Electronic Supplementary Material (ESI) for Organic & Biomolecular Chemistry

Supporting Information

Is the 2,3-carbon-carbon bond of indole really inert to oxidative cleavage by Oxone? – Synthesis of isatoic anhydrides from indoles

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1. General experimental remarks

All commercial reagents were ACS reagent grade and used without further purification. Dichloromethane was distilled from CaH2 immediately prior to use. Diethyl ether was distilled from Na/benzophenone. All commercial reagents were ACS reagent grade and used without further purification. NMR spectra were recorded on a Varian Inova 500 MHz NMR spectrometer at 500 MHz. Chemical shifts are reported in parts per million (ppm). Chemical shifts are referenced relative to tetramethylsilane (TMS).

2. General procedure for the preparation of the isatoic anhydrides 10a-10l

1 mmol indole compound in 10 mL solvent mixture was treated with 2.5 g (4 mmol) Oxone and the reaction mixture was stirred at room temperature overnight. After that time the reaction mixture was diluted with 25 mL of water and extracted with ethyl acetate. The extract was dried with sodium sulfate and the title compounds were isolated by crystallization or by chromatography.

3. ^{1}H NMR data of isatoic anhydrides (10a-10l)

Isatoic anhydride (10a).[1] Prepared from indole (**9a**) by stirring in a 4:1 mixture of DMF/H_2O for 16 h at room temperature. ^{1}H NMR (DMSO-d_6): δ 11.73 (s, br., 1H), 7.92 (d, *J* = 7.8 Hz, 1H), 7.74 (t, *J* = 7.8 Hz, 1H), 7.26 (t, *J* = 7.8 Hz, 1H), 7.16 (d, *J* = 7.8 Hz, 1H).

5-Bromoisatoic anhydride (10b). [2] Prepared from 5-bromo indole (**9b**) by stirring in a 4:1 mixture of DMF/H_2O for 16 h at room temperature. ^{1}H NMR

(DMSO-d_6): δ 11.85 (s, br., 1H), 7.96 (dd, *J* = 0.8, 8.7 Hz, 1H), 7.87 (dd, *J* = 2.3, 8.7 Hz, 1H), 7.09 (dd, *J* = 8.8, 0.8 Hz, 1H).

5-Chloroisatoic anhydride (10c). [3] Prepared from 5-chloro indole (**9c**) by stirring in a 4:1 mixture of DMF/H_2O for 16 h at room temperature. ^{1}H NMR (DMSO-d_6): δ 11.85 (s, br., 1H), 7.96 (dd, *J* = 0.8, 8.7 Hz, 1H), 7.87 (dd, *J* = 2.3, 8.7 Hz, 1H), 7.09 (dd, *J* = 8.8, 0.8 Hz, 1H).

5-Fluoroisatoic anhydride (10d). [4] Prepared from 5-fluoro indole (**9d**) by stirring in a 4:1 mixture of DMF/H_2O for 16 h at room temperature. ^{1}H NMR (DMSO-d_6): δ 11.19 (s, br., 1H), 7.36 (dd, *J* = 8.4, 2.6 Hz, 1H), 6.87 (dt, *J* = 8.4, 2.2 Hz, 1H), 6.74 (dd, *J* = 9.3, 2.2 Hz, 1H).

5-Methylisatoic anhydride (10e).[5] Prepared from 5-methyl indole (**9e**) by stirring in a 4:1 mixture of DMF/H_2O for 16 h at room temperature. ^{1}H NMR (DMSO-d_6): δ 11.61 (s, br., 1H), 7.69 (s Hz, 1H), 7.55 (d, *J* = 7.8 Hz, 1H), 7.05 (d, *J* = 8.7 Hz, 1H).

5-Nitroisatoic anhydride (10g). [6] Prepared from 5-nitro indole (**9g**) by stirring in a 4:1 mixture of CH_3CN/H_2O for 1 h at 40°C. ^{1}H NMR (DMSO-d_6): δ 12.34 (s, Br., 1H), 8.59 (s Hz, 1H), 8.51 (d, *J* = 7.8 Hz, 1H), 7.31 (d, *J* = 8.7 Hz, 1H).

4-Fluoroisatoic anhydride (10h). [4] Prepared from 6-fluoroindole (**9h**) by stirring in a 4:1 mixture of CH_3CN/H_2O for 1 h at 40°C. ^{1}H NMR (DMSO-d_6): δ 11.87 (s, br., 1H), 8.00 (ddd, *J* = 8.8, 6.0, 0.8 Hz, 1H), 7.11 (tdd, *J* = 8.8, 2.5, 1.1 Hz, 1H), 6.88 (ddd, *J* = 0.8, 2.5, 9.6, 2.5, 0.8 Hz, 1H).

3-Fluoroisatoic anhydride (10i). [7] Prepared from 7-fluoroindole (**9i**) by stirring in a 4:1 mixture of CH_3CN/H_2O for 1 h at 40°C. ^{1}H NMR (DMSO-d_6): δ 11.73 (s, br., 1H), 7.76 (dt, *J* = 8.0, 1.0 Hz, 1H), 7.67 (qd, *J* = 8.1, 1.2 Hz, 1H), 7.24 (dt, *J* = 4.6, 3.3 Hz, 1H).

6-Bromoisatoic anhydride. (10k) Prepared from 4-bromo-3-carbaldehyde by stirring in a 4:1 mixture of CH_3CN/H_2O for 1 h at 40°C. ^{1}H NMR: δ 11.82 (s, br., 1H), 7.56 (t, *J* = 7.8 Hz, 1H), 7.52 (d, *J* = 7.8 Hz, 1H), 7.14 (d, *J* = 7.8 Hz, 1H).

3-Bromoisatoic anhydride (10l). Prepared from 7-bromo-3-carbaldehyde by stirring in a 4:1 mixture of CH_3CN/H_2O for 1 h at 40°C. ^{1}H NMR: δ 11.08 (s, br., 1H), 8.02 (d, *J* = 7.8 Hz, 1H), 7.94 (d, *J* = 7.8 Hz, 1H), 7.19 (t, *J* = 7.8 Hz, 1H).

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5. Spectra