Bismuth-Catalyzed Benzylic Oxidations with *tert*-Butyl Hydroperoxide

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Experimental

Proton magnetic resonance spectra (¹H NMR) were recorded at 300 MHz. Chemical shifts (δ) are quoted in parts per million (ppm) and are referenced to the residual solvent peak, 7.26 for CDCl₃, and 2.52 for DMSO-d₆. Carbon magnetic resonance spectra (¹³C NMR) were recorded at 75 MHz. Chemical shifts (δ) are quoted in parts per million (ppm) and are referenced to the residual solvent peak, 77.0 for CDCl₃ and 39.7 for DMSO-d₆. Coupling constants (J) are quoted in Hertz (Hz) for both ¹H and ¹³C NMR. The following abbreviations were used to explain the multiplicities: s=singlet, d=doublet, dq=doublet of quartets, t=triplet, dt= doublet of triplets, q=quartet, m=multiplet. Reactions were monitored by Gas Chromatography Mass spectrometry.

General procedure for the oxidation of alkylarenes to ketones:

NaBH₄ (18 mg, 0.48 mmol) was added with vigorous stirring to a suspension of Bi₂O₃ (37 mg, 0.08 mmol) in distilled H₂O (1.5 mL) at room temperature giving a finely divided, black precipitate of bismuth metal. This was washed with H₂O (2 x 2 mL), then pyridine (0.8 mL), AcOH (0.08 mL), picolinic acid (20 mg, 0.16 mmol), substrate (0.8 mmol) and *t*-BuOOH in H₂O (70%; 0.66 mL, 4.8 mmol) were added. The mixture was sonicated for 30 min and heated at 100 °C for 16 h (sealed vessel), cooled, diluted with CH₂Cl₂, filtered through Celite® and rotary evaporated. The resulting oil was analyzed by NMR and GCMS and subsequently chromatographed to yield the corresponding ketone.

Ketones obtained are all known compounds, which are commercially available or previously described. Their analytical data are similar with those reported in the literature.

General procedure for the oxidation of methylarenes to arenecarboxylic acids:

A suspension of Bi(OTf)₃ (105 mg, 0.16 mmol), pyridine (0.8 mL), AcOH (0.13 mL), picolinic acid (10 mg, 0.08 mmol), substrate (0.8 mmol) and *t*-BuOOH in H₂O (70%; 0.77 mL, 5.6 mmol) was sonicated for 30 min and then heated at 110 °C for 20 h (sealed vessel). After cooling, EtOAc was added and the resulting suspension was washed with aqueous HCl (10%; 10 mL) and brine (10 mL). The organic layer was dried (MgSO₄), rotary evaporated and the resulting oil was analyzed (NMR and GCMS) and subsequently chromatographed to yield the corresponding carboxylic acid, which were commercially available and showed ¹H and ¹³C NMR spectra and mp identical with data reported except for 4-Bromo-naphthalene-1-carboxylic acid.

4-Bromo-naphthalene-1-carboxylic acid

[recrystallised from EtOAc/Hexane] Mp 215-218 °C (ref¹ 217-220 °C). IR (film) 3056-2875, 1696, 1279, 1252, 762 cm⁻¹. ¹H NMR (DMSO, 300 MHz) δ 7.77 (m, 2H), 8.00 (m, 2H), 8.25 (m, 1H), 8.91 (m, 1H), 13.43 (s, 1H) ppm. ¹³C NMR (DMSO, 75 MHz) δ 126.2, 126.8, 126.9, 128.0, 128.3, 128.4, 129.3, 129.9, 131.3, 131.7, 168.0 ppm. MS (CI+) *m/z* 250 (M + H)⁺, 268 (M + NH₄)⁺. HRMS calc for C₁₁H₁₁BrNO₂: (M + NH₄)⁺, 267.9963, found: (M + NH₄)⁺, 267.9973. Anal. calc. for C₁₁H₇BrO₂: C, 52.62, H, 2.81. Found: C, 52.55; H, 2.95.

¹ Bichan, D. J.; Yates, P. *Can. J. Chem.* **1975**, 53, 2054-2063.