Synthesis of 4*H*,5*H*-pyrano[3,2-*c*][1]benzopyran-5-ones in aqueous media

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The reaction of substituted cinnamonitriles with 4-hydroxycoumarin in water in the presence of triethylbenzylammonium chloride affords 2-amino-4-aryl-4*H*,5*H*-pyrano[3,2-*c*][1]benzopyran-5-one derivatives.

Keywords: fused pyrans, benzopyrans, coumarins, reactions in water, green chemistry

The need to reduce the amount of toxic waste and byproducts arising from chemical processes requires increasing emphasis on the use of less toxic and environmentally compatible materials in the design of new synthetic methods.[1] One of the most promising approaches uses water as a reaction medium.[2] Breslow,[3] who showed that hydrophobic effects could strongly enhance the rate of several organic reactions, rediscovered the use of water as a solvent in organic reactions in 1980s. In recent years, there has been increasing recognition that water is an attractive medium for many organic reactions.[4] The aqueous medium is less expensive, dangerous and environmentally-unfriendly in comparison with organic solvents. Generally, the low solubility[5] of most reagents in water is not an obstacle to the reactivity, which, on the contrary, is reduced by the use of cosolvents.

1-Benzopyran-2-one (coumarin) and its derivatives are natural compounds and are important chemicals in perfume, cosmetic and pharmaceutical industrial production.[6] Some coumarin derivatives have been reported to exhibit biological properties.[7-10] 4*H*,5*H*-pyrano[3,2-*c*][1]benzopyran-5-one derivatives are generally prepared by the reaction of 4-hydroxy-1-benzopyran-2-one (4-hydroxycoumarin) and substituted cinnamonitriles in an organic solvent (*e.g.* ethanol) in the presence of organic bases like piperidine.[11] Based on our previous studies on the use of water as solvent for carrying out carbon-carbon bond forming reactions under heterogeneous catalysis,[12-19] we now report the reaction of substituted cinnamonitriles (**1**) with 4-hydroxycoumarin (**2**) in water at 90 °C in the presence of a catalytic amount of triethylbenzylammonium chloride (TEBA) for 6–10 h, giving rise to 2-amino-4-aryl-4*H*,5*H*-pyrano[3,2-*c*][1]benzopyran-5-one derivatives (**3**) in 73–97 % yields (Scheme 1).

Table 1 summarises our results on the reactions of a number of substrates. Product structures were established on the basis of spectroscopic data, particularly ^{1}H NMR analysis, and were further confirmed by the X-ray crystal structure analysis of the product **3m**[20] (Fig.1).

In summary, the conversion of substituted cinnamonitriles and 4-hydroxycoumarin into 2-amino-4-aryl-4*H*,5*H*-pyrano[3,2-*c*][1]benzopyran-5-one derivatives can be efficiently performed in water as a solvent using a catalytic amount of TEBA. Compared to the previous methods, this new protocol has the advantages of good yields, low cost, simple operation and environmentally benign procedure.

Experimental

IR spectra were recorded on a FT IR-8101 spectrometer in KBr. ^{1}H NMR spectra were determined on an Inova 400 MHz spectrometer using $CDCl_3$ or DMSO-d_6 solutions. Chemical shifts (δ) are expressed in ppm downfield from internal tetramethylsilane. Microanalyses

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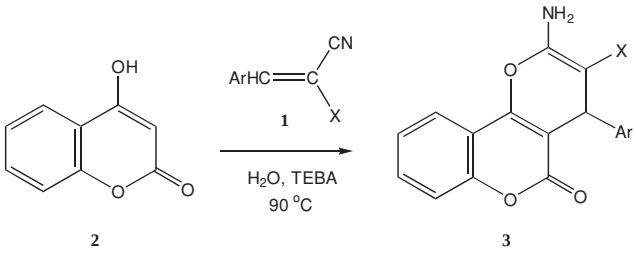

Scheme 1

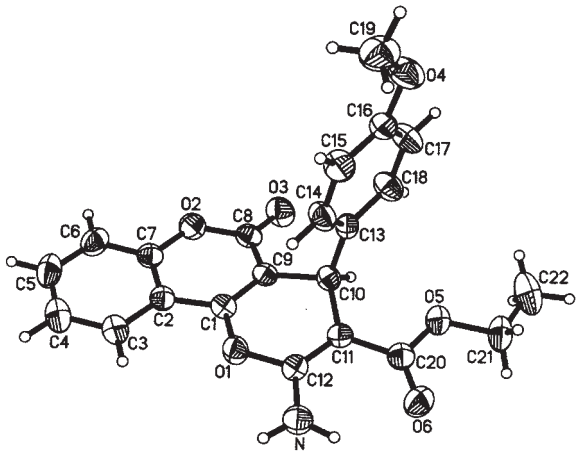

Fig. 1 The X-ray crystal structure of compound **3m**.

Table 1 4*H*,5*H*-pyrano[3,2-*c*][1]benzopyran-5-ones (**3**)

Entry	Ar	X	Reaction times/h	Isolated yield/%
3a	C_6H_5	CN	8	95
3b	4-$CH_3C_6H_4$	CN	8	73
3c	4-FC_6H_4	CN	10	93
3d	2-ClC_6H_4	CN	10	89
3e	3,4-$OCH_2OC_6H_3$	CN	10	90
3f	2,4-$Cl_2C_6H_3$	CN	10	92
3g	3,4-$(CH_3O)_2C_6H_3$	CN	10	89
3h	3-$NO_2C_6H_4$	CN	10	88
3i	C_6H_5	CO_2Et	8	90
3j	4-FC_6H_4	CO_2Et	6	89
3k	4-$CH_3C_6H_4$	CO_2Et	6	80
3l	4-ClC_6H_4	CO_2Et	8	93
3m	4-$CH_3OC_6H_4$	CO_2Et	8	89
3n	2,4-$Cl_2C_6H_3$	CO_2Et	10	89
3o	2-$NO_2C_6H_4$	CO_2Me	6	88
3p	5-Cl-2-$NO_2C_6H_3$	CO_2Me	8	93
3q	C_6H_5	CO_2Me	6	92
3r	4-$CH_3C_6H_4$	CO_2Me	7	93
3s	4-ClC_6H_4	CO_2Me	7	97

were carried out on a Perkin-Elmer 2400 II elemental analyser. X-ray diffraction was recorded using a Siemens P4 diffractometer.

General procedure for the synthesis of 2-amino-4-aryl-4H,5H-pyrano[3,2-c][1]benzopyran-5-one derivatives (**3**): A mixture of the substituted cinnamonitrile **1** (2 mmol), 4-hydroxycoumarin **2** (2 mmol) and TEBA (0.1 g) in H_2O (10 ml) was stirred for 6–10 h at 90 °C, then cooled to room temperature. The solid material formed was collected by filtration, washed with water and recrystallised from DMF/H_2O to give pure **3**.

2-Amino-5-oxo-4-phenyl-4H,5H-pyrano[3,2-c][1]benzopyran-3-carbonitrile (**3a**): m.p. 240–242 °C (Lit.[11] m.p. 242 °C).

2-Amino-4-(4-methylphenyl)-5-oxo-4H,5H-pyrano[3,2-c][1]benzopyran-3-carbonitrile (**3b**): m.p. 254–255 °C (Lit.[11] m.p. 255 °C). 2-Amino-4-(4-fluorophenyl)-5-oxo-4H,5H-pyrano[3,2-c][1] benzopyran-3-carbonitrile (**3c**): m.p. 260–262 °C. IR: ν/cm^{-1} 3380, 3191, 2195, 1716, 1678, 1639, 1605, 1507, 1494, 1460, 1379, 1225, 1213, 1173, 1157, 1114, 1061, 956, 905, 850, 757. ^{1}H NMR (DMSO-d_6): δ 4.49 (1H, s, CH), 7.11–7.15 (2H, m, ArH), 7.30–7.33 (2H, m, ArH), 7.41 (2H, s, NH_2), 7.45–7.52 (2H, m, ArH), 7.70–7.74 (1H, m, ArH), 7.90 (1H, d, *J* = 7.2 Hz, ArH). Anal. calcd for $C_{19}H_{11}FN_2O_3$: C 68.26, H 3.32, N 8.38; found C 68.19, H 3.41, N 8.52 %.

2-Amino-4-(2-chlorophenyl)-5-oxo-4H,5H-pyrano[3,2-c][1]benzopyran-3-carbonitrile (**3d**): m.p. 266–268 °C. IR: ν/cm^{-1}: 3401, 3180, 2200, 1710, 1675, 1636, 1602, 1457, 1380, 1328, 1306, 1270, 1259, 1212, 1173, 1112, 1062, 957, 904, 755. ^{1}H NMR (DMSO-d_6): δ 4.98 (1H, s, CH), 7.27–7.31 (3H, m, ArH), 7.42 (2H, s, NH_2), 7.47–7.53 (3H, m, ArH), 7.71–7.75 (1H, m, ArH), 7.91 (1H, d, *J* = 7.6 Hz, ArH). Anal. calcd for $C_{19}H_{11}ClN_2O_3$: C 65.06, H 3.16, N 7.99; found C 65.28, H 3.03, N 8.05 %.

2-Amino-4-(3,4-methylenedioxyphenyl)-5-oxo-4H,5H-pyrano[3,2-c][1]benzopyran-3-carbonitrile (**3e**): m.p. 244–246 °C. IR: ν/cm^{-1} 3399, 3318, 2191, 1705, 1690, 1607, 1495, 1383, 1361, 1257, 1235, 1067, 1036, 770. ^{1}H NMR (DMSO-d_6): δ 4.39 (1H, s, CH), 5.98 (2H, s, OCH_2O), 6.72–6.74 (1H, m, ArH), 6.82 (2H, s, ArH), 7.36 (2H, s, NH_2), 7.45–7.51 (2H, m, ArH), 7.69–7.73 (1H, m, ArH), 7.89 (1H, d, *J* = 8.4 Hz, ArH). Anal. calcd for $C_{20}H_{12}N_2O_5$: C 66.67, H 3.36, N 7.77; found C 66.86, H 3.21, N 7.89 %.

2-Amino-4-(2,4-dichlorophenyl)-5-oxo-4H,5H-pyrano[3,2-c][1]benzopyran-3-carbonitrile (**3f**): m.p. 248–250 °C. IR: ν/cm^{-1} 3463, 3297, 2200, 1716, 1674, 1631, 1608, 1590, 1470, 1376, 1321, 1210, 1172, 1111, 1062, 956, 845, 762. ^{1}H NMR (DMSO-d_6): δ: 4.98 (1H, s, CH), 7.34–7.41 (2H, m, ArH), 7.47–7.53 (4H, m, NH_2+ArH), 7.59 (1H, s, ArH), 7.72–7.75 (1H, m, ArH), 7.90 (1H, d, *J* = 7.2 Hz, ArH). Anal. calcd for $C_{19}H_{10}Cl_2N_2O_3$: C 59.24, H 2.62 N 7.27; found C 59.38, H 2.46, N 7.34 %.

2-Amino-4-(3,4-dimethoxyphenyl)-5-oxo-4H,5H-pyrano[3,2-c][1]benzopyran-3-carbonitrile (**3g**): m.p. 232–234 °C. IR: ν/cm^{-1} 3373, 3218, 2193, 1722, 1675, 1605, 1514, 1453, 1418, 1378, 1267, 1232, 1142 1051, 1024, 958, 765. ^{1}H NMR (DMSO-d_6): δ 3.72 (6H, s, 2 × CH_3O), 4.41 (1H, s, CH), 6.74 (1H, d, *J* = 8.4 Hz, ArH), 6.85–6.89 (2H, m, ArH), 7.34 (2H, s, NH_2), 7.45–7.51 (2H, m, ArH), 7.69–7.73 (1H, m, ArH), 7.90 (1H, d, *J* = 7.2 Hz, ArH). Anal. calcd for $C_{21}H_{16}N_2O_5$: C 67.02, H 4.28, N 7.44; found C 67.21, H 4.16, N 7.60 %.

2-Amino-4-(3-nitrophenyl)-5-oxo-4H,5H-pyrano[3,2-c][1]benzopyran-3-carbonitrile (**3h**): m.p. 254–255 °C. IR: ν/cm^{-1} 3325, 3183, 2199, 1717, 1674, 1606, 1528, 1377, 1346, 1259, 1172, 1111, 1055, 957, 764, 708. ^{1}H NMR (DMSO-d_6): δ 4.48 (1H, s, CH), 7.46–7.54 (4H, m, NH_2+ArH), 7.61–7.65 (1H, m, ArH), 7.72–7.75 (1H, m, ArH), 7.81 (1H, d, *J* = 8.4 Hz, ArH), 7.91–7.95 (2H, m, ArH), 8.12 (1H, d, *J* = 8.4 Hz, ArH). Anal. calcd for $C_{19}H_{11}N_3O_5$: C 63.16, H 3.07, N 11.63; found C 63.28, H 2.96, N 11.77 %.

Ethyl 2-amino-5-oxo-4-phenyl-4H,5H-pyrano[3,2-c][1]benzopyran-3-carboxylate (**3i**): m.p. 202–203 °C (Lit.[11] m.p. 196 °C). IR: ν/cm^{-1} 3416, 3309, 1688, 1670, 1611, 1544, 1493, 1376, 1279, 1253, 1194, 1085, 1055, 955, 760, 703. ^{1}H NMR (DMSO-d_6): δ 1.11 (3H, t, *J* = 7.2 Hz, CH_3), 3.99 (2H, q, *J* = 7.2 Hz, CH_2O), 4.70 (1H, s, CH), 7.13–7.16 (1H, m, ArH), 7.23–7.24 (4H, m, ArH), 7.44–7.51 (2H, m, NH_2), 7.68–7.72 (1H, m, ArH), 7.82 (2H, s, NH_2), 7.98 (1H, d, *J* = 8.4 Hz, ArH). Anal. calcd for $C_{21}H_{17}NO_5$: C 69.41, H 4.72, N 3.85; found C 69.38, H 4.84, N 3.69 %.

Ethyl 2-amino-(4-fluorophenyl)-5-oxo-4H,5H-pyrano [3,2-c][1]benzopyran-3-carboxylate (**3j**): m.p. 222 –224 °C. IR: ν/cm^{-1} 3500, 3300, 1720, 1690, 1660, 1610, 1530, 1490, 1290, 1200, 1175, 1100, 1055, 955, 845, 750. ^{1}H NMR (DMSO-d_6): δ 1.10 (3H, t, *J* = 7.2 Hz, CH_3), 3.99 (2H, q, *J* = 7.2 Hz, CH_2O), 4.69 (1H, s, CH), 7.03–7.08 (2H, m, ArH), 7.24–7.28 (2H, m, ArH), 7.44–7.52 (2H, m, ArH), 7.69–7.72 (1H, m, ArH), 7.86 (2H, s, NH_2), 7.97 (1H, d, *J* = 7.6 Hz, ArH). Anal. calcd for $C_{21}H_{16}FNO_5$: C 66.14, H 4.23, N 3.67; found C 66.35, H 4.08, N 3.79 %.

Ethyl 2-amino-4-(4-methylphenyl)-5-oxo-4H,5H-pyrano [3,2-c][1]benzopyran-3-carboxylate (**3k**): m.p. 191 –192 °C (Lit.[11] m.p. 190 °C).

Ethyl 2-amino-4-(4-chlorophenyl)-5-oxo-4H,5H-pyrano [3,2-c][1]benzopyran-3-carboxylate (**3l**): m.p. 191–192 °C (Lit.[11] m.p. 192 °C).

Ethyl 2-amino-4-(4-methoxyphenyl)-5-oxo-4H,5H-pyrano [3,2-c][1]benzopyran-3-carboxylate (**3m**): m.p. 160–162 °C (Lit.[11] m.p. 160 °C).

Ethyl 2-amino-4-(2,4-dichlorophenyl)-5-oxo-4H,5H-pyrano [3,2-c][1]benzopyran-3-carboxylate (**3n**): m.p. 197–198 °C. IR: ν/cm^{-1} 3415, 3293, 1721, 1691, 1655, 1611, 1522, 1491, 1325, 1279, 1251, 1197, 1086, 1048, 1027, 953, 860, 758. ^{1}H NMR (DMSO-d_6): δ 1.06 (3H, t, *J* = 7.2 Hz, CH_3), 3.96 (2H, q, *J* = 7.2 Hz, CH_2O), 5.06 (1H, s, CH), 7.29–7.34 (2H, m, ArH), 7.44–7.52 (3H, m, ArH), 7.69–7.73 (1H, m, ArH), 7.94–7.98 (3H, m, NH_2+ArH). Anal. calcd for $C_{21}H_{15}Cl_2NO_5$: C 58.35, H 3.50, N 3.24; found C 58.54, H 3.37, N 3.46 %.

Methyl 2-amino-4-(2-nitrophenyl)-5-oxo-4H,5H-pyrano [3,2-c][1]benzopyran-3-carboxylate (**3o**): m.p. 211 –212 °C. IR: ν/cm^{-1} 3411, 3278, 1710, 1690, 1613, 1531, 1500, 1352, 1280, 1183, 1040, 968, 830, 768. ^{1}H NMR (DMSO-d_6): δ 3.44 (3H, s, CH_3O), 5.63 (1H, s, CH), 7.44–7.53 (5H, m, ArH), 7.70–7.75 (1H, m, ArH), 7.91 (1H, d, *J* = 8.8 Hz, ArH), 7.99 (1H, dd, J_1 = 1.6 Hz, J_2 = 8.0 Hz, ArH), 8.03 (2H, s, NH_2). Anal. calcd for $C_{20}H_{14}N_2O_7$: C 60.92, H 3.58, N 7.10; found C 61.04, H 3.41, N 6.95 %.

Methyl 2-amino-4-(5-chloro-2-nitrophenyl)-5-oxo-4H,5H-pyrano [3,2-c][1]benzopyran-3-carboxylate (**3p**): m.p. 225–227 °C. IR: ν/cm^{-1} 3452, 3344, 1721, 1690, 1665, 1618, 1521, 1445, 1378, 1198, 1091, 968, 840, 748. ^{1}H NMR (DMSO-d_6): δ 3.44 (3H, s, CH_3O), 5.63 (1H, s, CH), 7.38–7.42 (1H, m, ArH), 7.43–7.47 (1H, m, ArH), 7.49–7.53 (1H, m, ArH), 7.55–7.59 (1H, m, ArH), 7.70–7.74 (1H, m, ArH), 7.85 (1H, dd, J_1 = 1.2 Hz, J_2 = 8.0 Hz, ArH), 7.98 (2H, s, NH_2), 8.00 (1H, dd, J_1 = 1.6 Hz, J_2 = 8.0 Hz, ArH). Anal. calcd for $C_{20}H_{13}ClN_2O_7$: C 56.02, H 3.06, N 6.53; found C 56.27, H 2.94, N 6.59 %.

Methyl 2-amino-3-cyano-4-phenyl-5-oxo-4H,5H-pyrano[3,2-c][1]benzopyran-3-carboxylate (**3q**): m.p. 211–213 °C. IR: ν/cm^{-1} 3431, 3298, 1721, 1690, 1613, 1510, 1490, 1373, 1280, 1183, 1086, 1040, 840, 743, 702. ^{1}H NMR ($CDCl_3$): δ 3.64 (3H, s, CH_3O), 4.93 (1H, s, CH), 6.45 (2H, s, NH_2), 7.13–7.18 (1H, m, ArH), 7.22–7.27 (2H, m, ArH), 7.28–7.38 (4H, m, ArH), 7.52–7.56 (1H, m, ArH), 7.81–7.83 (1H, m ArH). Anal. calcd for $C_{20}H_{15}NO_5$: C 68.76, H 4.33, N 4.01; found C 68.92, H 4.09, N 3.97 %.

Methyl 2-amino-4-(4-methylphenyl)-5-oxo-4H,5H-pyrano [3,2-c][1]benzopyran-3-carboxylate (**3r**): m.p. 204–206 °C. IR: ν/cm^{-1} 3406, 3293, 1700, 1690, 1650, 1540, 1500, 1445, 1383, 1285, 1194, 1081, 840, 748. ^{1}H NMR ($CDCl_3$): δ 2.27 (3H, s, CH_3), 3.64 (3H, s, CH_3O), 4.91 (1H, s, CH), 6.42 (2H, s, NH_2), 7.05 (2H, d, *J* = 8.0 Hz, ArH), 7.25 (2H, d, *J* = 8.0 Hz, ArH), 7.29–7.34 (2H, m, ArH), 7.52–7.56 (1H, m, ArH), 7.82 (1H, dd, J_1 = 1.6 Hz, J_2 = 8.0 Hz, ArH). Anal. calcd for $C_{21}H_{17}NO_5$: C 69.41, H 4.72, N 3.85; found C 69.58, H 4.53, N 3.93 %.

Methyl 2-amino-4-(4-chlorophenyl)-5-oxo-4H,5H-pyrano [3,2-c][1]benzopyran-3-carboxylate (**3s**): m.p. 227–229 °C. IR: ν/cm^{-1} 3380, 3268, 1726, 1700, 1650, 1614, 1520, 1490, 1440, 1360, 1280, 1188, 1081, 1050, 840, 748. ^{1}H NMR ($CDCl_3$): δ 3.64 (3H, s, CH_3O), 4.90 (1H, s, CH), 6.48 (2H, s, NH_2), 7.21 (2H, d, *J* = 8.4 Hz, ArH), 7.27 (2H, d, *J* = 8.4 Hz, ArH), 7.31–7.35 (2H, m, ArH), 7.54–7.58 (1H, m, ArH), 7.82 (1H, dd, J_1 = 1.6 Hz, J_2 = 8.0 Hz, ArH); Anal. calcd for $C_{20}H_{14}ClNO_5$: C 62.59, H 3.68, N 3.65; found C 63.08, H 3.51, N 3.79 %.

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