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

J. Málek and M. Černý

Institute of Chemical Process Fundamentals, Czechoslovak Academy of Sciences, Praha 6-Suchdol 2, CSR

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. 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 (I) with sodium bis-[2-methoxyethoxy]-aluminum hydride.

Whereas treatment of 1 with NaAlH₄(OCH₂CH₂OCH₂)₂ in boiling benzene under nitrogen gave the expected (±)-1-(2-naphthyl)-ethanol (yield: 97%, m.p. 73.0–73.5 °C), the reaction took an unusual course at a more elevated temperature.

From the reaction of 1 with the hydride in m-xylene at 140 °C, 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%).

1

NaAlH₄(OCH₂CH₂OCH₂)₂ / m-xylene, 140 °C

2a meso-
2b d,l-
3
The gross structures of \(2a\) and \(2b\) were established by elemental analysis as well as 1.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\(_3\))\(_2\)Si]. Compound \(2a\) shows a complex multiplet in the region of 2.7-7 (aromatic H), an unresolved multiplet centered at 7.05 (C=H), and a doublet at 8.86-8.92 (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; the spectrum displays another doublet at 8.86-8.92; 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 \(\delta\) 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 Khuransh 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-isopropyl-naphthalene was, however, detected in the reaction mixture, whereby this compound should correspond to the methylated products resulting from "hydrogenolysis methylolation" of benzophenone\(^2\). The absence of an aryl-activated benzylic C-atom in the case of \(1\) and the substantially higher stability of \(2a\) to \(2b\) 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 hydrogenolyc reactions of \(1\) and benzophenone with the hydride.

The conversion of \(1\) into \(2a\) to \(2b\) 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.

\(\pm\)1-(2-Naphthyl)-ethanol:

Ketone \(1\) (5.1 g, 0.04 mol) in benzene (50 ml) was mixed at room temperature with NaAlH\(_4\) (2.7 g, 0.04 mol) in benzene (50 ml) and refluxed under nitrogen for 10 min. The reaction mixture was cooled to 0 \(^\circ\)C, 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. 186 170/13 mm; m.p. 73.0-73.5. from light petroleum (b.p. 110-140\(^\circ\)C) (Ref.\(^6\), m.p. 73.0-73.5).

For comparison, the reaction was repeated using 1-acetyl-naphthalene under the same reaction conditions. The product was \((\pm\)1-(1-Naphthyl)-ethanol; yield: 4.94 g (96%); m.p. 65.5-66.0 \(^\circ\)C from ligroin (Ref.\(^6\), m.p. 65-66).