The Application of C_8K for Organic Synthesis: Reduction of Substituted Naphthalenes

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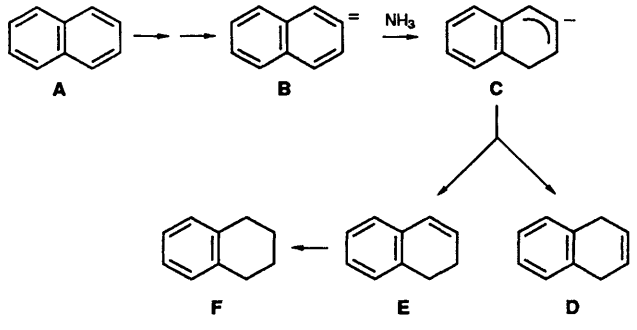
The reduction of disubstituted naphthalene derivatives by potassium–graphite intercalate C_8K is reported. The reduction is carried out at 0 °C in tetrahydrofuran. The C_8K–ether system suggests an alternative route for the Birch type reaction and the mechanism is discussed *vis-a-vis* the reaction in liquid ammonia.

Graphite reacts with potassium to form lamellar compounds of different stoichiometry depending on the precise conditions of the preparation.[1] The best known is the potassium–graphite intercalation compound of stoichiometry C_8K, in which each interlayer space in the graphite is occupied by a layer of potassium atoms, *i.e.* the so-called 'first stage' intercalate. The well defined three dimensional arrangement of potassium–graphite intercalate, C_8K, is characterized by a highly ordered structure that enables selective reactivity in comparison to dispersed potassium.[1]

The capability of C_8K as a catalyst and reactant in organic synthesis has been a subject of interest.[2] This intercalate has already been applied as a reducing agent to a wide variety of reactions, *e.g.* reduction of double bonds in α,β-unsaturated ketones, carboxylic acids, and Schiff's bases,[3] alkylation of carbon acids such as nitriles, esters[4] and imines,[5] reductive cleavage of carbon–sulfur bonds in vinylic[6] and allylic[7] sulfones and reductive coupling of aromatic acid esters,[8] ketones,[9,10] alkyl and aryl halides.[11,12]

The potential use of C_8K to reduce aromatic hydrocarbon systems had been hinted at earlier. Ishikawa *et al.*[13] have achieved full hydrogenation (high pressure, 100–150 bar) of the benzene ring in the presence of C_8K and H_2 at 250 °C. In addition, Beguin and Setton[14] have noted that in the hydrolysis of the quaternary intercalate, $KC_8(THF)_{0.4}(PhH)_{0.37}$, the benzene is transformed into a mixture of biphenyl and partly hydrogenated biphenyl derivatives.

In view of these studies, we devised a simple synthetic application for selective reductions of aromatic hydrocarbons and offer an alternative route for the Birch reduction and its modifications. The reduction of naphthalene derivatives with an alkali metal in liquid ammonia has received considerable attention.[15] Rabideau[16] has shown that the Birch reduction of naphthalene is sensitive to the reaction conditions: naphthalene **A** (Scheme 1) reacts with Li metal in liquid ammonia and forms dianion **B** that is protonated by ammonia and affords



Scheme 1 Reduction of naphthalene (Li–NH_3)

Table 1 C_8K Reduction of disubstituted naphthalenes

Naphthalene derivatives	Reduced naphthalene derivatives	Conversion[a,b] (%)			Yield[b] (%)		
		A	B	C	A[a]	B[a]	C
1	**2**	91	87	97	58	79	35
3	**4**, **5**[c]	74	40	98	66	14	46
6	**9**	78	40	99	74	40	42
7	**10**	86	54	98	56	20	41
8	**11**	83	79	100	47	57	60

[a] Based on ^1H NMR spectroscopy. [b] A, B and C refer to procedures A, B and C of the reductions with C_8K (see Experimental section). [c] The ratio of products obtained from procedures A, B and C are 50:50, 26:74 and 56:43, respectively.

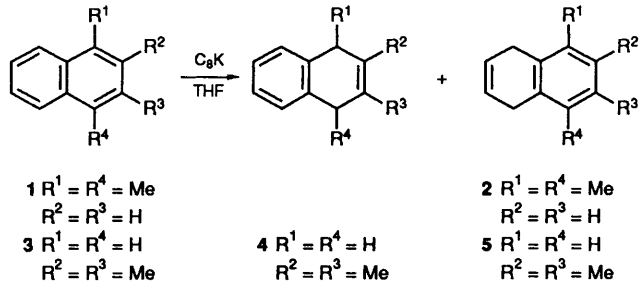
monoanion **C**. The latter is stable at low temperature (−78 °C). Upon elevation of the temperature (−33 °C), monoanion **C** undergoes protonation and gives the neutral 1,4-dihydronaphthalene **D**. An isomerization of 1,4-dihydronaphthalene **D** to 1,2-dihydronaphthalene **E** is observed when the dissolved lithium metal is converted into $LiNH_2$ on the addition of $FeCl_3$ and elevation of temperature. Tetrahydronaphthalene **F** is obtained when the reaction is performed in the presence of an excess of metal at −33 °C. In addition, monoanion **C** reacts with NH_4Cl at −78 °C to yield 1,4-dihydronaphthalene **D**.

Results and Discussion

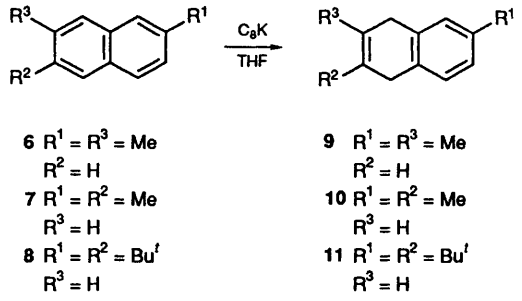
In the present study we report that the 'first stage' intercalation compound of potassium in graphite (C_8K) acts as a useful reducing agent towards disubstitued naphthalenes dissolved in tetrahydrofuran (THF).

Treatment of dialkylnaphthalenes with C_8K affords fair to good yields of 1,4-dihydronaphthalenes according to the conditions used (Table 1). The effect of electron donating groups on the Birch reduction of naphthalene derivatives is known.[16] In our study the reduction of 1,4-dimethylnaphthalene **1** occurs only on the unsubstituted ring and yields **2** while methyl substituents at the 2,3-positions of naphthalene, *i.e.* **3** promote reduction in both rings, and a mixture of 1,4-dihydro products **4** and **5** is obtained (Scheme 2). However, in 2,7-dimethylnaphthalene **6**, 2,6-dimethylnaphthalene **7** and 2,6-di-*tert*-butylnaphthalene **8** only one of the rings is reduced to give the 1,4-dihydronaphthalene derivatives, *i.e.* **9**, **10** and **11**, respectively (Scheme 3). The formation of the respective 1,2-dihydronaphthalene is not observed.

Best results were achieved under the following reaction conditions: 12.5 equiv. of C_8K, ice–water bath (0–5 °C) and reaction period of 4 h (procedure A, Table 1). No significant



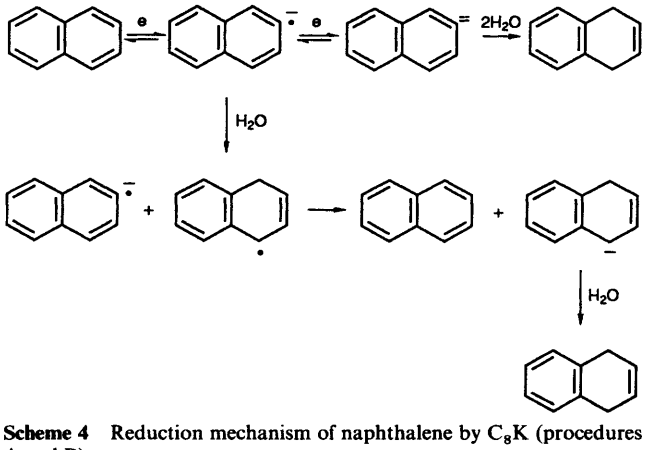
Scheme 2 Reduction products of substituted naphthalene derivatives (C_8K–THF)



Scheme 3 Reduction products of substituted naphthalene derivatives (C_8K–THF)

improvement was observed either when the reduction time was doubled or when the temperature was decreased to −15 °C. Elevation of the temperature to +85 °C (procedure B, Table 1) caused a decrease of conversions and yields. In the case of 1,4-dimethylnaphthalene **1** and 2,6-di-*tert*-butylnaphthalene **8** upon elevation of temperature, the yields were improved from 58 and 47 to 79 and 57%, respectively. In procedure B (Table 1) the reaction time was limited to one hour to avoid the formation of side products. In both procedures A and B, complete conversion was not obtained and a mixture of the product with the starting material was found.

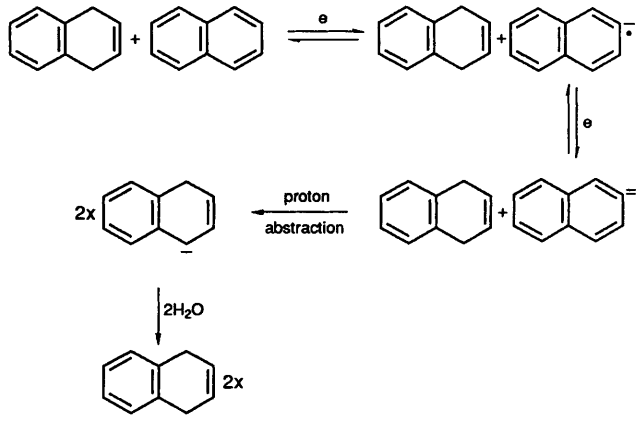
It should be noted that in the presence of a large excess of C_8K and upon elevation of the reaction temperature to +85 °C (reflux in THF), the products composition did not change. This observation is contrary to the results of the reduction by excess alkali metal in liquid ammonia at −33 °C where the complete reduction of one aromatic ring afforded 1,2,3,4-tetrahydronaphthalene derivatives. Our results suggest that in the reduction of dialkylnaphthalenes by C_8K, the THF, unlike ammonia, would not protonate the dianions and therefore the products of the monoanion could not be detected. As shown in Scheme 4,[17] the dianions are in equilibrium with their precursors. Thus, a rapid



Scheme 4 Reduction mechanism of naphthalene by C_8K (procedures A and B)

quench with an effective proton source such as water leads to protonation of the dianionic species to produce dihydro products. Water also caused the protonation of the radical-anionic species, which in a disproportionation reaction results in the neutral starting material and the dihydro products (Scheme 4).[17] Therefore, partial conversions were always obtained under the conditions depicted in procedures A and B (Table 1).

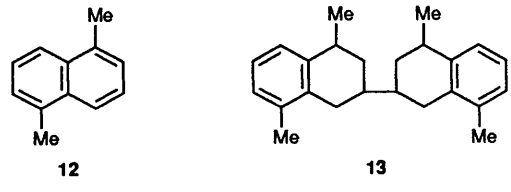
However, in this case, alcohol or ammonium chloride could not be used as a proton source as C_8K is decomposed under these conditions. One of our goals was to obtain high conversions, we therefore applied repeated reductions of the crude reaction products. This method of recycling (procedure C, Table 1) consists of two consecutive reactions. In each reaction three equiv. of C_8K were employed (0–5 °C, 2 h). Despite the high conversions, the yields were moderate (35–43%), excluding the reduction of 2,6-di-*tert*-butylnaphthalene **8**, in which the yield increased to 60%. The low yields may be attributed to adsorption of products on the graphite surface[18] or to the formation of insoluble products. Recycling according to procedure C did not afford further reduced products beyond dihydronaphthalene derivatives. Moreover, complete conversion to dihydro products was obtained only under conditions where at least an equivalent of the 1,4-dihydronaphthalene derivative is present. We therefore suggest that in the second step, the 1,4-dihydronaphthalene derivative serves as a proton source which forms stable monoanions from dianions. The protonation of the dianions is favoured because the latter are more basic than radical anions. Hence, the irreversible protonation of dianions should shift the equilibrium to the right and consequently only stable monoanionic species will exist (Scheme 5). In order to substantiate our conclusion, we carried



Scheme 5 The reduction process (C_8K–THF) in the presence of a proton donor

out an experiment where 2,6-dimethyl-1,4-dihydronaphthalene **10** was added to the starting material, *i.e.* **7**. Indeed, a significant increase in the yield of the reduction product was observed (70 *vs.* 56% after deduction of **10**).

Some information regarding possible dimerization processes in the course of reduction reactions by C_8K was gained from the formation of a dimeric tetralin derivative. The reaction of 1,5-dimethylnaphthalene **12** with 6.25 equiv. of C_8K at 85–90 °C (reflux in THF) affords, after repeated reductions, a dimer (ms)



12 **13**

assigned to 1,2,3,4,1′,2′,3′,4′-octahydro-1,5,1′,5′-tetramethyl-3,3′-binaphthyl **13** but the dimerization mechanism is as yet undefined.

From all the above it can be seen that C_8K is a useful reducing agent of naphthalene derivatives. Moreover, the reaction conditions are mild and the application of THF as medium affords a convenient solvent system as opposed to suspensions formed in liquid ammonia. The heterogenous graphite is easy to separate thus rendering the work-up procedure a simple one. The reaction does not afford perhydro derivatives of naphthalene and yields mainly dihydro products.

Experimental

General.—All C_8K preparations and reactions were carried out in flame-dried glassware under argon atmosphere. Synthetic graphite was purchased from BDH Chemicals Poole, UK. The disubstituted naphthalenes are commercially available (Aldrich, Fluka) and were of a high degree of purity. They were applied without further purification. Tetrahydrofuran (THF) was dried over potassium metal and distilled prior to use. Methylene chloride was distilled prior to application. NMR spectra were recorded using Bruker WP-200, WH-300 and AMX-400 pulsed FT spectrometers operating at 200.13, 300.13 and 400.13 MHz, respectively. Chemical shifts are reported in ppm downfield from Me_4Si; coupling constants (*J*) are given in Hz. Mass spectra were recorded on Varian MAT 311 instrument operating at 70 eV. Melting points (°C) are uncorrected.

Preparation of Potassium–Graphite Intercalate (C_8K).—In a three-necked round-bottomed flask flushed with argon and equipped with a magnetic stirrer, graphite (1.2 g) was flame dried and heated to 200 °C. After 15 min, potassium (0.5 g) was added in small pieces and the stirring at 200 °C was continued until a bronze-coloured C_8K was formed (*ca.* 10–20 min). The reagent was cooled to room temperature and kept under argon. For each reduction the correct amount of C_8K was prepared.

Reduction of Disubstituted Naphthalenes by C_8K.—*Procedure A.* The disubstituted naphthalene (1 mmol) in dry THF (50 cm^3) was added to freshly prepared C_8K (12.5 mmol). The mixture was stirred at 0 °C under argon and after 4 h, water (10 cm^3) was added. The reaction mixture was filtered through a fritted glass funnel and the filtered cake was washed with water (50 cm^3) and dichloromethane (50 cm^3). The filtrate was extracted with two portions (50 cm^3) of dichloromethane, the organic phase was dried ($MgSO_4$) and the solvent was evaporated under reduced pressure.

Procedure B. The steps are identical with procedure A, except that the reaction temperature was 85 °C (reflux). After 1 h the reaction mixture was cooled to room temperature and water (10 cm^3) was added.

Procedure C. To freshly prepared C_8K (25 mmol), disubstituted naphthalene (8 mmol) was added in dry THF (50 cm^3). The reaction mixture was stirred for 2 h at 0 °C and quenched with water. The work-up was identical with that given in procedure A. Then, the resultant crude product dissolved in dry THF (50 cm^3) was added to a three-fold molar amount of C_8K and identical conditions of preparation and work-up were used. The product was recrystallized from methanol or isopropyl alcohol and analysed by ^1H NMR spectroscopy, mass spectrometry and microanalysis.

Reaction of 1,4-*dimethylnaphthalene* **1** (*procedure C*). From 1,4-dimethylnaphthalene **1** (1.25 g) was obtained 5,8-dimethyl-1,4-dihydronaphthalene **2** (0.44 g, 35%), m.p. 40 °C from (Pr^iOH) (lit.,[19a,b] 29–31 °C, 45 °C) (Found: C, 91.0; H, 8.6. $C_{12}H_{14}$ requires C, 91.08; H, 8.84%), δ_H(200 MHz; $CDCl_3$) 6.93 (s, 2 H, Ar), 5.88 (t, 2 H, *J* 1.3, 2- and 3-H), 3.25 (d, 4 H, *J* 1.2, 1- and 4-H) and 2.19 (s, 6 H, 5- and 8-Me); *m/z* 158 (M^+, 48%), 143 (100) and 128 (78).

Reaction of 2,3-*dimethylnaphthalene* **3** (*procedure C*). From 2,3-dimethylnaphthalene **3** (1.25 g) was obtained a mixture (0.58 g, 46%) of 2,3-dimethyl-1,4-dihydronaphthalene **4** and 6,7-dimethyl-1,4-dihydronaphthalene **5**; δ_H(200 MHz; $CDCl_3$; **4*** and **5** mixture) 7.14* (s, 4 H, Ar), 6.91 (s, 2 H, Ar), 5.92 (t, 2 H, *J* 1.4, 2- and 3-H), 3.34 (d, 4 H, *J* 1.1, 1- and 4-H), 3.33* (s, 4 H, 1- and 4-H), 2.24 (s, 6 H, 6- and 7-Me) and 1.79* (s, 6 H, 2- and 3-Me); *m/z* 158 (M^+, 54%), 143 (100) and 128 (68).

Reaction of 2,7-*dimethylnaphthalene* **6** (*procedure C*). From 2,7-dimethylnaphthalene **6** (0.63 g) was obtained 2,7-dimethyl-1,4-dihydronaphthalene **9** (0.27 g, 42%), m.p. 34 °C (from MeOH) (Found: C, 89.25; H, 8.55. $C_{12}H_{14}$ requires C, 91.08; H, 8.84%); δ_H(300 MHz; $CDCl_3$) 7.03–6.92 (m, 3 H, Ar) 5.59 (dt, 1 H, *J* 5.5 and 1.6, 3-H), 3.31 (br s, 2 H, 1-H), 3.24 (d, 2 H, *J* 5.4, 4-H), 2.29 (s, 3 H, 7-Me) and 1.78 (s, 3 H, 2-Me); *m/z* 158 (M^+, 74%), 143 (100) and 128 (45).

Reaction of 2,6-*dimethylnaphthalene* **7** (*procedure C*). From 2,6-dimethylnaphthalene **7** (1.25 g) was obtained 2,6-dimethyl-1,4-dihydronaphthalene **10**, m.p. 58 °C (from Pr^iOH) (lit.,[20] 61.5–62.5 °C) (Found: C, 91.35; H, 8.55. $C_{12}H_{14}$ requires C, 91.08; H, 8.84%); δ_H(300 MHz; $CDCl_3$) 7.01–6.92 (m, 3 H, Ar), 5.57 (unres. m, 1 H, 3-H), 3.31 (br s, 2 H, 1-H), 3.24 (d, 2 H, *J* 5.1, 4-H), 2.28 (s, 3 H, 6-Me) and 1.79 (s, 3 H, 2-Me); *m/z* 158 (M^+, 58%), 143 (100) and 128 (37).

Reaction of 2,6-*di*-tert-*butylnaphthalene* **8** (*procedure C*). From 2,6-di-*tert*-butylnaphthalene **8** (0.96 g) was obtained 2,6-di-*tert*-butyl-1,4-dihydronaphthalene **11** (0.58 g, 60%), m.p. 85 °C (from Pr^iOH) (Found: C, 90.0; H, 10.45. $C_{18}H_{26}$ requires C, 89.19; H, 10.72%); δ_H(200 MHz; $CDCl_3$) 7.21–7.09 (m, 3 H, Ar), 5.71 (m, 1 H, 3-H), 3.38–3.32 (m, 4 H, 1-H and 4-H), 1.31 (s, 9 H, 6-H) and 1.10 (s, 9 H, 2-H); *m/z* 242 (M^+, 99%), 227 (100), 185 (98), 155 (62) and 128 (79).

Reaction of 1,5-*Dimethylnaphthalene* **12**.—To freshly prepared C_8K (12.5 mmol) was added 1,5-dimethylnaphthalene (0.31 g, 2 mmol) in dry THF (50 cm^3) and the reaction mixture was refluxed (85–90 °C). After 2 h the reaction mixture was cooled to room temperature and water (10 cm^3) was added. The mixture was worked up as described in procedure A. The crude product (0.30 g) in dry THF (50 cm^3) was added to C_8K (12.5 mmol) and identical conditions of preparation and work-up were applied.

Recrystallization of the crude product (0.25 g) from benzene–isopropyl alcohol (1 : 1) gave white crystals (22 mg, 7%) of a dimer tentatively assigned to 1,2,3,4,1′,2′,3′,4′-octahydro-1,5,1′,5′-tetramethyl-binaphthyl **13**, m.p. 160–161 °C; δ_H(400 MHz; $CDCl_3$) 7.04–6.96 (m, 6 H, Ar), 3.07 (m, 2 H), 2.75 (m, 2 H), 2.39 (m, 2 H), 2.23 (s, 6 H), 1.93 (m, 2 H), 1.88 (m, 2 H), 1.69 (m, 2 H) and 1.29 (d, 6 H, *J* 7.2); *m/z* 318 (M^+, 86%), 159 (93), 157 (100) and 128 (22).

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