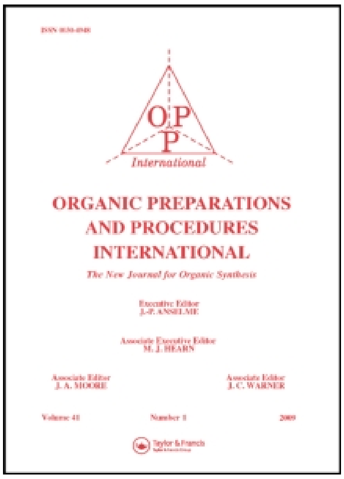

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A CONVENIENT SYNTHESIS OF 2-BENZYLNAPHTHALENE AND 2-BENZYL-1,2,3,4-TETRAHYDRONAPHTHALENE

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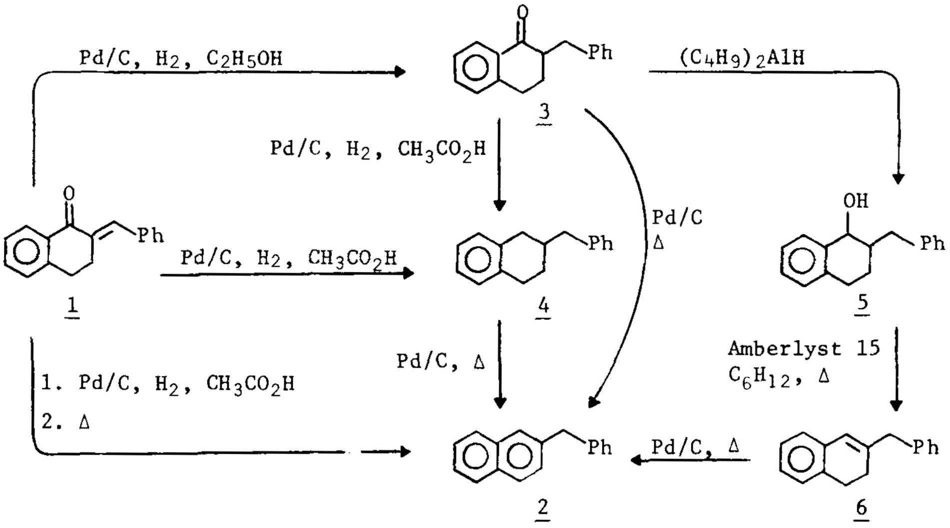
The reactions in Scheme I were used to prepare pure hydrocarbon standards in high yields for the American Petroleum Institute.[3] Of particular interest is the conversion of 2-benzylidene-3,4-dihydro-1(2H)-naphthalenone (1) to 2-benzylnaphthalene (2) in 95% yield. Hydrogenolysis of 2-benzyl-3,4-dihydro-1(2H)-naphthalenone (3) gave 2-benzyl-1,2,3,4-tetrahydronaphthalene (4) in 97% yield. The products of these reactions were free of other isomers in contrast to electrophilic alkylation reactions.[4] However, 2,3-benzofluorene was observed as a side product (*ca.* 3%) in the formation of 2 but not of 4 or 6. The identity of 2,3-benzofluorene was established by comparison of its nmr and mass spectra with those of 1,2-, 2,3-, and 3,4-benzofluorene.

The dehydrogenation of naphthalenones and other unsaturated ketones[5a] and particularly 1[5b] frequently leads to phenols.[6] However, in some cases,[7a,b,c] naphthalenes may be obtained in high yields and hydrogenation, hydrogenolysis and dehydrogenation (Scheme I) provide attractive routes to aromatic hydrocarbons.

The formation of 2 from 1 probably proceeds through 3 and 4 by successive hydrogenation and dehydrogenation. At this time, there is no evidence that 2-benzyl-1,2,3,4-tetrahydro-1-naphthol (5) or 3-benzyl-1,2-dihydronaphthalene (6) are involved. However, it should be noted that

SCHEME I



catalytic dehydrogenation of 3 and 5 leads to mixtures of products whereas dehydrogenation of 4 and 6 gives 2 in high yield. The intermediates 3, 4, 5, and 6 were prepared separately and the indicated conversions[c] to 2 were carried out.

The preparation of 5 by reduction of 3 with diisobutylaluminum hydride is, in our opinion, superior to reduction with lithium aluminum hydride and is recommended.[9] The dehydration[10] of 5 to 6 with Amberlyst 15 is convenient and provides an attractive alternate route to 2.

EXPERIMENTAL[11]

2-Benzylidene-3,4-dihydro-1(2H)-naphthalenone (1).— The ketone 1 was prepared by condensation of 1460 g (10 mole) of 3,4-dihydro-1(2H)-naphthalenone and 1265 g (11 mole) benzaldehyde in a vigorously agitated[12] mixture of 8 l. of 95% ethanol and 1 l. of H_2O containing 545 g (13 mole) of sodium hydroxide. The reaction mixture was stirred for 5 hours at 20-30° at which time gas chromatography[13] showed less than 1% of starting ketone remained.

The reaction mixture was centrifuged and water was added to the centrifuged liquid to cause additional crystallization. The product was crystallized from hot isopropyl alcohol to give 2140 g (97%) of 1: mp 107° [lit.[14a] mp 107°]; nmr (CCl_4) δ 8.07 (m, 1, Ar$\underline{H}$ *peri* to carbonyl), 7.77 (t, 1, vinylic), 7.33 (m, 8, Ar$\underline{H}$), 2.97 (m, 4, $-C\underline{H}_2-C\underline{H}_2-$);[14b] mass spectrum *m/e* (rel. intensity) 234 (100), 115 (13), 91 (13), 90 (13), 89 (9), and 77 (5).

2-Benzylnaphthalene (2).

A. From 1.— A 400 g sample of 1 was hydrogenated at 65° and 50-60 psi in 750 ml acetic acid in the presence of 40 g of 10% Pd/C catalyst for 25 hr.[14a] The excess hydrogen was vented, and the entire hydrogenation flask contents were transferred to a 2-l. round-bottomed flask equipped with heating mantle, magnetic stirring bar, short Vigreus column, and distillation receiver. The acetic acid was distilled rapidly and heating was continued until the flask temperature rose to 300° and dehydrogenation took place. Gas chromatography of the crude product showed the ratio napthalene:2:2,3-benzofluorene (2:197:1).[15] Distillation through a 16-in. vacuum-jacketed Vigreux column gave 339 g (91%) of crystalline 2. A portion of the distillate was dissolved in petroleum ether (bp 60-68°) and the solution was passed through a short column of acid-washed alumina to remove colored impurities. The product 2 was obtained as colorless crystals: bp 154° (0.05 mm) [lit.[16] bp 350° (760 mm)]; mp 54-55° [lit.[9] 54-55°]; nmr (CCl_4) δ 7.0-7.7 (m, 7, $C_{10}\underline{H}_7$), 7.08 (s, 5, $C_6\underline{H}_5$), 3.92 (s, 2, $C\underline{H}_2$); mass spectrum *m/e* (rel. intensity) 218 (100), 217 (44), 215 (23), 202 (20), 141 (11), and 115 (10).

B. From 4.— A 2.00 g sample of 4 and 0.20 g of 10% Pd/C were placed in a 4 ml flask equipped with a condenser. The system was flushed with helium for 5 minutes and the flask was slowly lowered into a molten metal bath at 325° C. Heating was continued until hydrogen evolution ceased (17 min).

The mixture was cooled, ether was added, and the catalyst was filtered. Glpc showed 2:4 (98:2).

C. From 6.— The above procedure was applied to 6 and glpc studies showed 2:6 (99:1).

2-Benzyl-3,4-dihydro-1(2H)-naphthalenone (3).— A 234 g (1 mole) sample of 1 dissolved in 500 ml of 95% ethanol was hydrogenated in the presence of 5.9 g (2.5%) of 10% Pd/C catalyst at 33° and 55 psi for 2 hr. The hydrogenation was stopped when glpc studies showed absence of 1. The crude product was filtered and recrystallized from 95% ethanol to give 221 g of 3 (94%): mp 53.5-54° [lit.[9] 53-54°]; bp 150-155° (0.04 mm) [lit.[9] 155-159° (0.01 mm)]; nmr (CCl_4) δ 7.96 (m, 1, ArH *peri* to carbonyl), 7.13 (m, 8, ArH), 3.40 (m, 1, CH-C=O), 2.4-3.0 (m, 4, $ArCH_2$), 1.3-2.3 (m, 2, CH_2 β to aromatic ring); mass spectrum *m/e* (rel. intensity) 236 (59), 145 (48), 118 (22), 117 (20), 115 (18), and 91 (100).

2-Benzyl-1,2,3,4-tetrahydronaphthalene (4).

A. From 1.— A 234 g (1 mole) sample of 1 dissolved in 500 ml acetic acid was hydrogenated in the presence of 23 g of 10% Pd/C catalyst at 66° for 19 hr. at which time glpc studies showed that all of 1 was consumed. The catalyst was filtered and the crude product was distilled to give 4 (92%): mp 38-39°, bp 133° (0.04 mm) [lit.[17] bp 194-195° (13 mm)]; nmr (CCl_4) δ 7.13 (s, 5, C_6H_5), 6.92 (s, 4, C_6H_4), 2.58 (m, 6, $ArCH_2$), 1.0-2.4 (m, 3, β -CH-CH_2): mass spectrum *m/e* (rel. intensity) 222 (72), 132 (59), 131 (100), 130 (62), 129 (34), and 92 (99).

B. From 3.— The application of the above procedure to 3 yielded 4 (97%).

2-Benzyl-1,2,3,4-tetrahydro-1-naphthol (5).— A 493 g (2.1 mole) sample of 3 dissolved in 1200 ml of dry benzene was added dropwise over a 2.5 hr period to a well-stirred solution of 371 g (2.6 mole) of diisobutylaluminum hydride[18a] in 1 l. of benzene at room temperature in a nitrogen atmosphere.[18b] The solution was withdrawn and cautiously poured onto several liters of crushed ice. The mixture was acidified to Ph 3 with conc. hydrochloric acid. Additional benzene (2 l.) was added, the layers were separated, and the organic phase was dried ($MgSO_4$) and concentrated to give 450 g (90%) of crude 5 which was recrystallized from petroleum ether (bp 60-68°): mp 118-119° [lit.[9] 119-120°]; nmr ($CDCl_3$) δ 7.35 (m, 1, Ar$\underline{H}$ *peri* to hydroxyl), 7.05-7.30 (m, 8, Ar$\underline{H}$), 4.40 (d, 1, C$\underline{H}$-O), 2.2-3.2 (m, 4, ArC$\underline{H}$), 1.1-2.2 (m, 3, C$\underline{H}$-C$\underline{H}_2$ β to aromatic ring), 2.09 (s, 1, O$\underline{H}$); mass spectrum *m/e* (rel. intensity) 220 (51), 147 (25), 146 (62), 129 (100), 128 (37), and 91 (80).

3-Benzyl-1,2-dihydronaphthalene (6).— A 46.0 g sample of 5 was dissolved in 100 ml cyclohexane, 4.6 g of Amberlyst 15 were added,[10] and the mixture was stirred at reflux temperature for 1 hr. The reaction mixture was filtered, dried ($MgSO_4$), and the product was distilled through a vacuum-jacketed Vigreux column to give 41.1 g (97%) of 6: bp 125° (0.05 mm) [lit.[9] bp 126° (0.1 mm)]; nmr (CCl_4) δ 7.11 (s, 5, $C_6\underline{H}_5$-), 6.93 (m, 4, $C_6\underline{H}_4$=), 6.14 (m, 1, vinylic), 3.32 (s, 2, Ar-C$\underline{H}_2$-C=C), 2.61 (m, 2, ArC$\underline{H}_2$), 2.01 (m, 2, allylic); mass spectrum *m/e* (rel. intensity) 220 (59), 141 (25), 129 (100), 128 (36), 115 (14), and 91 (31).

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(10) Literature on the use of Amberlyst 15 resin may be obtained from the Rohm and Haas Co., Independence Mall West, Philadelphia, Pa. 19105.

(11) Mass spectra were obtained at 70 eV on a C.E.C. 110 mass spectrometer using direct probe loading in the ion source. Nmr data were obtained from a Varian HR-60 spectrometer. Line positions are reported as ppm

from internal tetramethylsilane (δ scale). The catalytic hydrogenations were carried out in a 3.5 l. stainless steel vessel using a model 3920 Parr shaker-type hydrogenator.

(12) An E-2 Vibromixer, Chemapec Inc., Hoboken, N. J., was used.

(13) The gas chromatography studies using a Hewlett-Packard model 5750 instrument were made at 240° on an 0.25-in. x 12-ft column of 80-100 mesh Chromosorb G (acid-washed) treated with DMCS and coated with 5% silicone rubber UC W-98.

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