported in Scheme 1 and Table-1&2 and confirmed by measuring melting points and $^{1}H$ and $^{13}C$ NMR spectra under deuterated chloroform as the NMR solvent.*

***Key Words:*** *Chalcone, phosphonium ionic liquid, Claisen-Schmidt condensation.*

## 1. INTRODUCTION:

One-pot synthesis allows compounds to be prepared without having to isolate and purify the intermediates, thereby reducing waste and increasing reaction efficiency. Reacting three or more components in a single operation can avoid the use of large amounts of solvents for each step and expensive purification techniques. Chalcones, also known as α,β-unsaturated ketones, are abundant in edible plants and are considered to be precursors of flavonoids and isoflavonoids. Chalcones bear a very good synthon so that a variety of novel heterocycles with good pharmaceutical profiles can be designed. Chalcone epoxides (α,β-epoxyketones) not only undergo the usual reactions of epoxides, but are also susceptible to several useful reactions owing to the presence of carbonyl groups. Chalcones and chalcone epoxides display an enormous number of biological activities, including anti-cancer, anti-microbial, anti-inflammatory, anti-oxidant, and anti-viral [1]. The reaction combines two or more molecules through carbon-carbon bond formation. Aldol condensation can proceed under acidic or basic conditions. Under basic conditions, the reaction of carbonyl compound enolates with an aldehyde or a ketone forms a β-hydroxy carbonyl compound. The β-hydroxy carbonyl compound is also called an aldol because it contains both an aldehyde group and the hydroxyl group of an alcohol. An aldol is a structural unit found in many naturally occurring molecules and pharmaceuticals [2-3].The mechanism for the base-catalyzed Claisen-Schmidt condensation between benzaldehyde and acetophenone is a base removes a proton from the acetophenone to form an enolate ion. Then, the enolate ion adds to the benzaldehyde followed by the protonation, resulting in the aldol product. The dehydration of the aldol under basic conditions results in the α,β-unsaturated ketone [4].




1a-i Substituted Aldehyde

2 Acetophenone

3a-i Chalcone

3a =A - H , 3b =A - 4-Cl , 3c =A -4-Me , 3d =A - 4-OMe , 3e =A - 4-NO2 , 3f =A -2-Cl , 3g =A -2-Me , 3h =A -3-Cl , 3i =A =-3-Me

**Scheme 1 One pot synthesis of Chalcones by Claisen-Schmidt condensation**

**i = NaOH / MeOH**

**ii = Phosphonium - Ionic liquid**

**Phosphonium Ionic Liquid catalyzed Green Synthesis of Chalcones**

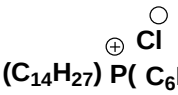



**Figure 1.** Representation of tetradecyl-(trihexyl)-phosphonium chloride ionic liquid **[PhosIL-Cl]**

## 2. MATERIALS AND METHODS:

### 2.1. Conventional method:

5 mmol of substituted benzaldehyde, acetophenone (5 mmol), and methanol (10.0 mL) into a 50-mL round-bottomed flask along with a magnetic stir bar. To the substituted benzaldehyde is a solid, stirred the mixture until it became homogeneity. The solution should be cooled to room temperature before proceeding to the next step. While stirring at room temperature, add 1.0 mL of 30% aqueous NaOH solution to the reaction mixture over a period of 3-5 minutes. The first step, Claisen - Schmidt condensation is carried out at room temperature under basic conditions using aqueous NaOH as the base catalystThen stirred the reaction for another 90-120 minutes at room temperature to give solid chalcone product. Gently heat the reaction mixture in a hot water bath for few minutes to dissolve the chalcone. Collect products **(3a-i)** by vacuum filtration. Wash the product in the funnel with cold distilled water. Let the product dry at the vacuum and transfer it to a pre-weighed vial and weigh the products. Reaction totally maintains 1-2 hrs conventionally poor yields (62-80%) are observed based on the type of the aldehyde.

### 2.2. Ionic liquid green method:

To attend green protocols with high yields of products the Claisen – Schmidt /Crossed Aldol condensation reaction is optimized standard molar ratio of a series of substituted benzaldehydes (1 mmol) (1a-i) and acetophenone (1 mmol) with phosphonium chloride as ionic liquid catalyzed (2ml) one – pot synthesis of series of chalcones by means of nearly 70-75$^0$C (3a-i) with yields (80-92%) were described (**shown in Scheme 1,fig 1 and Table-1)** with catalytic recyclables.**(Table-2)** The chalcone is recovered by vacuum filtration. The product can be analyzed by melting point and characterized by $^1$H and $^{13}$CNMR spectra.

## 3. RESULTS AND DISCUSSION:

**Table 1. Synthesis of Chalcone using Phosphonium Ionic Liquid**

| Entry | Time (h) | Yield (%)[b] | M.P.($^0$C) Found | M.P.($^0$C)[Lit][c] |
|---|---|---|---|---|
| 3a | 3 | 90 | 56-57 | 54-56[6] |
| 3b | 2.5 | 90 | 174-175 | 173-174[6] |
| 3c | 2.5 | 80 | 179-181 | 183-184[5] |
| 3d | 3.5 | 85 | 110-112 | 111-113[7] |
| 3e | 4 | 80 | 195-196 | 192-194[7] |
| 3f | 2.5 | 92 | 96-98 | 100-101[6] |
| 3g | 3 | 80 | 132-134 | 130-131[6] |
| 3h | 3 | 85 | 97-99 | 101-102[7] |
| 3i | 2.5 | 80 | 177-179 | 175-176[6] |

[a]Reaction Condition: Acetophenone (1 mmol), substituted benzaldehydes (1 mmol) in [PhosIL-Cl] 2ml was stirred at 75$^0$C temperatures.
[b]Isolated and unoptimized yield.
[c]Literature melting point.

**Table 2. Recyclables of the Phosphonium Ionic Liquid**

| Entry | Yield (%) of [PhosIL-Cl] | | |
|---|---|---|---|
| | Recycle1 | Recycle2 | Recycle3 |
| 3a | 90 | 86 | 80 |
| 3b | 88 | 85 | 78 |
| 3c | 92 | 88 | 80 |

## 4. CONCLUSION:

We have described green approaches to develop the chalcones with high purity and effective yields of products. Herewith a simple and effective process has been described reported using recyclables phosphonium ionic liquid. The selectivity of method of reaction additional attractive and useful.

**REFERENCES:**

1. Ritter, M.; Martins, R. M.; Dias, D.; Pereira, C. M. P. *Lett. Org. Chem.* **2014**, *11* (7), 498–508.
2. Ho, T. L.; Liu, S. H. *Synth. Commun.* **1983**, *13*, 685–690.
3. Vashchenko, V.; Kutulya, L.; Krivoshey, A. *Synthesis* **2007**, *14*, 2125–2134.
4. Yamaguchi, K.; Mori, K.; Mizugaki, T.; Ebitani, K.; Kaneda, K. *J. Org. Chem.* **2000**, *65*, 6897–6903.
5. 5.Denmark, S,E.; Wong, K,T.; Su,X,J. Am.Chem.Soc.,**1999**, 121,4982.
6. 6.Miquel,J.F.Bull.Soc. Chim, Fr., **1961**,1369.
7. 7.Shen, J.;Wang,H.; Sun, Y.; J.Mol.Catal.A: Chem,**2008**,280,24-28.

**$^{1}$H and $^{13}$C NMR Spectral data of synthesized various chalcones (3a-i)**

**3a:** $^{1}$H NMR (400 MHz, CDCl3) δ 8.01 (d, J = 8.0 Hz, 2H), 7.61(t, J = 6.4 Hz, 1H), 7.49 (t, J = 7.6 Hz, 2H), 7.38 (m, 5H), 4.27 (d, J = 2 Hz, 1H),4.08 (d, J = 2 Hz, 1H);
$^{13}$C NMR (100 MHz, CDCl3) δ 192.5, 135.4, 134.1, 129.2, 129.0, 128.9, 128.5, 125.7, 61.1, 59.5.

**3b:** $^{1}$H NMR (400 MHz, CDCl3) δ 7.98 (d, J = 7.6 Hz, 2H), 7.62 (t, J = 7.2 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.0 Hz, 2H), 4.24 (d, J = 2 Hz, 1H), 4.05 (d, J = 2 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl3) δ 192.8, 135.5, 135.0, 134.2, 134.1, 129.1, 129.0, 128.5, 127.2, 61.0, 58.8.

**3c:** $^{1}$H NMR (400 MHz, CDCl3) δ 8.00 (d, J = 8.0 Hz, 2H), 7.61 (t, J = 6.8 Hz, 1H), 7.48 (t, J = 8.0 Hz, 2H), 7.26 (d, J = 8.0 Hz, 2H), 7.20 (d, J = 8.0 Hz, 2H), 4.29 (d, J = 2 Hz, 1H), 4.05 (d, J = 2 Hz, 1H), 2.38 (s, 3H); $^{13}$C NMR (100 MHz, CDCl3) δ 193.3, 139.2, 135.6, 134.1, 132.6, 129.6, 128.9, 128.4, 125.9, 61.2, 59.6, 21.4.

**3d:** $^{1}$H NMR (400 MHz, CDCl3) δ 7.99 (d, J = 7.6 Hz, 2H), 7.60 (t, J = 7.6 Hz, 1H), 7.47 (t, J = 7.6 Hz, 2H), 7.28 (d, J = 8.4 Hz, 2H), 6.91 (d, J = 8.4 Hz, 2H), 4.29 (d, J = 2 Hz, 1H), 4.01 (d, J = 2 Hz, 1H), 3.83 (s, 3H); $^{13}$C NMR (100 MHz, CDCl3) δ 193.3, 160.4, 135.6, 134.0, 130.3, 128.9, 128.5, 127.3, 114.3, 61.2, 59.5, 55.5.

**3e:** $^{1}$H NMR (400 MHz, CDCl3) δ 7.98 (d, J = 7.6 Hz, 2H), 7.61 (t, J = 7.2 Hz, 1H), 7.48 (t, J = 7.6 Hz, 2H), 7.36 (d, J = 8.0 Hz, 2H), 7.29 (d, J = 8.4 Hz, 2H), 4.24 (d, J = 2 Hz, 1H), 4.04 (d, J = 2 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl3) δ 192.2, 148.4, 142.9, 135.3, 134.4,129.1, 128.5, 126.7, 124.2, 60.9, 58.1.

**3f:** $^{1}$H NMR (400 MHz, CDCl3) δ8.09 (d, J = 7.3 Hz, 2H), 7.15-7.61 (m, 9H), 4.34 (d, J = 2 Hz, 1H), 4.11 (d, J= 2 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl3) δ 192.8, 134.9, 134.1, 133.9, 133.7, 129.8, 129.5, 128.9, 128.5, 126.2, 124.8, 60.1, 57.2.

**3g:** $^{1}$H NMR (400 MHz,CDCl3) δ 8.00 (d, J = 7.4 Hz, 2H), 7.74 (t, J = 7.2 Hz, 1H), 7.58 (t, J = 7.3 Hz, 2H),7.25-7.15 (m, 4H), 4.21 (d, J = 2 Hz, 1H), 4.02 (d, J = 2 Hz, 1H), 2.35 (s, 3H); $^{13}$C NMR (100 MHz, CDCl3) δ 192.2, 139.5, 135.9, 135.7, 134.6, 129.9, 129.1, 128.9,128.2, 126.8, 123.5, 61.5, 59.2, 21.4.

**3h:** $^{1}$H NMR (400 MHz, CDCl3) δ 7.97 (d, J = 7.1 Hz, 2H), 7.60 (t, J = 7.0 Hz, 1H), 7.47 (t, J = 7.4 Hz, 2H), 7.23-7.31 (m, 4H), 4.22 (d, J = 2 Hz, 1H), 4.02 (d, J = 2 Hz, 1H); $^{13}$C NMR (100 MHz, CDCl3) δ 192.6, 137.9, 134.8, 134.6, 134.2, 130.5, 129.3, 129.0, 128.5, 125.8, 60.9, 58.6.

**3i:** $^{1}$H NMR (400 MHz, CDCl3) δ 7.99 (d, J = 7.4 Hz, 2H), 7.77 (t, J = 7.2Hz, 1H), 7.60 (t, J = 7.3 Hz, 2H), 7.27-7.16 (m, 4H), 4.28 (d, J = 2 Hz, 1H), 4.02(d, J = 2 Hz, 1H), 2.36 (s, 3H); $^{13}$C NMR (100 MHz, CDCl3) δ 193.2, 139.1, 135.9,135.8, 134.1, 130.0, 129.0, 128.8, 128.4, 126.4, 123.1, 61.1, 59.6, 21.5.