

SYNTHESIS OF 1,2,3,4-TETRAHYDRONAPHTHALENE-1-<sup>13</sup>C, NAPHTHALENE-1-<sup>13</sup>C,  
AND 1-NAPHTHALENOL-1-<sup>13</sup>C

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## SUMMARY

The synthesis of 1,2,3,4-tetrahydronaphthalene-1-<sup>13</sup>C, naphthalene-1-<sup>13</sup>C, and 1-naphthalenol-1-<sup>13</sup>C in 98, 81, and 82% overall yields respectively from 4-phenylbutanoic-1-<sup>13</sup>C acid is described.

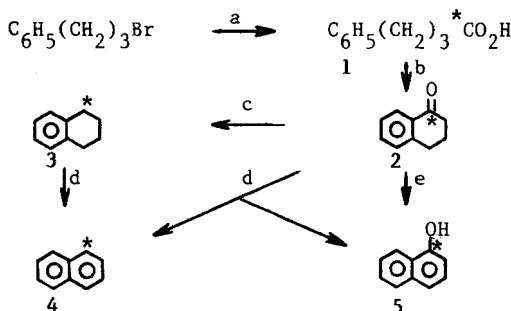
Key Words: 4-phenylbutanoic-1-<sup>13</sup>C acid, 3,4-dihydro-1(2H)-naphthalenone-1-<sup>13</sup>C, 1,2,3,4-tetrahydronaphthalene-1-<sup>13</sup>C, naphthalene-1-<sup>13</sup>C and 1-naphthalenol-1-<sup>13</sup>C.

## INTRODUCTION

Coal liquefaction solvents have been the subject of several studies designed to gain a better understanding of the role of solvent molecules in the conversion of coal to coal liquids (1). These investigations have proven useful in elucidating the kinetics and mechanisms of the reactions utilizing these solvents.

Several solvents and related compounds bearing a specific <sup>13</sup>C label (sym-octahydrophenanthrene-1-<sup>13</sup>C, phenanthrene-1-<sup>13</sup>C, 9-methylphenanthrene-9-<sup>13</sup>C, 1-phenol-1-<sup>13</sup>C) (2), as well as 1,2,3,4-tetrahydroquinoline-2-<sup>13</sup>C (3) have previously been prepared for use in this study. These labeled compounds and the currently synthesized ones were used to study solvent, solvent-solvent, and solvent-coal reactions including isomerization, cracking, adduction and hydrogen-transfer reactions (1). As a continuation of our earlier preparation of <sup>13</sup>C-labeled compounds (3), the title compounds were synthesized. 4-Phenylbutanoic-1-<sup>13</sup>C acid (1) was prepared as shown, and then cyclized to 3,4-dihydro-1(2H)-naphthalenone-1-<sup>13</sup>C (2). 1,2,3,4-Tetrahydronaphthalene-1-<sup>13</sup>C (3) was

prepared from **2** in 99% yield by hydrogenation. Two routes were investigated for the conversion of **2** to naphthalene-1-<sup>13</sup>C (**4**) and 1-naphthalenol-1-<sup>13</sup>C (**5**). The first was to heat neat ketone **2** with Pd/C at 230 °C for 3 h. This gave both **4** (25% yield) and **5** (30% yield). Carrying the reaction out at 260 °C is reported to increase the yield of **4** (37% yield) at the expense of **5** (18% yield) i.e. **5** is converted to **4** under these conditions (**4a**). While direct conversion of **2** to **4** and **5** is advantageous when both products are required, the low yield (total 55%) prompted separate syntheses for **4** (82%) and **5** (82%) from **2** as shown in the reaction scheme.



<sup>a</sup>Mg,  $C_6H_6 \cdot THF$ ; <sup>13</sup>CO<sub>2</sub>. <sup>b</sup>PPA,  $\Delta$ . <sup>c</sup>Pd/C, H<sub>2</sub>, acetic acid,  $\Delta$ . <sup>d</sup>Pd/C,  $\Delta$ .

<sup>e</sup>Br<sub>2</sub>, ether; DMF, Li<sub>2</sub>CO<sub>3</sub>, LiBr,  $\Delta$ .

An alternate route for directly converting **2** to **4** in 70-75% yield is available (**4b**). This consists of heating **2** at 250 °C in the presence of a 1:1 mixture of NaOH:KOH.

#### EXPERIMENTAL

**4-Phenylbutanoic-1-<sup>13</sup>C Acid (1).** Labeled carbon dioxide (<sup>13</sup>CO<sub>2</sub>, 0.21 mol) was generated by adding 200 mL of H<sub>3</sub>PO<sub>4</sub> to an aqueous slurry of 46.1 g of Ba<sup>13</sup>CO<sub>3</sub> (92% <sup>13</sup>C). In a three-necked flask was placed 6.7 g (0.28 mol) of Mg turnings and 300 mL of 9:1 benzene:tetrahydrofuran (THF) solution. This mixture was brought to reflux as 50 g (0.25 mol) of 3-phenyl-1-propylbromide was added slowly through an addition funnel. After the reaction was initiated, reflux was maintained an additional 45 min with most of the Mg reacted.

The Grignard reagent was transferred by siphoning to a stainless steel

reactor (5). After cooling the reactor to liquid nitrogen temperature, <sup>13</sup>CO<sub>2</sub> was added and the system was gradually warmed (overnight), after which unreacted <sup>13</sup>CO<sub>2</sub> was recovered (6). The reactor was disconnected and its contents were poured over 500 g of ice, acidified with hydrochloric acid and then extracted with ethyl ether (3x). The combined ether layers were washed 2x with saturated Na<sub>2</sub>CO<sub>3</sub> (ca. 1-L), dried (MgSO<sub>4</sub>), filtered, and concentrated to 10 g of neutral product.

The Na<sub>2</sub>CO<sub>3</sub> extracts containing the labeled acid were acidified with hydrochloric acid followed by extraction (2x) with ethyl ether. The organic layer was dried (MgSO<sub>4</sub>), filtered, and concentrated to 26.9 g of **1** (76.2% yield) as white crystals, mp 50-51 °C (lit. (7) 52 °C for unlabeled acid): IR (melt) 2955 (-CO<sub>2</sub>H), 1660 (C=O), 745, 700 (C=CH bend) cm<sup>-1</sup>; <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 2.65-3.1 (m, 2, ArCH<sub>2</sub>CH<sub>2</sub>), 7.05-7.25 (m, 5, ArH), 11.04 (s, 1, CO<sub>2</sub>H); <sup>13</sup>C-NMR (CDCl<sub>3</sub>) ppm 26.0, 33.2, 34.8, 125.7, 128.1, 140.8, 180.0; MS m/z (rel. intensity), 165.2 (M<sup>+</sup>, 1.6), 163.2 (4.7), 147.2 (11.5), 104.3 (84.7), 91.2 (100).

**3,4-Dihydro-1(2H)-naphthalenone-1-<sup>13</sup>C (2).** The labeled acid **1** (61.0 g, 0.37 mol) was added to 500 g of polyphosphoric acid and mechanically stirred. The mixture was heated at 95-105 °C for 1 h then poured over ice and stirred to yield greenish-white crystals. The product was extracted with ether, dried (MgSO<sub>4</sub>), filtered, concentrated, and Kugelrohr distilled to give 54 g (99% yield) of colorless labeled ketone **2**: bp 64 °C/0.1 mm (lit. (8) 129 °C/12 mm for unlabeled ketone); IR (neat) 1575 (C=O), 1625 (C=C str), 760, 725 (C=CH bend) cm<sup>-1</sup>; <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 1.90-2.20 (pentet, J=6 Hz, 2, ArCH<sub>2</sub>CH<sub>2</sub>), 2.48-2.68 (q, J=7 Hz, 2, ArCH<sub>2</sub>), 2.82-2.96 (t, J=6 Hz, 2, ArCOCH<sub>2</sub>), 7.10-7.46 (m, 3, ArH), 7.85-8.05 (m, 1, ArH peri to C=O); <sup>13</sup>C-NMR (CDCl<sub>3</sub>) ppm 22.7, 29.0, 38.5, 125.8, 126.2, 128.1, 131.8, 132.6, 143.7, 197.1; MS m/z (rel. intensity), 147.1 (M<sup>+</sup>, 58.1), 119.0 (100), 115.0 (14.5), 91.0 (15.5), 90.0 (70.7), 89.0 (25.7).

**1,2,3,4-Tetrahydronaphthalene-1-<sup>13</sup>C (3).** A mixture, containing 56.8 g (0.39 mol) of **2** and 5 g Pd/C in 500 mL acetic acid, was hydrogenated at

70-80 °C and 35 psig. After hydrogen uptake ceased, the mixture was filtered, concentrated, neutralized with  $\text{Na}_2\text{CO}_3$ , extracted with isohexane, dried ( $\text{MgSO}_4$ ), concentrated and Kugelrohr distilled to give 50.6 g of **3** (99% yield): bp 35 °C/0.13 mm (lit. (8) 79.4 °C/10 mm for the unlabeled hydrocarbon); IR (neat) 1500, 1450 (C=C str), 740 (C=CH bend)  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  1.70-1.90 (m, 4,  $\text{ArCH}_2\text{CH}_2$ ), 2.00-2.20 (m, 1,  $\text{Ar}^{13}\text{CH}_a\text{H}_b$ ), 2.65-2.90 (m, 2,  $\text{ArCH}_2$ ), 3.30-3.50 (m, 1,  $\text{Ar}^{13}\text{CH}_a\text{CH}_b$ ), 7.05 (s, 4, ArH);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ) ppm 23.3, 29.3, 125.1, 128.8, 136.6; MS  $m/z$  (rel. intensity), 133.1 ( $\text{M}^+$ , 69.2), 129.1 (31.4), 105.1 (100), 104.1 (60.7), 92.1 (33.6), 91.1 (37.4).

**Naphthalene-1- $^{13}\text{C}$  (4).** Labeled **3** (1.52 g, 0.011 mol) was heated at 180-200 °C with 0.2 g of 10% Pd/C until  $\text{H}_2$  evolution ceased. The mixture was then brought to reflux for an additional 15 min. After cooling, the solid was dissolved in ether and filtered through Dicalite to remove the catalyst. The ether was concentrated, leaving an off-white product which was chromatographed on silica gel with cyclohexane as solvent. After concentrating, hydrocarbon **4** (1.24 g, 83% yield) was obtained as white crystals, mp 76 °C. Additional purification via picrate formation and regeneration gave **4**: mp 80 °C (lit. (9) 80.5 °C for unlabeled hydrocarbon): IR (KBr) 1575 (C=C str), 785 (ArH bend)  $\text{cm}^{-1}$ ;  $^1\text{H-NMR}$  ( $\text{CDCl}_3$ )  $\delta$  7.05-7.90 (m, ArH);  $^{13}\text{C-NMR}$  ( $\text{CDCl}_3$ ) ppm 126.0, 128.1, 133.7; MS  $m/z$  (rel. intensity), 129.2 ( $\text{M}^+$ , 100), 128.2 (19.0), 127.1 (6.92), 103.2 (6.35), 102.1 (4.33).

**Naphthalenol-1- $^{13}\text{C}$  (5).** To a solution of **2** (40.0 g, 0.27 mol) in 500 mL of anhydrous ethyl ether at room temperature was added one drop of bromine. The solution, which rapidly decolorized, was then cooled to 5 °C using an ice bath. The remainder of the bromine (43.8 g, 0.27 mol) was added dropwise over a 20 min period, allowing each drop to decolorize before more was added. The solution was kept below 5 °C during the addition, allowed to warm to room temperature, ether was removed and dimethylformamide (DMF) (800 mL, Fisher), lithium carbonate (32.8 g, 0.44 mol), and lithium bromide (38.6 g, 0.44 mol) were added to the flask (10). The mixture was then heated at 153 °C (reflux) for 1 h, cooled, acidified with conc. HCl,

and extracted with ethyl ether (3x). The combined ether layers were washed with 10% NaOH (2x), dried (MgSO<sub>4</sub>), filtered, and concentrated to give 2 g of 2 (5% recovery of starting material).

The NaOH extracts containing 5 were acidified with hydrochloric acid and extracted with ethyl ether (3x). The extract was then dried (MgSO<sub>4</sub>), filtered, and concentrated to 35.6 g of crude 5. Kugelrohr distillation of the crude material gave 32.3 g (82%) of 5: mp 91-93 °C (lit. (11) 96 °C for unlabeled 1-naphthalenol); IR (KBr) 3300 (broad OH stretch), 770 (ArH bend), 790 cm<sup>-1</sup>; <sup>1</sup>H-NMR (CDCl<sub>3</sub>) δ 8.18 (m, 1H, ArH), 7.8 (m, 1H, ArH), 7.46 (m, 3H, ArH), 7.27 (m, 1H, ArH), 6.75 (m, 1H, ArH), 5.73 (d, 1H, OH); <sup>13</sup>C-NMR (CDCl<sub>3</sub>) ppm 151.1, 127.6, 127.5, 126.3, 125.7, 125.3, 125.1, 121.4, 120.8, 120.5, 109.9, 109.5, 107.2; MS m/z (rel. intensity), 145.1 (100), 144.1 (6.7), 116.6 (33.9), 215.1 (74.6), 89.1 (7.0); exact mass (M<sup>+</sup>) 145.0610, required for C<sub>9</sub><sup>13</sup>CH<sub>8</sub>O (M<sup>+</sup>) 145.0609.

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