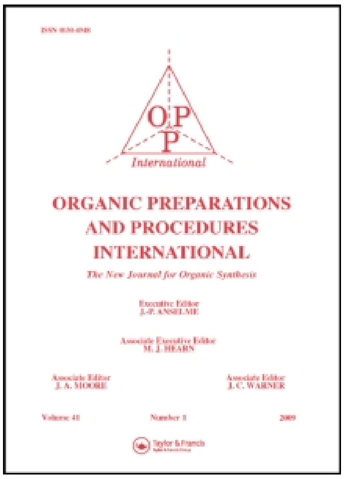

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SYNTHESIS OF 2-(1-NAPHTHYLMETHYL)-3,4-DIHYDRONAPHTHALENE, 2-(1-NAPHTHYLMETHYL)-1,2,3,4-TETRAHYDRONAPHTHALENE, 7a, 8, 9, 13b-TETRAHYDRO-7*H*-DIBENZ [*a, k L*] ANTHRACENE, AND 5,6-DIHYDRO-4*H*-DIBENZ[*a, k L*]ANTHRACENE

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SYNTHESIS OF 2-(1-NAPHTHYLMETHYL)-3,4-DIHYDRONAPHTHALENE, 2-(1-NAPHTHYLMETHYL)-1,2,3,4-TETRAHYDRONAPHTHALENE, 7a,8,9,13b-TETRAHYDRO-7H-DIBENZ[*a*,*kl*]ANTHRACENE, AND 5,6-DIHYDRO-4H-DIBENZ[*a*,*kl*]ANTHRACENE

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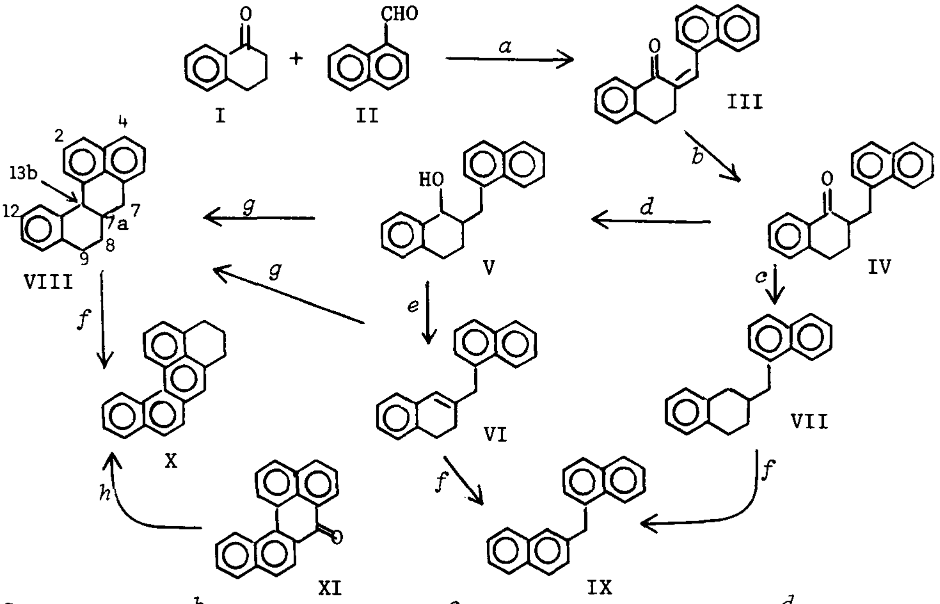
This paper describes the synthesis of three new hydrocarbons — 2-(1-naphthylmethyl)-3,4-dihydronaphthalene (VI), 2-(1-naphthylmethyl)-1,2,3,4-tetrahydronaphthalene[2a] (VII), and 7a,8,9,13b-tetrahydro-7H-dibenz[*a*,*kl*]anthracene (VIII). Also described is a procedure for converting the latter hydrocarbon to 5,6-dihydro-4H-dibenz[*a*,*kl*]anthracene (X)[2b] as shown in the scheme below.



${}^{a}OH^{-}$, C_2H_5OH. ^{b}Pd/C, H_2, C_2H_5OH. ${}^{c}NH_2NH_2$, OH^{-}, glycol, Δ. ^{d}DIBAH. ${}^{e}CH_3CO_2H$, Δ. ^{f}Pd/C, Δ. ^{g}A-15, $C_6H_5CH_3$, Δ. ${}^{h}P_4$, HI, CH_3CO_2H, Δ.

The preparation of III, a precursor to all the new hydrocarbons in the scheme, is readily accomplished by an aldol condensation of I and II in 73% yield. Hydrogenation of III to IV occurred in 67% yield. Of the two routes shown for converting IV to IX,[2b] the preferred approach is via VII,[2b] since a 62% yield is obtained in two steps. The other route involving reduction[3] of IV to V occurred in 49% overall yield. However, V and VI[2b] can be conveniently cyclized with Amberlyst-15[4] sulfonic acid resin (A-15) to the new hydrocarbon VIII.[2b] That cyclization occurs predominately at C-8 of the naphthalene ring of V or VI, as opposed to C-2, was established by Pd/C dehydrogenation of VIII to 5,6-dihydro-4H-dibenz[*a*,*kl*]anthracene (X). The latter was identified by direct comparison with a sample synthesized via the hydriodic acid-red phosphorus reduction[5a,b] of 7H-dibenz[*a*,*kl*]anthracen-7-one (XI). This selective cyclization to VIII suggests a general synthesis route for substituted 5,6-dihydro-4H-dibenz[*a*,*kl*]anthracenes.

The *cis* assignment of protons at C-7a and C-13b of VIII is preferred because of the observed small coupling constant ($J_{7a,13b}$= 4.2 Hz) for the proton at C-13b and because of the lack of a significant low-field shift for the absorptions due to C-1 and C-13 protons. The models of the two conformers of VIII in the *cis* configuration show dihedral angles of 57° and 66° (calculated[6] coupling constant for intermediate angle of 60°, 2.5 Hz), whereas the model of the *trans* isomer shows a near diaxial relationship (calculated[6] coupling constant for 180°, 15.7 Hz) between protons at C-7a and C-13b. The model of the *trans* isomer of VIII also shows interaction for C-1 and C-13 protons, and a downfield aromatic shift similar to that noted for X should be observed. The absence of this shift as well as the good agreement between calculated and observed coupling constants for the C-13b proton leads us to believe that the *cis* isomer of VIII was isolated.

SYNTHESIS OF 2-(1-NAPHTHYLMETHYL)-3,4-DIHYDRONAPHTHALENE

EXPERIMENTAL[7]

3,4-Dihydro-2-(1-naphthylmethylene)-1(2H)-naphthalenone (III). — A 146.0 g (1.0 mole) sample of I and a 156.0 g (1.0 mole) sample of II were dissolved in 3 ℓ of stirred 95% ethanol in a 5-ℓ flask under a nitrogen atmosphere. Sodium hydroxide (40 g, 1 mole) in 75 ml of water was then added. A blue color developed which faded in 15 min. as crystals formed in the solution. Stirring was continued for 5 hr at 20-28°. The reaction mixture was filtered and the collected solid was washed with 95% ethanol (2 x 250 ml) and water (2 x 250 ml). These wet crystals were then dissolved in toluene, the water layer was separated, the solution was dried ($MgSO_4$), and the volume was reduced by rotary evaporation until the product crystallized. The cooled suspension was then filtered to give 208 g (0.73 mole, 73%) of white, granular crystals of III, mp 131-133°, lit.[8] 131°.

Mass spectrum (70 eV) *m/e* (rel intensity) 284 (M^+, 63), 283 (100), 165 (18), 141 (9), 128 (11), and 90 (13); pmr ($CDCl_3$) δ 8.34 (s, 1, vinylic), 8.26-8.12 (m, 1, ArH), 8.04-7.68 (m, 3, ArH), 7.56-7.05 (m, 7, ArH), and 2.82 (s, 4, $ArCH_2CH_2$).

3,4-Dihydro-2-(1-naphthylmethyl)-1(2H)-naphthalenone (IV).— The purified ketone III (85 g, 0.297 mole) was added to a 1-ℓ stainless steel hydrogenation vessel containing 750 ml of 95% ethanol and 2.2 g of 10% Pd/C catalyst.[9a] The vessel was evacuated, hydrogen was introduced, and the vessel was then shaken at 10 psi for five hr.[9b] Crystals that formed during the hydrogenation were dissolved in toluene and this solution was then filtered through Dicalite[9c] to remove catalyst. The filtrate was rotary evaporated to yield a dark red oil. This oil was eluted with toluene through a 5-cm (O.D.) column containing layers (top to bottom) of 2 cm of basic alumina, 3 cm of acid alumina, and 5 cm of silica to give 57 g (0.2 mole, 67%) of colorless IV, mp 89.0-90.5°, lit.[10] 92-93°.

Mass spectrum (70 eV) *m/e* (rel intensity) 286 (M^+, 44), 142 (16), 141 (100), 128 (14), 115 (26), and 90 (20); pmr ($CDCl_3$) δ 8.21-7.94 (m, 2, ArH), 7.84-7.52 (m, 2, ArH), 7.48-6.88 (m, 7, ArH), 4.15 (q, 1, ArCOCH), 2.96-2.42 (m, 4, $ArCH_2$) and 2.05-1.37 (m, 2, $ArCH_2C\underline{H}_2$).

1,2,3,4-Tetrahydro-2-(1-naphthylmethyl)-1-naphthol (V).— A sample (286 g, 1 mole) of IV dissolved in toluene (1.7 ℓ) was added to a stirred solution of DIBAH[3] (288 g, 2 moles) and dry toluene (1 ℓ) at 10° over a 40-min. period. The reaction was stirred for an additional 60 min. and ethyl acetate (100 cc) was carefully added. The contents of the flask were poured onto ice (2 kg) and conc. HCl (700 ml) was added. The layers were separated and the toluene extract was washed with water (3 ℓ), dried ($MgSO_4$), and concentrated. Petroleum ether[11] (1.5 ℓ) was added to precipitate a solid which was collected by filtration and then dried to give 262 g (0.91 mole, 91%) of colorless V, mp 113-115°, lit.[12] 114°.

Mass spectrum (70 eV) *m/e* (rel intensity) 288 (M^+, 10), 270 (56), 146 (65), 142 (100), 141 (89), and 115 (59); pmr ($CDCl_3$) δ 8.22-7.97 (m, 1, ArH), 7.89-6.82 (m, 10, ArH), 4.50 (d, 1, $ArC\underline{H}OH$, J=8 cps), 3.70, 3.57 (d of d, 1, $ArCHOHC\underline{H}$, J=5 cps), 2.88-2.52 (m, 4, $ArCH_2$), 2.24-1.32 (m, 2, $ArCH_2C\underline{H}_2$), and 1.99 (s, 1, $ArCHO\underline{H}$).

2-(1-Naphthylmethyl)-3,4-dihydronaphthalene (VI).— A sample (70 g, 0.24 mole) of V was dissolved in 225 ml of acetic acid and was then heated at reflux for 24 hr. The acetic acid volume was reduced to 50 ml by rotary evaporation and the concentrate was diluted with water (450 ml). This solution was extracted with ether (3 x 500 ml) and the ether layer was then washed twice with saturated sodium carbonate solution and once with water, dried ($MgSO_4$), and concentrated to give 43 g (0.16 mole, 66%) of VI, mp 100-102°.

Mass spectrum (70 eV) *m/e* (rel intensity) 270 (M^+, 94), 142 (100), 141 (70), 129 (90), 128 (44), 127 (17); pmr ($CDCl_3$) δ 8.16-7.92 (m, 1, ArH), 7.90-6.61 (m, 2, ArH), 7.59-7.26 (m, 4, ArH), 7.16-6.78 (m, 4, ArH), 6.25-6.08 (m, 1, ArCH=C), 3.91 (s, 2, $ArC\underline{H}_2C{=}CH$), 2.76 (t, 2, $ArCH_2$, J=8 cps), 2.24 (t, 2, $ArCH_2C\underline{H}_2$, J=8 cps).

Calcd. for $C_{21}H_{18}$; C, 93.29; H, 6.71. Found: C, 93.48; H, 6.52.

SYNTHESIS OF 2-(1-NAPHTHYLMETHYL)-3,4-DIHYDRONAPHTHALENE

2-(1-Naphthylmethyl)-1,2,3,4-tetrahydronaphthalene (VII).— A sample of IV (60 g, 0.21 mole), hydrazine hydrate (40 ml), KOH (28 g, 0.5 mole), and diethylene glycol (800 ml) were added to a 1.2-ℓ stainless steel reaction vessel[13] and this reaction mixture was slowly heated to 250°. This temperature was maintained until 256 ml of distillate was obtained (2.5 hr). The cooled reaction mixture was added to 2 ℓ of deionized water, and this solution was then extracted with benzene (2 x 1 ℓ). The aqueous layer was acidified with conc. HCl and was again extracted with benzene (1 ℓ). The benzene extracts were combined and washed with 10% HCl (500 ml). A dark brown solid appeared which was removed by filtering. Rotary-evaporation gave a second brown solid which was eluted through a column of neutral alumina (5.0 cm x 90 cm) with petroleum ether[11] to give 39 g (0.14 mole, 68%) of colorless, crystalline VII, mp 102-104°.

Mass spectrum (70 eV) *m/e* (rel intensity) 272 (M^+, 42), 142 (100), 141 (55), 131 (82), 115 (35), and 91 (24); pmr ($CDCl_3$) δ 8.10-7.91 (m, 1, ArH), 7.88-7.61 (m, 2, ArH), 7.53-7.20 (m, 4, ArH), 7.12-6.88 (m, 4, ArH), 3.06 (d, 2, $ArCH_2$, J=7 cps), 2.93-2.36 (m, 4, $ArCH_2$), and 2.34-1.22 (m, 3, $ArCH_2C\underline{H}C\underline{H}_2$).

Anal. Calcd. for $C_{21}H_{20}$: C, 92.60; H, 7.40. Found: C, 92.54; H, 7.30.

7a,8,9,13b-Tetrahydro-7H-dibenz[*a,kl*]anthracene (VIII) from 1,2,3,4-Tetrahydro-2-(1-naphthylmethyl)-1-naphthol (V).— Toluene (30 ml) and V (2.0 g, 0.007 mole) were combined with 0.2 g of A-15[4] catalyst and this suspension was heated at reflux for 24 hr. The cooled suspension was filtered and the filtrate was rotary evaporated to dryness to give 1.9 g (0.007 mole, 100%) of VIII, mp 125-135°. Two recrystallizations from isooctane[14] gave 1.4 g (0.0052 mole, 75%) of VIII, mp 142-144°.

Mass spectrum (70 eV) *m/e* (rel intensity) 270 (M^+, 100), 241 (17), 179 (54), 165 (75), 129 (28), and 117 (19); pmr ($CDCl_3$) δ 7.80-7.60 (m, 2, isolated ArH), 7.49-6.90 (m, 8, ArH), 4.30 (d, 1, Ar_2CH, J=4.2 cps), 3.34-2.44 (m, 5, $ArC\underline{H}_2CH_2C\underline{H}C\underline{H}_2Ar$), and 2.17-1.40 (m, 2, $ArCH_2C\underline{H}_2$).

Anal. Calcd. for $C_{21}H_{18}$: C, 93.29; H, 6.71. Found: C, 93.17; H, 6.61.

The mother liquor from the first isooctane[14] recrystallization contained VIII and an unknown compound (ratio ~ 1:1 by glc). The unknown compound represented a 3-4% impurity in the original reaction mixture. A field ionization mass spectral scan showed the presence of a single parent ion peak at *m/e* 270. Aromatization of this mother liquor with Pd/C gave two new hydrocarbons as seen by glc analysis. A low potential mass spectrum showed two parent ion peaks at *m/e* 268 (corresponding to X) and another at *m/e* 266. The latter may arise from dibenzo[*a*,*kl*]fluorene, the aromatized product resulting from cyclization at C-2 of V or VI.

7a,8,9,13b-Tetrahydro-7H-dibenz[*a*,*kl*]anthracene (VIII) from 2-(1-naphthylmethyl)-3,4-dihydronaphthalene (VI).— The above cyclization procedure applied to VI gave VIII in 80% yield.

1,2'-Dinaphthylmethane (IX) from 2-(1-Naphthylmethyl)-1,2,3,4-Tetrahydronaphthalene (VII).— Catalyst (0.2 g of 10% Pd/C)[9a] and VII (2.0 g, 0.007 mole) were heated for 2 hr under nitrogen in a 25-ml round-bottom flask using a Wood's metal bath at 250-300°. After cooling, the product and catalyst was transferrred with benzene and the benzene solution was filtered. The filtrate was then diluted to 100.0 ml and the yield (90%) of IX (mp 96-97°, lit.[15] 96°) was determined by glc.[16]

Mass spectrum (70 eV) *m/e* (rel intensity) 268 (M^+, 100), 267 (53), 266 (16), 265 (23), 252 (17), and 141 (15); pmr ($CDCl_3$) δ 8.14-7.20 (m, 14, ArH) and 4.55 (s, 2, $ArCH_2$).

1,2'-Dinaphthylmethane (IX) from 2-(1-Naphthylmethyl)-3,4-dihydronaphthalene (VI).— The above dehydrogenation procedure applied to VI gave IX in 81% yield.[16]

5,6-Dihydro-4H-dibenz[*a*,*kl*]anthracene (X).— Catalyst (0.2 g of 10% Pd/C)[9a] and VIII (2.0 g, 0.007 mole) were added to a 100-ml round-bottom flask, flushed with nitrogen, and then heated in a molten salt bath at 290-300° for 45 min. After cooling, the residue was dissolved in benzene

(75 ml), filtered to remove catalyst, and rotary-evaporated to give 1.9 g of yellow solid. This solid was passed through a 1.4-cm x 5-cm column of neutral alumina with petroleum ether eluant[11] in a continuous-extraction, glass-fritted apparatus[17] to give 1.8 g (0.0067 mole, 91%) of X as colorless crystals, mp 138-140°,[18] lit.[5] 139°.

Mass spectrum (70 eV) *m/e* (rel intensity) 268 (M^+, 100) 267 (21), 266 (13), 265 (18), 253 (11), and 252 (18); pmr ($CDCl_3$) δ 9.18-8.79 (m, 2, ArH at C-1 and C-13), 8.01-7.10 (m, 8, ArH), 3.15 (t, 4, $ArCH_2$, J=6 cps), and 2.07 (q, 2, $ArCH_2\underline{CH_2}$, J=6 cps); uv max (95% ethanol) 200 nm (log ε 4.56), 221 (4.60), 232 (4.38), 248 (4.00), 259 (4.16), 269 (4.47), 277 (4.76), 287 (4.92), 298 (4.20), 3.08 (4.05), 321 (4.05), and 334 (3.83).

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1. a) American Petroleum Institute Graduate Research Assistant, 1973-74; Lambda Chi Alpha Graduate Scholarship, 1973-74; Continental Oil Company Fellowship, 1975.
   b) Undergraduate Research Assistant, 1970-72.
   c) American Petroleum Institute Graduate Research Assistant, 1969-73; Continental Oil Company Fellowship, 1973; Ph.D., Oklahoma State University, 1973.

2. a) Hydrocarbons VII and IX have been carefully purified and have been made available to the Energy Relations Group at the Bartlesville ERDA station for thermodynamic studies.
   b) Correspondence regarding samples of hydrocarbons VI-X should be directed to A. J. Streiff, American Petroleum Institute, Carnegie-Mellon University, Pittsburgh, Pa. 15213.

3. We thank Mr. T. F. Davenport, Jr., Ethyl Corporation, Commercial Development Division, for literature and a sample of diisobutylaluminum hydride (DIBAH).

4. We thank Dr. C. T. Dickert, Rohm and Haas Company, Philadelphia, Pa. for samples of Amberlyst-15 sulfonic acid resin. Literature describing its use may be obtained from this source.

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9. a) The 10% Pd/C was purchased as a stock item from Engelhard Industries.
   b) A Parr Model 3921 hydrogenation apparatus was used.
   c) Dicalite is a diastomaceous earth filteraid commercially available from Grefco, Inc., Dicalite Division, Arlington, Texas 76010.

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16. No starting material remained after dehydrogenation; the only products were IX, naphthalene, 1-methylnaphthalene, and 2-methylnaphthalene. The naphthalenes presumably result from degradation of IX. The products were identified through glc studies on a 0.25-in. (O.D.) x 11-ft copper column containing acid-washed, DMCS-treated Chromosorb G coated with 5% UC W-98 using a Hewlett-Packard 5750B instrument operating at 170° with dual flame ionization units.

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18. The mp of a mixture of X from this source and from XI showed no depression.

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