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# (2-CHLORO-2-NITROETHENYL)BENZENES AS SYNTHONS: A GENERAL METHOD FOR THE PREPARATION OF 2,3-DIHYDRO-2-NITRO-3-PHENYL-4*H*-FURO[3,2-c][1]BENZOPYRAN-4-ONES AND 3-PHENYL-4*H*-FURO[3,2-c][1]BENZOPYRAN-4-ONES

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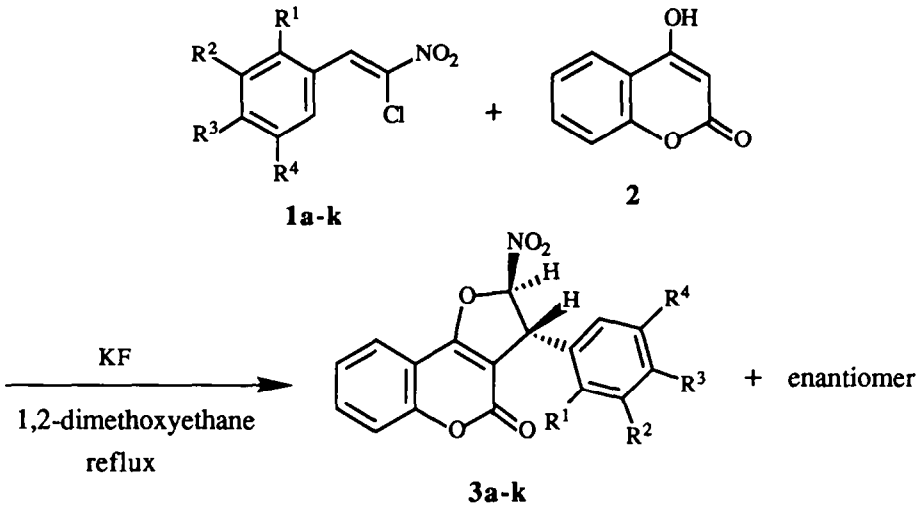
**Abstract**: we describe a convenient and general method for the preparation of 2,3-dihydro-2-nitro-3-phenyl-4*H*-furo[3,2-c][1]benzopyran-4-ones from 4-hydroxycoumarin and (2-chloro-2-nitroethenyl)benzenes in the presence of potassium fluoride. Using the same starting materials and by replacing potassium fluoride with triethylamine the hitherto unknown 3-phenyl-4*H*-furo[3,2-c][1]benzopyran-4-ones are obtained in a one-pot procedure.

In the course of our investigations on the use of (2-chloro-2-nitroethenyl)benzenes in organic synthesis[1-3], we studied the reactions of these compounds with 4-hydroxycoumarin in an attempt to prepare novel furocoumarines with photobiological properties.

We initially carried out the reaction in the presence of potassium fluoride considering that this weak base has been fruitfully used, on various occasions, by Yoshikoshi and co-workers to carry out Michael additions of β-dicarbonyl derivatives with simple nitroolefins giving acylfurans[4,5], tricarbonyl compounds[4,6], 2-phenylthio-2,3-dihydrofurans[7-9] or (hydroxyimino)dihydrofurans[8] depending on the particular reagents and reaction conditions employed.

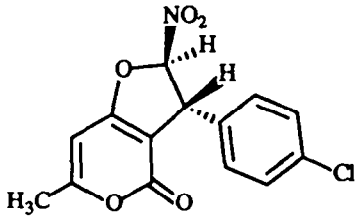
We describe herein the condensation of (2-chloro-2-nitroethenyl)benzenes **1a-k** with 4-hydroxycoumarin **2** under reflux in 1,2-dimethoxyethane in the presence of potassium fluoride giving good yields of 2,3-dihydro-2-nitro-3-phenyl-4*H*-furo[3,2-c][1]benzopyran-4-ones **3a-k**.These novel furobenzopyrans were obtained in the exclusively *trans* configuration.




| 1,3,5 | $R^1$ | $R^2$ | $R^3$ | $R^4$ |
|---|---|---|---|---|
| **a** | H | H | H | H |
| **b** | Cl | H | H | H |
| **c** | H | Cl | H | H |
| **d** | H | H | Cl | H |
| **e** | $NO_2$ | H | H | H |
| **f** | H | $NO_2$ | H | H |
| **g** | H | H | $NO_2$ | H |
| **h** | $OCH_3$ | H | H | H |
| **i** | H | $OCH_3$ | H | H |
| **j** | H | H | $OCH_3$ | H |
| **k** | H | $OCH_3$ | $OCH_3$ | $OCH_3$ |

This reaction was performed with various substrates bearing electron-withdrawing or electron-donating substituents on the aromatic ring, and was found to be quite general (Table1). Moreover, we also checked that this condensation takes place with α-pyrones hydroxylated in the 4-position. Thus, the representative chlorinated compound **1d** reacts with

4-hydroxy-6-methyl-2-pyrone to give 3-(4-chlorophenyl)-2,3-dihydro-6-methyl-2-nitro-4*H*-furo[3,2-c][1]pyran-4-one (**4**) (Table 1).




**4**

The spectral data for compounds **3a-k** and **4** are listed in Table 2. The weak $^3J$ coupling constants (2.1-3.0 Hz) for the neighbouring protons $H_2$ and $H_3$ in the $^1H$ NMR spectra indicates a *trans* configuration. A complementary crystallographic study of the 3-(3-chlorophenyl)-2,3-dihydro-2-nitro-4*H*-furo[3,2-c][1]benzopyran-4-one(**3c**), selected as a representative of its class of compounds, confirms the *trans* configuration as illustrated by the ORTEP diagram depicted in figure 1.

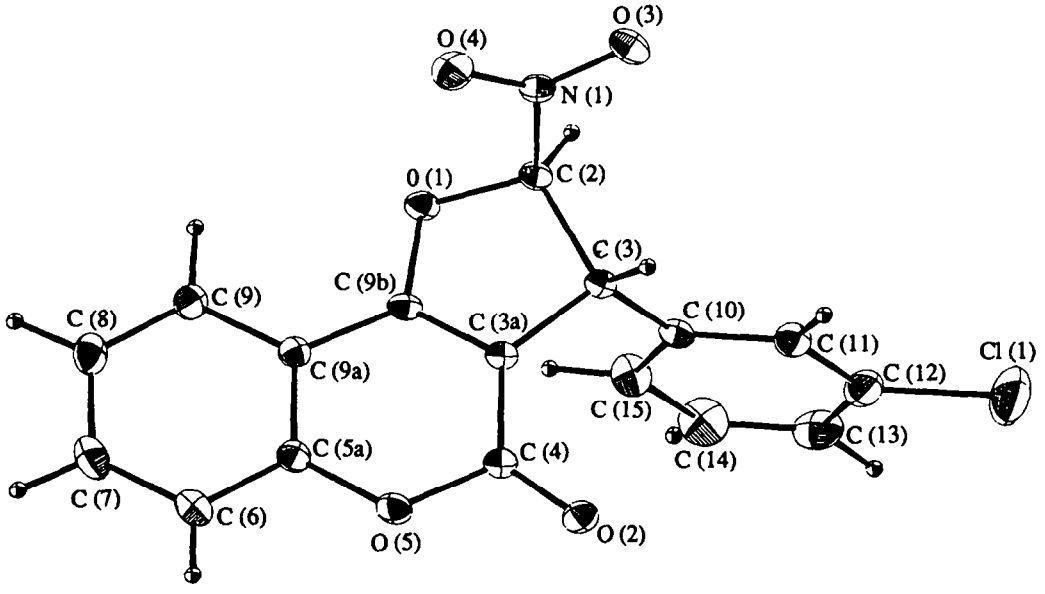



Figure 1. An ORTEP stereoview of the molecule of **3c**.
The thermal ellipsoids are drawn at a 30% probability level.

**Table 1**: Preparation of compounds **3a-k** and **4**.

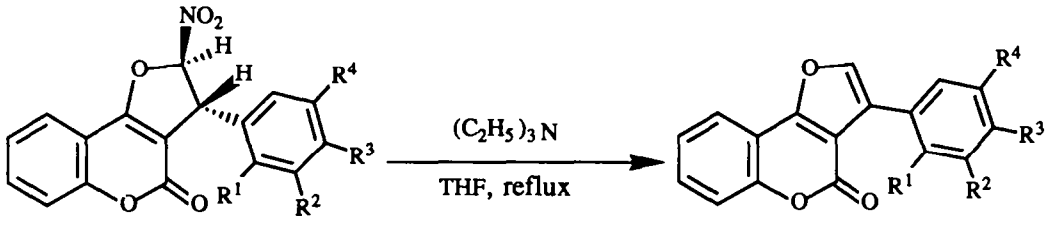
| Compound | Reaction time (h) | Yield[a] (%) | melting point (°C) ( recrystallization solvent) | Molecular formula (molecular weight) | Analysis (%) Calculated / (found) C | H | N |
|---|---|---|---|---|---|---|---|
| **3a** | 16 | 86 | 144-144.5 (cyclohexane) | $C_{17}H_{11}NO_5$ (309.3) | 66.02 (65.90) | 3.58 (3.67) | 4.53 (4.45) |
| **3b** | 10 | 76 | 202-203 (cyclohexane/benzene) | $C_{17}H_{10}ClNO_5$ (343.7) | 59.40 (59.49) | 2.93 (3.03) | 4.07 (3.98) |
| **3c** | 7 | 90 | 141-142 (cyclohexane/benzene) | $C_{17}H_{10}ClNO_5$ (343.7) | 59.40 (59.59) | 2.93 (3.02) | 4.07 (3.97) |
| **3d** | 14 | 88 | 164-165 (cyclohexane/benzene) | $C_{17}H_{10}ClNO_5$ (343.7) | 59.40 (59.32) | 2.93 (2.99) | 4.07 (4.02) |
| **3e** | 20 | 73 | 223-224 (benzene) | $C_{17}H_{10}N_2O_7$ (354.3) | 57.64 (57.62) | 2.85 (2.93) | 7.91 (7.86) |
| **3f** | 4 | 70 | 212-214 (benzene/acetonitrile) | $C_{17}H_{10}N_2O_7$ (354.3) | 57.64 (57.81) | 2.85 (2.83) | 7.91 (7.88) |
| **3g** | 5 | 35 | 219-221 (trichloroethylene/acetonitrile) | $C_{17}H_{10}N_2O_7$ (354.3) | 57.64 (57.71) | 2.85 (2.93) | 7.91 (7.83) |
| **3h** | 30 | 93 | 180-181 (cyclohexane/benzene) | $C_{18}H_{13}NO_6$ (339.3) | 63.72 (63.59) | 3.86 (3.77) | 4.13 (4.08) |
| **3i** | 10 | 83 | 174-175 (cyclohexane/benzene) | $C_{18}H_{13}NO_6$ (339.3) | 63.72 (63.91) | 3.86 (3.93) | 4.13 (4.06) |
| **3j** | 30 | 86 | 159-159.5 (cyclohexane/benzene) | $C_{18}H_{13}NO_6$ (339.3) | 63.72 (63.46) | 3.86 (3.76) | 4.13 (4.04) |
| **3k** | 24 | 93 | 197-198[b] (benzene/heptane) | $C_{20}H_{17}NO_8$ (399.4) | 60.15 (60.03) | 4.29 (4.21) | 3.51 (3.48) |
| **4** | 8 | 81 | 161-161.5 (cyclohexane/benzene) | $C_{14}H_{10}ClNO_5$ (307.7) | 54.65 (54.48) | 3.28 (3.37) | 4.55 (4.48) |

[a] Yield of pure recrystallized product [b] Allotropic change at 190-192 °C

**Table 2**: Spectral data of compounds **3a-k** and **4**.

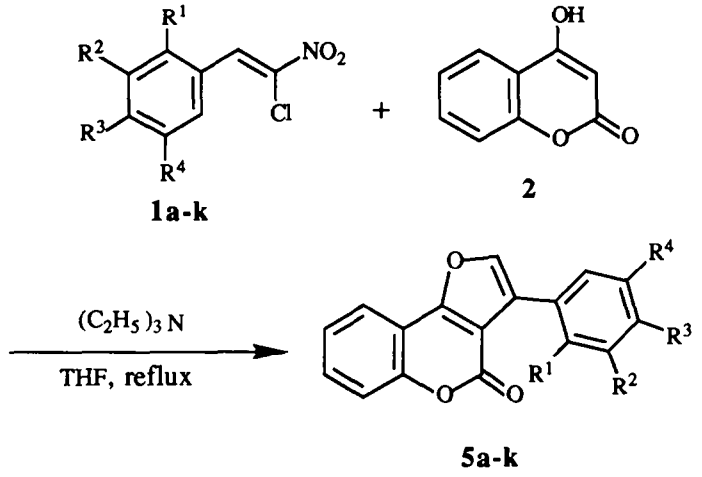
| Compound | IR $\nu_{C=O}$ ($cm^{-1}$) | MS (70 eV) *m/z* (%) | $^1$H-NMR ($CDCl_3$/TMS) δ, J (Hz) |
|---|---|---|---|
| **3a** | 1734 | 309 | 4.95 (br d, 1H, J = 2.1); 6.22 (d, 1H, J = 2.1); 7.08-7.54 (m, 7H arom); 7.55-7.73 (m, 1H arom); 7.74-7.96 (m, 1H arom) |
| **3b** | 1734 | 343, 345 | 5.42 (br d, 1H, J = 2.4); 6.24 (d, 1H, J = 2.4); 6.95-7.58 (m, 6H arom); 7.59-7.76 (m, 1H arom); 7.77-7.94 (m, 1H arom) |
| **3c** | 1735 | 343, 345 | 4.91 (br d, 1H, J = 2.3); 6.19 (d, 1H, J = 2.3); 7.10-7.47 (m, 5H arom); 7.48 (br s, 1H arom); 7.57-7.77 (m, 1H arom); 7.78-7.97 (m, 1H arom) |
| **3d** | 1734 | 343, 345 | 4.91 (br d, 1H, J = 2.4); 6.18 (d, 1H, J = 2.4); 7.07-7.52 (m, 6H arom); 7.58-7.74 (m, 1H arom); 7.75-7.95 (m, 1H arom) |
| **3e** | 1734 | 354 | 5.66 (br d, 1H, J = 3.0); 6.37 (d, 1H, J = 3.0); 6.98-7.93 (m, 7H arom); 8.03-8.22 (m, 1H arom) |
| **3f** | 1736 | 354 | 5.07 (br d, 1H, J = 2.4); 6.25 (d, 1H, J = 2.4); 7.20-7.80 (m, 5H arom); 7.81-7.98 (m, 1H arom); 8.07-8.33 (m, 2H arom) |
| **3g** | 1736 | 354 | 5.06 (br d, 1H, J = 2,4); 6.23 (d, 1H, J = 2.4); 7.32-7.59 (m, 2H arom); 7.48 and 8.27 (AA'BB' system, 4H arom); 7.63-7.79 (m, 1H arom); 7.80-7.99 (m, 1H arom) |
| **3h** | 1733 | 339 | 3.84 (s, 3H); 5.21 (br d, 1H, J = 2.7); 6.25 (d, 1H, J = 2.7); 6.81-7.14 (m, 3H arom); 7.23-7.53 (m, 3H arom); 7.75-7.72 (m, 1H arom); 7.73-7.90 (m, 1H arom) |
| **3i** | 1734 | 339 | 3.73 (s, 3H); 4.84 (br d, 1H, J = 2.1); 6.15 (d, 1H, J = 2.1); 6.70-6.90 (m, 3H arom); 7.13-7.38 (m, 2H arom); 7.42 (br s, 1H arom); 7.50-7.68 (m, 1H arom); 7.69-7.91 (m, 1H arom) |
| **3j** | 1734 | 339 | 3.78 (s, 3H); 4.89 (br d, 1H, J = 2.1); 6.18 (d, 1H, J = 2.1); 6.89 and 7.18 (AA'BB' system, 4H); 7.27-7.53 (m, 2H arom); 7.57-7.74 (m, 1H arom); 7.75-7.96 (m, 1H arom) |
| **3k** | 1734 | 399 | 3.82 (s, 9H); 4.88 (br d, 1H, J = 2.4); 6.22 (br d, 1H, J = 2.4); 6.43 (s, 2H arom); 7.28-7.57 (m, 2H arom); 7.58-7.76 (m, 1H arom); 7.78-7.98 (m, 1H arom) |
| **4** | 1737 | 307, 309 | 2.37 (br s, 3H); 4.75 (br d, 1H, J = 2.3); 6.01 (d, 1H, J = 2.3); 6.25 (br s, 1H); 7.15 and 7.37 (AA'BB' system, 4H arom) |

In further experiments in which we refluxed compounds **3a-k** with triethylamine in tetrahydrofuran, we obtained an almost quantitative yield of the corresponding denitrified compounds **5a-k** according to the following reaction scheme:




**3a-k** **5a-k**

This indicated that (2-chloro-2-nitroethenyl)benzenes **1a-k** could be condensed directly with 4-hydroxycoumarin (**2**) by refluxing in tetrahydrofuran in the presence of triethyl amine to give very good yields of 3-phenyl-4*H*-furo[3,2-c][1]benzopyran-4-ones **5a-k** in a one-flask process. These compounds have not previously been described.




**1a-k** **2**

**5a-k**

In this case, the reaction was also found to be quite general. Under identical conditions, 4-hydroxy-6-methyl-2-pyrone afforded 3-(4-chlorophenyl)-6-methyl-4*H*-furo[3,2-c]pyran-

**Table 3**: Preparation of compounds **4a-k** and **6**.

| Compound | Reaction time (h) | Yield[a] (%) | melting point (°C) ( recrystallization solvent) | Molecular formula (molecular weight) | Analysis (%) Calculated / (found) C | H | N |
|---|---|---|---|---|---|---|---|
| **5a** | 2 | 89 | 171.5-172.5 (benzene/heptane) | $C_{17}H_{10}O_3$ (262.3) | 77.86 (77.76) | 3.84 (3.75) | - ( - ) |
| **5b** | 3 | 83 | 192-193 (cyclohexane/benzene) | $C_{17}H_9ClO_3$ (296.7) | 68.82 (68.65) | 3.06 (2.98) | - ( - ) |
| **5c** | 3 | 89 | 177-178 (isopropyl ether/benzene) | $C_{17}H_9ClO_3$ (296.7) | 68.82 (68.60) | 3.06 (3.10) | - ( - ) |
| **5d** | 4 | 90 | 184-185 (cyclohexane/benzene) | $C_{17}H_9ClO_3$ (296.7) | 68.82 (68.89) | 3.06 (3.02) | - ( - ) |
| **5e** | 0.5 | 89 | 231-232.5 (acetonitrile/trichloroethylene) | $C_{17}H_9NO_5$ (307.3) | 66.45 (66.25) | 2.95 (2.86) | 4.56 (4.51) |
| **5f** | 0.5 | 92 | 256-258 (1,2-dichloroethane/trichloroethylene) | $C_{17}H_9NO_5$ (307.3) | 66.45 (66.65) | 2.95 (2.94) | 4.56 (4.49) |
| **5g** | 0.25 | 92 | 255-256 (nitromethane) | $C_{17}H_9NO_5$ (307.3) | 66.45 (66.72) | 2.95 (2.93) | 4.56 (4.44) |
| **5h** | 14 | 82 | 134-134.5 (cyclohexane) | $C_{18}H_{12}O_4$ (292.3) | 73.97 (73.88) | 4.14 (4.03) | - ( - ) |
| **5i** | 2 | 88 | 133-134 (benzene/heptane) | $C_{18}H_{12}O_4$ (292.3) | 73.97 (73.97) | 4.14 (4.06) | - ( - ) |
| **5j** | 9 | 84 | 149-149.5 (benzene/heptane) | $C_{18}H_{12}O_4$ (292.3) | 73.97 (74.12) | 4.14 (4.14) | - ( - ) |
| **5k** | 3 | 90 | 167-168 (benzene/heptane) | $C_{20}H_{16}O_6$ (352.3) | 68.18 (68.13) | 4.58 (4.53) | - ( - ) |
| **6** | 2 | 83 | 132-133[b] (benzene/heptane) | $C_{14}H_9ClO_3$ (260.7) | 64.51 (64.67) | 3.48 (3.38) | - ( - ) |

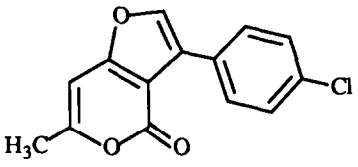
[a] Yield of pure recrystallized product [b] Allotropic change at 118-120 °C

**Table 4**: Spectral data of compound **5a-k** and **6**.

| Compound | IR<br>$\nu_{C=O}$ ($cm^{-1}$) | MS (70 eV)<br>*m/z* (%) | $^1$H-NMR ($CDCl_3$/TMS)<br>δ, J (Hz) |
|---|---|---|---|
| **5a** | 1741 | 262 | 7.23-7.58 (m, 6H arom); 7.73 (s, 1H); 7.62-7.98 (m, 3H arom) |
| **5b** | 1742 | 296, 298 | 7.22-7.65 (m, 7H arom); 7.76 (s, 1H); 7.82-7.99 (m, 1H arom) |
| **5c** | 1741 | 296, 298 | 7.22-7,78 (m, 7H arom); 7.73 (s, 1H); 7.81-8.00 (m, 1H arom) |
| **5d** | 1740 | 296, 298 | 7.23-7.58 (m, 3H arom); 7.36 and 7.68 (AA'BB' system, 4H arom); 7.73 (s, 1H); 7.80-7.97 (m, 1H arom) |
| **5e** | 1742 | 307 | 7.29-7.80 (m, 6H arom); 7.71 (s, 1H); 7.81-8.03 (m, 1H arom); 8.12-8.32 (m, 1H arom) |
| **5f** | 1746[a] | 307 | 7.38-7.77 (m, 4H arom); 7.92-8.06 (m, 1H arom); 7.95 (s, 1H); 8.20-8.38 (m, 2H arom); 8.61-8.69 (m, 1H arom) |
| **5g** | 1747[a] | 307 | 7.27-7.67 (m, 3H arom); 7.87 (s, 1H); 7.86-7.99 (m, 1H arom); 7.96 and 8.29 (AA'BB' system, 4H arom) |
| **5h** | 1741 | 292 | 3.85 (s, 3H); 6.87-7.15 (m, 2H arom); 7.16-7.72 (m, 5H arom); 7.80 (s, 1H); 7.75-7.98 (m, 1H arom) |
| **5i** | 1741 | 292 | 3,87 (s, 3H); 6.78-7.06 (m, 1H arom); 7.18-7.65 (m, 6H arom); 7.75 (s, 1H); 7.81-7.98 (m, 1H arom) |
| **5j** | 1740 | 292 | 3.83 (s, 3H); 6.95 and 7.68 (AA'BB' system, 4H arom); 7.22-7.57 (m, 3H arom); 7.67 (s, 1H); 7.80-7.98 (m, 1H arom) |
| **5k** | 1736 | 352 | 3.88 (s, 3H); 3.92 (s, 6H); 7.05 (s, 2H arom); 7.28-7.68 (m, 3H arom); 7.76 (s, 1H); 7.82-7.98 (m, 1H arom) |
| **6** | 1742 | 260, 262 | 7.05 (d, 3H, J = 0.9); 6.40 (d, 1H, J = 0.9); 7.56 (s, 1H); 7.35 and 7.68 (AA'BB' system, 4H arom) |

(a): KBr pellet.

4-one **6** by condensation with 1-chloro-4-(2-chloro-2-nitroethenyl) benzene (**1d**):



**6**

The yields and physicochemical parameters of compounds **5a-k** and **6** are reported in Table 3 and 4. It should be noted that lower yields of the furobenzopyranones **3** and **5** were obtained by using other solvents (*e.g.* acetonitrile, toluene).

## EXPERIMENTAL

Melting points were measured on a Köfler hot-stage apparatus and are uncorrected. Infrared spectra were recorded on a Perkin-Elmer 1710 spectrophotometer either as chloroform solutions or KBr discs. Electron impact mass spectra were obtained using a Nermag Ribermag R10-10C spectrometer at 70 eV. $^1$H NMR spectra were determined either at 90 MHz with a Varian EM 390 spectrometer or, in the case of difficultly soluble products, at 270 MHz using a Bruker HX270 apparatus, for deuteriochloroform solutions with tetramethylsilane as internal reference. Microanalysis were performed by the "Service d'Analyse du C.N.R.S., Vernaison". Silica gel (Merck, 230-400 Mesh ASTM) was used for column chromatography. Commercially available reagents and solvents were used without further purification. Starting (2-chloro-2-nitroethenyl)benzenes **1a-k** were prepared according to a previously reported method[3].

*General procedure for the synthesis of* 2,3-*dihydro*-2-*nitro*-3-*phenyl*-4*H*-*furo*[3,2-c][1]*benzopyran*-4-*ones* **3a-k**:

A 50 mL round-bottomed flask fitted with a condenser is charged with the appropriate (2-chloro-2-nitroethenyl)benzene **1a-k** (5 mmol), 4-hydroxycoumarin (**2**, 1.62g, 10 mmol), anhydrous 1,2-dimethoxyethane (25 mL) and potassium fluoride (0.58 g, 10 mmol). The reaction flask is placed in an oil bath, and the mixture is smoothly refluxed with stirring under inert atmosphere for the required times indicated in Table 1. Rotary evaporation of the solvent *in vacuo* leaves a residue which is taken up with dichloromethane (50 mL). An

insoluble material is filtered off and thoroughly rinsed with several portions of dichloromethane. The filtrate is evaporated to dryness, then column-chromatographed on silica gel [100g, eluting with pure dichloromethane for **3a-d** and **3h-k**, a mixture dichloromethane/cyclohexane (65:35) for **3e**, or a mixture dichloromethane/ cyclohexane (75:25) for **3f** and **3g**]. Removal of the solvents under reduced pressure followed by recrystallization gives the analytically pure products **3a-k** (Table 1).

*General procedure for the synthesis of* 3-*phenyl*-4*H*-*furo*[3,2-c] [1]*benzopyran*-4-*ones* **5a-k**:

The appropriate (2-chloro-2-nitroethenyl)benzene **1a-k** (10 mmol), 4-hydroxycoumarin (**2**, 1.78g, 11 mmol), dry tetrahydrofuran (50 mL) and anhydrous triethylamine (5.06g, 6.97 mL, 50 mmol) are placed in a 100 mL round-bottomed flask fitted with a condenser and a drying tube. The mixture is gently refluxed with stirring, using an oil bath, for the required times reported in Table 3. Rotary evaporation under reduced pressure of the volatil components leaves a crude material:

- In the cases of **4a-e** and **4h-k** this crude product is directly chromatographed over a silica gel column (150 g, eluent dichloromethane). Removal of the solvent *in vacuo* followed by recrystallization provides analytically pure compounds (Table 3).
- In the cases of **4f** and **4g**, the product is scarcely soluble in dichloromethane. In these instances, the crude material is taken up with a mixture dichloromethane/methanol (50:50, 200 mL), refluxed with vigourous stirring for 1 hour, then allowed to cool to room temperature. The solid is isolated by suction. The filtrate is evaporated, then chromatographed on a silica gel column (150 g, eluent dichloromethane). After removal of the solvent, the resulting solid and the previously filtered product are recrystallized together to afford **4f** or **4g** in the reported yields (Table 3).

The 3-(4-chlorophenyl)-2,3-dihydro-6-methyl-2-nitro-4*H*-furo[3,2-c]pyran-4-one (**4**) and 3-(4-chloro-phenyl)-6-methyl-4*H*-furo[3,2-c]pyran-4-one (**6**) are respectively prepared according to the same procedures (Tables 1 and 3).

*Single crystal X-ray analysis of* **3c**:

Cristallographic and refinement parameters are summarized in Table 5. The data were collected on a Philips PW 1100 diffractometer using graphite-monochromated Mo-K$\alpha$ radiation ( $\lambda$ = 0.71073 Å ). The structure was solved by the Patterson method and subsequent Fourier maps. An absorption correction was applied using the program DIFABS of CRYSTALS[10]. In the final refinement, anisotropic thermal parameters were used for the non-hydrogen atoms and isotropic temperature factors were used for the hydrogen atoms. Least squares refinements were carried out in two blocks. The atoms were corrected from anomalous dispertion. Interatomic bond lenghts and bond angles are listed in tables 6 and 7, respectively[11].

**Table 5**: Crystal and Refinement Parameters for compound **3c**.

| | | |
|---|---|---|
| Molecular formula | | $C_{17}H_{10}ClNO_5$ |
| Molecular weight | | 343.7 |
| Crystal system | | Triclinic |
| Space group | | P-1 |
| a, Å | | 7.507(3) |
| b, Å | | 9.400(3) |
| c, Å | | 12.003(3) |
| α | | 98.15(3) |
| β | | 101.62(3) |
| γ | | 101.17(3) |
| V, Å$^3$ | | 799(1) |
| Z | | 2 |
| ρ calc, g.cm$^{-3}$ | | 1.43 |
| F (000) | | 352 |
| Reflections for lattice parameters | number | 25 |
| | range | 17-18 |
| Temperature, °C | | 18 |
| Crystal size, mm | | 0.70 x 0.60 x 0.55 |
| Radiation | | Mo-Kα |
| Monochromator | | Graphite |
| Scan type | | ω - 2θ |
| Scan width | | 1.6 + 0.34 tan θ |
| θ range, deg | | 1-25 |
| Standard reflections | | two, measured every two hours |
| μ, cm$^{-1}$ | | 2.61 |
| Nb of measured reflections | | 2561 |
| Nb of reflections used $I \geq 3\sigma(I)$ | | 2162 |
| Min and max height in final Δρ, e Å$^{-3}$ | | -0.48 and 0.25 |
| Nb of refined parameters | | 279 |
| $R = [\ \Sigma\|\Delta F\| / \Sigma\|F_o\|]$ | | 0.056 |
| $R_w = [\ \Sigma w(\Delta F)^2 / \Sigma w F_o^2\ ]^{1/2}$ <br> $w = 1.$ | | 0.052 |

**Table 6**: Bond Lenghts (Å) for compound **3c**.

| | | | | | |
|---|---|---|---|---|---|
| Cl (1) | C (12) | 1.729(5) | O (1) | C (2) | 1.407(4) |
| O (1) | C (9b) | 1.377(4) | O (2) | C (4) | 1.209(4) |
| O (3) | N (1) | 1.221(3) | O (4) | N (1) | 1.202(3) |
| O (5) | C (4) | 1.383(4) | O (5) | C (5a) | 1.381(4) |
| N (1) | C (2) | 1.549(4) | C (2) | C (3) | 1.548(4) |
| C (3) | C (3a) | 1.503(4) | C (3) | C (10) | 1.513(4) |
| C (3a) | C (4) | 1.430(4) | C (3a) | C (9b) | 1.337(4) |
| C (5a) | C (6) | 1.373(5) | C (5a) | C (9a) | 1.402(4) |
| C (6) | C (7) | 1.372(6) | C (7) | C (8) | 1.394(6) |
| C (8) | C (9) | 1.370(5) | C (9) | C (9a) | 1.400(5) |
| C (9a) | C (9b) | 1.422(4) | C (10) | C (11) | 1.361(5) |
| C (10) | C (15) | 1.401(5) | C (11) | C (12) | 1.389(6) |
| C (12) | C (13) | 1.388(7) | C (13) | C (14) | 1.343(7) |
| C (14) | C (15) | 1.377(6) | | | |

**Table 7**: Bond Angles (deg.) for compound **3c**.

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| C (9b) | 0 (1) | C (2) | 105.9(2) | C (5a) | O (5) | C (4) | 123.2(2) |
| O (4) | N (1) | O (3) | 125.5(3) | C (2) | N (1) | O (3) | 114.8(3) |
| C (2) | N (1) | O (4) | 119.6(3) | N (1) | C (2) | O (1) | 106.8(3) |
| C (3) | C (2) | O (1) | 108.9(2) | C (3) | C (2) | N (1) | 108.1(2) |
| C (3a) | C (3) | C (2) | 98.4(2) | C (10) | C (3) | C (2) | 114.2(3) |
| C (10) | C (3) | C (3a) | 115.4(3) | C (4) | C (3a) | C (3) | 128.7(3) |
| C (9b) | C (3a) | C (3) | 110.2(3) | C (9b) | C (3a) | C (4) | 121.1(3) |
| O (5) | C (4) | O (2) | 116.9(3) | C (3a) | C (4) | O (2) | 127.6(3) |
| C (3a) | C (4) | O (5) | 115.5(3) | C (6) | C (5a) | O (5) | 117.4(3) |
| C (9b) | C (5a) | O (5) | 121.7(3) | C (9a) | C (5a) | C (6) | 120.9(3) |
| C (7) | C (6) | C (5a) | 119.2(4) | C (8) | C (7) | C (6) | 121.1(4) |
| C (9) | C (8) | C (7) | 120.0(4) | C (9a) | C (9) | C (8) | 119.8(4) |
| C (9) | C (9a) | C (5a) | 119.0(3) | C (9b) | C (9a) | C (5a) | 114.4(3) |
| C (9b) | C (9a) | C (9) | 126.5(3) | C (3a) | C (9b) | O (1) | 113.3(3) |
| C (9a) | C (9b) | O (1) | 122.6(3) | C (9a) | C (9b) | C (3a) | 124.1(3) |
| C (11) | C (10) | C (3) | 120.5(3) | C (15) | C (10) | C (3) | 120.8(3) |
| C (15) | C (10) | C (11) | 118.7(3) | C (12) | C (11) | C (10) | 120.9(4) |
| C (11) | C (12) | Cl (1) | 119.9(4) | C (13) | C (12) | Cl (1) | 119.7(4) |
| C (13) | C (12) | C (11) | 120.5(4) | C (14) | C (13) | C (12) | 117.7(4) |
| C (15) | C (14) | C (13) | 123.4(5) | C (14) | C (15) | C (10) | 118.8(4) |

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11) Supplementary data are available on request from the Cambridge Crystallographic Data Center, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K. Any request should be accompanied by the full literature citation for this communication.