Synthesis of Peri-Substituted Naphthalenes and Tetralins

Naser Pourahmady,[1] Euin H. Vickery, and Edmund J. Eisenbraun*

Department of Chemistry, Oklahoma State University, Stillwater, Oklahoma 74078

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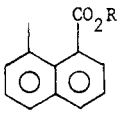
Synthesis of 1-ethyl-8-methylnaphthalene and 1-isopropyl-8-methylnaphthalene along with several 1,2,3,4-tetrahydro derivatives is described. The difficulties encountered in the synthesis and purification of these peri-substituted hydrocarbons are discussed.

Peri-substituted naphthalenes and the corresponding tetralins are of interest because this substitution provides a type of steric environment important in spectroscopic and thermodynamic studies of molecules having crowded substituents.[2]

In this paper, we describe approaches to the synthesis of the new peri-substituted hydrocarbons 1-ethyl-8-methylnaphthalene (**7**) and 1-isopropyl-8-methylnaphthalene (**12**) and the tetrahydro derivatives **4**, **8a**, **9**, and **11a** shown in Scheme I.

Unlike the other disubstituted naphthalene derivatives, peri-substituted naphthalenes cannot be synthesized by Friedel–Crafts condensation. Duswalt and Mayer[3a] prepared 13 of the 14 possible ethylmethylnaphthalenes by alkylating 1- and 2-methylnaphthalene. Sterically hindered 1-ethyl-8-methylnaphthalene was not found among the products. We did not anticipate that the preparation of **7** and **12** should present unusual synthesis problems other than some expected yield decrease through steric interference from peri substitution, and we initially hoped that hydrogenolysis[3b] of **1** would provide 8-methyl-1-naphthoic acid (**13a**) which could then be converted to **7**

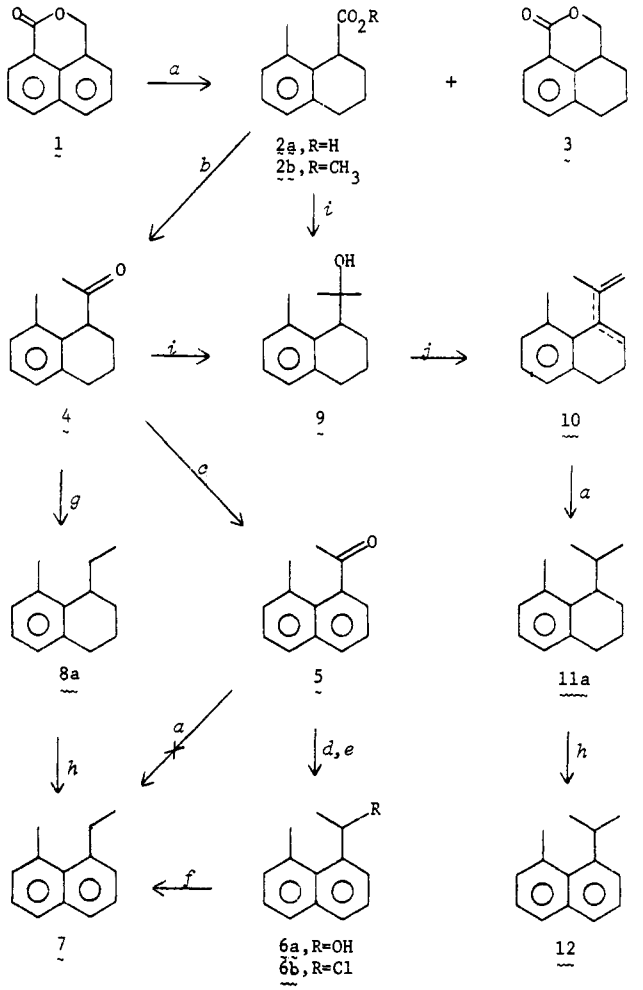


13a, R=H

13b, R=CH_3

via **5**. Instead, ring hydrogenation[4a] took place to give **2a** and **3** (72:28). All attempts at controlling hydrogenolysis to favor formation of **13a** failed.[5a] A separate incomplete hydrogenation of **1** provided a low yield of **13a** as evidenced by GC/MS studies of the methyl ester **13b** obtained with diazomethane. Ester **13b** appeared to be unaffected by treatment with a solution of commercial methyllithium,[5b] and hence we were forced to consider other alternatives. Our final objective was to prepare highly purified samples

Scheme I



[a] H_2, Pd/C, acetic acid, Δ. [b] $SOCl_2$, $(CH_3)_2Cd$. [c] Pd/C, Δ. [d] DIBAH, benzene, Δ. [e] Concentrated HCl. [f] Li-$(Et)_3BH$. [g] N_2H_4, KOH, DEG, Δ. [h] Pd/C, Δ, *p*-cymene. [i] CH_3Li, ether or CH_3MgBr, ether. [j] $CuSO_4$, Δ.

of **7** and **12** for thermodynamic studies,[6] and, consequently, routes with high yields and minimal side products were essential. The best overall route for **7**, not the shortest, became that of **2a** → **4** → **5** → **6a** → **6b** → **7** in 44% overall yield. The route **2a** → **4** → **8a** → **7** gave 22% yield. For the synthesis of **12** we found the route **2a** → **4** → **9** → **10** → **11a** → **12** to give the best overall yield (30%). This route is preferable to that of **2a** → **2b** → **9** because of the greater mixture of products (**2b**/**4**/**9** ratio of 17:25:58) formed in the latter sequence. This was improved by using **4**, which resulted in a 62% yield of **9** obtained as a mixture of **9** and **4** (68:32). Since other well-developed reactions

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(5) (a) Hydrogenation at room temperature and low pressure (below 55 psi) did not take place. Increasing the pressure above 55 psi and the temperature above 60 °C (to 90 °C) changed the product ratio to favor the lactone **3**. Birch reduction of **1** gave a low yield of 1,4-dihydro-8-methyl-1-naphthoic acid. (b) A mixture of esters **2b**/**13b** (9:1) was treated, as described for **2b**, with methyllithium. A GC/MS study showed that **2b** was converted to **4** but that **13b** remained and none of the expected reaction products of **13b** appeared in the GC/MS trace. (c) A rotary evaporator operating at water aspirator pressure and using a warm water bath served to remove solvent.

(6) To be published by: Good, W. D., et al. U.S. Department of Energy, Bartlesville Energy Technology Center, Bartlesville, OK.

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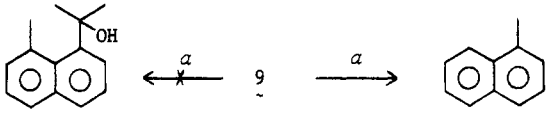
Scheme II



14

[a] Pd/C, Δ.

were found to be unsatisfactory in the synthesis of **7** and **12**, we were forced to use the stated routes, and a discussion of our findings is offered as follows.

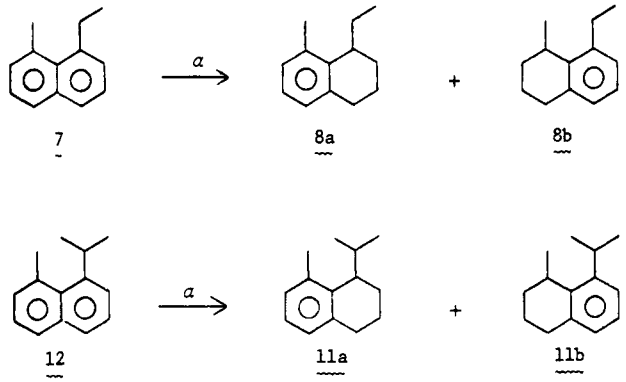
Methyllithium in ether, THF, or a mixture of ether–THF failed to react with **2a** probably because of the formation of insoluble salts,[4b] with **2a** being recovered unchanged. The use of ether and THF gave comparable results. We found that the acid chloride of **2a** reacted directly with dimethylcadmium but not with methyllithium. Acid **2a** was recovered from the latter reaction.

We sought conversion of **4** to **7** via **8a**, but this was blocked by a low-yield Wolff–Kishner reaction which gave impure **8a** (42%). We then aromatized **4** to **5** at 280 °C with Pd/C in 65% yield. Temperature control of this reaction was critical. Ketone **5** was extremely unreactive toward typical carbonyl reagents. For example, in the preparation of the 2,4-dinitrophenylhydrazone,[7] a 24-h reflux period was required to obtain a 30% yield. Further, a stable picrate of **5** is not obtained nor was there any apparent color change on mixing it with an alcohol solution of picric acid whereas methyl 1-naphthyl ketone and methyl 2-naphthyl ketone readily form stable picrates and show color changes. Our attempts to hydrogenolyze[3a] **5** to **7** with Pd/C in acetic acid were frustrated by hydrogenation of the nucleus to **4**. In an attempt to aid hydrogenolysis, we reduced ketone **5** to the alcohol **6a** with metal hydride but found that on subsequent catalytic hydrogenation, ring reduction of **6a** rather than hydrogenolysis to **7** persisted. Mixed hydride[8] (LAH plus $AlCl_3$) reduction of **5** gave **7** accompanied by 15–30% of 1-ethyl-7-methylnaphthalene regardless of mode of addition and alteration of conditions (solvent, reaction time, and ratio of reactants). Migration of *peri*-methyl groups in the presence of Friedel–Crafts catalysts is known.[9] Conventional Wolff–Kishner[10] and Clemmensen[11] reductions of **5** to **7** were not satisfactory because of low yield and impure products. These failures to obtain **7** caused us to prepare **6b** from purified (99.99%) **6a** which was readily dehalogenated to **7** with Super-Hydride.[12] Though three steps are involved in the route **5** → **6a** → **7**, this sequence gave an overall yield of 91%.

For the synthesis of **12** we considered **2b** and **4** as starting materials. Ketone **5** was not used to prepare **12** because of its unreactivity toward methyllithium and methylmagnesium bromide. In these reactions, enolization favored through steric hindrance is so pronounced that none of **14** could be detected as a product.

We attempted Pd/C aromatization of **9** → **14** but found that formation of 1-methylnaphthalene, resulting from

Scheme III



7 8a 8b

12 11a 11b

[a] H_2, Pd/C, ethyl acetate.

dealkylation, was the predominant product as shown in Scheme II. However, dehydration of **9** with hot $CuSO_4$[13] followed by hydrogenation and subsequent aromatization afforded **12** with no significant loss of the side chain provided the dehydrogenation was carried out in the presence of refluxing *p*-cymene.[14]

Direct aromatization of **10** to **12** was less satisfactory since the side-chain double bond survived as shown by GC/MS ($C_{14}H_{14}$, *m/e* 182). Subsequent hydrogenation of this reaction product to **12** ($C_{14}H_{16}$) was troublesome because of the ease of hydrogenation of the aromatic nucleus. Increased bulk in *peri*-alkyl substitution decreases the resistance of the aromatic nucleus to hydrogenation,[15] and the ring with a bulkier substituent is preferentially reduced. We found that **12** hydrogenated more readily than **7**, and hydrogenation of the ring bearing the bulkier substituent is favored in each case. Since standards **7**, **8a**, **11a**, and **12** were available, LC analysis with UV detection permitted an easy determination of the ratios of the resulting tetralins in Scheme III. In these hydrogenations, all of **7** and **12** were consumed, and the ratios of 1,8-dialkyltetralins were 78:22 **8a**/**8b** and 86:14 **11a**/**11b**.

Experimental Section

All melting and boiling points are uncorrected. Vacuum distillations were carried out by using a Kugelrohr apparatus and glassware (two bulbs fitted with ⅋ 19/38 or ⅋ 24/40 joints) purchased from Aldrich Chemical Co. Infrared spectra were recorded on a Perkin-Elmer 681 instrument. Proton and ^{13}C NMR spectra were determined at 100.1 and 25.2 MHz on a Varian XL-100A with tetramethylsilane as an internal standard in $CDCl_3$. GC/MS spectra were provided by Conoco Inc., Ponca City, OK, employing a Finnigan Model 4023 system with a 30-m SP-2100 glass capillary column. GC analyses were obtained with a Varian 3700 capillary gas chromatograph and a Varian Aerograph, Model 550. Analytical and preparative high-pressure LC separations were performed on a Waters Associates analytical system and a Prep LC 500 system. Microanalyses were carried out by Galbraith Laboratories, Inc., Knoxville, TN.

8-Methyl-1,2,3,4-tetrahydro-1-naphthoic Acid (2a). Lactone **1** (300 g, 1.63 mol), prepared as described,[16] was hydrogenated in 3 L of acetic acid by using Pd/C (20 g, 5%) at 55–60 psi at 60 °C for 24 h. The solution was filtered, concentrated,[5c] poured into water, and extracted with ether. The ether layer was washed

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with $NaHCO_3$ solution and concentrated[5c] to 87 g (29%) oof lactone **3**: mp 65–66 °C; ^1H NMR ($CDCl_3$) δ 7.80 (d, 1, Ar H ortho to CO), 7.30 (m, 2, Ar H), 4.40 and 4.00 (q, 1, CH_2OCO), 3.20–2.60 (m, 3, benzylic protons); ^{13}C NMR ($CDCl_3$) 164.96 (carbonyl), 138.32, 135.05, 133.82, 127.34, 126.65, and 124.05(aromatic), 71.64 (CH_2O), 33.35 (ArCH), 27.71 ($ArCH_2$), 23.72, and 21.56 ppm (aliphatic). Anal. Calcd for $C_{12}H_{12}O_2$: C, 76.57; H, 6.42; O, 17.00. Found: C, 76.73; H, 6.63; O, 16.51.

The bicarbonate extract was acidified, extracted with ether, dried ($MgSO_4$), and concentrated[5c] to 218 g (72%) of acid **2a**, mp 146–148 °C (lit.[17] mp 150 °C). Recrystallization from ethyl acetate gave the following: mp 148–149 °C; ^1H NMR ($CDCl_3$) δ 11.1 (s, 1, CO_2H), 7.2–6.9 (m, 3, Ar H), 3.8 (t, 1, Ar**C**HCO_2H), 2.8 (t, 2, Ar CH_2), 2.2 (d, 3, Ar CH_3), 1.8 (m, 4, CH_2); ^{13}C NMR ($CDCl_3$) 181.35 (CO_2H), 137.15, 136.97, 131.43, 127.49, 127.02, and 126.73 (aromatic), 42.08, 29.44, 27.26, 19.61 and 19.38 ppm (aliphatic).

Methyl 8-Methyl-1,2,3,4-tetrahydro-1-naphthoate (2b). A 19-g (0.1 mol) sample of acid **2a** in 300 mL ether was treated with an excess of diazomethane in ether.[21] The ether solution was then washed with 10% sodium bicarbonate, dried ($MgSO_4$), and concentrated[5c] to 20 g (98%) of ester **2b**: bp 125–126 °C (Kugelrohr, 0.1 mm): ^1H NMR ($CDCl_3$) δ 7.18–6.84 (m, 3, Ar H), 3.82 (t, 1, Ar CHCO), 3.64 (s, 3, CH_3O), 2.80 (t, 2, Ar CH_2), 2.15 (s, 3, Ar CH_3), 2.30–1.70 (m, 4, CH_2); ^{13}C NMR ($CDCl_3$) 174.44 (CO), 136.65, 136.43, 131.74, 127.05, 126.58, and 126.06 (aromatic), 51.32, 41.96, 29.20, 27.13, 19.34, and 18.87 ppm (aliphatic); MS *m/e* (relative intensity) 204 (M^+, 9), 145 (100), 129 (8), 115 (4).

8-Methyl-1,2,3,4-tetrahydro-1-naphthyl Methyl Ketone (4). A 114-g (0.54 mol) sample of the acid chloride of **2a**, prepared as described,[18] was dissolved in 900 mL of benzene and then added during 1 h to a mechanically stirred suspension of 1 mol (in 1 L of benzene) of dimethylcadmium.[19] After the exothermic reaction had subsided, the stirred mixture was refluxed for 1 h, cooled, and poured into ice-cold dilute hydrochloric acid. Ether extraction followed by distillation (Kugelrohr; bp 129 °C, 0.05 mm) and recrystallization from petroleum ether (bp 60 °C) gave 86 g (85%) of **4** as a white crystalline product: mp 37–38 °C; IR (CCl_4) 1720 cm^{-1} (CO); ^1H NMR ($CDCl_3$) δ 7.10–6.90 (m, 3, Ar H), 3.8 (t, 1, Ar CHCO), 2.8 (t, 2, Ar CH_2), 2.15 (s, 3, Ar CH_3), 2.10 (s, 3, CH_3CO), 2.00 (m, 2), 1.6 (m, 3, Ar H); ^{13}C NMR ($CDCl_3$) 209.93 (CO), 137.33, 136.39, 132. 86, 127.61, 126.96, and 126.38 (aromatic), 50.49, 29.71, 28.04, 26.50, 19.69, and 19.64 ppm (aliphatic); MS *m/e* (relative intensity) 188 (M^+, 16), 145 (100), 130 (30), 115 (20), 105 (24), 43 (27). Anal. Calcd for $C_{13}H_{16}O$: C, 82.93; H, 8.57. Found: C, 82.82; H, 8.78.

8-Methyl-1-naphthyl Methyl Ketone (5). Ketone **4** (56.5 g, 0.3 mol) was heated at 280–290 °C with 3 g of 10% Pd/C for 12 h until H_2 evolution ceased. The cooled mixture was dissolved in ether and filtered through Dicalite. Concentration[5c] by rotary evaporation gave 48 g of yellow oil which was shown by HPLC (C-18 column, 4:1 acetonitrile/water) to be ketone **5** and 1-methylnaphthalene in a 4:1 ratio in that order of elution. Addition of 100 mL of petroleum ether, refrigeration, and filtration gave 36 g (65%) of crude **5**. A second recrystallization from isohexane removed 1-methylnaphthalene and gave 32.5 g (58%) of ketone **5**: mp 39–40 °C; ^1H NMR ($CDCl_3$) δ 7.8–7.4 (m, 6, Ar H), 2.65 (s, 3, Ar CH_3), 2.50 (d, 3, CH_3CO); ^{13}C NMR ($CDCl_3$) 205.81 (CO), 140.24, 134.43, 133.36, 131.03, 129.71, 128.51, 126.85, 125.92, 124.28, and 123.66 (aromatic), 31.80 (CH_3CO), 23.64 ppm (Ar CH_3); IR (KBr) 1690 cm^{-1} (CO). Anal. Calcd for $C_{13}H_{12}O$: C, 84.75; H, 6.58. Found: C, 84.94; H, 6.65.

DIBAH Reduction of Ketone 5 to Alcohol 6a. Ketone **5** (38.6 g, 0.21 mol) in 250 mL of dry benzene was added dropwise to a stirred solution of 72 g (0.5 mol) of DIBAH in 500 mL of benzene at room temperature. The mixture was stirred at room temperature for 2 h and then at 50 °C for 0.5 h, cooled, and poured into ice–water. Concentrated hydrochloric acid was added to pH 2. Ether extraction and concentration[5c] gave 38.5 g (99%) of alcohol **6a**. Recrystallization from isohexane gave 36.0 g of white needles: mp 78–79 °C; ^1H NMR ($CDCl_3$) δ 7.70–7.20 (m, 6, Ar H), 5.8 (q, 1, OH), 2.7 (s, 3, Ar CH_3), 2.6 (m, 1, Ar CH), 1.2 (d, 3, CH_3CHOH); ^{13}C NMR ($CDCl_3$) 143.42 (×2), 134.99, 133.15, 130.18, 128.87, 127.90, 124.66, 124.54, and 123.46 (aromatic), 66.30 (CHOH), 26.06 (CH_3CHOH), 25.65 ppm (Ar CH_3). Anal. Calcd for $C_{13}H_{14}O$: C, 83.83; H, 7.58. Found: C, 83.64; H, 7.51.

Conversion of Alcohol 6a to Chloride 6b. Alcohol **6a** (36.5 g, 0.194 mol), 2 L of *n*-hexane, and 100 mL of concentrated HCl were mixed thoroughly with a Vibromixer for 30 min at room temperature. The mixture was transferred to a separatory funnel, washed with 10% sodium bicarbonate, and then several times with water, dried ($MgSO_4$), and concentrated to give 38 g (95%) of liquid chloride **6b**: ^1H NMR ($CDCl_3$) δ 7.80–7.00 (m, 6, Ar H), 6.20 (q, 1, Ar CHCl), 2.80 (s, 3, Ar CH_3), 1.80 (d, 3, CH_3CHCl); ^{13}C NMR ($CDCl_3$) 139.28, 134.99, 132.63, 130.88, 130.07, 127.99, 125.80, 124.89, 124.78, and 124.46 (aromatic), 55.79, 26.88, and 25.24 ppm (aliphatic).

1-Ethyl-8-methylnaphthalene (7) from Chloride 6b. A solution of chloride **6b** (37 g, 0.18 mol) in 500 mL dry THF was added dropwise to an ice-cold solution of 0.3 mol of Super-Hydride (lithium triethylborohydride) in 300 mL of THF. The mixture was stirred at room temperature for 2 h, poured into 1 L of ice–water, extracted with *n*-hexane, washed with dilute hydrochloric acid and water, dried ($MgSO_4$), and concentrated[5c] to 29.5 g (97%) of hydrocarbon **7**: mp 5–7 °C; bp 101–102 °C (0.1 mm); ^1H NMR ($CDCl_3$) δ 7.64–7.10 (m, 6, Ar H), 3.17 (q, 2, methylene), 2.76 (s, 3, Ar CH_3), 1.20 (t, 3, CH_3CH_2); ^{13}C NMR ($CDCl_3$) 141.35, 135.54, 134.14, 131.84, 129.59, 127.96, 127.72, 127.67, 124.81, and 124.54 (aromatic), 29.65, 25.33, and 17.34 ppm (aliphatic); MS *m/e* (relative intensity) 170 (64), 155 (100), 141 (10), 128 (12), 115 (14), 77 (20), 63 (8).

Purification of 1-Ethyl-8-methylnaphthalene (7). Picric acid (41.5 g, 0.18 mol) and 28 g (0.165 mol) of **7** (ca. 99%) were dissolved in 200 mL of boiling methanol. When the mixture cooled, the picrate of **7** crystallized as bright orange needles. Further cooling to −10 °C and filtering gave 52 g of product, mp 96–98 °C. Two recrystallizations from 150–175 mL of methanol gave 43.5 (69%) and 38 g (60%) of product, mp 97–97.5 °C. A dried 27-g sample of the purified picrate was decomposed to **7** as described[20] by using a column of basic alumina and *n*-hexane as the eluant to give 18.5 g (0.109 mol) of **7**, mp 6–7 °C (99.98% purity).

1-Ethyl-8-methyl-1,2,3,4-tetrahydronaphthalene (8a). A sample of ketone **4** (3.5 g, 19 mmol) was deoxygenated[10] by using hydrazine hydrate (5 mL, 85%), KOH (2.5 g, 45 mmol), and diethylene glycol (75 mL) to give 1.4 g (42%) of liquid tetralin **8a** [bp 92–94 °C (0.1 mm), further purified by elution through a column of alumina with *n*-hexane: ^1H NMR ($CDCl_3$) δ 6.90 (m, 3, Ar H), 2.70 (m, 3, benzylic), 2.26 (s, 3, Ar CH_3), 2.00–1.20 (m, 6), 1.00 (t, 3, CH_3CH_2); ^{13}C NMR ($CDCl_3$) 140.29, 136.01, 135.66, 127.64, 126.79, and 125.04 (aromatic), 36.45, 29.53, 27.02, 25.08, 18.99, 17.85, and 12.63 ppm (aliphatic); MS *m/e* (relative intensity) 174 (M^+, 12), 145 (100), 128 (12), 115 (10), 69 (68).

α,α,8-Trimethyl-1,2,3,4-tetrahydro-1-naphthalenemethanol (9). Method A. A 150-mL solution of methylmagnesium bromide (Aldrich, 2.9 M in ether) was added dropwise to an ice-cold solution of 9.4 g (50 mmol) of ketone **4** in 300 mL of ether. The mixture was stirred at room temperature for 6 h, heated at reflux for 1 h, poured into acidic ice–water, washed with water, dried ($MgSO_4$), and concentrated.[5c] The crude product (9.2 g) was found to be a **9**/**4** (68:32) mixture by HPLC (silica column, methylene chloride). Alcohol **9** was isolated by using a silica column (methylene chloride) and was found to be identical with that obtained from methylation of ester **2b** (method B): ^1H NMR ($CDCl_3$) δ 7.00–6.80 (m, 3, Ar H), 3.12 (q, 1, Ar CH), 2.90–2.60 (m, 2, Ar CH_2), 2.32 (s, 3, Ar CH_3), 2.20- 1.50 (m, 4, CH_2), 1.14 and 1.17 (s, 3, CH_3COH); ^{13}C NMR ($CDCl_3$) 140.13, 137.09, 135.93, 127.58, 126,35, and 125.22 (aromatic), 75.23 (COH), 43.31, 29.47, 29.12, 26.78, 24.48, 20.57, 20.19 ppm.

Method B. To an 80-mL (1.8 M) solution of methyllithium in ether at reflux temperature was added dropwise a solution of 9.2 g (0.045 mol) of ester **2b** in 150 mL of dry ether. The solution was stirred at room temperature for 15 h and cooled in an ice bath, and 30 mL of dilute hydrochloric acid was added slowly. The

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ether layer was washed with 10% hydrochloric acid and then with water, dried ($MgSO_4$), and concentrated[5c] to 8.9 g of crude product. The product was analyzed by high-pressure LC (silica column, methylene chloride) and GC/MS, and it was found to be a mixture (58:25:17) of alcohol **9**, ketone **4**, and unreacted ester **2b**. Alcohol **9** was separated from the mixture on a silica column by using methylene chloride as the eluant.

Dehydration of Alcohol 9. A mixture of alcohol **9** (4 g, 19.6 mmol and anhydrous copper(II) sulfate (0.75 molar equiv) was heated at 120 °C for 1 h.[13] The cooled mixture was diluted with ether, filtered through Dicalite, concentrated,[5c] and distilled [Kugelrohr, bp 92–95 °C (0.5 mm)] to give 3.5 g (96%) which was identified as a 29:71 mixture of alkenes represented by **10** as shown by GC/MS studies. Attempts to separate the alkenes by column chromatography (silica) or fractional distillation were unsuccessful. Anal. Calcd for $C_{14}H_{18}$ (mixture): C, 90.26; H, 9.74. Found: C, 90.39; H, 9.81.

1-Isopropyl-8-methyl-1,2,3,4-tetrahydronaphthalene (11a). A mixture of alkenes **10** (3.5 g, 18.8 mmol) was hydrogenated at 50 °C and 40 psi in 100 mL of acetic acid by using 700 mg of 5% Pd/C as described for **1** to give 3.2 g (91%) of hydrocarbon **11a** which was purified by elution through a column of silica with *n*-hexane and distillation [Kugelrohr, bp 82 °C (0.2 mm)]: ^1H NMR ($CDCl_3$) δ 6.95 (m, 3, Ar H), 2.27 (s, 3, Ar CH_3), 0.89 (d, 3, CH_3CH), 0.86 (d, 3, CH_3CH); ^{13}C NMR ($CDCl_3$) 140.01, 137.89, 135.54, 127.67, 126.33, and 124.87 (aromatic), 40.45, 31.02, 28.89, 23.99, 21.21, 19.90, 19.46, and 19.41 ppm (aliphatic); MS *m/e* (relative intensity) 188 (M^+, 4), 145 (100), 130 (6), 43 (5). Anal. Calcd for $C_{14}H_{20}$: C, 89.29; H, 10.71. Found: C, 89.05; H, 10.57.

1-Isopropyl-8-methylnaphthalene (12). A sample of 1.5 g (9 mmol) of hydrocarbon **11a**, 5 mL of cymene, and 150 mg of 10% Pd/C was refluxed for 55 h, cooled, filtered through Dicalite, concentrated[5c] under reduced pressure, and then dissolved in 15 mL of hot 95% ethanol containing 2.5 g of picric acid. When the mixture cooled, the picrate of **12** crystallized as orange needles. Filtration gave 3.2 g or product, mp 108–109 °C. The picrate was decomposed on a column of basic alumina by using *n*-hexane[20] to give 0.9 g (60%) of **12**: bp 104–105 °C (Kugelrohr, 0.1 mm); ^1H NMR ($CDCl_3$) δ 7.65–7.10 (m, 6, Ar H), 4.12 (m, 1, CH_3CH); ^{13}C NMR ($CDCl_3$) 146.28, 135.46, 133.65, 131.58, 130.20, 128.16, 127.56, 124.75, 124.37, 123.61, 29.67, 26.18, 25.15 ppm (×2); MS *m/e* (relative intensity) 184 (M^+, 74), 169 (100), 154 (72), 141 (45), 115 (35), 83 (56), 76 (50). Anal. Calcd for $C_{14}H_{16}$: C, 91.25; H, 8.75. Found: C, 91.41; H, 8.65.

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Registry No. **1**, 518-86-5; **2a**, 81603-28-3; **2a** acid chloride, 81603-45-4; **2b**, 81603-29-4; **3**, 81603-30-7; **4**, 81603-31-8; **5**, 67757-66-8; **5** 2,4-DNP, 81603-32-9; **6a**, 81603-33-0; **6b**, 81603-34-1; **7**, 61886-71-3; **7** picrate, 81603-35-2; **8a**, 81603-36-3; **8b**, 81603-37-4; **9**, 81603-38-5; **10** (isomer 1), 81603-39-6; **10** (isomer 2), 81603-40-9; **10** (isomer 3), 81603-41-0; **11a**, 81603-42-1; **11b**, 81603-43-2; **12**, 81603-44-3; **13a**, 19310-98-6; **13b**, 15724-49-9; 1-ethyl-7-methylnaphthalene, 31032-92-5; 1-methylnaphthalene, 90-12-0; methyl bromide, 74-83-9.

Identification of Configurational Isomers of Some 3,3′-Disubstituted 1,1′-Biindans and Related Compounds

Norman E. Heimer, Massoud Hojjatie, and Charles A. Panetta*

Department of Chemistry, University of Mississippi, University, Mississippi 38677

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rac- and *meso*-3,3′-biindan-1-ones have been prepared for the first time and the configuration of the former has been identified by X-ray diffraction analysis. The configuration of the following compounds were then related to these two diastereomers by unambiguous syntheses: *rac*- and *meso*-3,3′-biindan-1-ol, two isomers of *rac*-3,3′-dichloro-1,1′-biindan, two isomers of *rac*-3,3′-dibromo-1,1′-biindan, *rac*-1,1′-biindan, *rac*-1,1′-bi-1*H*-indene, and one racemic pair of 1-(1-indanyl)-2-indene. All, but the last three (whose configurations were previously unknown) are new compounds.

The configurations of several 1,1′-biindans and 1,1′-bi-1*H*-indene were required for a research project. Only one form each of the known 1,1′-biindan (**1**)[1] and 1,1′-bi-1*H*-indene (**2**)[2] have been reported, but as far as we can determine, the configurations were never identified. The other desired compounds (**3–6**) were never reported in the literature.

rac-3,3′-Biindan-1-one (**3**) was prepared for the first time and its configuration was identified unequivocally by X-ray diffraction analysis (Tables I and II and Figure 1). A second, lower melting isomer of **3** was assumed to be the meso form. The configurations of the other compounds reported in this paper were then related to these two diastereomers by chemical interconversion (outlined in Scheme I).

1,1′-Bi-1*H*-indene (**2**) was prepared by the usual method of coupling indenylmagnesium bromide in the presence of cupric chloride.[2] The product mixture, in a typical experiment, consisted of recovered indene (26%), crystalline **2** (mp 100 °C, 68%), and viscous oil. Gas and liquid chromatography of the oil revealed two components: one, with the greater retention time (volume), was identical with that of crystalline **2**; the other component was assumed to be an isomer of **2** (mainly by comparison of the infrared and NMR spectra of the crystalline and oily samples).

Hydrochlorination[3] of crystalline **2** afforded two crystalline isomers of 3,3′-dichloro-1,1′-biindan (**4**): the first (mp 160–161 °C) in 76% yield and the second (mp 130–131 °C) in 17% yield. These same two isomers were obtained in reduced yields (30% and 17%, respectively) after hydrochlorination of an oily (mixed isomer) sample of **2**. No other pure (crystalline) dichloro isomers could be obtained from the hydrochlorination of the oily or crystalline bi-

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