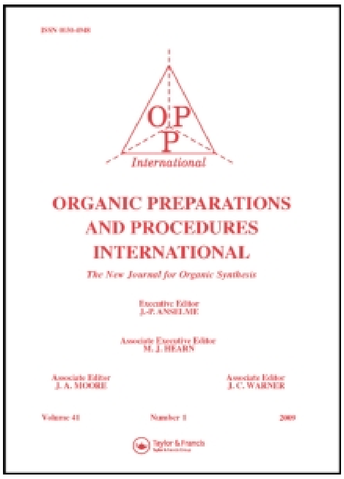

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SYNTHESIS OF 1-HYDROXY-7-PHENOXYNAPHTHALENE

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and 750 cm^{-1}. H NMR (CCl_4): δ 1.8 (s, 3H, $\underline{CH_3}$-C=), 4.46 (s, 2H, -$O\underline{CH_2}$), 4.9, 5 (2H, CH_2=C<), 5.46 (s, 1H, OH), 6.76 (m, 4H, aromatic).

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SYNTHESIS OF 1-HYDROXY-7-PHENOXYNAPHTHALENE

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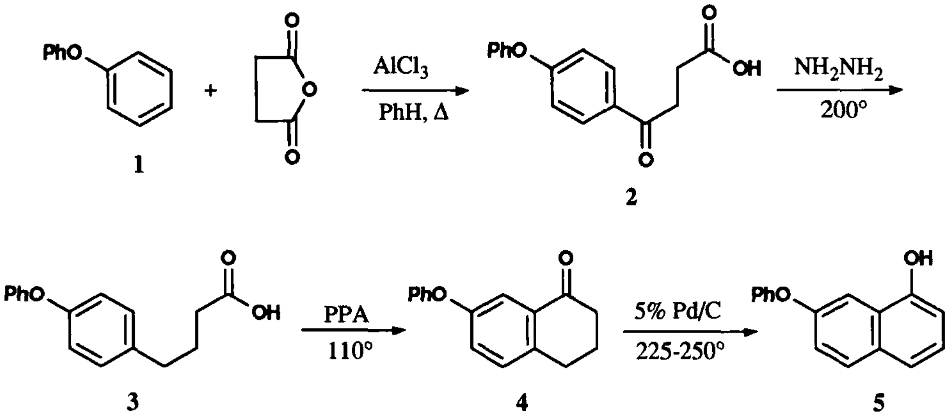
Cleavage of diaryl ethers containing one-to-three rings and a hydroxyl group is an important pathway for depolymerization of low rank coals, and oil shales, into synthetic liquid fuels.[1] There are no reports in the literature on the synthesis of such structures to allow study of their reactivity. Preparation of 7-phenoxy-1-hydroxynaphthalene (**5**) is now reported *via* the synthesis of a tetralone derivative (**4**) in which the phenoxy group is already built in the bicyclic system.

Treatment of the diphenyl ether (**1**) with succinic anhydride in the presence of $AlCl_3$ by a literature procedure[2] gave 3-(p-phenoxybenzoyl)propionic acid (**2**) in 90% yield. Clemmensen reduction[3] of the carbonyl function of **2** gave (**3**) 4-(4-phenoxyphenyl)butyric acid[3] in only 40% yield. However, Wolf-Kishner reduction[3] in diethylene glycol at 200° for 4 hrs furnished **3** as a crystalline solid, in 80% yield. Cyclization of **3** with polyphosphoric acid[4] afforded the expected bicyclic ketone, 7-phenoxy-1-tetralone (**4**) in 25% yield, together with some polymer. Dehydrogenation of **4** to 1-hydroxy-7-phenoxynaphthalene (**5**) (70% yield) was accomplished with 5% Pd/C in refluxing 1,3,5-triisopropylbenzene for 6 hrs.



EXPERIMENTAL SECTION

Melting points were determined on a hot stage microscope and are uncorrected. ^1H and ^{13}C NMR spectra were recorded on Varian VXR 300 spectrometer. Chemical shifts are in parts per million (δ) relative to TMS. Coupling constants (J) are in Hertz (Hz). Elemental analysis was performed on a Carlo Erba-1106 instrument. Mass spectra were recorded at 70 ev on GC/MS ITD 700 mass spectrometer.

4-Oxo-4-(4-phenoxyphenyl)butyric Acid (2).- To a mixture of 68 g (0.4 mole) of diphenyl ether, 40 g (0.4 mole) of powdered succinic anhydride and 200 mL of benzene were added six 5 g portions of anhydrous $AlCl_3$. Each time the flask was swirled gently until the reaction subsided (ca. 15 min). The mixture was heated at reflux for 3 hrs, allowed to cool overnight and poured onto crushed ice (1 kg). The solidified product was collected and dried. The crude acid was extracted with 2% NaOH and the aqueous solution acidified with 5% HCl. The precipitated white solid was collected and dried to give 97 g (90%) of colorless solid, mp.115-117° (lit[2] 117°). ^1H NMR: δ 2.79 (t, 2 H, J = 7.5, CO-C$\underline{H}_2$), 3.26 (t, 2 H, J = 7, C$\underline{H}_2$$CO_2H$), 6.99 (d, 2 H, J = 7), 7.06 (d, 2 H, J = 8), 7.19 (t, 1 H J = 7.5), 7.39 (t, 2 H, J = 7), 7.95 (d, 2 H, J = 8). ^{13}C NMR: δ 28.0, 32.8, 117.3, 120.1, 124.6, 130.0, 130.3, 131.0, 155.3, 162.1, 178.8, 196.4. M^+ 270 (100% r.i.).

4-(4-Phenoxyphenyl)butyric Acid (3).- A mixture of 25 g (0.01 mole) of **2**, 17.5g of KOH, 200 mL of diethylene glycol, 12.5 mL of 85% $N_2H_4 H_2O$ was refluxed (230 - 240 °) for 1 hr and kept at 200° for 4-5 hrs. The resulting mixture was cooled, diluted with water, acidified with 5% HCl and extracted with chloroform. The extract was washed with water, dried over $MgSO_4$ and the solvent removed to yield **3** (17g, 80% yield) mp. 63-65° (lit[3] 64-66°C). ^1H NMR: δ 1.94 (quint, 2 H, J = 7.5, CH_2-C$\underline{H}_2$-CH_2), 2.37 (t, 2 H, J = 7, C$\underline{H}_2$-Ar), 2.64 (t, 2 H, J=7, C$\underline{H}_2$$CO_2H$), 6.91-7.32 (m, 9H). ^{13}C NMR: δ 26.3, 33.3, 34.2, 118.5, 119.0, 122.9, 129.6, 136.1, 155.3, 157.5, 180.1 (C=O). $M^{+\cdot}$ 256 (100%).

7-Phenoxy-1-tetralone (4).- A mixture of 12.8 g (0.05 mole) of **3** in 50 g of polyphosphoric acid was heated at 110° for 12 hrs. The resulting mixture was allowed to stand overnight and was poured onto crushed ice. The dark red solution was extracted with $CHCl_3$, washed with 5% NaOH, water, and dried over $MgSO_4$. The $CHCl_3$ was removed and the residue was purified by two triturations with petroleum ether to give 3.0 g (25%) of compound **4**, mp. 67-68° (petroleum ether). ^{1}H NMR: δ 2.11 (quint, 2 H, J = 7, CH_2-$\underline{CH_2}$-CH_2), 2.60-2.64 (t, 2 H, J = 8, CH_2-Ar), 2.90-2.94 (t, 2 H, J = 7, Ar-CO-$\underline{CH_2}$), 7.00 (d, 2 H, J = 7), 7.06-7.63 (m, 5 H), 7.63 (d, 1 H, J = 3.5). ^{13}C NMR: δ 23.3, 29.0, 38.9, 116.2, 118.8, 123.5, 124.5, 130.3, 139.3, 156.0, 156.9, 197.7 (C=O). $M^{+\cdot}$ 238 (100%).

Anal. Calcd. for $C_{16}H_{14}O_2$: C, 80.65; H, 5.92. Found: C, 80.92; H, 6.00.

1-Hydroxy-7-phenoxynaphthalene (5).- A mixture of **4** (1.19 g, 0.005 mole), 5% Pd/C and 1,3,5-triisopropylbenzene (5 mL) was heated at 225-250° for 6 hrs, under an Argon atmosphere. The resulting reaction mixture was cooled, diluted with water and extracted with $CHCl_3$. The organic solution was filtered from the undissolved material, washed with water and dried over $MgSO_4$. Evaporation of the solvent afforded a thick oil which solidified on trituration with hexane to give **5** (0.83 g, 70%), mp. 97-99° (from hexane). ^{1}H NMR: δ 5.72-5.74 (b, 1 H, -O$\underline{H}$), 6.73 (d, 1 H, J = 7), 7.01-7.39 (m, 9H), 7.68-7.81 (m, 2 H). ^{13}C NMR: δ 108.8, 109.2, 118.9, 120.3, 120.5, 123.3, 124.6, 125.3, 129.7, 129.8, 131.5, 150.9, 154.6, 157.3. HRMS Calcd. for $C_{16}H_{12}O_2$: 236.0837. Found: 236.0840.

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