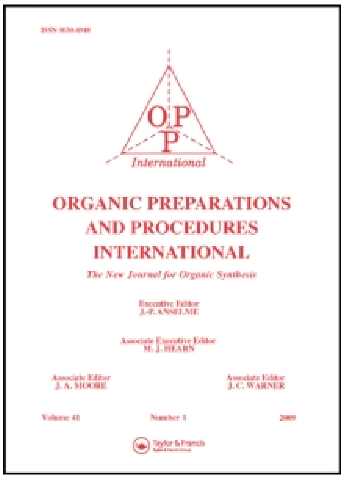

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SYNTHESIS OF 2-HEXYLNAPHTHALENE

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SYNTHESIS OF 2-HEXYLNAPHTHALENE

Submitted by B. Dewprashad and E. J. Eisenbraun*
(06/15/88)

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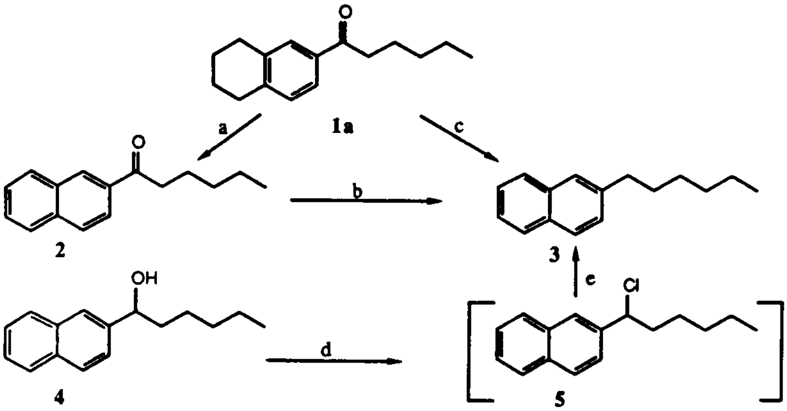
The reaction sequence (1a→2→3) was used to prepare 3 as a high-purity, model hydrocarbon for precise thermodynamic studies of fossil fuel constituents by the National

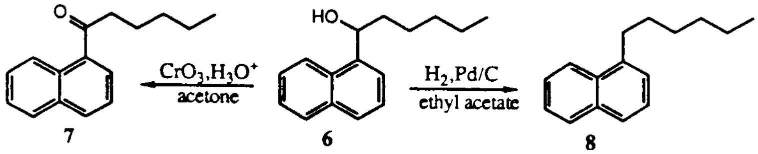


a) Pd/C, p-cymene, Δ. b) NH_2NH_2, OH^-, DEG, Δ. c) Pd/C, Δ. d) Conc. HCl, toluene. e) H_2, Pd/C, C_2H_5OH.

Institute for Petroleum and Energy Research. This route is preferred over 4→5→3, in which 4 is readily prepared from 2-naphthaldehyde and n-pentylmagnesium bromide, because the former route gives less observed impurities and provides crystalline intermediates (semicarbazone of 1a and crystalline 2) for purification.

The acylation of tetralin was expected to produce some 1-(5,6,7,8-tetrahydronaphthyl)-1-hexanone (1b) but we were unable to directly detect its presence. However, an indication of the ratio of 1a:1b was gained by aromatizing the crude acylation product in refluxing p-cymene in the presence of Pd/C.[1] Under these conditions, products indicating deoxygenation of the side-chain were not observed. Capillary GC/MS of the reaction products showed 2:7 (50/1). The semicarbazone of 1a was prepared, recrystallized and regenerated to the starting ketone as an initial step. Dehydrogenation conditions were found which converted 1a directly to 3 in 91% yield.[2,3] However, aromatization to 2, using Pd/C in refluxing p-cymene, was included because it afforded, via recrystallization, an intermediate purification point.

To meet the purity requirement (70 g, 99.9+%) for 3, it was essential to know whether isomer 8 was present. Unfortunately, 3 and 8 could not be distinguished by capillary GC nor by high pressure liquid chromatography. Thus, 7 and 8, shown below, were prepared for use as GC standards. Capillary GC showed that ketone 7 was absent in the sample of purified ketone 2 used to prepare 3. Hence, the sample of purified 3 did not contain 8.



EXPERIMENTAL SECTION

2-(5,6,7,8-Tetrahydronaphthyl)-1-hexanone (1a).- Tetralin (3.54 kg, 26.8 moles), hexanoyl chloride (1.53 kg, 11.4 moles) and 4.0 L nitroethane were combined and vigorously stirred.[4] An ice-salt bath was used for cooling and a nitrogen sweep excluded moisture. Aluminum chloride (1.6 kg, 12 moles) was added through Gooch tubing during 1 hr with the temperature remaining at 0-5°. The cooling bath was then drained and washed free of ice. Stirring was maintained for 30 min and the reaction was then poured onto ice, extracted with ether, washed with water and brine, dried ($MgSO_4$), filtered, concentrated and distilled. The yield of ketone distilling at 167-170°/1 mm was 67%. A 1.69 kg sample of the ketone was converted to the semicarbazone, mp. 148-152°, in 95% yield. The latter was recrystallized to mp. 157-158° from isopropyl alcohol and 500 g was cleaved with hydrochloric acid and ether to 1a in 91% yield: ^{1}H NMR ($CDCl_3$): δ 7.60 (m, 2H), 7.60 (d, 1H), 2.86 (t, 2H), 2.75 (m, 4H), 1.70 (m, 6H), 1.35 (m, 4H), 0.9 (t, 3H); ^{13}C NMR ($CDCl_3$): δ 220.0 (40), 142.7 (82), 137.3 (83), 134.6 (87), 129.3

(196), 128.9 (179), 125 (200), 38.4 (81.6), 31.6 (184), 29.6 (173), 29.4 (178), 24.3 (178), 23.1 (194), 22.9 (181), 22.6 (166), 14.0 (143); MS, m/e (rel. intensity): 230 (17), 174 (100), 175 (26), 159 (64), 160 (43), 131 (29), 91 (36), 77 (7).

Anal. Calcd. for $C_{17}H_{25}N_3O$: C, 71.04; H, 8.77. Found: C, 71.22; H, 8.64

Conversion of 1a to (2-Napthyl)-1-hexanone (2).- Purified 1a (390 g, 1.69 mole) from above was aromatized by heating for 24 hrs in refluxing p-cymene (400 mL) containing 5% Pd/C (33 g).[1] The filtered and concentrated product weighed 297 g (78%) and showed mp. 66-68°. Further recrystallization from n-hexane gave 2, mp. 67-68°; ^1H NMR ($CDCl_3$): δ 8.44 (s, 1H), 8.02 (dd, 1H), 7.95 (d, 1H), 7.82 (m, 2H), 7.50 (m, 2H), 2.02 (t, 2H), 1.75 (m, 2H), 1.38 (m, 4H), 0.92 (t, 3H); ^{13}C NMR: δ 224.5 (40), 135.5 (53), 134.4 (53), 132.5 (56), 129.6 (187), 129.5 (200), 128.3 (194), 128.3 (194), 127.7 (176), 126.7 (161), 123.9 (158), 38.6 (159), 31.6 (156), 24.2 (157), 22.6 (134), 14.0 (127); MS, m/e (rel. intensity): 226 (8), 170 (56), 116 (20), 115 (100), 127 (77).

Anal. Calcd. for $C_{16}H_{18}O$: C, 84.91; H, 8.02. Found: C, 85.33; H, 8.12

GC/MS ratio of 2 and 7 from aromatization of crude 1a.- Crude ketone 1a was treated with Pd/C in refluxing p-cymene as described for the preparation of 2. GC/MS studies using a J and W silica column (DB-17, film thickness 0.5 μm, 0.253 mm x 30 M) programmed at 5°/min from 180-225° showed a small peak (ca. 2% of 7) at 11 min with m/e 226 (20), 170 (70), 155 (100), 127 (55). The peak corresponding to 2, m/e 226 (19), 170 (68), 155 (100), 127 (60), appeared at 13 min.

Conversion of 2 to 2-Hexylnaphthalene (3).- Hydrocarbon (3) was prepared by heating ketone 2 (99.9% purity, 235 g, 1.04 mole), hydrazine hydrate (225 mL) and potassium hydroxide (225 g, 4.00 mole) in 1500 mL diethylene glycol. The product was eluted through a silica column with n-hexane to give 195 g (0.92 mole) of 3 (99.9% pure, 96% yield). The product was further purified to 99.9+% by distillation at 115-112°/3mm. lit.[5] bp. 124°/0.7 mm. ^1H NMR ($CDCl_3$): δ 7.60-8.10 (m, 7H), 3.06 (t, 2H), 2.05 (m, 2H), 1.60 (m, 6H)), 1.21 (t, 3H); ^{13}C NMR ($CDCl_3$): δ 140.3 (30), 133.6 (23), 131.8 (23), 127.6 (131), 127.5 (135), 127.3 (214), 126.1 (108). 125.6 (106), 124.8 (121), 36.0 (119), 31.7 (103), 31.4 (14), 31.2 (107), 28.9 (107), 22.5 (93), 14.0 (86). MS m/e (rel. intensity): 212 (31), 143 (11), 141 (100), 115 (12), 42 (77).

Direct conversion of 1a to 3.- A sample of 1a (25 g, 0.109 mole), purified via its semicarbazone, was heated at 224° in the presence of 2.5 g of 5% Pd/C for 6 hrs. The product, dissolved in ether, was filtered and concentrated to 21.0 g (91%) of 3.[2,3]

1-Naphthyl-1-hexanol (6).- 1-Naphthaldehyde (23.4 g, 0.15 mole) in 100 mL anhydrous ether was added dropwise to a stirred solution of 100 mL of pentylmagnesium bromide (0.2 mole) in ether during 0.5 hr. The reaction mixture was heated at reflux for an additional hour, cooled, quenched with 300 mL of 25% ammonium chloride, and extracted with ether (2 x 200 mL). The extract was washed (saturated Na_2CO_3, water), dried ($MgSO_4$), filtered, concentrated and distilled (Kugelrohr, 130°/0.3 mm) to give 27.2 g (80%) of 6. ^1H NMR ($CDCl_3$): δ 7.35-8.10

(m, 7H), 5.35 (t, 1H), 2.30 (s, 1H), 1.75-1.95 (m,2H), 1.20-1.55 (m, 6H), 0.65-0.95 (t, 3H); ^{13}C NMR ($CDCl_3$): δ 140.6 (73), 134 (64), 130 (56), 128 (227), 127.7 (230), 125.9 (227), 125.8 (21), 125.4 (381), 123.2 (225.9), 122.8 (217), 71.2 (210), 38.3 (209), 31.8 (216), 25.9 (209), 22.0 (183), 14.0 (173).

Conversion of 6 to (1-Naphthyl)-1-hexanone (7).- A 0.6 g (0.003 mole) sample of 6 in 25 mL of cold acetone was magnetically stirred and oxidized by the dropwise addition of chromic acid (Jones reagent[6]) until a permanent orange color resulted. Isopropyl alcohol was added to consume excess reagent and the reaction mixture was concentrated, ether was added and the mixture was dried ($MgSO_4$), filtered and concentrated. The concentrate was dissolved in toluene, filtered through a 0.5" bed of silica, concentrated and distilled to give 0.45 g of 7. ^{1}H NMR ($CDCl_3$): δ 8.62 (d, 1H), 7.86 (d, 1H(, 7.76 (m, 2H), 7.32-7.36 (m, 3H), 2.96 (t, 2H), 1.74 (m, 2H), 1.44 (m, 4H), 0.88 (t, 3H); ^{13}C NMR ($CDCl_3$): δ 204.9 (28), 136.3 (40), 133.9 (66), 132.2 (190), 130.1 (52), 128.3 (200), 127.7 (192), 127.2 (199), 126 (200), 125.8 (200), 124.3 (192), 42.1 (151), 31.5 (179), 24.4 (182), 22.5 (168), 14.0 (141). MS, m/e (rel. intensity): 226 (11), 170 (23), 155 (100, 127 (54).

Conversion of 6 to 1-Hexylnaphthalene (8).- Kugelrohr distillation at 130°/0.3 mm of 6 (23 g, 0.10 mole) in the presence of anhydrous $CuSO_4$[7] (18.4 g, 0.115 mole) gave 17.3 g of colorless dehydration product which was directly hydrogenated (Pd/C, 1.5 g of 5%) in ethyl acetate (150 mL) at 50 psi for 10 min. The catalyst was removed by filtration and Kugelrohr distillation at 115-120°/0.3 mm gave 16.5 g (77%) of 8. Hydrocarbon 8 was further purified through picrate formation and regeneration. ^{1}H NMR ($CDCl_3$): δ 7.95 (m, 1H), 7.75 (m, 1H), 7.60 (m, 1H), 7.20-7.40 (m, 4H), 2.95 (t, 2H), 1.70 (m, 2H), 1.30 (m, 4H), 0.85 (t, 3H). ^{13}C NMR ($CDCl_3$): δ 138.9 (64), 133.9 (41), 131.9 (37), 128.7 (170), 126.4 (169), 125.8 (188), 125.5 (196), 125.5 (197), 125.3 (187), 123.8 (186), 33.1 (160), 31.8 (148), 30.8 (159), 29.5 (152), 22.7 (134), 14.1 (127).

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