SHORT PAPER

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A new, safe and convenient procedure for reduction of naphthalene and anthracene: synthesis of tetralin in a one-pot reaction[†]

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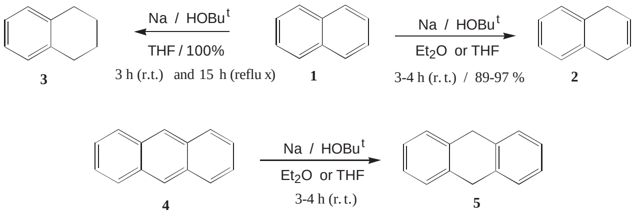
Reduction of naphthalene and anthracene with sodium and *tert*-butyl alcohol gave 1,4-dihydronaphthalene and 9,10-dihydroanthracene respectively in high yields at room temperature (r.t.) as the sole products. The synthesis of tetralin from naphthalene was carried out in a one-pot reaction *via* 1,4-dihydronaphthalene. The reduced products were easily isolated.

Keywords*:* reductions, sodium, naphthalene, anthracene, *tert*-butyl alcohol

Reduction reactions of aromatic compounds such as the Birch reduction and related reactions are important in synthetic organic chemistry, and therefore these reactions have been investigated by many chemists.[1] The reduction products or intermediates formed in these reactions serve as starting materials for many target molecules.[2] The reduction of aromatic rings by solutions of alkali metals in liquid ammonia was discovered by Wooster and Godfrey,[3] who reacted toluene with sodium in ammonia followed by the addition of water. They reported a “highly unsaturated liquid product”, which was not identified further. The real development of this reaction was to follow in the work by Birch.[4] This reaction is generally referred to as the Birch reduction, although in some cases it is simply called metal–ammonia reduction. Wild and Nelson[5] found adding alcohol last to be advantageous, as opposed to having it present when the metal is added, and it was subsequently discovered that it should be avoided altogether with polynuclear compounds.

Depending on the reaction conditions, naphthalene (**1**) is reduced to different products. Naphthalene is converted to 1,2,3,4-tetrahydronaphthalene (tetralin) (**3**), or *cis*- or *trans*-decahydronaphthalene (decalin) by catalytic hydrogenation.[1a,e,6] The reduction of naphthalene with sodium and ethanol gives 1,4-dihydronaphthalene (**2**) at high temperatures (60–145°C).[2a] It is possible to effect the reduction of naphthalene selectively with metal-ammonia, amine, *etc.* solutions to form dihydro, tetrahydro, hexahydro or octahydro derivatives.[1a,e,7] In a similar way, anthracene is also reduced to different products, depending on the conditions.[1a,c,d,e,2c,6b,8] For the reduction of anthracene to 9,10-dihydroanthracene, Na and ethanol at a high temperature (50°C) are extensively used.[8]

We reduced naphthalene (**1**) and anthracene (**4**) with sodium and HOBu^t in diethyl ether (Et_2O) or tetrahydrofuran (THF) at r.t. for 3–4 h. The reduction products are 1,4-dihydronaphthalene (**2**) and 9,10-dihydroanthracene (**5**), respectively (Scheme 1). In the reductions of naphthalene, there are some differences when THF is used instead of Et_2O: a navy blue colour appears when metallic Na is added to the solution of naphthalene, and it disappears when HOBu^t is added. Only unreacted Na was removed from the THF reaction mixture by gravity filtration because NaOBu^t was dissolved in THF. For the reduction of anthracene (**4**) to 9,10-dihydroanthracene (**5**), a similar procedure was used (Scheme 1). However, larger amounts of Et_2O and THF were used because of the low solubility of anthracene in these solvents. The yields are 89–97 % in the reduction reactions.



Scheme 1

Compared to the reduction procedure of naphthalene (**1**)[2a] and anthracene (**4**)[8] with sodium-ethanol to 1,4-dihydronaphthalene (**2**) and 9,10-dihydroanthracene (**5**), respectively, the procedure with sodium-HOBu^t yielding the same products has certain advantages. These include the following:

(1) The reduction reactions are carried out at room temperature. The reaction temperatures are much lower than those in the other procedures (50–145 °C).

(2) The reactions are much safer because they are less exothermic in the presence of HOBu^t. HOBu^t is used in the new procedure while ethanol is used in the others as the source of proton. However, unreacted Na is removed by gravity filtration. NaOBu^t is also removed by filtration when Et_2O was used as solvent.

(3) The reduction products are easily isolated. Distillation and crystallisation are not necessary for the reaction products because they are pure enough.

(4) Synthesis of tetralin (**3**) from naphthalene (**1**) is possible *via* 1,4-dihydronaphthalene (**2**) in a one-pot reaction.

In the reductions of aromatic compounds, alcohols are extensively used as the source of proton or acid. The reactions of alcohols with metals, radical anions, monoanions or dianions are exothermic. The acidity of the alcohols used is important in these reactions. HOBu^t has a significantly higher pK_a of 18, about 100 times less acidic than a primary alcohol such as ethanol (pK_a 15.9). Therefore, the reactions of HOBu^t with these anions are slow, and the reaction conditions are mild.

To synthesize tetralin (**3**) (Scheme 1), 5 equivalents (eq.) metallic Na and HOBu^t were added to the naphthalene solution (1.0 eq.). After the mixture was stirred at r.t. for 3 h, it was refluxed for 15 h. The work-up of the mixture was

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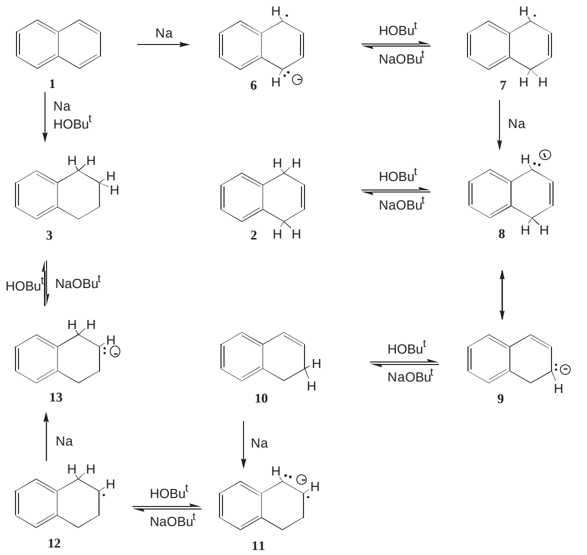
[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

performed as described above, and tetralin was obtained quantitatively. It was observed that this reaction occurred very slowly at room temperature.

To observe the formation of 1,2-dihydronaphthalene (**10**) in the reaction medium, naphthalene (**1**) was reduced to 1,4-dihydronaphthalene (**2**) in THF (Schemes 1 and 2). After unreacted Na was removed by gravity filtration, the mixture was stirred at room temperature for 7 days. ^{1}H NMR analysis of the reaction mixture indicated the presence of 1,2-dihydronaphthalene (**10**), 1,4-dihydronaphthalene (**2**) and naphthalene (**1**).



The following reaction mechanism may be proposed in order to explain the formation of 1,4-dihydronaphthalene (**2**), 1, 2-dihydronaphthalene (**10**) and tetralin (**3**) (Scheme 2). Naphthalene (**1**) and metallic Na react to give the radical anion **6**. This anion may be converted into 1,4-dihydronaphthalene (**2**) *via* intermediates **7** and **8** in the presence of HOBu^t and Na. As known, Na and alcohol do not generally reduce isolated double bonds. Therefore, 1,4-dihydronaphthalene (**2**) must be converted into 1,2-dihydronaphthalene (**10**) *via* intermediates **8** and **9**, respectively. The isomerisation of 1,4-dihydronaphthalene (**2**) to 1,2-dihydronaphthalene (**10**), which is found in the reaction medium, is brought about by the NaOBu^t/HOBu^t. Then 1,2-dihydronaphthalene (**10**) and Na also react to give radical anion **11**. Radical anion **11** may also be converted into tetralin (**3**) *via* intermediates **12** and **13** in the presence of HOBu^t and Na.

In summary, we have found a new, safe and convenient procedure for the reduction of naphthalene (**1**) and anthracene (**4**) to 1,4-dihydronaphthalene (**2**) and 9,10-dihydroanthracene (**5**), respectively. The structures and purities of 1,4-dihydronaphthalene (**2**), 1,2-dihydronaphthalene (**10**), tetralin (**3**) and 9,10-dihydroanthracene (**5**) were determined by NMR spectroscopy. The synthesis of tetralin (**3**) from naphthalene (**1**) was carried out in a one-pot reaction *via* 1,4-dihydronaphthalene (**2**). The reduced products were easily isolated. Further reactions of aromatic compounds with metals (Na, Li etc.) and HOBu^t are under investigation.

Experimental

Reductions of naphthalene with Na and HOBu^t: In Et$_2$O: To a solution of naphthalene (**1**) (5.0 g, 39 mmol) in dry Et$_2$O (80 ml) was added metallic Na (2.25 g, 98 mmol) in small pieces over a period of 10-15 minutes, and then a solution of HOBu^t (7.25 g, 98 mmol) in dry Et$_2$O (10 ml) was slowly added over 10–20 minutes. After stirring at room temperature for 3 h, unreacted Na and solid NaOBu^t were removed by gravity filtration and washed with Et$_2$O (25 ml). The combined organic layer was washed with water (2 × 30 ml), dried over CaCl$_2$ and then the Et$_2$O was evaporated. The reduction product 1,4-dihydronaphthalene (**2**) (4.52 g, 89 %) was obtained as the sole product.

Caution: After separating unreacted Na, it must be disposed of carefully using an alcohol such as HOBu^t or isopropyl alcohol.

In THF: Naphthalene (**1**) was also reduced to 1,4-dihydronaphthalene (**2**) in THF. In this case, work-up was slightly different, in that only unreacted Na was removed by filtration due to the solubility of NaOBu^t in THF, and the sodium washed with THF (10–15 ml). The combined solutions were evaporated, Et$_2$O (100 ml) was added, and the ether layer was washed with water (2 × 30 ml). The solvent was dried over CaCl$_2$ and removed *in vacuo* to give 1,4-dihydronaphalene (**2**) (4.90 g, 96.5 %) as the sole product.

Reductions of anthracene with Na and HOBu^t: In these reductions, the solutions of anthracene (**4**) (5.0 g, 39 mmol) in dry Et$_2$O (350 ml) or THF (200 ml) was used. However, the solids (unreacted Na and NaOBu^t or unreacted Na) were washed with more solvent (such as 40 ml of Et$_2$O and 25 ml of THF). From solutions of anthracene with Et$_2$O and THF, 9,10-dihydroanthracene (**5**) was obtained in yields of 90 % (4.55 g) and 96 % (4.90 g), respectively.

Synthesis of tetralin: To a solution of naphthalene (**1**) (5.0 g, 39 mmol) in THF (140 ml) was added metallic Na (4.50 g, 196 mmol) in small pieces over a period of 15-25 minutes, and then a solution of HOBu^t (14.50g, 196 mmol) in THF (20 ml) was slowly added over 20 minutes. After stirring at room temperature for 3 h, it was refluxed for 15 h. The solution was cooled and the solvent was evaporated. Et$_2$O (150 ml) was added, and the ether layer was washed with water (3 × 50 ml), and organic layer was washed with water (2 × 50 mL), dried over CaCl$_2$ and then the Et$_2$O was evaporated. The reduction product tetralin (**3**) was quantitatively obtained as the sole product.

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