One-Step Synthesis of *meso*- and *d,l*-Bis-[2-naphthyl]-butanes from 2-Acetylnaphthalene[1]

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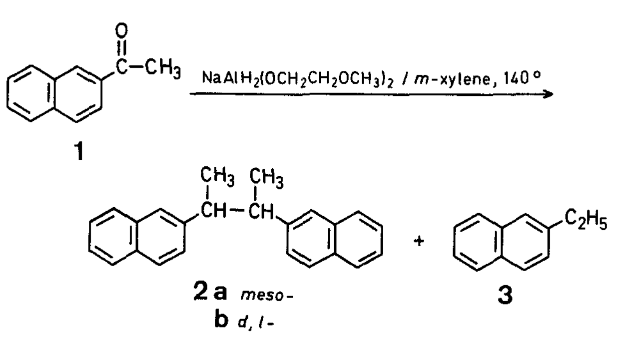
In a previous communication we described the reaction of benzophenone with sodium bis-[2-methoxyethoxy]-aluminum hydride which in one step affords 2,2-diphenylpropane as the major product, accompanied by 1,1-diphenylcyclopropane[2]. To investigate the synthetic possibilities of this new reaction, we extended the study to other carbonyl compounds; we now report the results of the reaction of 2-acetylnaphthalene (**1**) with sodium bis-[2-methoxyethoxy]-aluminum hydride.

Whereas treatment of **1** with $NaAlH_2(OCH_2CH_2OCH_3)_2$ in boiling benzene under nitrogen gave the expected (±)-1-(2-naphthyl)-ethanol (yield: 97%; m.p. 73.0–73.5°[3]), the reaction took an unusual course at a more elevated temperature.

From the reaction of **1** with the hydride in *m*-xylene at 140°, we isolated colorless, crystalline compounds to which we assigned structures **2a** (yield: 27%, m.p. 157.0–157.5°) and **2b** (yield: 16%, m.p. 96.0–96.5°), respectively, and a liquid compound identified by G.L.C. analysis as **3** (yield: 37%).



The gross structures of **2a** and **2b** were established by elemental analysis as well as I.R. spectral data, both of which are identical for the two compounds. Final proof of the structure of hydrocarbons **2a** and **2b** was provided by the N.M.R. spectra [in $CDCl_3$ relative to $(CH_3)_4Si$]. Compound **2a** shows a complex multiplet in the region of 2.7 τ (aromatic H), an unresolved multiplet centered at 7.05 τ (C—H), and a doublet at 8.86–8.92 τ (C—CH_3). Compound **2b** shows an unresolved multiplet formed by overlap of two different aromatic proton resonances, as well as an unresolved multiplet for C—H. Apart from an intense doublet for C—CH_3 at 8.62–8.68 τ, the spectrum displays another doublet at 8.86–8.92 τ in an integration ratio of 1:4 (indicating the presence of 20% of the higher melting hydrocarbon **2a**).

In analogy to the differences found in the N.M.R. spectra of *meso*- and *d,l*-2,3-diphenylbutanes[4], the higher melting hydrocarbon **2a**, the C—CH_3 groups of which resonate 0.24 δ p.p.m. higher than those of the lower melting **2b**, is assigned the *meso*-2,3-bis-[2-naphthyl]-butane structure, and the hydrocarbon **2b** taken to be the *d,l*-isomer. Unfortunately, comparison of our *d,l*-isomer with the product prepared earlier by Kharasch via a 3-step synthesis from 2-vinylnaphthalene, and believed to be **2b**, was not possible because of a lack of physical and structural data in the literature which would characterize the latter compound[5].

The formation of **3** from **1** is in accordance with the transient formation of diphenylmethane from benzophenone under similar reaction conditions; no 2-isopropylnaphthalene was, however, detected in the reaction mixture, whereby this compound should correspond to the methylated products resulting from "hydrogenolytic methylation" of benzophenone[2]. The absence of an aryl-activated benzylic C-atom in the case of **1** and the substantially higher stability of **2a**–**2b** toward disproportionation compared to that of the relatively unstable 1,1,2,2-tetraphenylethane[2] which is transiently formed during the reduction of benzophenone, are probably responsible for the different course of hydrogenolytic reactions of **1** and benzophenone with the hydride.

The conversion of **1** into **2a**–**2b** represents, to our knowledge, the first example of a single-step transformation of alkyl aryl ketones to diarylalkanes by use of a metallic hydride; similar results obtained in the reactions of acyl-substituted condensed aromatic hydrocarbons indicate the general character of this reaction.

(±)-1-(2-Naphthyl)-ethanol:

Ketone **1** (5.1 g, 0.04 mol) in benzene (50 ml) was mixed at room temperature with $NaAlH_2(OCH_2CH_2OCH_3)_2$ (8.7 g, 0.04 mol) in benzene (50 ml) and refluxed under nitrogen for 10 min. The reaction mixture was cooled to 0°, diluted with ether, and decomposed with 20% sulfuric acid. The solvent layer was combined with the ether extract of the aqueous layer, and the solution washed with 10% aqueous sodium hydrogen carbonate, then with water, and dried with sodium sulfate. The solvents were removed and the residue was distilled in vacuo; yield: 5.0 g (97%); b.p. 168–170°/13 mm; m.p. 73.0–73.5°, from light petroleum (b.p. 110–140°) (Ref.[3], m.p. 73.0–73.5°).

For comparison, the reaction was repeated using 1-acetylnaphthalene under the same reaction conditions. The product was (±)-*1-(1-Naphthyl)-ethanol*; yield: 4.94 g (96%); m.p. 65.5–66.0°, from ligroin (Ref.[6], m.p. 65–66°).

***meso*-2,3-Bis-[2-naphthyl]-butane (2a), *d,l*-2,3-Bis[2-naphthyl]-butane (2b), and 2-Ethylnaphthalene (3):**

Ketone **1** (8.5 g, 0.05 mol) in *m*-xylene (47 g) was added to solid $NaAlH_2(OCH_2CH_2OCH_3)_2$ (20.5 g, 0.1 mol) (prepared from the commercial hydride solution in benzene by solvent evaporation in vacuo), and the mixture refluxed (140°) under nitrogen. The homogeneous solution turned from deep blue to brown and, according to G.L.C. analysis, was free of 1-(2-naphthyl)-ethanol after 2 hr; after refluxing for a further 30 min, the mixture was cooled to 0°, decomposed (discoloration) with 20% sulfuric acid, the solvent layer combined with the ether extract of the aqueous layer, the solution successively washed with 10% aqueous sodium hydrogen carbonate, with water, and dried with sodium sulfate. Removal of the solvents gave an oily residue (8.24 g) which was dissolved in hot ethanol (100 ml) and cooled to −70°; the crystalline product (2.57 g) which separated was recrystallized once from ethanol. Subsequent sublimation in vacuo (0.2 torr, bath temperature 160°) gave colorless needles of meso-*2,3-bis-[2-naphthyl]-butane* (**2a**); yield: 2.1 g (27%); m.p. 157.0 to 157.5°.

$C_{24}H_{22}$	calc.	C 92.86	H 7.14
(310.4)	found	93.11	7.29

The mother liquor from the separation of crude crystalline **2a** (after cooling to −70°) was freed from ethanol and distilled in vacuo (14 torr); the distillate obtained was identified by G.L.C. analysis and by comparison with an authentic sample as *2-ethylnaphthalene* (**3**); yield: 2.9 g (37%); b.p. 123–124°/14 torr (Ref.[7], b.p. 122.5°/12 torr).

The oily residue resulting from the isolation of **3** was fractionally distilled in vacuo (0.2 torr) and the fraction (1.5 g) boiling at 170–175°/0.2 torr solidified on standing. Recrystallization of this material from ethanol (2 times) afforded colorless needles of d,l-*2,3-bis-[2-naphthyl]-butane* (**2b**), containing, according to N.M.R. analysis, 20% **2a**; yield: 1.2 g (16%); m.p. 96.0–96.5°.

$C_{24}H_{22}$	calc.	C 92.86	H 7.14
(310.4)	found	92.99	7.09

I.R. (CS_2) of **2a** and **2b**: (CH_3) 2974 (s), 1376 (m), 1456 (m), 2875 (w) cm^{-1}; (C—H) 2905 (w) cm^{-1}.

Received: October 18, 1972

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