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A novel and convenient synthesis of 4-hydroxy-6-methyl-3-(1-(phenylimino) ethyl)-2*H*-pyran-2-one derivatives under ultrasound irradiation

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ABSTRACT

A facile, efficient and environment-friendly protocol for the synthesis of 4-hydroxy-6-methyl-3-(1-(phenylimino)ethyl)-2*H*-pyran-2-one derivatives has been developed by the convenient ultrasound-mediated condensation of amine with dehydroacetic acid. This method provides several advantages over current reaction methodologies including a simple work-up procedure, shorter reaction times and higher yields.

1. Introduction

The Schiff base (or azomethine), named after Hugo Schiff, has a wide range of applications. For example, it can be used as a catalyst, nonlinear optical materials, electroluminescent materials and so on. In recent years, scientists have found that the Schiff base plays a very important role in catalytic and electronic transfer processes of organisms [1]. The synthesis of novel Schiff bases and the research of their physiological activities has become important due to their anticancer and antimicrobial activities [2–4]. As a part of drug development programs, numerous methods for the synthesis of various kinds of Schiff base have been reported [5–9].

In recent years, ultrasound has become a highly useful method for performing a wide range of chemical reactions and processes, including chemical synthesis, materials production and water treatment [10–12]. Most of the effects arise from cavitation [13,14]. Furthermore, the application of ultrasound irradiation in organic reactions is also rapidly increasing. A large number of organic reactions can be carried out in a higher yield, shorter reaction time and milder conditions under ultrasonication [15–22].

In order to expand the application of ultrasound in the synthesis of organic compounds, we wish to report a novel and efficient method for the synthesis of 4-hydroxy-6-methyl-3-(1-(phenylimino) ethyl)-2*H*-pyran-2-one derivatives **3** via an efficient condensation of amine **1** and dehydroacetic acid **2** in ethanol in the presence of *p*-toluenesulfonic acid (*p*-TSA) under ultrasonic irradiation (Scheme 1).

2. Methods

2.1. Apparatus and analysis

All reagents were purchased from commercial sources and used without further purification. Ultrasonication was performed in a KQ-250E medical ultrasound cleaner with a frequency of 40 kHz and an output power of 250 W. Melting points are uncorrected. IR spectra were recorded on a Varian F-1000 spectrometer in KBr with absorptions in cm^{-1}. ^1H NMR were determined on a Varian Invoa-300/400 MHz spectrometer in $CDCl_3$ solution. *J* values are in Hz. Chemical shifts are expressed in ppm downfield from internal standard TMS. HRMS analyses were carried out using TOF-MS. X-ray diffractions were recorded on a Siemens P4 diffractometer. The reaction flask was located at the maximum energy area in the cleaner, and the surface of the reactants was placed slightly lower than the level of the water. Observation of the surface of the reaction solution during vertical adjustment of vessel depth will show the optimum position by the point at which maximum surface disturbance occurs. The reaction temperature was controlled by addition or removal of water from ultrasonic bath.

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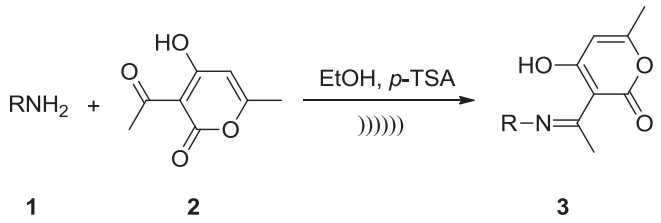

Scheme 1. Synthesis of 4-hydroxy-6-methyl-3-(1-(phenylimino)ethyl)-2*H*-pyran-2-one derivatives.

2.2. Classical procedure for the synthesis of 4-hydroxy-6-methyl-3-(1-(phenylimino)ethyl)-2H-pyran-2-one derivatives (**3**)

A 100 mL flask was charged with amine **1** (10 mmol), dehydroacetic acid **2** (10 mmol) and *p*-TSA (0.5 mmol) in ethanol (30 mL). The mixture was stirred at reflux. After the completion of the reaction (monitored by TLC), the reaction was allowed to cool, and the ethanol was evaporated under reduced pressure. The solid residue was washed with ethanol to afford the pure product as solid.

2.3. Ultrasound-promoted synthesis of 4-hydroxy-6-methyl-3-(1-(phenylimino)ethyl)-2H-pyran-2- one derivatives (**3**)

A 100 mL flask was charged with amine **1** (10 mmol), dehydroacetic acid **2** (10 mmol) and *p*-TSA (0.5 mmol) in ethanol (10 mL). The mixture was sonicated in the water bath of an ultrasonic cleaner at 30 °C. After the completion of the reaction (monitored by TLC), the reaction was allowed to cool, the ethanol was evaporated under reduced pressure. The solid residue was washed with ethanol to afford the pure product as solid.

2.4. Data spectra of products

2.4.1. Compound **3a**

4-hydroxy-6-methyl-3-(1-(p-tolylimino)ethyl)-2*H*-pyran-2-one. White solid; m.p. 154–156 °C (lit.[23a] m.p. 155 °C); IR (KBr, cm^{-1}): 3398, 3036, 2929, 1701, 1650, 1565, 1471, 1383, 1067, 946, 837, 764; ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 2.16 (s, 3H, CH_3), 2.39 (s, 3H, CH_3), 2.58 (s, 3H, CH_3), 5.75 (s, 1H, CH), 7.05 (d, J = 6.3 Hz, 2H, ArH), 7.24 (d, J = 6.0 Hz, 2H, ArH), 15.66 (s, 1H, OH).

2.4.2. Compound **3b**

3-(1-((4-chlorophenyl)imino)ethyl)-4-hydroxy-6-methyl-2*H*-pyran-2-one. White solid; m.p. 138–140 °C (lit.[23b] m.p. 140 °C); IR (KBr, cm^{-1}): 3404, 3079, 2725, 1718, 1651, 1568, 1466, 1327, 1091, 949, 845, 719; ^1H NMR (300 MHz, $CDCl_3$): δ (ppm) 2.10 (s, 3H, CH_3), 2.47 (s, 3H, CH_3), 5.80 (s, 1H, CH), 7.39 (d, J = 8.7 Hz, 2H, ArH), 7.54 (d, J = 8.7 Hz, 2H, ArH), 15.72 (s, 1H, OH); HRMS calculated for $C_{14}H_{12}{}^{35}Cl\ NO_3$ [M^+]: 277.0505, found: 277.0503.

2.4.3. Compound **3c**

3-(1-((4-methoxyphenyl)imino)ethyl)-4-hydroxy-6-methyl-2*H*-pyran-2-one. Yellow solid; m.p. 174–175 °C (lit.[23c] m.p. 180–182 °C); IR (KBr, cm^{-1}): 3439, 3089, 2929, 1695, 1619, 1563, 1472, 1331, 1069, 945, 833, 715; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.16 (s, 3H, CH_3), 2.58 (s, 3H, CH_3), 3.84 (s, 3H, CH_3), 5.75 (s, 1H, CH), 6.96 (d, J = 8.8 Hz, 2H, ArH), 7.10 (d, J = 8.8 Hz, 2H, ArH), 15.59 (s, 1H, OH).

2.4.4. Compound **3d**

3-(1-((3-chloro-4-methylphenyl)imino)ethyl)-4-hydroxy-6-methyl-2*H*-pyran-2-one. Light yellow solid; m.p. 167–169 °C; IR (KBr, cm^{-1}): 3440, 3081, 2984, 1707, 1656, 1563, 1471, 1359, 1067, 954, 830,765; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.13 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 2.56 (s, 3H, CH_3), 5.72 (s, 1H, CH), 6.95 (d, J = 8.0 Hz, 1H, ArH), 7.16 (s, 1H, ArH), 7.27 (d, J = 8.0 Hz, 1H, ArH), 15.77 (s, 1H, OH); HRMS calculated for $C_{15}H_{14}{}^{35}Cl\ NO_3$ [M^+]: 291.0662, found: 291.0660.

2.4.5. Compound **3e**

4-hydroxy-6-methyl-3-(1-((4-nitrophenyl)imino)ethyl)-2*H*-pyran-2-one. Gray solid; m.p. 198–200 °C; IR (KBr, cm^{-1}): 3429, 3128, 2927, 1726, 1650, 1567, 1469, 1339, 1062, 945, 857,725; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.19 (s, 3H, CH_3), 2.66 (s, 3H, CH_3), 5.80 (s, 1H, CH), 7.37 (d, J = 8.4 Hz, 2H, ArH), 8.34 (d, J = 8.0 Hz, 2H, ArH), 16.39 (s, 1H, OH); HRMS calculated for $C_{14}H_{12}N_2O_5$ [M^+]: 288.0746, found: 288.0743.

2.4.6. Compound **3f**

3-(1-((2-chlorophenyl)imino)ethyl)-4-hydroxy-6-methyl-2*H*-pyran-2-one. White solid; m.p. 158–160 °C (lit.[23d] m.p. 156 °C); IR (KBr, cm^{-1}): 3435, 3081, 2927, 1697, 1642, 1563, 1460, 1365, 1062, 946, 855,757; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.17 (s, 3H, CH_3), 2.53 (s, 3H, CH_3), 5.78 (s, 1H, CH), 7.24 (t, J = 7.6 Hz, 1H, ArH), 7.32–7.38 (m, 2H, ArH), 7.53 (dd, J_1 = 1.6 Hz, J_2 = 7.2 Hz, 1H, ArH), 15.91 (s, 1H, OH).

2.4.7. Compound **3g**

3-(1-((3-chlorophenyl)imino)ethyl)-4-hydroxy-6-methyl-2*H*-pyran-2-one. White solid; m.p. 116–117 °C (lit.[23a] m.p. 118 °C); IR (KBr, cm^{-1}): 3429, 3063, 2647, 1706, 1652, 1568, 1467, 1385, 1070, 997, 839, 796; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.14 (s, 3H, CH_3), 2.58 (s, 3H, CH_3), 5.73 (s, 1H, CH), 7.07 (d, J = 7.6 Hz, 1H, ArH), 7.19 (s, 1H, ArH), 7.33–7.40 (m, 2H, ArH), 15.91 (s, 1H, OH).

2.4.8. Compound **3h**

3-(1-(benzylimino)ethyl)-4-hydroxy-6-methyl-2*H*-pyran-2-one. Light yellow solid; m.p. 79–80 °C (lit.[23c] m.p. 79–81 °C); IR (KBr, cm^{-1}): 3442, 3057, 2917, 1700, 1643, 1571, 1472, 1387, 1059, 995, 874, 728; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.12 (s, 3H, CH_3), 2.67 (s, 3H, CH_3), 4.69 (d, J = 5.6 Hz, CH_2), 5.68 (s, 1H, CH), 7.26–7.31 (m, 2H, ArH), 7.34 (d, J = 6.8 Hz, 1H, ArH), 7.39 (t, J = 7.6 Hz, 2H, ArH), 14.54 (s, 1H, OH); HRMS calculated for $C_{15}H_{15}NO_3$ [M^+]: 257.1052, found: 257.1052.

2.4.9. Compound **3i**

3-(1-((4-fluorophenyl)imino)ethyl)-4-hydroxy-6-methyl-2*H*-pyran-2-one. White solid; m.p. 147–148 °C; IR (KBr, cm^{-1}): 3422, 3079, 2927, 1725, 1661, 1575, 1477, 1329, 1063, 998, 831, 771; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.16 (s, 3H, CH_3), 2.57 (s, 3H, CH_3), 5.75 (s, 1H, CH), 7.15 (d, J = 6.4 Hz, 4H, ArH), 15.75 (s, 1H, OH); HRMS calculated for $C_{14}H_{12}F\ NO_3$ [M^+]: 261.0801, found: 261.0799.

2.4.10. Compound **3j**

3-(1-(benzo[*d*][1,3]dioxol-5-ylimino)ethyl)-4-hydroxy-6-methyl-2*H*-pyran-2-one. Gray solid; m.p. 184–185 °C; IR (KBr, cm^{-1}): 3441, 3088, 2917, 1693, 1650, 1566, 1471, 1364, 1037, 931, 869, 779; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.15 (s, 3H, CH_3), 2.57 (s, 3H, CH_3), 5.74 (s, 1H, CH), 6.03 (s, 2H, OCH_2O), 6.62 (d, J = 8.8 Hz, 2H, ArH), 6.83 (d, J = 7.6 Hz, 1H, ArH), 15.58 (s, 1H, ArH); HRMS calculated for $C_{15}H_{13}NO_5$ [M^+]: 287.0794, found: 287.0796.

2.4.11. Compound **3k**

4-hydroxy-6-methyl-3-(1-(quinolin-6-ylimino)ethyl)-2*H*-pyran-2-one. White solid; m.p. 196–198 °C; IR (KBr, cm^{-1}): 3427, 3044, 2925, 1717, 1650, 1574, 1479, 1365, 1063, 941, 836, 793; ^1H NMR (400 MHz, $CDCl_3$): δ (ppm) 2.19 (s, 3H, CH_3), 2.68 (s, 3H,

Table 1
The model reaction catalyzed by *p*-TSA in different solvents under ultrasound irradiation[a].

Entry	Solvent	Temperature (°C)	Time (h)	Yield[b] (%)
1	Ethanol	30	4	86
2	Methanol	30	5.5	76
3	Toluene	30	24	40
4	Acetonitrile	30	24	38
5	THF	30	24	32
6	Dioxane	30	24	35
7	Water	30	7	65
8	Ethanol	40	4	85
9	Ethanol	50	4	87

[a] Reaction conditions: *p*-toluidine (10 mmol), dehydroacetic acid (10 mmol), *p*-TSA (0.5 mmol), solvent (10 mL) and the ultrasonic power 250 W, irradiation frequency 40 kHz.
[b] Yields of isolated products.

Table 2
Synthesis of 4-hydroxy-6-methyl-3-(1-(phenylimino)ethyl)-2*H*-pyran-2-one derivatives **3** under ultrasonic irradiation[a].

Entry	R	Product	MP (°C)	Traditional method		Sonochemical method	
				Time (h)	Yield[b] (%)	Time (h)	Yield[b] (%)
1	4-$CH_3C_6H_4$	**3a**	154–156	4	69	4	86
2	4-ClC_6H_4	**3b**	138–140	9	67	7.5	78
3	4-$CH_3OC_6H_4$	**3c**	174–175	3.5	50	3.5	80
4	4-CH_3-3-ClC_6H_3	**3d**	167–169	5	88	4	95
5	4-$NO_2C_6H_4$	**3e**	198–200	40	41	20	69
6	2-ClC_6H_4	**3f**	158–160	10	52	8	79
7	3-ClC_6H_4	**3g**	126–127	10	74	9	85
8	$C_6H_5CH_2$	**3h**	79–80	1.5	77	1	86
9	4-FC_6H_4	**3i**	147–148	12	69	7	88
10	3,4-$OCH_2OC_6H_3$	**3j**	184–185	6	74	5	88
11	quinoline-6-yl	**3k**	196–199	20	50	9	62
12	2,6-$Cl_2C_6H_3$	**3l**	–	36	Trace	20	Trace

[a] Reaction conditions: amine (10 mmol), dehydroacetic acid (10 mmol), *p*-TSA (0.5 mmol), ethanol (10 mL) and the ultrasonic power 250 W, irradiation frequency 40 kHz.
[b] Yields of isolated products.

CH_3), 5.18 (s, 1H, CH), 7.48–7.54 (m, 2H, ArH), 7.85 (s, 1H, ArH), 8.20 (t, J = 9.6 Hz, 2H, ArH), 8.98 (s, 1H, ArH), 16.12 (s, 1H, OH); HRMS calculated for $C_{17}H_{14}N_2O_3$ [M^+]: 294.1004, found: 294.1005.

3. Results and discussion

To achieve suitable conditions for the synthesis of 4-hydroxy-6-methyl-3-(1-(phenylimino) ethyl)-2*H*-pyran-2-one derivatives **3**, various reaction conditions have been investigated in the reaction of *p*-toluidine **1a** and dehydroacetic acid **2** as a model reaction.

Initially, we examined the effect of the solvent through some experiments. To search for the optimal solvent, the ultrasonic-assisted reaction of the aromatic amine and dehydroacetic acid was examined using ethanol, methanol, toluene, acetonitrile, tetrahydrofuran (THF), dioxane and water as solvent. The results were listed in Table 1. Methanol and water afforded moderate yields of the desired products (Table 1, entries 2 and 7). Poor results were observed when the reactions were carried out in toluene, acetonitrile, THF and dioxane. The reactions took a long time and the yields were low (Table 1, entries 3–6). Nevertheless, the reaction using ethanol as the solvent gave the best result (Table 1, entry 1). Thus, ethanol was chosen as the solvent for all further reactions.

Next, we attempted to further improve the yield by performed experiments in 30, 40 and 50 °C under ultrasonic irradiation (Table 1). The effect, however, was not remarkable. Therefore, the temperature was not the main factor affecting the reaction.

In order to apply this reaction to a library synthesis, we have extended the reaction of aryl amine with aliphatic and heterocyclic amine under similar conditions (ethanol/30 °C/ultrasound/*p*-TSA), furnishing the respective 4-hydroxy-6-methyl-3-(1-(phenylimino) ethyl)-2*H*-pyran-2-one in good yields (Scheme 1). The optimized results are summarized in Table 2. We found that the results were excellent in terms of yields using aryl amine carrying electron-donating substituents. Under the same conditions, however, the reactions with aryl amine carrying electron-withdrawing groups required a longer time and the yields of some products notably decreased (Table 2, entries 2,5,7,9). It was also found that the ortho-substituted aromatic amines generally gave very low yields, even trace of the products, probably due to the large steric effect of 2,6-dichloroaniline (Table 2, entry 6,12). That is to say, steric factors played a key role in affecting the rates of reaction and the reactions required a longer time.

To find the specific effect of ultrasound on this reaction, all previously mentioned reactions were carried out under the same conditions in the absence of ultrasound irradiation (Table 2). It was observed that the reaction times increased considerably and the yields of the products decreased under conventional reflux conditions. Thus, ultrasonic irradiation was found to have a beneficial effect on the synthesis of 4-hydroxy-6-methyl-3-(1-(phenylimino) ethyl)-2*H*-pyran-2-one derivatives which was superior to the traditional method with respect to yields, reaction times, simplicity and safety.

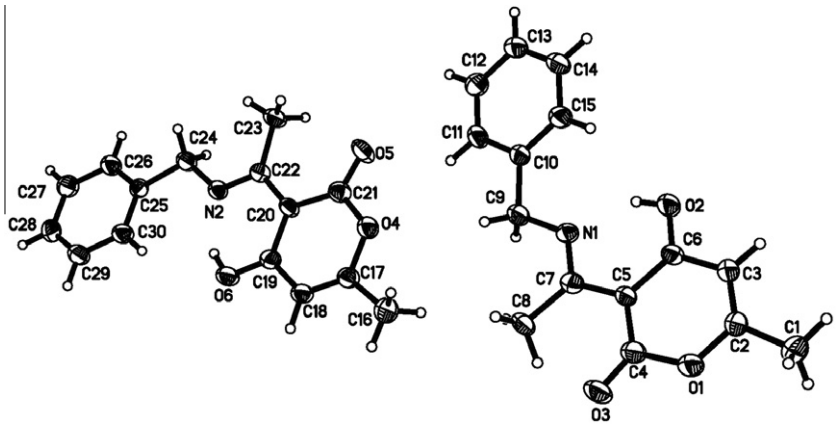

Fig. 1. X-ray crystal structure of 3h.

To the best of our knowledge, this new procedure provides the first example of an efficient and ultrasound-promoted approach for the synthesis of 4-hydroxy-6-methyl-3-(1-(phenylimino)ethyl)-2*H*-pyran-2-one. This method is the most simple and convenient and would be applicable for the synthesis of different types of nitrogen-containing heterocyclic compounds. The structures of all the synthesized compounds were established by their IR and ^{1}H NMR. The HRMS analyses of compound **3b**, **3d**, **3e**, **3h**, **3i**, **3j** and **3k** that are unknown compounds were performed. The structure of **3h** was further confirmed by X-ray diffraction analysis [24]. The molecular structure of the product **3h** is shown in Fig. 1.

4. Conclusion

In conclusion, we have found an efficient and practical procedure for the preparation of 4-hydroxy-6-methyl-3-(1-(phenylimino) ethyl)-2*H*-pyran-2-one from amine and dehydroacetic acid in ethanol under ultrasonic irradiation at 30 °C in the presence of *p*-TSA. Based on those results, we demonstrated that compared with traditional methods (reflux method), ultrasound irradiation can speed up the reaction remarkably and is more convenient and efficient.

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[24] Crystallographic data for **3h** have been deposited at the Cambridge Crystallographic Data Centre with the deposition number CCDC 806998. Copies of these data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ, UK; Fax: +44 1223 336 033; or e-mail: deposit@ccdc.cam.ac.uk).