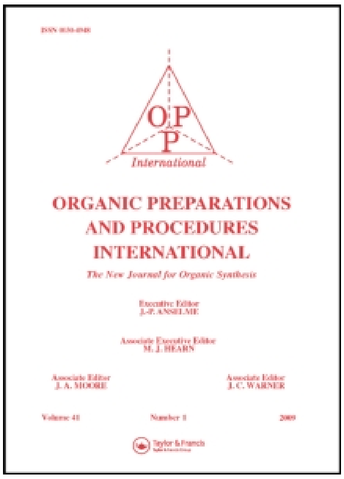

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# PURIFICATION OF 1,2-DIHYDRONAPHTHALENE- AN IMPORTANT INTERMEDIATE IN THE HYDROPROCESSING OF NAPHTHALENE

Mike D. Cagle[a]; Sharbil J. Firsan[a]; E. J. Eisenbraun[a]
[a] Department of Chemistry, Oklahoma State University, Stillwater, OK

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9. Small quantities (<10%) of N-1,N-4-disubstituted piperazines can be detected by TLC and isolated. The attribution of the N-4 regioisomer to the compounds **2a-d** was based on the Nuclear Overhauser Enhancement (NOE) of H-$3_{eq}$ (3%), H-$5_{eq}$ (2%) and H-$3_{ax}$ /H-$5_{ax}$ (1.5% overall) at 400 MHz (Varian VXR 400S) by irradiating the $CH_2$ in the side-chain of **2a**; structures **2b-d** were attributed by analogy.

10. A higher yielding hydrogenation procedure ($PtO_2$, 60 psi, 60°, 86%) is given in ref. 7.

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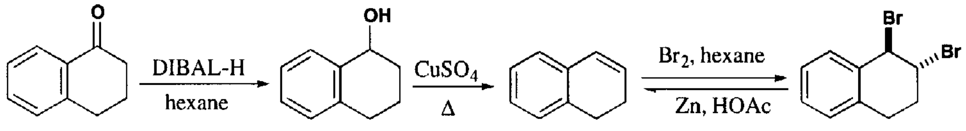
# PURIFICATION OF 1,2-DIHYDRONAPHTHALENE- AN IMPORTANT INTERMEDIATE IN THE HYDROPROCESSING OF NAPHTHALENE

*Submitted by* (09/07/93)

Mike D. Cagle, Sharbil J. Firsan and E. J. Eisenbraun*

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

1,2-Dihydronaphthalene (**3**) is an important intermediate in the hydroprocessing of naphthalene which in turn, is a useful model in studies of the hydroprocessing of aromatic constituents of fossil fuels.[1] Knowledge of the precise thermochemical properties of **3** is essential for introducing improvements in refinery design and other petroleum processing technology.[2] Determination of these properties has been precluded thus far by the unavailability of **3** of the required purity. To meet this need, we prepared 68+ g of **3** (≥ 99.97% purity).[3]



**1** **2** **3** **4**

While **3** and its 1-tetralol (**2**) precursor are commercially available,[4] they were synthesized starting with 1-tetralone (**1**) in order to minimize the presence of impurities boiling in the same range as **3**. Thus, treatment of freshly distilled **1** with DIBAL-H in hexane and dehydrating the resulting **2** by distilling from anhydrous copper(II) sulfate[5] afforded **3** in 98% initial purity. These reagents were selected in preference to the previously reported use of $NaBH_4$ in alcohols[6,7] and conc. HCl in acetic acid[6] because of the scale involved and in order to avoid formation of octahydrobenzo[j]fluoranthenes during exposure of **3** to strong protic acids.[8] Our previous attempts at achieving the desired high purity by subjecting **3** to the following treatments failed: (i) fractional distillation under reduced pressure using packed and spinning band columns, (ii) chromatography on acidic and basic alumina, on silica gel impregnated with silver nitrate, on basic alumina impregnated with 5% picric acid, and using a [3-(2,4-dinitroanilino)propyl]silica (DNAP) column,[9] and finally (iii) by reaction with mercuric acetate and decomposition of the resulting adduct with mineral acid.[10]

Successful ultrapurification was ultimately accomplished by preparing the dibromide **4**,[6,11] repeatedly recrystallizing from ether, and cleanly debrominating it to **3** with zinc in acetic acid.[12,13] The final step involved distillation of **3** under reduced pressure and sealing under vacuum in glass ampoules.[14] 1,2-Dihydronaphthalene (**3**) thus obtained showed 99.97% purity by capillary gas chromatography.

The value of this purification procedure, which is analogous to Fieser's purification of cholesterol *via* its dibromide,[15] lies in its simplicity, the generation of gram quantities of ultra pure material, and its potential applicability to similar compounds.

## EXPERIMENTAL SECTION

Melting points determined with a Thomas-Hoover Unimelt apparatus are uncorrected. NMR spectra ($^1H$ at 300 MHz and $^{13}C$ at 75 MHz) were recorded using a Varian XL300 spectrometer. The chemical shifts are in ppm down field from TMS as internal standard. Mass spectra were obtained from a VG-analytical ZAB 2-SE-high resolution, reverse geometry instrument. Gas chromatographic data was obtained from a Varian 3700 instrument with FID 60 m x 0.247 mm fused silica column interior coated with 0.25 μm of DB-5ms (J & W Scientific); flow rate = 21.7 cm/min or 1.4 mL/min; temp. program = 60° (10 min) to 300° at 10°/min.

**(±)-1,2,3,4-Tetrahydro-1-naphthalenol (2)**.- A solution of freshly distilled 1-tetralone (**1**) (275.8 g, 1.89 mol) in hexane (200 mL) was added dropwise (25-60°, 4.5 hrs) under nitrogen to a solution of diisobutylaluminum hydride in hexane (800 mL). The resulting turbid reaction mixture was stirred for 0.5 hr and was then treated cautiously with methyl acetate (200 mL) over 4 hrs, during which time the solvent began to reflux and vigorous gas evolution took place. This was followed by dropwise addition (0°, 3 hrs) of methanol (200 mL). The resulting thick white suspension was poured onto ice-water, acidified, and then extracted with ether (4 x 500 mL). The combined ether extracts were washed with brine and saturated $NaHCO_3$, dried ($MgSO_4$), and concentrated to 319 g of pale-yellow oil. Kugelrohr distillation (90-100°/0.06 mm; lit.[16] bp. 89°/1 mm) gave 261 g (93%) of **2**. The NMR and MS data agreed with reported values.[17]

**1,2-Dihydronaphthalene (3).**[6,11c]

**Method A- From 2.**- Kugelrohr-distillation of 50-g (0.34 mol) batches of **2** mixed with anhydrous copper(II) sulfate (40 g, 0.25 mol) was used for dehydration.[5] The distillates from five such dehydrations were combined, washed (sat'd $NaHCO_3$ 100 mL, brine 100 mL), dried ($MgSO_4$), filtered, and fractionated using a 20-cm Vigreux column (55°/0.2 mm; lit.[6] bp 78-80°/9 mm) to give 146 g (66%) of **3** in 98% purity. Our earlier attempts at dehydrating **2** to **3** using oxalic acid, 80% sulfuric acid, or trifluoroacetic anhydride gave side products.

**Method B- From Dibromide 4.**- Zinc dust (63 g, 0.96 mol) and acetic acid (50 mL) were added at 0° to a solution of dibromide **4** (233 g, 0.80 mol) in ether (2.5 L).[12] After 1 hr at 0°, the mixture was allowed to warm to 25°, stirred at 25° for 2 hrs, washed (5% HCl, 200 mL; sat'd $NaHCO_3$, 2 x 250 mL; brine, 250 mL), dried ($MgSO_4$), filtered, and concentrated to a light oil. Fractional distillation through a 20-cm Vigreux column (45°/0.05 mm) yielded 68.2 g (65%) of **3** of 99.97% purity by capillary gas chromatography.

**(±)-*trans*-1,2-Dibromo-1,2,3,4-tetrahydronaphthalene (4)**[6,11].- Bromine (180 g, 1.13 mol) was added dropwise at 0°, in the dark, to a solution of **3** (146 g, 1.13 mol) in hexane (1 L). After addition, excess bromine was destroyed with cyclohexene (10 mL). Concentration and repeated recrystallization from ether afforded 233 g (71%) of **4** as white crystals, mp 70.5-71° (lit.[11a] mp 68-68.5°), purity 99.97%; $^1$H NMR ($CDCl_3$)[11a]: δ 2.03-2.24 (m, 1H, H-3), 2.60-3.06 (m, 2H, H-4), 3.11-3.36 (m, 1H, H-3), 4.90 (s, 1H, H-2),[18] 5.63 (s, 1H, H-1), 7.00-7.39 (m, 4H, Ar); $^{13}$C NMR ($CDCl_3$,) δ 24.39, 25.04 and 51.48 (aliphatic C̲H's), 126.56, 128.80, 129.11, and 131.13 (aromatic C̲H), 132.70 and 134.32 (quaternary aromatic C̲). HRMS m/z 289.9129 ($M^+$); Calcd. ($C_{10}H_{10}$ $^{79}$Br $^{81}$Br) 289.9129.

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