One-Pot Synthesis of Substituted Coumarins Catalyzed by Silica Gel Supported Sulfuric Acid Under Solvent-Free Conditions

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Abstract: A remarkable acceleration in the synthesis of substituted coumarins *via* Pechmann reaction catalyzed by silica gel supported sulfuric acid (H_2SO_4/silica gel) at 120 °C in high yields under solvent-free reaction condition with short reaction times is described. This methodology offers momentous improvements over various options for the synthesis of coumarins with regard to yield of products, simplicity in operation and green aspects by avoiding toxic catalysts and solvents.

Keywords: Pechmann reaction, phenols, reaction mechanism, Coumarin derivatives, H_2SO_4/silica gel, solvent-free.

INTRODUCTION

Coumarin and its derivatives form an important class of benzopyrones found in Nature. They are structural subunits in many complex natural products and have shown numerous biological activities, such as antitumor [1], anti-HIV (NNRTI) [2], antioxidation [3], tumor necrosis factor-a (TNF-a) inhibition [4], antimicrobial activity [5], serine protease inhibition [6] and anticancer activity [7]. The widespread biological activities of coumarin derivatives have aroused great interest in the area of synthetic chemistry and pharmacology.

Coumarins could be synthesized by various methods, such as Pechmann [8], Perkin [9], Knoevenagel [10], Reformatsky [11], Witting [12], Claisen [13] and flash vacuum pyrolysis reaction [14]. However, the Pechmann reaction is one of the simplest and direct methods for the synthesis of coumarins since it proceeds from very simple starting materials, namely, phenols and β-keto esters or α,β-unsaturated carboxylic acids utilizing various catalysts, such as sulfuric acid [8], trifluoroacetic acid [15], phosphorus pentoxide [16], $ZrCl_4$ [17], $TiCl_4$ [18] and ionic liquids [19]. However, most of these procedures require long duration (24 h [20], 20 h [21]), high temperature (150°C) [21] and also microwave irradiation [22]. Also there have been some attempts to find alternative, environmentally benign synthesis routes. On those lines, Nafion-H [23], zeolite H-BEA, modified zirconia [24], Amberlyst 15 [25], montmorillonite clay [26] and other solid acids have been employed for this purpose in the Pechmann condensation.

It has been realized in recent years that sulfuric acid adsorbed on silica gel could be used as a multipurpose acid catalyst [27-31]. In continuation of our work on the development of useful synthetic methodologies by employing solid acid catalysts [32-35], we observed that H_2SO_4/silica gel is an efficient catalyst for the synthesis of coumarins *via* Pechmann condensation. In this communication, we are disclosing our findings on H_2SO_4/silica gel catalyzed Pechmann condensation of a series of phenols and β-keto esters to coumarins under solvent free conditions.

EXPERIMENTAL

Preparation of H_2SO_4/Silica Gel

A solution of 1 mL conc. H_2SO_4 in 15 mL acetone is added to a dispersion of 50 g silica gel (Merck 230-400 mesh, 60 Å) in 100 mL acetone and stirred at room temperature for 1 h. The solvent was removed under reduced pressure. A yellow–brown powder was obtained, which can be stored in a desiccator for long periods of time without any appreciable loss of activity.

Typical Reaction Procedure

In a typical experiment, H_2SO_4/silica gel (100mg) was dispersed in a mixture of phenols (2 mmol) and β- keto esters (2.4mmol) in a 25-mL batch reactor equipped with a distillation condenser. The content was stirred vigorously at 120 °C. The progress of the reaction was monitored by TLC. At the end of the reaction, the reaction mixture was treated with CH_3OH and filtered to recover the catalyst. It was reused for several times without loss of activity. The filtrate was evaporated under reduced pressure to obtain the crude product. Thus obtained product was washed with water, filtered and dried at 100 °C. The product was purified by dissolving in 20 mL 1 M NaOH and then regenerated with 10 mL 2 M H_2SO_4 solution. NMR, IR and mass spectroscopic techniques were used to analyze the products and compared with the authentic samples.

RESULTS AND DISCUSSION

The reaction of phenols and β-keto esters in the presence of catalytic amount of H_2SO_4/silica gel afforded the corresponding coumarin derivatives (Scheme **1**). The reactions were clean and affording exclusively coumarins in high yields in a relatively short times. It is an established fact in the literature that Pechmann reaction proceeds through trans-

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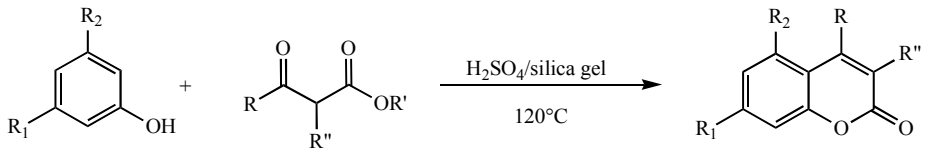
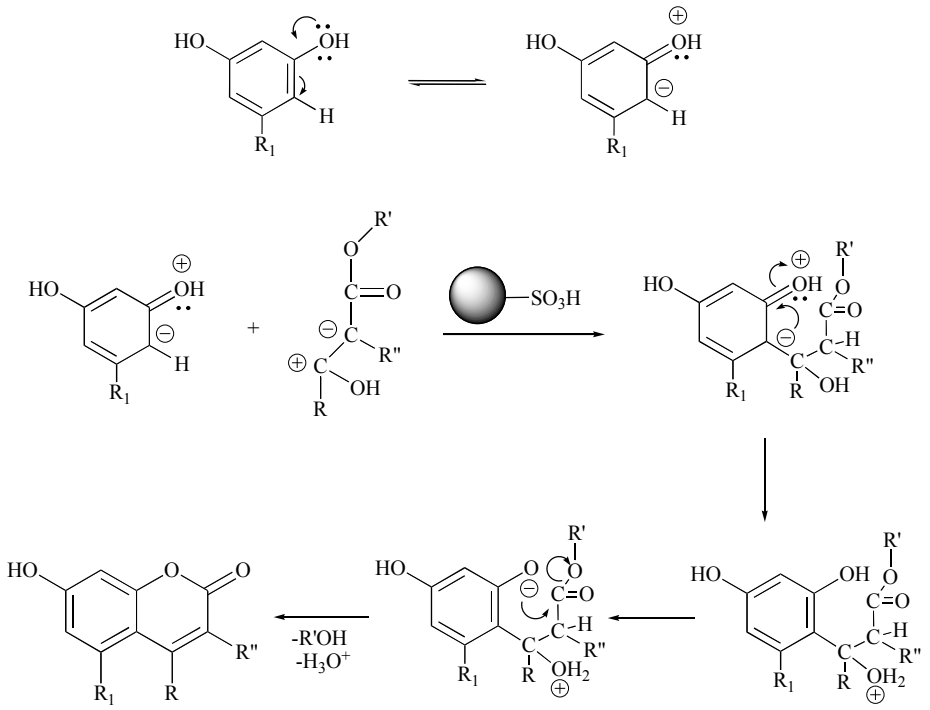


Scheme 1. Pechmann condensation reaction of phenols with β-keto esters to substituted coumarins.



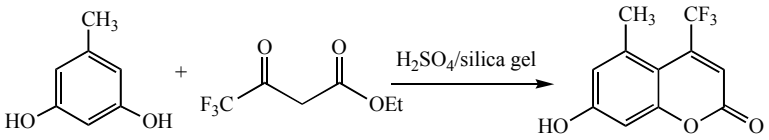
Scheme 2. Plausible mechanism for the pechmann condensation of phenols and β–keto esters by H_2SO_4/silica gel.

esterification and intramolecular hydroxyalkylation, followed by dehydration [18, 24]. These three steps are all typical acid-catalyzed reactions. Therefore, the outcome of the Pechmann reaction depends very much on the Brønsted acidity of the catalysts [16]. We have given a plausible mechanism for the Pechmann condensation of phenols and β–keto esters by H_2SO_4/silica gel in Scheme **2**.

To optimize the reaction conditions such as temperature, solvent and amount of catalyst (H_2SO_4/silica gel), we selected the highest time taking reaction that is the reaction between orcinol and ethyltrifluoroacetoacetate as a model reaction. The results are collected in Table **1**. Lower catalytic activity is observed for various organic solvents such as toluene, MeOH, CH_2Cl_2 under reflux condition and 50mg H_2SO_4/silica gel catalyst, which probably due to interference of solvent with active site of the catalyst (Table **1**, entry **6-8**). On the contrary, reaction worked well under solvent-free condition (Table **1**, Entry **1-5**). On increasing reaction temperature from 60 to 120°C, product yield and time were found to be more favorable at 120°C (Table **1**, entry **1-4**). Again increasing the catalyst amount the reaction moved faster (Table **1**, entry **1, 5**). Interestingly, no reaction took place in the absence of catalyst for 2 days of reaction time.

The sulfated silica gel solid acid catalyst was evaluated for liquid phase synthesis of coumarins in solvent free conditions and summarized in Table **2**. Different types of β-keto esters were used namely, ethyl acetoacetate (Table **2**, entries **1-6** and 20), methyl acetoacetate (Table **2**, entries **7-10**), methyl cyclohexanone-2-corboxylate (Table **2**, entries **11-13**), ethyl trifluoro acetoacetate (Table **2**, entries **14**, **15**) and α-methyl ethyl acetoacetate (Table **2**, entries **16-19**). Reactions of phloroglucinol with ethyl acetoacetate, methyl acetoacetate and α-methyl ethyl acetoacetate (Table **2**, entries **4**, **10**, **19**) took place very fast within 3, 3 and 18 min, respectively. This is mainly due to the presence of three hydroxyl groups that cooperate in activating the aromatic ring for hydroxyalkylation. Similarly, reactions of pyrogallol with ethyl acetoacetate, methyl acetoacetate and α-methyl ethyl acetoacetate (Table **2**, entries **3**, **9**, **18**) took place in 6, 7 and 26 min, respectively, which are slower than that of the reactions of phloroglucinol presumably due to steric hindrance of hydroxyl groups. Again reaction of pyrogallol with methyl cyclohexanone-2-corboxylate was completed within 3 min. The reactions of resorcinol with ethyl acetoacetate, methyl acetoacetate, α-methyl ethyl acetoacetate, methyl cyclohexanone-2-corboxylate and ethyl trifluoro acetoacetate (Table **2**, entries **2**, **8**, **17**, **12** and **15**) occurred within 5, 7, 10, 5 and 65 min, respectively. This could be due to the presence of only two hydroxyl groups, which are meta to each other. However, in the case of orcinol, the reactions (Table **2**, entries **1**, **7**, **16**, **11** and **14**) were somewhat slower than that of the reactions of resorcinol that could be due to the steric hindrance of methyl group ortho to the position of hydroxyalkylation. Table **1** compares the activities of various β-keto esters with various phenols, Reactivity order for β–keto esters is found to be ethyl acetoacetate ≈methyl acetoace-

Table 1. Effect of Temperature, Solvent, Amount of Catalyst (H_2SO_4/Silica Gel) on the Synthesis of Coumarins



S. No.	Catalyst Amount (mg)	Oil Bath Temperature (^oC)	Solvent	Time (min[c]), (hrs[d]), (Days[e])	Yield (%)[b]
1.	50	120	-	110[e]	73
2.	50	100	-	5.5[d]	71
3.	50	80	-	11[d]	78
4.	50	60	-	16[d]	85
5.	100	120	-	70[e]	87
6.	50	120	Toluene	20[d]	75
7.	50	120	CH_3OH	24[d]	60
8.	50	120	CH_2Cl_2	24[d]	62
9.	-	120	-	02[e]	NR

[b]Isolated yields.
NR - No Reaction.

tate > methyl cyclohexanone-2-corboxylate > α–methyl ethyl acetoacetate > ethyl trifluoro acetoacetate. The o-hydroxy phenol and m-methoxy phenol (Table **2**, entry **5**, **6** Table **1**) are found to be inactive and gallic acid (Table **2**, entry **20**) is also less active may be due to steric hindrance by acid (COOH) group to the position of ortho to hydroxyalkylation. Interestingly, with H_2SO_4/silica gel catalyst a 95% yield was obtained in just 3 min. All products were characterized by comparison of their ^{1}H NMR, mass and IR spectra with those of authentic samples, and then we conclude that selectively one product (A) is forming during the reaction (Scheme **3**). The spectral data for some selected representative compounds are given below:

7-Hydroxy-4, 5-dimethyl-chromen-2-one (Entry 1, Table 2)

^{1}HNMR ($CDCl_3$ + DMSO, 200 MHz): δ 9.85 (bs, 1H, OH), 6.51 (s, 2H, aromatic protons), 5.88 (s, 1H, allylic CH), 2.97 (attributable to residual water in product), 2.58 (s, 3H, Me), 2.30 (s, 3H, Me) ppm. IR (Neat): ν 3251, 1627, 1443, 1379, 1133, 1080, 908, 681, 535 cm^{-1}. EIMS: *m/z* –190 [M^+].

7-Hydroxy-4-methyl-chromen-2-one (Entry 2, Table 2)

^{1}HNMR ($CDCl_3$ + DMSO, 200 MHz): δ 7.36 - 7.41 (q, J = 6.00, J = 1.50, 1H, aromatic proton), 6.71 – 6.76 (m, 2H, aromatic protons), 5.99 (d, J = 1.50, 1H, allylic CH), 2.37 (d, J = 1.50, 3H, Me) ppm. IR (Neat): ν 3155, 1678, 1400, 1227, 1057, 974, 844, 748 cm^{-1}. EIMS: *m/z* –176 [M^+].

7,8-Dihydroxy-4-methyl-chromen-2-one (Entry 3, Table 2)

^{1}HNMR ($CDCl_3$ + DMSO, 200 MHz): δ 6.96 (d, J = 8.81 Hz, 1H, aromatic proton), 6.78(d, J = 8.81 Hz, 1H, aromatic proton), 5.99 (s, 1H, olefinic CH), 2.38 (s, 3H, Me) ppm, OH is unobserved. IR (Neat): ν 3424, 1842, 1660, 1593, 1450, 1332, 1276, 1072, 910, 804, 504 cm^{-1}. EIMS: *m/z* – 192 [M^+].

5,7-Dihydroxy-4-methyl-chromen-2-one (Entry 4, Table 2)

^{1}NMR ($CDCl_3$ + DMSO, 200 MHz): δ 6.24 (d, J = 2.19 Hz, 1H, aromatic proton), 6.19 (d, J = 2.19 Hz, 1H, aromatic proton), 5.70 (s, 1H, olifinic proton), 2.11 (s, 3H, Me) ppm, OH is unobserved. IR (Neat): ν 3447, 1865, 1660, 1618, 1530, 1456, 1160, 815, 750, 570 cm^{-1}. EIMS: *m/z* – 192 [M^+].

7-Hydroxy-4, 5-dimethyl-chromen-2-one (Entry 7, Table 2)

^{1}HNMR ($CDCl_3$ + DMSO, 200 MHz): δ 10.02 (bs, 1H, OH) 6.52 (s, 2H, aromatic protons), 5.89 (s, 1H, allylic proton), 3.24 (attributable to residual water in product) 2.58 (s, 3H, Me), 2.31 (s, 3H, Me) ppm. IR (Neat): ν 3251, 1627, 1443, 1379, 1133, 1080, 908, 681, 535 cm^{-1}. EIMS: *m/z* – 190 [M^+].

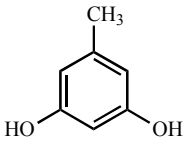
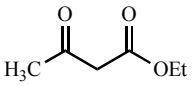
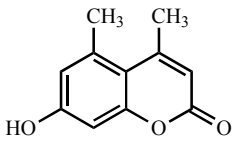
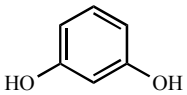
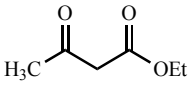
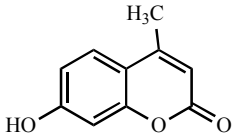
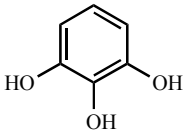
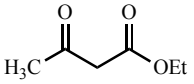
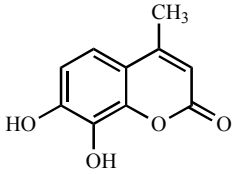
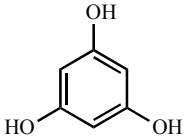
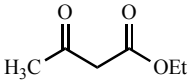
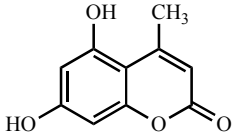
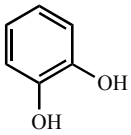
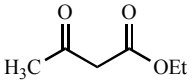
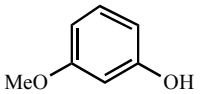
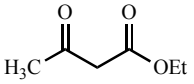
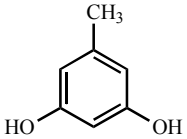
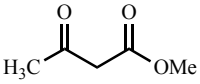
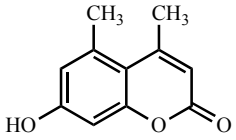
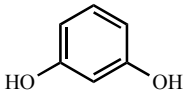
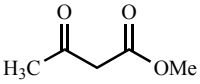
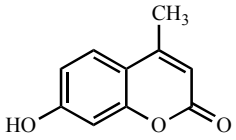
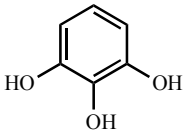
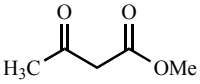
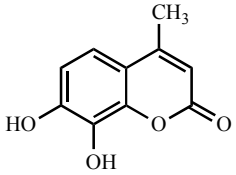
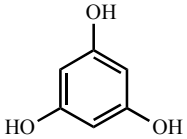
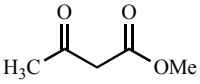
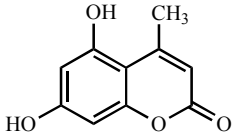
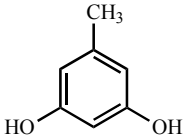
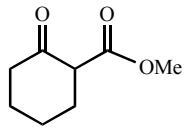
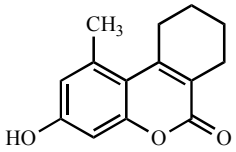
7-Hydroxy-4-methyl-chromen-2-one (Entry 8, Table 2)

^{1}HNMR ($CDCl_3$ + DMSO, 200 MHz): δ 9.90 (bs, 1H, OH) 7.37 - 7.41 (q, J = 1.46, J = 0.73, 1H), 6.70 – 6.76 (m, 2H), 5.98 (d, J = 1.46, 1H), 3.08 (attributable to residual water in product) 2.37 (d, J = 1.46, 3H, Me) ppm. IR (Neat): 3160, 1658, 1380, 1242, 1024, 996, 856, 787, 666 cm^{-1}. EIMS: *m/z* – 176 [M^+].

7,8-Dihydroxy-4-methyl-chromen-2-one (Entry 9, Table 2)

^{1}HNMR ($CDCl_3$ + DMSO, 200 MHz): δ 6.97 (d, *J* = 8.81 Hz, 1H, aromatic proton), 6.77 (d, *J* = 8.81 Hz, 1H, aromatic proton), 5.99 (s, 1H, olefinic proton), 3.59 (attributable to residual water in product), 2.37 (s, 3H, Me) ppm, OH is unobserved. IR (Neat): ν 3420, 1839, 1597, 1447, 1325, 1270, 1061, 901, 784, 515 cm^{-1}. EIMS: *m/z* – 192 [M^+].

Table 2. H_2SO_4/Silica Gel Catalyzed Pechmann Condensation in Solvent Free Conditions

Entry	Phenol	β-Keto Ester	Product[a]	Time (min)	Yield %
1				10	92
2				05	80
3				06	86
4				03	95
5			----	60	NR
6			----	180	NR
7				12	87
8				07	86
9				07	89
10				03	92
11				25	89

(Table 2) contd…..

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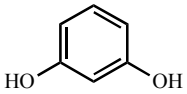
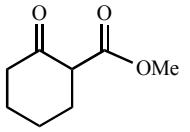
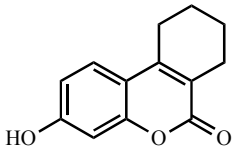
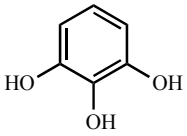
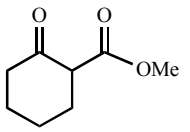
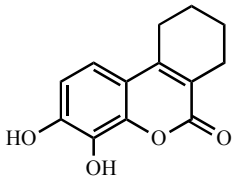
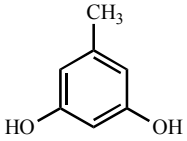
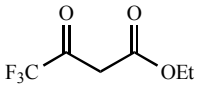
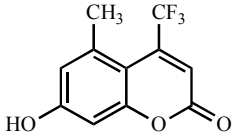
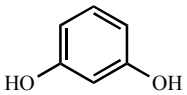
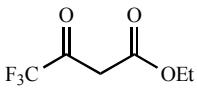
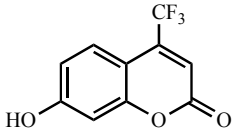
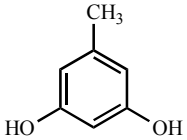
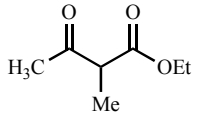
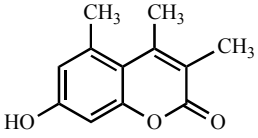
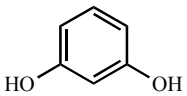
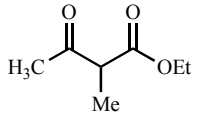
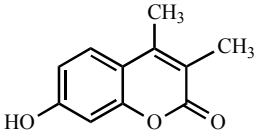
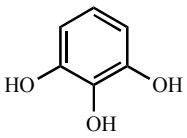
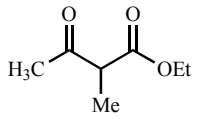
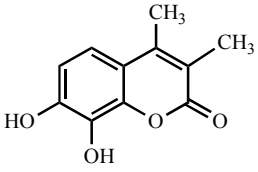
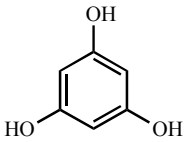
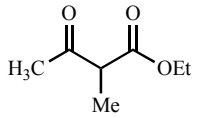
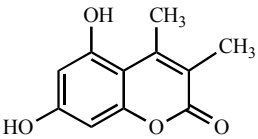
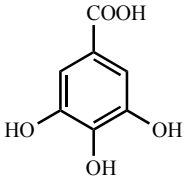
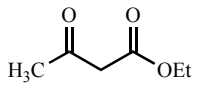
12				05	91
13				03	91
14				110	73
15				65	81
16				40	75
17				10	82
18				26	78
19				18	85
20			----	90	NR

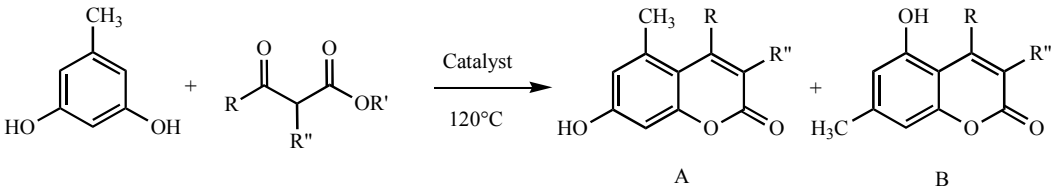
[a] The structures of the products were determined from their spectroscopic (1H NMR and MS) data.
[b] Isolated yield.

5,7-Dihydroxy-4-methyl-chromen-2-one (Entry 10, Table 2)

^{1}NMR ($CDCl_3$ + DMSO, 200 MHz): δ 6.24 (d, J = 2.19 Hz, 1H, aromatic proton), 6.18 (d, *J* = 2.19 Hz, 1H, aromatic proton), 5.71 (s, 1H, olifinic proton), 2.54 (s, 3H, Me) ppm, OH is unobserved. IR (Neat): ν 3473, 1876, 1660, 1618, 1533, 1416, 1156, 815, 723, 646, 582 cm^{-1}. EIMS: *m/z* –192 [M$^+$].

3-Hydroxy-1-methyl-7,8,9,10-tetrahydro-benzo[c]chromen-6-one (Entry 11, Table 2)

^{1}NMR ($CDCl_3$ + DMSO, 200 MHz): δ 9.84 (s, 1H, OH), 6.49 (s, 2H, aromatic protons), 2.98- 3.13 (m, 2H, cyclohexyl), 2.36- 2.51 (m, 2H, cyclohexyl), 2.29 (s, 3H, Me) 1.62- 1.83 (m, 4H, cyclohexyl) ppm. IR (KBr): ν 3222,



Scheme 3. Selectivity of the product for the pechmann condensation.

2933, 2861, 1667, 1600, 1267, 1091, 826, 737, 527 cm^{-1}. EIMS: *m/z* – 230 [M^+].

3-Hydroxy-7,8,9,10-tetrahydro-benzo[c]chromen-6-one (Entry 12, Table 2)

^{1}NMR ($CDCl_3$ + DMSO, 200 MHz): δ 9.79 (s, 1H, OH), 7.30- 7.40 (m, 1H, aromatic proton), 6.64- 6.73(m, 1H, aromatic protons), 3.02 (due to water remaining in product), 2.67- 2.81 (m, 2H, cyclohexyl), 2.38- 2.55 (m, 2H, cyclohexyl), 1.69- 1.84 (m, 4H, cyclohexyl) ppm. IR (KBr): ν 3214, 2937, 1678, 1613, 1564, 1151, 1102, 1040, 852, 754, 497 cm^{-1}. EIMS: *m/z* – 216 [M^+].

3,4-Dihydroxy-7, 8, 9, 10-tetrahydro-benzo[c]chromen-6-one (Entry 13, Table 2)

^{1}NMR ($CDCl_3$ + DMSO, 200 MHz): δ 9.09 (bs, 2H, OH), 6.90 (d, *J* = 8.32 Hz, 1H, aromatic proton), 6.73(d, *J* = 8.32 Hz, 1H, aromatic proton), 3.02 (due to water remaining in product), 2.66- 2.84 (m, 2H, cyclohexyl), 2.40- 2.60 (m, 2H, cyclohexyl), 1.63- 1.98 (m, 4H, cyclohexyl) ppm. IR (KBr): ν 3464, 2946, 1674, 1616, 1580, 1508, 1382, 1318, 1095, 975, 807, 762 cm^{-1}. EIMS: m/z – 232 [M^+].

7-Hydroxy-5-methyl-4-trifluoromethyl-chromen-2-one (Entry 14, Table 2)

^{1}NMR ($CDCl_3$ + DMSO, 200 MHz): 10.52 (s, 1H, OH proton), 6.54-6.66 (m, 3H, aromatic protons), 3.17 (due to water remaining in product), 2.34 (s, 3H, CH_3) ppm. IR (KBr): ν 3420, 3162, 2955, 1725, 1618, 1512, 1309, 1213, 1161, 926, 863, 695, 656, 539 cm^{-1}. EIMS: *m/z* – 244 [M^+].

7-Hydroxy-4-trifluoromethyl-chromen-2-one (Entry 15, Table 2)

^{1}NMR ($CDCl_3$ + DMSO, 200 MHz): one broad singlet observed at δ 10.58, 7.46-7.52 (dd, *J* = 6.25 Hz, *J* = 2.34 Hz, 1H, aromatic proton), 6.75-6.90 (m, 2H, aromatic protons), 6.51 (s, 1H, allylic proton) 3.30 (due to water remaining in product) ppm. IR (KBr): ν 3399, 3104, 2921, 1714, 1609, 1405, 1286, 1193, 1131, 891, 857, 655, 624, 498 cm^{-1}. EIMS: *m/z* – 230 [M^+].

7-Hydroxy-3,4,5-trimethyl-chromen-2-one (Entry 16, Table 2)

^{1}NMR ($CDCl_3$ + DMSO, 200 MHz): δ 9.78 (bs, 1H, OH), 6.51 (s, 2H, aromatic protons), 3.10 (due to water) 2.60 (s, 3H, Me), 2.29 (s, 3H, Me), 2.09 (s, 3H, Me) ppm. IR (KBr): ν 3210, 1673, 1618, 1281, 1117, 1061, 827, 745, 538 cm^{-1}. EIMS: *m/z* – 204 [M^+].

7-Hydroxy-3,4,-dimethyl-chromen-2-one (Entry 17, Table 2)

^{1}NMR ($CDCl_3$ + DMSO, 200 MHz): δ 7.39 (d, *J* = 8.08 Hz, 1H, aromatic proton), 6.64- 6.78 (m, 2H, aromatic protons), 2.34 (s, 3H, Me), 2.11 (s, 3H, Me) ppm, OH is unobserverved. IR (KBr): ν 3189, 1677, 1616, 1566, 1319, 1236, 1149, 1097, 857, 762, 730 cm^{-1} EIMS: *m/z* – 190 [M^+].

7,8-Dihydroxy-3,4,-dimethyl-chromen-2-one (Entry 18, Table 2)

^{1}NMR ($CDCl_3$ + DMSO, 200 MHz): δ 6.96 (d, *J* = 8.81 Hz, 1H, aromatic proton), 6.75 (d, *J* = 8.81 Hz, 1H, aromatic proton), 2.35 (s, 3H, Me), 2.13 (s, 3H, Me) ppm, OH is unobserverved. IR (KBr): ν 3425, 3065, 1673, 1581, 1347, 1303, 1109, 816, 764 cm^{-1}. EIMS: m/z – 206 [M^+].

5,7-Dihydroxy-3, 4,-dimethyl-chromen-2-one (Entry 19, Table 2)

^{1}NMR ($CDCl_3$ + DMSO, 200 MHz): δ 9.75 (s, 1H), 6.20 (dd, *J* = 9.06 Hz, J = 3.02 Hz, 2H, aromatic protons), 2.56 (s, 3H, Me), 2.06 (s, 3H, Me), 1.24 (s, 1H) ppm. IR (KBr): ν 3269, 2920, 1675, 1615, 1561, 1383, 1358, 1285, 1167, 1056, 836, 742, 559 cm^{-1}. EIMS: *m/z* – 206 [M^+].

CONCLUSION

In summary, a convenient method has been developed for the Pechmann reaction of phenols and β-keto esters catalyzed by H_2SO_4/silica gel. Use of inexpensive and reusable catalyst, solvent-free condition, short reaction time, high yield and ease of purification of the product are the key features of this elegant protocol for which it may be considered as an effective alternative to the existing methodologies. The pronounced advantage of this novel catalytic system is expected to contribute to the development of more benign Pechmann condensation reactions of phenols with β-keto esters.

ACKNOWLEDGEMENTS

BT thanks the Department of Science and Technology, New Delhi, for a Research Fellowship under SERC Scheme (SP/S1/PC-31/2004). MKP is the recipient of Senior Research Fellowship of CSIR, New Delhi.

REFERENCES

[1] Weber, U.S.; Steffen, B.; Siegers, C.P. *Res. Commun. Mol. Pathol. Pharmacol.*, **1998**, *99*, 193.
[2] Patil, A.D.; Freyer, A.J.; Drake, S.E.; Haltiwanger, R.C.; Bean, M.F.; Taylor, P.B.; Caranfa, M.J.; Breen, A.L.; Bartus, H.R.; Johnson, R.K.; Hertzberg, R.P.; Westley, J.W. *J. Med. Chem.*, **1993**, *36*, 4131.
[3] Yun, B.S.; Lee, I.K.; Ryoo, I.J.; Yoo, I.D. *J. Nat. Prod.*, **2001**, *64*, 1238.
[4] Cheng, J.F.; Ishikawa, A.; Ono, Y.; Arrhenius, T.; Nadzan, A. *Bioorg. Med. Chem.*, **2003**, *13*, 3647.
[5] Zaha, A.A.; Hazem, A. *Microbiologica.*, **2002**, *25*, 213.
[6] Whittaker, M.; Floyd, C.D.; Brown, P.; Gearing, A.J.H. *Chem. Rev.*, **1999**, *99*, 2735.
[7] Maly, D.J.; Leonetti, F.; Backes, B.J.; Dauber, D.S.; Harris, J.L.; Craik, C.S.; Ellman, J.A. *J. Org. Chem.*, **2002**, *67*, 910.
[8] Pechmann, V.H.; Duisberg, C. *Chem. Ber.*, **1884**, *17*, 929.

[9] Johnson, J.R. *Org. React.*, **1942**, *1*, 210.
[10] Brufola, G.; Fringuelli, F.; Piermatti, O.; Pizzo, F. *Heterocycles*, **1996**, *43*,1257.
[11] Shirner, R.L. *Org. React.*, **1942**, *1*, 1.
[12] Yavari, I.; Hekmat, S.R.; Zonouzi, A. *Tetrahedron Lett.*, **1998**, *39*, 2391.
[13] Cairns, N.; Harwood, L.M.; Astles, D.P. *J. Chem. Soc. Perkin Trans.*, **1994**, *1*, 3101.
[14] Cartwright, G.A.; McNab, W. *J. Chem. Res. (S)*, **1997**, 296.
[15] Woods, L.L.; Sapp, J. *J. Org. Chem.*, **1962**, *27*, 3703.
[16] Robertson, A.; Sandrock, W.F.; Henry, C.B. *J. Chem. Soc.*, **1931**, 2426.
[17] Sharma, G.V.M.; Janardhan, R.J.; Sree, L.P.; Radha, K.P. *Tetrahedron Lett.*, **2005**, *46*, 6119.
[18] Valizadeha, H.; Shockravi, A. *Tetrahedron Lett.*, **2005**, *46*, 3501.
[19] Potdar, M.K.; Mohile, S.S.; Salunkhe, M.M. *Tetrahedron Lett*., **2001**, *42*, 9285.
[20] Rodriguez-Dominguez, J.C.; Kirsch, G. *Tetrahedron Lett.*, **2006**, *47*, 3279.
[21] Selvakumar, S.; Chidambaram, M.; Singh, A.P. *Catal. Commun.*, **2007**, *8*, 777.
[22] Frere, S.; Thiery, V.; Besson, T. *Tetrahedron Lett.*, **2001**, *42*, 2791.
[23] Chaudhari, D.A. *Chem. Ind.*, **1983**, 568.
[24] Naik, M.A.; Mishra, B.G.; Dubey, A. *Colloids Surf. A Physicochem. Eng. Aspects*, **2008**, *317*, 234.
[25] Gunnewegh, E.A.; Hoefnagel, A.J.; van Bekkum, H. *J. Mol. Catal. A: Chem.*, **1995**, *100*, 87.
[26] Fre`re, S.; Thie´ry, V.; Besson, T. *Tetrahedron Lett.*, **2001**, *42*, 2791
[27] Heravi, M.M.; Ajami, D.; Ghassemzadeh, M. *Synth. Commun.*, **1999**, *29*, 1013.
[28] Oskooie, H.A.; Heravi, M.M.; Sadnia, A.; Jannati, F.; Behbahani, F.K. *Monatsh. Chem.*, **2008**, *139*, 27.
[29] Wu, H.; Shen, Y.; Fan, L.-y.; Wan, Y.; Zhang, P.; Chen, C.-f.; Wang, W.-x. *Tetrahedron*, **2007**, *63*, 2404.
[30] Shaterian, H.R.; Ghashang, M.; Feyzi, M. *Appl. Catal. A Gen.*, **2008**, *345*, 128.
[31] Mohammadpoor-Baltork, I.; Mirkhani, V.; Moghadam, M.; Tangestaninejad, S.; Zolfigol, M.A.; Abdollahi-Alibeik, M.; Khosropour, A.R.; Kargar, H.; Hojati, S.F. *Catal. Commun.*, **2008**, *9*, 894.
[32] Reddy, B.M.; Patil, M.K.; Reddy, B.T. *Catal. Lett.*, **2008**, *125*, 97.
[33] Reddy, B.M.; Patil, M.K.; Reddy, B.T.; Park, S.-E. *Catal. Commun.*, **2008**, *9*, 950.
[34] Reddy, B.M.; Patil, M.K.; Rao, K.N.; Reddy, G.K. *J. Mol. Catal. A Chem.*, **2006**, *258*, 302.
[35] Reddy, B.M.; Patil, M.K.; Reddy, B.T. *Catal. Lett.*, **2008**, *126*, 413.

Received: January 3, 2009 Revised: February 2, 2009 Accepted: February 3, 2009