RSC Advances

PAPER

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Cite this: *RSC Adv.*, 2014, **4**, 39667

A practical one-pot synthesis of coumarins in aqueous sodium bicarbonate *via* intramolecular Wittig reaction at room temperature†

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Received 11th July 2014
Accepted 19th August 2014

DOI: 10.1039/c4ra06996j

www.rsc.org/advances

An efficient, simple and relatively inexpensive method for the synthesis of coumarins in aqueous sodium bicarbonate at ambient temperature has been developed. It features an intramolecular Wittig reaction of substituted 2-formylphenyl 2-bromoacetate in saturated aqueous sodium bicarbonate. Its advantages include benign reaction conditions, easy work-up and good overall yield with short reaction time. Various substituted coumarins have been synthesized by utilizing this methodology.

Introduction

Solvent free organic reactions and reactions in aqueous conditions have greatly influenced and attracted the chemist's interest as an integral part of green chemistry.[1,2] Recently these reactions without the use of harmful organic solvents have drawn much more attention. Use of water as a medium for organic reactions has a large number of desired advantages as it is a cost-effective, non-toxic, non-hazardous and environmentally benign solvent where isolation of the organic products can be performed by simple phase separation.[3] A wide range of stabilized ylides and aldehydes have been extensively used in aqueous media during the Wittig reaction as an important carbon–carbon bond forming reaction. Despite, the poor solubility of reactants, acceptable yields are obtained and the rate of the reactions in water is unexpectedly accelerated as it lowers the energy of the transition state for the Wittig reaction.[4]

The coumarin scaffold and its derivatives exhibit diverse biological and pharmaceutical properties such as anti-HIV, anticoagulant, antibacterial, antioxidant and anticancer are well known.[5,6] Some of them also display a broad range of applications as additives to perfumes and cosmetics, as photographic sensitizers and solar collectors, as fluorescent markers in biochemistry and as tunable dye lasers.[7,8] Because of the significance of this heterocyclic system and their diverse pharmacological properties, many strategies for the synthesis of substituted coumarins have been developed, which include Perkin,[9] Wittig,[10] Knoevenagel,[11] Reformatsky,[12] and Pechmann[13] reactions and more recently palladium-catalyzed carbonylative annulations.[14]

Notably, most of the methods for the synthesis of coumarins reported to date have been developed without attention to its environmental impact, making the development of new reliable high-yielding eco-friendly methods for the synthesis of coumarins an important subject. The intramolecular Wittig reaction has been extensively used as an excellent method for the C–C bond-forming process in the synthesis of natural products.[15] The first synthesis of coumarin *via* intramolecular Wittig reaction was reported as a short paper by Desai *et al.*[16] wherein they have used toxic chloroform and pyridine and failed to isolate any intermediates and obtained the product in very low yield (26–30%).

Results and discussion

During the course of our investigation to develop novel greener synthetic methods for the synthesis of biologically active heterocyclic compounds, we herein report an efficient, simple and relatively inexpensive method for the synthesis of coumarins *via* intramolecular Wittig reaction under very mild and environmentally benign conditions: in saturated aqueous sodium bicarbonate and at ambient temperature (Scheme 1). The main objective of this work was to explore the synthesis of coumarin derivatives in aqueous media *via* the intramolecular Wittig reaction.

Based on the concept of preparing phosphoranes *in situ* during the Wittig process, we attempted the one pot synthesis of coumarin *via* intramolecular Wittig reaction in saturated aqueous sodium bicarbonate, which proceeded in decent yields with short reaction time (20–30 min).

In order to establish the optimal reaction conditions in terms of various organic and inorganic bases in water media, the Wittig salt **3a** was chosen as model substrate. As shown in Table 1,

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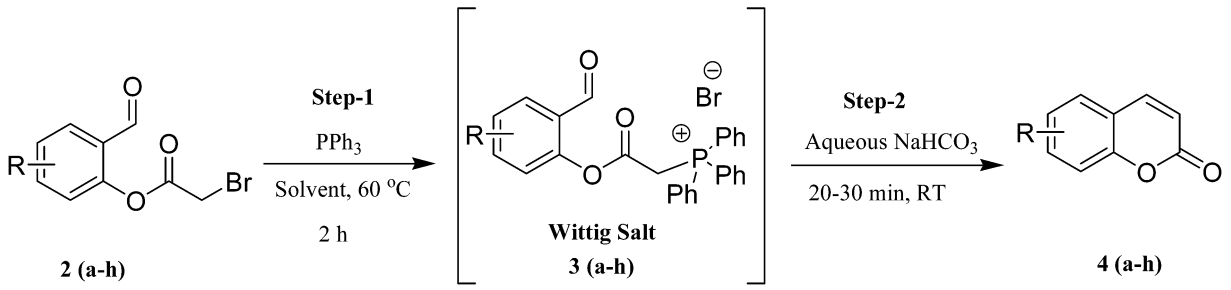
† Electronic supplementary information (ESI) available. See DOI: 10.1039/c4ra06996j



Scheme 1 Aqueous sodium bicarbonate mediated synthesis of coumarins *via* intramolecular Wittig reaction at room temperature.

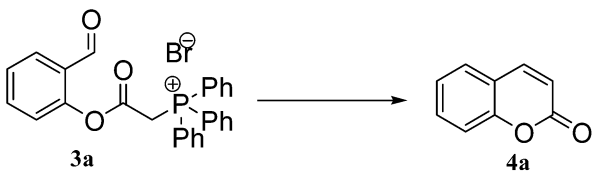
various organic bases, such as triethylamine, pyridine, piperidine, DBU and DMAP have been applied to promote this model reaction in water at 25 °C, only low yields (12–20%) of the desired product **4a** were obtained (Table 1, entries 1–5). The reaction was then carried out with various inorganic bases, such as NaOH, KOH, Na_2CO_3, K_2CO_3 and $NaHCO_3$ which again afforded the desired product **4a** in low yield at room temperature (Table 1, entries 7–9). Longer reaction time and higher temperature did not further promote the reaction (Table 1, entries 11). Only a trace amount of the desired product was obtained when the reaction was conducted in pure water without a base at 80 °C for 8 h (Table 1, entry 13). When we carried out the reaction in saturated aqueous $NaHCO_3$, to our delight **4a** was produced in 70% yield with short reaction time (30 min) at room temperature (Table 1, entries 12). In saturated Na_2CO_3 solution the product yield was lowered to 18% (Table 1, entry 15) and stirring for longer time in saturated Na_2CO_3 resulted in decomposition of the formed product, this might be due to strong alkali (pH = 12) nature of saturated Na_2CO_3 which might be cleaving the coumarin ring.

The reaction with saturated $NaHCO_3$ at elevated temperature (Table 1, entries 14) resulted in the decomposition of the formed product due to dehydration of $NaHCO_3$ to Na_2CO_3, which increases the basicity of the reaction media resulting in the cleavage of coumarin ring.

Among all the bases evaluated in water, saturated aqueous $NaHCO_3$ mediated intramolecular Wittig reaction afforded the coumarin **4a** in decent yield with short reaction time (20–30 min) at room temperature. The remarkable activation in the reaction rate is due to, lowering of energy of the transition state for the Wittig reaction by saturated aqueous sodium bicarbonate. This prompted us to explore the potential of this protocol for the synthesis of various coumarin derivatives.

Encouraged by this promising result, the substrate scope was further extended to a variety of substituted 2-formylphenyl 2-

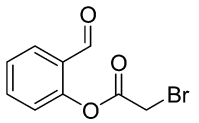
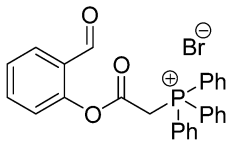
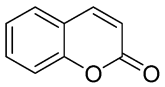
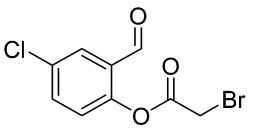
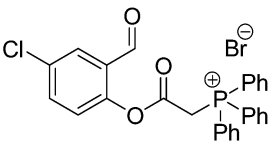
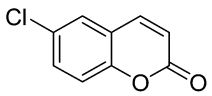
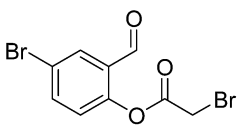
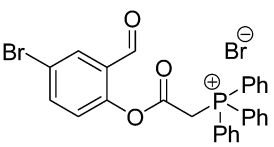
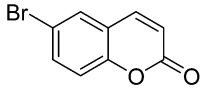
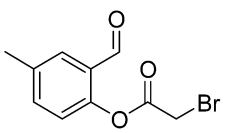
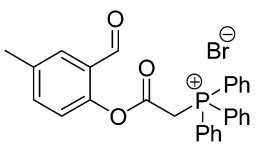
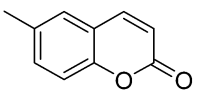
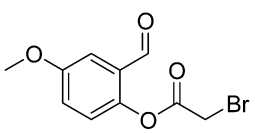
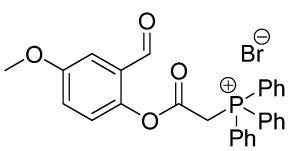
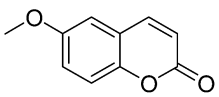
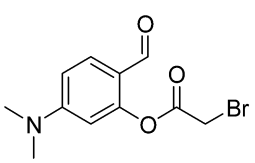
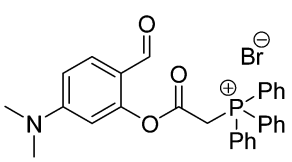
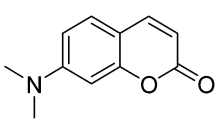
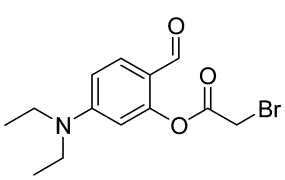
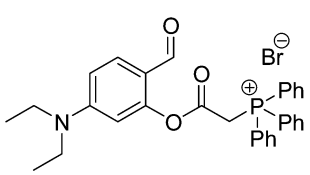
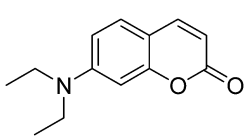
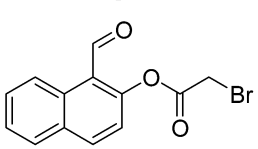
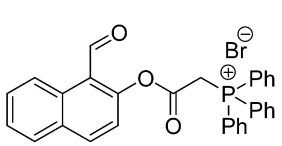
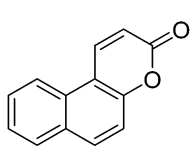
Table 1 Optimization of base, time and temperature in water for the synthesis of coumarin **4a** *via* intramolecular Wittig reaction[a]



Entry	Solvent	Base (equivalent)	Time (min)	Temperature	Yield[a] (%)
1	Water	Triethylamine (2.2)	300	25 °C	10
2	Water	Pyridine (2.2)	300	25 °C	12
3	Water	Piperidine (2.2)	300	25 °C	12
4	Water	DBU (2.2)	300	25 °C	22
5	Water	DMAP (2.2)	300	25 °C	18
6	Water	NaOH (2.2)	300	25 °C	18
7	Water	KOH (2.2)	300	25 °C	15
8	Water	Na_2CO_3 (2.2)	300	25 °C	25
9	Water	K_2CO_3 (2.2)	300	25 °C	28
10	Water	$NaHCO_3$ (2.2)	300	25 °C	30
11	Water	Na_2CO_3 (5.0)	8 h	85 °C	30
12	Water	$NaHCO_3$ (saturated)	30	25 °C	70
13	Water	—	8 h	85 °C	Trace
14	Water	$NaHCO_3$ (saturated)	20	60 °C	20
15	Water	Na_2CO_3 (saturated)	30	25 °C	18

[a] Isolated yield after column purification.

Table 2 Synthesis of coumarins (**4a–h**) under optimized conditions

Entry	Substrates (**2a–h**)	Wittig salt[a] (**3a–h**)	Products (**4a–h**)	Time[b] (min)	Yield[c] (%)
1	 **2a**	 **3a**	 **4a**	30	70
2	 **2b**	 **3b**	 **4b**	30	68
3	 **2c**	 **3c**	 **4c**	30	68
4	 **2d**	 **3d**	 **4d**	30	72
5	 **2e**	 **3e**	 **4e**	25	75
6	 **2f**	 **3f**	 **4f**	30	72
7	 **2g**	 **3g**	 **4g**	30	72
8	 **2h**	 **3h**	 **4h**	30	70

[a] Wittig salts (**3a–h**) were obtained in quantitative yields in 2 h at 60 °C and used immediately for the second step reaction because of their hygroscopic nature. [b] Time required for step-2. [c] Overall isolated yield after column purification.

bromoacetates (**2a–h**) (Table 2). As is apparent from Table 2, the reaction is highly versatile and efficient with various substituents such as chloro (**2b**), bromo (**2c**), methyl (**2d**), methoxy (**2e**), *N*,*N*-dimethyl (**2f**) and *N*,*N*-diethyl (**2g**) which yielded the corresponding coumarins **4a–h** in 65–75% yield.

Further to test the feasibility of a large-scale reaction, the reaction of 4-bromo-2-formylphenyl 2-bromoacetate (**2c**) (31 mmol) and triphenylphosphine (31 mmol) was investigated. The reaction could afford 4.6 g of **4c** in 65% yield after column purification. Hence, this protocol could be used as a practical method to synthesize the bioactive coumarins.

The required substituted 2-formylphenyl 2-bromoacetates (**2a–h**) were readily obtained by modification of a literature method[17] from substituted salicylaldehydes and bromoacetyl bromide in THF/NaH at 0 °C. After work-up, the 2-formylphenyl 2-bromoacetates (**2a–h**) were obtained in 80–90% yield with sufficient purity which can be directly used for the next step reaction. These aldehydes (**2a–h**) were converted to the corresponding Wittig salts (**3a–h**) by reacting with triphenylphosphine in ethylacetate for 2 h at 60 °C in quantitative yields. Since these Wittig salts were hygroscopic, they were immediately used for the one-pot synthesis of coumarins (**4a–h**) *via* intramolecular Wittig reaction in saturated aqueous sodium bicarbonate. The products were isolated by simple extraction with ethylacetate and purified by column chromatography on silica.

The reactions of salicylaldehydes having electron-donating groups furnished slightly greater yields of coumarins compared to that without electron-donating groups or with an electron-withdrawing group. However the reaction of 5-nitro salicylaldehyde with bromoacetyl bromide did not proceed because of the strong electron withdrawing nature of the nitro group. Similarly 3,5-dichloro salicylaldehyde did not react with bromoacetyl bromide because of steric hindrance of 3-chloro substituent.

Conclusion

In conclusion, we have developed an efficient, simple and relatively inexpensive one-pot method for the synthesis of coumarins *via* intramolecular Wittig reaction in saturated aqueous $NaHCO_3$ at room temperature. The methodology offers several advantages such as using green solvent, one-pot manner, ambient temperature, high reaction rates, good yields and simplicity in the extraction of the product, which make it a useful and attractive strategy in the synthesis of various substituted coumarins.

Experimental

General information

All reagents were of analytical grade and were used directly. Thin-layer chromatography (TLC) was performed on silica gel plates (60 F254; Merck). Column chromatography was performed using silica (60–120 mesh size; Merck). Melting points were determined in open capillaries and are uncorrected. The IR spectra were recorded on Nicolet Impact 410 FT IR spectrophotometer using KBr pellets. ^{1}H and ^{13}C NMR were recorded on Bruker 300 MHz and 400 MHz FT NMR spectrometer in $CDCl_3$ and DMSO-d_6 by using TMS as internal standard.

Typical procedure for the synthesis of 2*H*-chromen-2-one (4a)

A mixture of 2-formylphenyl 2-bromoacetates **2a** (2 mmol, 0.5 g) and triphenylphosphine (2 mmol, 0.55 g) in ethyl acetate (5 mL) was stirred at 60 °C for 2 h. The progress of the reaction was monitored by TLC (eluent: EtOAc–hexane, 2 : 8). After completion of the reaction, the mixture was cooled to room temperature and the separated Wittig salt **3a** was filtered and washed with cold ethyl acetate (5 mL). The obtained Wittig salt **3a** (2 mmol, 1.0 g) was taken in saturated aqueous $NaHCO_3$ (5 mL) and stirred vigorously for 30 min at room temperature. The progress of the reaction was monitored by TLC (eluent: EtOAc–hexane, 2 : 8). After completion of the reaction, the crude reaction mixture was extracted with ethyl acetate (3 × 10 mL), the combined organic layer was washed with H_2O (10 mL) and dried over Na_2SO_4. The solvent was evaporated under reduced pressure and the residue was purified by column chromatography on silica (60–120, eluent: EtOAc–hexane, 2 : 8) to afford the pure products in 65–75% yields (Table 2). The physical data (mp, NMR) of all the known compounds were found to be identical with those reported in the literature.

2*H*-Chromen-2-one (4a)[18]

Yield: 0.210 g (70%); white solid; mp: 68–69 °C. IR (KBr): 1696, 1602, 1383, 1237, 1067, 985, 856, 758, 572, 525, 426 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.70 (d, J = 9.6 Hz, 1H), 7.56–7.48 (m, 2H), 7.35–7.26 (m, 2H), 6.42 (d, J = 9.6 Hz, 1H); ^{13}C NMR (400 MHz, $CDCl_3$): δ 161.2, 154.4, 143.9, 132.3, 128.3, 124.8, 119.2, 117.3, 117.1.

6-Chloro-2*H*-chromen-2-one (4b)[19]

Yield: 0.221 g (68%); colorless solid; mp: 152–153 °C. IR (KBr): 1699, 1602, 1383, 1237, 1067, 950, 895, 830, 820, 730, 590, 530, 500 cm^{-1}; ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.56 (d, J = 9.6 Hz, 1H), 7.41–7.43 (m, 2H), 7.21 (d, J = 7.0 Hz, 1H), 6.39 (d, J = 9.6 Hz, 1H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 159.5, 151.9, 141.7, 131.3, 129.2, 126.6, 119.3, 117.8, 117.3.

6-Bromo-2*H*-chromen-2-one (4c)[20]

Yield: 0.237 g (68%); light brownish solid; mp: 162–164 °C. IR (KBr): 1690, 1600, 1383, 1237, 1067, 950, 895, 830, 730, 620, 590, 530, 500 cm^{-1}. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.53–7.57 (m, 3H), 7.15 (d, J = 7.0 Hz, 1H), 6.39 (d, J = 9.6 Hz, 1H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 159.9, 152.9, 142.1, 134.6, 130.2, 120.3, 118.6, 117.8, 116.9.

6-Methyl-2*H*-chromen-2-one (4d)[21]

Yield: 0.224 g (72%); colorless solid; mp: 73–75 °C. IR (KBr): 1717, 1684, 1575, 1380, 1262, 1189, 1167, 1105, 911, 841, 820, 813 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$): δ 7.69 (J = 9.3 Hz, 1H), 7.40.7.20 (m, 3H), 6.43 (d, J = 9.3 Hz, 1H), 2.43 (s, 3H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 161.0, 152.0, 143.4, 134.1, 132.8, 127.6, 118.5, 116.5, 116.4, 20.7.

6-Methoxy-2*H*-chromen-2-one (4e)[21]

Yield: 0.242 g (75%); colorless solid; mp: 100–102 °C. IR (KBr): 1705, 1570, 1491, 1451, 1286, 1261, 1185, 886, 808, 684 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.64 (d, $J = 9.6$ Hz, 1H), 7.22 (d, $J = 9.0$ Hz, 1H), 7.07 (dd, $J = 9.0$, 2.7 Hz, 1H), 6.89 (d, $J = 2.7$ Hz, 1H), 6.35 (d, $J = 9.9$ Hz, 1H), 3.82 (s, 3H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 160.9, 155.9, 148.3, 143.2, 119.4, 119.0, 117.7, 116.9, 109.9, 55.7.

7-(Dimethylamino)-2*H*-chromen-2-one (4f)[22]

Yield: 0.238 g (72%); purple powder; mp: 161–162 °C. IR (KBr): 1685, 1570, 1491, 1451, 1286, 1261, 1185, 886, 808, 684 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$): δ 7.54 (d, $J = 9.3$ Hz, 1H), 7.25 (d, $J = 2.8$ Hz, 1H), 6.61 (dd, $J = 8.7$ Hz, 2.3 Hz, 1H), 6.49 (d, $J = 2.2$ Hz, 1H), 6.06 (d, $J = 9.3$ Hz, 1H), 3.82 (s, 3H), 2.9 (s 6H). ^{13}C NMR (300 MHz, $CDCl_3$): δ 162.1, 156.3, 152.9, 143.7, 128.5, 109.8, 109.0, 108.8, 98.1, 40.2.

7-(Diethylamino)-2*H*-chromen-2-one (4g)[23]

Yield: 0.248 g (72%); yellowish powder; mp: 93–95 °C. IR (KBr): 1680, 1570, 1491, 1451, 1286, 1261, 1185, 886, 808, 684 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 7.45 (d, $J = 9.2$ Hz, 1H), 7.13 (d, $J = 2.4$ Hz, 1H), 6.48 (d, $J = 8.8$ Hz, 1H), 6.42 (d, $J = 2.0$ Hz, 1H), 5.95 (d, $J = 9.2$ Hz, 1H), 3.33 (q, $J = 14.2$ Hz, 4H), 1.14 (t, $J = 6.8$ Hz, 6H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 162.3, 156.7, 150.7, 143.7, 128.7, 109.1, 108.6, 108.3, 97.5, 44.7, 12.4.

3*H*-Benzo[*f*]chromen-3-one (4h)[24]

Yield: 0.234 g (70%); yellowish powder; mp: 117–119 °C. IR (KBr): 1705, 1278, 1257, 1200, 1119 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$): δ 8.47 (d, $J = 9.7$ Hz, 1H), 8.21 (d, $J = 8.4$ Hz, 1H), 7.97 (d, $J = 9.0$ Hz, 1H), 7.90 (d, $J = 8.1$ Hz, 1H), 7.71–7.66 (m, 1H), 7.59–7.54 (m, 1H), 7.44 (d, $J = 9.2$ Hz, 1H), 6.56 (d, $J = 9.8$ Hz, 1H). ^{13}C NMR (400 MHz, $CDCl_3$): δ 160.9, 153.9, 139.1, 133.1, 130.3, 129.0, 128.3, 126.1, 121.3, 117.1, 115.6, 113.0.

Acknowledgements

The authors gratefully acknowledge the financial assistance from UGC, New Delhi under UPE-FAR-I program, F. no. 14-3/2012 (NS/PE) and DST, New Delhi under major research project no. SR/S1/OC-58/2011. One of the authors NSB thank Sigma-Aldrich Chemicals Private Limited, Bangalore India for technical support.

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