

Phototransformation of some *N*-(2-hydroxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)aryl/heterylamides

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Photoreorganisation of few *N*-(2-hydroxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)aryl/heterylamides **1** to *N*-benzoyl-3-oxo-1,3-dihydro-2-benzofuran-1-carboxamides **2** is described

Keywords: arylamides, heterylamides, carboxamides, Norrish Type-I reactions, photoreorganisation

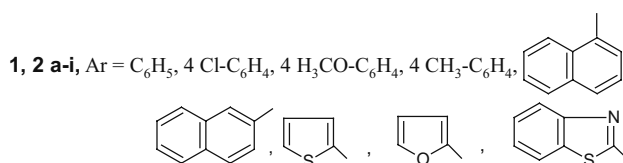
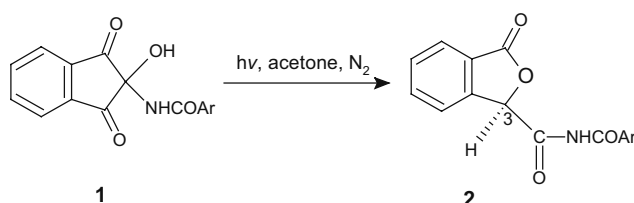
2,2-Disubstituted 1*H*-indene-1,3(2*H*)-diones carrying alkyl, aryl or aralkyl substituents are known to undergo facile photoisomerisation to afford the corresponding ylidene-2-benzofuran-1(3*H*)-ones¹ in excellent yields *via* Norrish Type-I reactions. Recently, we reported² that the inclusion of an aryl group at C-2 did not change the course of this phototransformation and it still led to the formation of isomeric (*E/Z*)-3-alkylidene-2-benzofuran-1(3*H*)-ones. However, when an alkoxy group was introduced at C-2 it conferred stereoselectivity to the transformation and led to the exclusive formation of (*Z*)-3-alkoxy-3-[(4-methoxyphenyl)methylene]-2-benzofuran-1(3*H*)-ones from 2-alkoxy-2-(4-methoxyphenyl)-1*H*-indene-1,3(2*H*)-diones.³

With a view to examine the influence of other polar groups such as hydroxyl and aryl/heterylamido at C-2 in 2,2-disubstituted 2*H*-indene-1,3-dione molecules on the manner of this photoreaction we report here the results of our studies on the synthesis and the photobehaviour of some *N*-(2-hydroxy-1,3-dioxo-1,3-dihydro-2*H*-inden-2-yl)aryl/heterylamides **1**.

N-(2-hydroxy-1,3-dioxo-1,3-dihydro-2*H*-inden-2-yl)aryl/heterylamides **1a–i** were prepared by refluxing a benzene solution of a mixture of ninhydrin hydrate and a suitable aryl/heterylamides for 1.0–1.5 h according to the procedure prescribed for *N*-(2-hydroxy-1,3-dioxo-1,3-dihydro-2*H*-inden-2-yl)benzamide.⁴

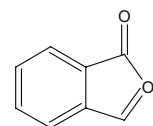
Next the photoirradiation of **1a–i** in dry acetone with light from 450 W Hanovia lamp through a pyrex filter under N₂ atmosphere for 5–7 h led to the isolation of **2a–i** as white crystalline solids in excellent yields (90–92%).

The structures of **2a–i** became evident from their IR, ¹H NMR and mass spectra: $\nu_{\max}/\text{cm}^{-1}$ 3280 (N–H), 1775–1780 (C=O, lactone), 1720–1725 (C=O, isobenzofuranamide) and 1680–1690 (C=O, arylamide). The most distinguishing

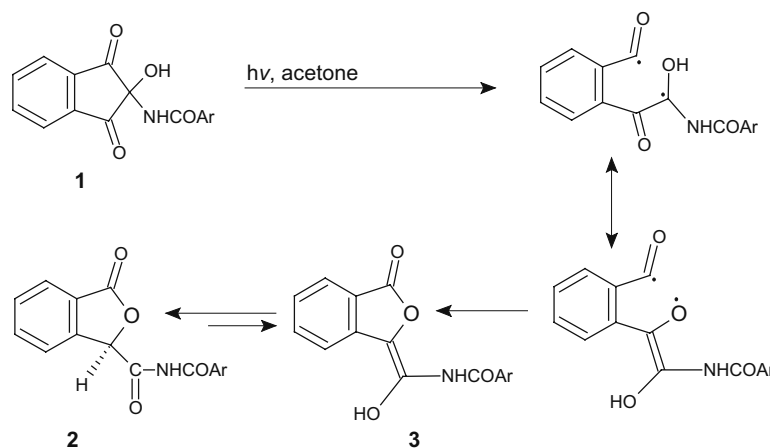


Scheme 1

feature of their ¹H NMR spectra was the appearance of a one proton singlet in the region δ 6.60–6.80 due to C-3 proton and a highly acidic imidic proton (exchangeable with D₂O) in the region δ 11.0–11.60. Further confirmation of their structure came from the mass spectra which displayed a medium intensity peak at *m/z* 133 due to the ion



The formation of **2** from **1** can be easily rationalised in terms of α -cleavage of 1*H*-indene-1,3(2*H*)-dione followed by reorganisation of the resulting 1,5-biradical intermediate with concomitant tautomerisation of the initially formed enolic benzofuranone **3**.



Scheme 2

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Thus it is concluded that the inclusion of hydroxyl and aryl/heterylamidogroup at C-2 did not alter the course of the phototransformation which still involved α -cleavage of the 2*H*-indene-1,3-dione moiety followed by reorganisation of the resulting 1,5-biradical to afford **3** which tautomerises to give **2**.

Experimental

Melting points were determined in open capillaries using a sulfuric acid bath and are uncorrected. Elemental analysis data was recorded on Exeter analytical CE 440 and Perkin-Elmer 2400 instruments. IR spectra were recorded as Nujol mulls on a Perkin-Elmer 842 spectrophotometer and ¹H NMR spectra were recorded on a 90 MHz Perkin-Elmer R-32 instrument in CDCl₃ + DMSO-*d*₆ or CDCl₃ using TMS as an internal standard. Mass spectra were recorded at 70eV using KRATOS MS-50 instrument.

General method for the synthesis of *N*-(2-hydroxy-1,3-dioxo-2,3-dihydro-1*H*-inden-2-yl)aryl/heterylamides **1a-i**

A mixture of ninhydrin hydrate (10.0 g, 56 mmol) and benzamide (6.8 g, 56 mmol) in benzene was refluxed for 1.0–1.5 h. and the water formed was removed by azeotropic distillation. The mixture was cooled and the solid so deposited was filtered, recrystallised from an ethanol-hexane mixture to give **1a-i** as pale yellow crystals.

1a: 88% yield, m.p. 143°C (Lit.⁴ m.p. 143–144°C), v_{\max}/cm^{-1} 3300, 3240, 1754 and 1724, 1660; δ_{H} 7.10–7.34 (m, 3H), 7.40 (br s, 1H), 7.61 (dd, 2H, $J = 8.0$ and 2.5 Hz), 7.72–8.08 (m, 5H).

1b: 92% yield, m.p. 209–210°C, (Found: C, 60.9; H, 3.2; N, 4.4; C₁₆H₁₀ClNO₄ requires C, 60.8; H, 3.2; N, 4.4%); v_{\max}/cm^{-1} 3348, 3287, 1750 and 1710, 1647; δ_{H} 7.30 (d, 2H, $J = 8.25$ Hz), 7.72–8.10 (m, 7H), 9.65 (br s, 1H).

1c: 94% yield, m.p. 178–179°C, (Found: C, 65.7; H, 4.05; N, 4.8; C₁₇H₁₃NO₅ requires C, 65.6; H, 4.2; N, 4.5%); v_{\max}/cm^{-1} 3380, 3318, 1754 and 1718, 1642; δ_{H} 3.82 (s, 3H), 6.87 (d, 2H, $J = 8.75$ Hz), 7.43 (br s, 1H), 7.84 (d, 2H, $J = 8.75$ Hz), 7.88–8.10 (m, 4H), 8.77 (br s, 1H).

1d: 96% yield, m.p. 170–171°C, (Found: C, 69.2; H, 4.4; N, 4.7; C₁₇H₁₃NO₄ requires C, 69.1; H, 4.4; N, 4.7%); v_{\max}/cm^{-1} 3380, 3320, 1754 and 1716, 1645; δ_{H} 2.32 (s, 3H), 7.12 (d, 2H, $J = 8.5$ Hz), 7.72 (d, 2H, $J = 8.5$ Hz), 7.77–8.12 (m, 5H), 8.58 (br s, 1H).

1e: 91% yield, m.p. 180–181°C, (Found: C, 72.6; H, 4.0; N, 4.2; C₂₀H₁₃NO₄ requires C, 72.5; H, 4.0; N, 4.2%); v_{\max}/cm^{-1} 3378, 3320, 1758 and 1730, 1638; δ_{H} 7.33–7.75 (m, 5H), 7.78–8.25 (m, 7H), 8.50 (br s, 1H).

1f: 93% yield, m.p. 177–178°C, (Found: C, 72.9; H, 4.0; N, 4.4; C₂₀H₁₃NO₄ requires C, 72.5; H, 4.0; N, 4.2%); v_{\max}/cm^{-1} 3360, 3320, 1754 and 1718, 1650; δ_{H} 7.35–7.55 (m, 2H), 7.65–8.05 (m, 9H), 8.43 (d, 1H, $J = 2.0$ Hz), 9.00 (br s, 1H).

1g: 89% yield, m.p. 155–156°C, (Found: C, 58.7; H, 3.05; N, 4.6; C₁₄H₉NO₄S requires C, 58.5; H, 3.2; N, 4.9%); v_{\max}/cm^{-1} 3380, 3320, 1753 and 1715, 1650; δ_{H} 6.98 (dd, 1H, $J = 4.8$ and 3.5 Hz), 7.42 (dd, 1H, $J = 4.8$ and 1.2 Hz), 7.67 (dd, 1H, $J = 3.5$ and 1.2 Hz), 7.72 (s, 1H), 7.78–8.05 (m, 4H), 8.70 (br s, 1H).

1h: 86% yield, m.p. 152–153°C, (Found: C, 62.05; H, 3.1; N, 5.4; C₁₄H₉NO₅ requires C, 62.0; H, 3.35; N, 5.2%); v_{\max}/cm^{-1} 3460, 3280, 1754 and 1724, 1654; δ_{H} 6.44 (dd, 1H, $J = 3.5$ and 1.7 Hz), 7.06 (dd, 1H, $J = 3.5$ and 0.85 Hz), 7.53 (dd, 1H, $J = 1.70$ and 0.85 Hz), 7.80–8.12 (m, 5H), 8.82 (br s, 1H).

1i: 88% yield, m.p. 174–176°C, (Found: C, 60.4; H, 2.8; N, 8.4; C₁₇H₁₀N₂O₄S requires C, 60.3; H, 3.0; N, 8.3%); v_{\max}/cm^{-1} 3287, 1754 and 1719, 1669; δ_{H} 7.47–7.57 (m, 2H), 7.88–7.96 (m, 4H), 8.05–8.10 (m, 3H), 8.32 (br s, 1H).

Photolysis of *N*-(2-hydroxy-1,3-dioxo-1,3-dihydro-2*H*-inden-2-yl)aryl/heterylamides **1a-i**

General procedure

A deoxygenated solution of **1** (0.5 g) in dry acetone (90 cm³) was irradiated in a pyrex vessel with light from 450W Hanovia lamp for

5.0–7.0 h. Solvent was removed and the resulting photolysate was crystallised using acetone-ethanol mixture to afford the corresponding *N*-benzoyl-3-oxo-1,3-dihydro-2-benzofuran-1-carboxamide **2** as white needles.

2a: 90% yield, m.p. 210–212°C, (Found: C, 68.5; H, 3.85; N, 5.2; C₁₆H₁₁NO₄ requires C, 68.3; H, 3.9; N, 5.0%); v_{\max}/cm^{-1} 3250, 1775, 1725 and 1689; δ_{H} 6.65 (s, 1H), 7.30–7.60 (m, 4H), 7.65–7.90 (m, 3H), 7.90–8.05 (dd, 2H, $J = 9.0$ and 2.5 Hz), 11.50 (br s, 1H); m/z 281 (M⁺, 39), 133 (30.6), 105 (100), 104 (22), 78 (32.4), 77 (57.5), 76 (41), 51 (32).

2b: 88% yield, m.p. 215–216°C, (Found: C, 60.9; H, 3.1; N, 4.45; C₁₆H₁₀ClNO₄ requires C, 60.8; H, 3.2; N, 4.4%); v_{\max}/cm^{-1} 3260, 1788, 1728 and 1627; δ_{H} 6.61 (s, 1H), 7.42–8.02 (m, 8H), 11.60 (br s, 1H); m/z 315 (5.1), 141 (29.7), 139 (100), 133 (24.4), 111 (23.4), 105 (87.5), 77 (12).

2c: 92% yield, m.p. 200–202°C, (Found: C, 65.7; H, 4.0; N, 4.7; C₁₇H₁₃NO₅ requires C, 65.6; H, 4.2; N, 4.5%); v_{\max}/cm^{-1} 3280, 1780, 1718 and 1682; δ_{H} 3.89 (s, 3H), 6.78 (s, 1H), 7.00 (d, 2H, $J = 8.5$ Hz), 7.50–7.80 (m, 3H), 7.90 (d, 1H, $J = 8.5$ and 2.5 Hz), 8.05 (d, 2H, $J = 8.5$ Hz), 10.95 (br s, 1H); m/z 294 (19.9), 263 (11.4), 136 (12.8), 135 (100), 133 (5.2), 77 (19.6).

2d: 92% yield, m.p. 183–184°C, (Found: C, 69.5; H, 4.05; N, 4.6; C₁₇H₁₃NO₄ requires C, 69.1; H, 4.4; N, 4.7%); v_{\max}/cm^{-1} 3280, 1785, 1722 and 1687; δ_{H} 2.42 (s, 3H), 6.80 (s, 1H), 7.30 (d, 2H, $J = 8.5$ Hz), 7.50–7.80 (m, 3H), 7.80–8.02 (m, 3H), 11.10 (br s, 1H); m/z 295 (M⁺, 3.3), 135 (27.5), 133 (43.9), 119 (100), 105 (16.5), 91 (40.7), 65 (15.0).

2e: 86% yield, m.p. 193–194°C, (Found: C, 73.0; H, 3.25; N, 4.45; C₂₀H₁₃NO₄ requires C, 72.5; H, 4.0; N, 4.2%); v_{\max}/cm^{-1} 3240, 1790, 1715 and 1682; δ_{H} 6.53 (s, 1H), 7.35–8.10 (m, 9H), 8.15–8.40 (m, 2H), 7.80–8.02 (m, 3H), 11.50 (br s, 1H); m/z 171 (72.7), 170 (24.0), 155 (68.1), 134 (37.7), 133 (100), 127 (72.0), 126 (20.6), 105 (48.3).

2f: 84% yield, m.p. 203–204°C, (Found: C, 72.9; H, 3.4; N, 4.5; C₂₀H₁₃NO₄ requires C, 72.5; H, 4.0; N, 4.2%); v_{\max}/cm^{-1} 3280, 1775, 1715 and 1690; δ_{H} 6.78 (s, 1H), 7.40–8.10 (m, 9H), 8.63 (d, 1H), 12.50 (br s, 1H); m/z 171 (86.3), 155 (100), 134 (28.4), 133 (72.5), 127 (94.4), 105 (37.7), 77 (42.4), 51 (25.7).

2g: 86% yield, m.p. 192–193°C, (Found: C, 58.9; H, 3.0; N, 4.6; C₁₄H₉NO₄S requires C, 58.5; H, 3.2; N, 4.9%); v_{\max}/cm^{-1} 3260, 1782, 1708 and 1672; δ_{H} 6.87 (s, 1H), 7.15 (dd, 1H, $J = 4.8$ and 3.5 Hz), 7.50–8.0 (m, 5H), 8.15 (d, 1H, $J = 3.5$ Hz), 11.50 (br s, 1H); m/z 287 (M⁺, 6.6), 134 (13.5), 133 (27.2), 111 (100), 105 (11.4), 83 (7.9), 77 (12.4).

2h: 88% yield, m.p. 167–168°C, (Found: C, 62.1; H, 3.15; N, 5.45; C₁₄H₉NO₅ requires C, 62.0; H, 3.35; N, 5.2%); v_{\max}/cm^{-1} 3260, 1787, 1715 and 1677; δ_{H} 6.17 (s, 1H), 6.53 (dd, 1H, $J = 3.5$ and 1.8 Hz), 7.34 (d, 1H, $J = 3.5$ Hz), 7.50–8.00 (m, 5H), 11.80 (br s, 1H); m/z 271 (M⁺, 5.6), 134 (53.7), 133 (93.2), 105 (40.9), 95 (100), 77 (38.6), 76 (19.0).

2i: 90% yield, m.p. 178–179°C, (Found: C, 60.5; H, 2.75; N, 8.3; C₁₇H₁₀N₂O₄S requires C, 60.3; H, 3.0; N, 8.3%); v_{\max}/cm^{-1} 3268, 1786, 1720 and 1680; δ_{H} 6.19 (s, 1H), 7.55–7.67 (m, 3H), 7.50–8.00 (m, 5H), 7.75–8.01 (m, 1H), 8.20–8.23 (dd, 1H, $J = 8.5$ and 2.5 Hz), 10.71 (br s, 1H); m/z 338 (M⁺, 5.8), 205 (59.5), 162 (100), 134 (44), 133 (54.2), 105 (19.1), 77 (21.2).

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