on starting imine) of the oxazolidinone **27c**: ^{1}H NMR ($CDCl_3$) δ 1.07–2.27 (m, 10 H, $(CH_2)_5$), 2.87 (s, 3 H, CH_3N), 3.25 (s, 2 H, CH_2N). Anal. Calcd for $C_9H_{15}NO_2$: C, 63.88; H, 8.93; N, 8.28. Found: C, 63.77; H, 8.82; N, 8.01.

1-[(Methylamino)methyl]cyclohexanol (12c) was prepared by hydrolysis of oxazolidone **27c** by the method of Adams and Segur.[14] A solution of 0.19 g (3.4 mmol) of potassium hydroxide and 0.143 g (0.844) of **27c** in 0.7 mL of absolute ethanol was heated at reflux under nitrogen for 2 h. After being cooled to room temperature, the suspension was diluted with enough water to dissolve the precipitated inorganic salts. The resulting solution was extracted with four 3-mL portions of dichloromethane, and the dichloromethane extracts were combined and dried. Filtration and evaporation of the solvent at reduced pressure of a rotary evaporator followed by purification of the residue by Kugelrohr distillation at 85 °C (0.6 mm) afforded amino alcohol **12c** as a colorless liquid: yield, 0.091 g (75%); IR (neat) 3300 cm^{-1} (NH, OH); ^{1}H NMR ($CDCl_3$) δ 0.80–2.33 (m, 10 H, $(CH_2)_5$), 2.45 (s, 3 H, CH_3N), 2.48 (s, 2 H, CH_2N).

1-[(Dimethylamino)methyl]cyclohexanol (29). A suspension of 0.060 g (1.50 mmol) of 95% lithium aluminum hydride in 2 mL of anhydrous diethyl ether was stirred under nitrogen at 0 °C. A solution of 0.085 g (0.510 mmol) of oxazolidone **27c** in 1 mL of anhydrous diethyl ether was added dropwise. After the addition was complete, the suspension was allowed to warm to room temperature and stirred for an additional 20 h. The suspension was cooled to 0 °C, and 1 mL of isopropyl alcohol was added. After sequential addition of 0.05 mL of water, 0.05 mL of 15% aqueous sodium hydroxide, and 0.15 mL of water, the suspension was filtered, the solids were washed well with diethyl ether, and the ether portions were combined. The ether solution was extracted with three 10-mL portions of 10% aqueous hydrochloric acid, and the aqueous extracts were combined and made basic to pH paper with 15% aqueous sodium hydroxide. The aqueous solution was extracted with three 20-mL portions of dichloromethane, and the dichloromethane extracts were combined and dried ($MgSO_4$). Filtration and evaporation of the solvent at reduced pressure on a rotary evaporator, followed by purification of the residue by Kugelrohr distillation at 90 °C (0.7 mm), afforded dimethylamino alcohol **29** as a colorless liquid: yield, 0.0571 g (72%); IR (neat) 3390 cm^{-1} (OH); ^{1}H NMR ($CDCl_3$) δ 0.97–1.90 (m, 10 H, $(CH_2)_5$), 2.28 (s, 2 H, CH_2N), 2.37 (s, 6 H, $N(CH_3)_2$), 3.18 (br s, 1 H, OH).

A small portion of amino alcohol **29** was converted to the hydrochloride salt by bubbling anhydrous hydrogen chloride through a diethyl ether solution. The melting point of the hydrochloride was 171–175 °C (lit.[19] mp 172–174 °C).

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Registry No. **1**, 2043-61-0; **2**, 123-72-8; **3**, 78-84-2; **4**, 42540-33-0; **5**, 93-53-8; **6a**, 85664-56-8; **6b**, 60795-42-8; **6c**, 89332-91-2; **7a**, 72552-75-1; **7b**, 5857-79-4; **8a**, 85664-55-7; **8b**, 5857-80-7; **9a**, 85664-57-9; **9b**, 100812-00-8; **10a**, 85664-58-0; **10b**, 100812-01-9; **11a**, 85664-62-6; **11b**, 100812-02-0; **11c**, 100812-03-1; **12a**, 65055-38-1; **12b**, 7592-90-7; **12c**, 75541-95-6; **13a**, 100812-10-0; **13a** (imine pivalate), 85664-60-4; **13b**, 68058-00-4; **13b** (imine pivalate), 100812-04-2; **14a**, 14537-89-4; **14a** (imine pivalate), 85664-61-5; **14b**, 7527-65-3; **14b** (imine pivalate), 100812-05-3; **15a**, 100812-11-1; **15a** (imine pivalate), 100812-06-4; **15b**, 100812-12-2; **15b** (imine pivalate), 100812-07-5; **16a**, 55915-75-8; **16a** (imine pivalate), 100812-08-6; **16b**, 67102-79-8; **16b** (imine pivalate), 100812-09-7; **17a**, 100812-13-3; **17b**, 100812-14-4; **18**, 100812-16-6; **19**, 100812-15-5; **21**, 6830-84-8; **26a**, 100812-17-7; **26b**, 100812-18-8; **26c**, 100812-19-9; **27a**, 100812-21-3; **27b**, 100812-22-4; **27c**, 95891-59-1; **28**, 100812-20-2; **29**, 21095-16-9; *N-tert*-butylhydroxylamine, 16649-50-6; *N*-cyclohexylhydroxylamine hydrochloride, 25100-12-3; *N*-methylhydroxylamine hydrochloride, 4229-44-1; pivaloyl chloride, 3282-30-2; cyclohexanecarbonyl chloride, 2719-27-9; methyl chloroformate, 79-22-1.

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Metal–Ammonia Reduction of Naphthalene at –33 °C: Formation of Oligomeric Compounds

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Naphthalene (**1**) has been reductively protonated in a dry ammonia/cosolvent mixture at –33 °C using Li, Na, K, and Mg. In addition to 1,4-dihydro-, 1,2-dihydro-, and 1,2,3,4-tetrahydronaphthalene (**2–4**, respectively) substantial amounts (20–70%) of oligomeric compounds were formed in the case of Li and Na. The reactions have been followed in time in order to obtain insight into the influence of the metal on the reaction course. The results indicate that the oligomerization proceeds via an anionic reaction mechanism by attack of the naphthalene monoanion onto the olefinic bond of 1,2-dihydronaphthalene.

Recently the formation of dimeric species of tetralin (**4**) was reported when this compound was used as a hydrogen-donating solvent in coal liquefaction.[1,2] This bitetralyl formation is thought to occur via intermediately formed dihydronaphthalene species. In order to get a better mechanistic insight into such dimerization reactions we have now studied the metal–ammonia reduction of naphthalene (**1**) to **4** since dihydronaphthalene species are accepted to play an important role in this reaction (Scheme I).

In the course of the reaction of **1** with alkali metals in ammonia the mono- and dianion of **1** were proved to be formed.[3] The dianion formation proceeds through an

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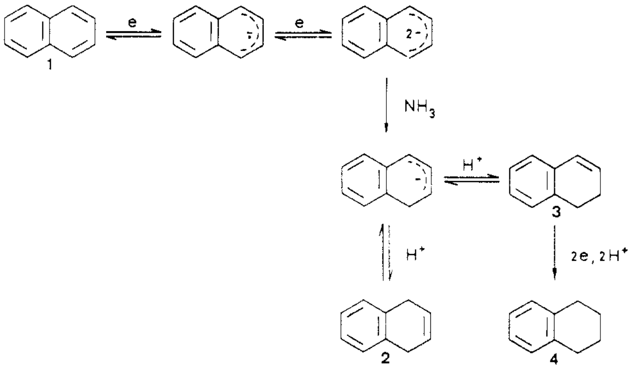
0022-3263/86/1951-1389$01.50/0

Scheme I



intermediate radical anion (see Scheme I). Protonation of the radical anion by ammonia is not very likely since this species is known to be less basic than the monoanion,[4] which is quite stable under these conditions,[5] and since another electron easily adds to the radical anion.

The dianion is protonated to yield naphthalene monoanion, which in its turn can be protonated or quenched to give the kinetically favored 1,4-dihydronaphthalene (**2**) and the more stable 1,2-dihydronaphthalene (**3**). When using tetrahydrofuran instead of ammonia the dianion of naphthalene is only formed when Li is the reducing agent and not with Na.[6] In ammonia at −33 °C and with excess Li or Na **4** is the main product while with 2 mol equiv of Li **3** is obtained via isomerization of the initially formed **2**.[7,8]

Oligomeric species were found in the reduction of **3**[9] or **1**[10] with Na in liquid ammonia and in primary and secondary amines[10,11] as well as with Mg in liquid ammonia.[12] However, no quantitative data as to the extent of formation in relation to reaction time were given. Because in tetrahydrofuran protonation cannot occur before quenching, no dimerization has been reported when reducing **1** in this solvent, but dimerization was found when coal was reductively alkylated in tetrahydrofuran with **1** as electron-transfer agent.[13] Dimerization of **2** and **3** was also found to take place by base-catalyzed reactions in Me_2SO and ethylenediamine at room temperature, and an anionic reaction scheme was suggested.[10]

So far all studies concerning naphthalene reduction in liquid ammonia at −33 °C were undertaken by quenching the reaction mixture after a defined reaction time or by having a proton donor present in situ.[14] In the present study using Li, Na, K, or Mg as the reducing metal the reactions were followed by quenching each time part of the reaction mixture. Under these conditions substantial amounts of oligomeric compounds were found. The mechanism of oligomerization could be deduced from additional experiments in which **2** and **3** were reacted with metal amide in ammonia.

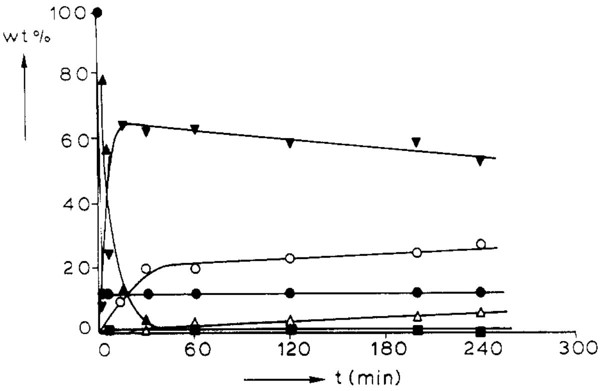


Figure 1. Reaction of naphthalene (10 g) in 400 mL of ammonia and 100 mL of diethyl ether with 2 mol equiv of Li at −33 °C: (●) **1**; (▲) **2**; (▼) **3**, (■) **4**; (○) dimer; (△) trimer.

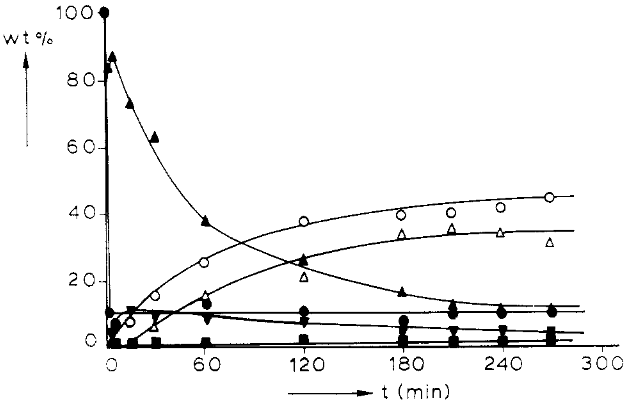


Figure 2. Reaction of naphthalene (10 g) in 400 mL of ammonia and 100 mL of diethyl ether with 2 mol equiv of Na at −33 °C: (●) **1**; (▲) **2**; (▼) **3**; (■) **4**; (○) dimer; (△) trimer.

Results and Discussion

Reduction of Naphthalene. The result of the reaction of **1** with 2 mol equiv of Li in dry ammonia at −33 °C is shown in Figure 1.

Li was quantitatively consumed during the first 2 min of the reaction as can be seen from the fast decrease in concentration of **1**. In a duplo experiment with a slight excess of Li all of **1** disappeared within 2 min and 10% of **4** was formed. It should be realized that the concentration of the different products in Figure 1 reflects the sum of both the quench product and the product already present in solution. Quenching of the reaction mixture will protonate the monoanion in a kinetically determined fashion favoring **2**. Formation of the more stable **3** in the solution before quenching can take place by isomerization of **2** with a one-step mechanism[8] or by relatively slow protonation of the monoanion by the solvent. The reaction mixture had throughout the first 30 min a deep red color, which changed to orange while the amount of **2** decreased to zero after 45 min.[15] This means that component **2** in Figure 1 is mainly to be considered as a quench product, whereas **3** is the actual species present in the solution after 30 min which is in equilibrium with the monoanion in low concentration. From the slow increase in dimer and trimer

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[15] A red color indicates the presence of the monoanion. A blue color originates from metal-ammonia complexes together with solvated electrons. Radical anions have a green color. The change of colors is very pronounced when performing the reduction of 1 with only 1 mol equiv of Li.

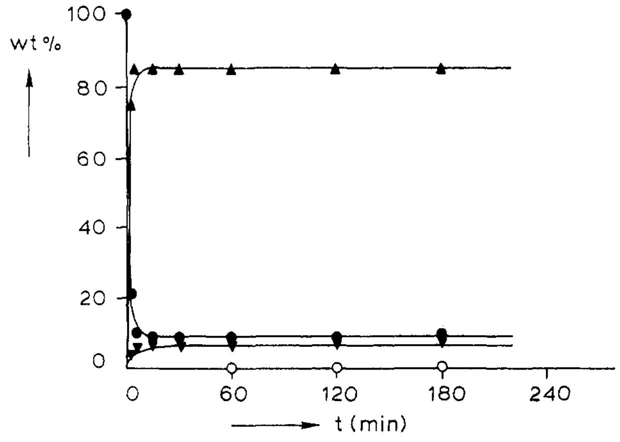


Figure 3. Reaction of naphthalene (10 g) in 400 mL of ammonia and 100 mL of diethyl ether with 2 mol equiv of K at −33 °C: (●) 1; (▲) 2; (▼) 3; (■) 4; (○) dimer.

formation after 30 min and the change in color it seems that oligomer formation is a reaction between the monoanion and 3. More than 25% oligomeric products were formed after 240 min. As a consequence of the oligomerization reaction interconversion should occur between compound 3 and the monoanion. This was confirmed by reacting 3 with 3 mol equiv of $LiNH_2$ at −33 °C, whereby 3% dimeric compounds were found after 60 min, in addition to 1% 1, 95% 3, and 1% 4.[16,17]

Reaction of 1 with 4 mol equiv of Li in dry ammonia for 2 min resulted in 66% 2, 24% 4, and 10% 1 after quenching, whereas after 100 min 100% 4 was formed. With 4 mol equiv of Na 84% 4, 9% 1, 2% 3, and 5% oligomeric products were obtained after 150 min. These results show that part of the monoanion is protonated by ammonia to yield 2 followed by a slow isomerization into 3 which in its turn is fastly converted to 4. The latter reaction is faster with Li than with Na as was shown by the absence of 3 and the much shorter time necessary for 100% conversion of 1 in the reaction with Li.

The fact that no oligomeric products were found in the reaction with 4 mol equiv of Li is explained by the very low concentration of 3 when more than 2 mol equiv of metal is used. The conversion of 3 into 4 is apparently much faster than the oligomerization reaction.

The deep red color throughout the reaction of 1 with 2 mol equiv of Na, Figure 2, points to the presence of a substantial concentration of monoanion.

As a consequence the concentration of 3 is low, which explains the relatively slow formation of oligomeric material (>70% after 240 min).

The reaction of 1 with 2 mol equiv K, Figure 3, showed upon quenching after short (5 min) or long (180 min) reaction times nearly the same product distribution.

Traces of dimer (up to 0.5%) were found after 60 min. Quenching of the samples with ethyl iodide gave only ethylated products together with some naphthalene, showing that the monoanion is apparently very slowly protonated under these conditions. The experiments show that the rate of protonation of the monoanion by ammonia depends on the cation: Li > Na > K.

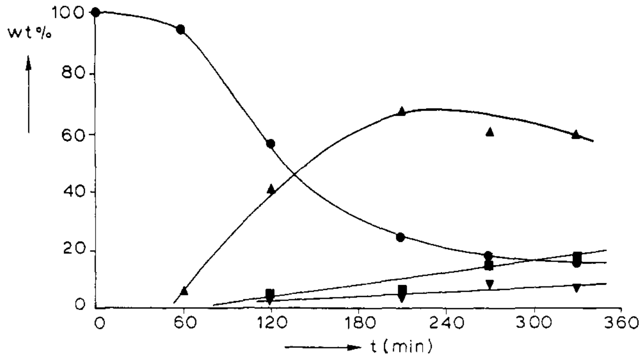


Figure 4. Reaction of naphthalene (10 g) in 400 mL of ammonia and 100 mL of diethyl ether with 2 mol equiv of Mg (powder) at −33 °C: (●) 1; (▲) 2; (▼) 3; (■) 4.

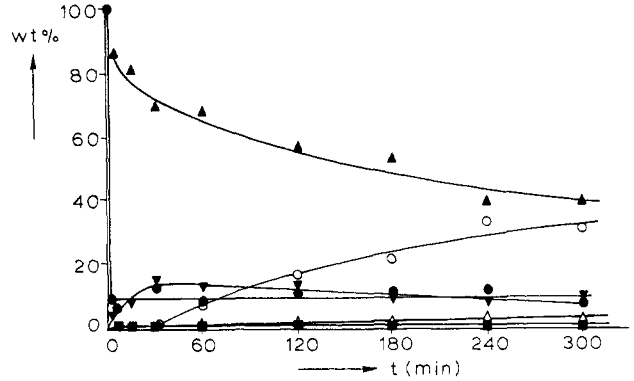
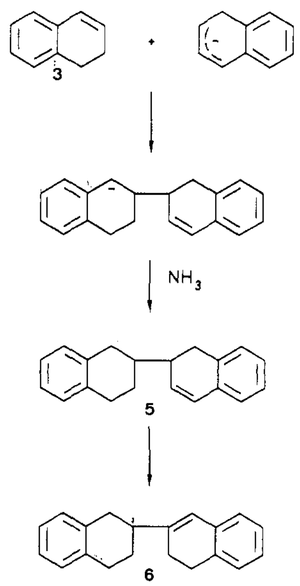


Figure 5. Reaction of naphthalene (10 g) in 400 mL of ammonia and 100 mL of hexane with 2 mol equiv of Na at −33 °C: (●) 1; (▲) 2; (▼) 3; (■) 4; (○) dimer; (△) trimer.

Scheme II



Because Mg is insoluble in ammonia, the electron transfer in the reaction between 1 and 2 mol equiv of Mg powder is a surface-controlled reaction. Because no red color was observed it is likely that the products (see Figure 4) are formed during quenching of the radical anion. No dimeric products were found even after 6 h.

The main dimer compound (>80% of dimer fraction) in the reaction with Li is 1,1′,2,2′,3,4-hexahydro-2,2′-binaphthyl (5). A possible pathway toward 5 is presented in Scheme II.

After 15 min reaction of 1 with 2 mol equiv of Na the main dimeric compound is 5, but as the reaction proceeds 5 goes through a maximum and the main dimeric compound becomes the isomeric 1,2,3,3′,4,4-hexahydro-2,2′-binaphthyl (6) (40% of the dimeric compounds), which

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(16) Oligomerization was much more pronounced upon reaction of 3 with 3 mol equiv of $NaNH_2$ for 60 min: 21% dimers and 7% trimers, in addition to 13% 1, 51% 2, 7% 3 and 1% 4.

(17) Formation of 1 has been explained by the loss of hydride from the monoanion.[18]

presumably is thermodynamically more stable than **5**. The presence of a dimeric monoanion was confirmed by quenching the reaction mixture (120 min, 2 mol equiv of Na used) with CH_3I which yielded a methylated hexahydrobinaphthyl compound as was shown by mass spectrometry.

The product distribution of the reduction of naphthalene is highly temperature dependent: reaction at −70 °C for 240 min with both Li and Na results in the formation of 70% **2**, 1% **4**, and just traces of **3** and oligomers.

The cosolvents diethyl ether and tetrahydrofuran, both miscible with ammonia, gave identical results. However, when hexane, which is immiscible with ammonia, was used as cosolvent, both dimer and trimer formation are much slower (Figure 5). It should be noted that in the ammonia–hexane system the monoanion is present in the ammonia, whereas **3** and **5** are mainly present in the hexane phase. Thus the oligomerization will be slower than in diethyl ether.

In contrast to the literature[10] the order of addition of Na and the naphthalene diethyl ether solution to the ammonia had no effect upon the ultimate result. When 200 mL instead of 400 mL of ammonia were used even tetrameric compounds were detected amounting to 5% after 360 min.

A different product distribution at prolonged reaction times, after evaporation of the ammonia, has been observed with all the metals. The effect was most pronounced with K where after evaporation of the ammonia the diethyl ether layer contained 48% **1**, 11% **3**, 0.5% **4**, 20% dimers, and 20% trimers. Quenching of these reactive mixtures at room temperature resulted in a distinct rise in temperature, which might well be the cause of the effect.

Reaction of 1,4-Dihydronaphthalene (2) with Alkali Metal Amide at −33 °C. In order to support the postulated mechanism of formation of dimers (Scheme II) some experiments were performed with **2** and alkali metal amide in ammonia. Oligomer formation was expected to occur because **2** isomerizes to **3** at −33 °C in the presence of metal amide whereby the monoanion is the intermediate product. When adding a solution of **2** in diethyl ether to 1 mol equiv of metal amide in ammonia at −33 °C all of the insoluble solid amide disappeared within 30 min under formation of the monoanion as indicated by the deep red color. Performing the experiment with a diethyl ether solution of 62% **2**, 35% **1**, 2% **3** and 1% **4** and 1 mol equiv of $LiNH_2$ (equivalency based on metal/2 molar ratio) 16% dimers and 3% trimers had been formed after 120 min. Similar experiments with 1 mol equiv of $NaNH_2$ and 1 mol equiv of KNH_2 and a diethyl ether solution of 90% **2**, 5% **1**, and 5% **3** showed 57% respectively 30% oligomer formation after 240 min. Dimerization has been reported by reacting **3** with strong bases like KOH, NaH, and BuLi at room temperature[10] but was overlooked by earlier workers in the isomerization of **2** into **3** with $LiNH_2$, $NaNH_2$, and KNH_2 at −33 °C.[18] It was found that isomerization hardly occurred at −70 °C, showing the temperature dependence of the proton abstraction reaction.

Product distribution in the oligomer fraction with metal amide is the same as in the reduction of **1** with that particular metal. The oligomer formation by KNH_2 shows that during the reaction between **1** and K metal (Figure 3) the observed products **2** and **3** almost completely result from quenching as dimeric products are only observed after prolonged reaction times. In the experiment with **2** and KNH_2 not only the monoanion is produced but also **3** via a probable one-step isomerization similar to the isomerization step found earlier between **2** and $LiNH_2$.[8] In accordance with the proposed mechanism the presence of both monoanion and **3** leads to extensive oligomer formation.

Experimental Section

General Procedures. GLC analyses were performed on a Packard-427 GC with Chrom WHP 80–100 mesh column and FID to separate monomeric compounds and on a Varian Model 3700 equipped with an on-column injector, FID, and a CPSil 8 CB (10 m, 0.32-mm diameter) column to separate the monomeric from the oligomeric compounds. GC–MS was performed with a Varian MAT 44 S mass spectrometer equipped with a CPSil 5 column. ^1H NMR spectra were determined with a Varian T-60 spectrometer.

Metal–Ammonia Reduction of Naphthalene at −33 °C. Dry ammonia (400 mL) was distilled into the reaction vessel, and small pieces of the alkali metal (usually 2 mol equiv) were added to the ammonia. After 30 min the reduction was started by adding rapidly 10 g of naphthalene in 100 mL of diethyl ether. Sampling was performed by sucking a few milliliters of the reaction mixture into a cold mixture of ammonium chloride and diethyl ether. After addition of water and extraction by diethyl ether the organic layer was analyzed by GC and GC–MS.

Reaction between 1,4-Dihydronaphthalene and Metal Amide. $LiNH_2$ and KNH_2 were prepared in situ by adding a trace of dry $FeCl_3$ to a blue solution of Li or K in ammonia at −33 °C, after which the amide precipitated.

Solutions containing >60% 1,4-dihydronaphthalene were obtained by reduction of naphthalene with Na in ammonia at −70 °C followed by rapid quenching with aqueous NH_4Cl. The reaction was started by adding a solution of 1,4-dihydronaphthalene (5 g) in diethyl ether (50 mL) to 1 mol equiv of metal amide in 200 mL of distilled ammonia.

1,1′,2,2′,3,4-Hexahydro-2,2′-binaphthyl (5). The monomeric fraction from a naphthalene reduction experiment with Li in liquid ammonia at −33 °C was removed from the oligomer fraction by vacuum distillation. The oligomer fraction contained 80% **5**: GC–MS *m/e* (relative intensity) 261 (4), 260 (15), 131 (25), 130 (35), 129 (100), 128 (71), 127 (9), 115 (9), 104 (7), 91 (13); ^1H NMR (CCl_4) δ 7.0 (m, 8 H), 6.0 (m, 2 H), 3.0–0.6 (m, 10 H).

1,2,3,3′,4,4′-Hexahydro-2,2′-binaphthyl (6). The dimeric fraction from a naphthalene reduction experiment with Na in liquid ammonia at −33 °C was isolated by distillation [bp 225 °C (1.5 kPa)] followed by chromatography through a short silica gel column using ligroin (60–80 °C) as the eluens. The fraction contained 65% of **6**: GC–MS *m/e* (relative intensity) 261 (7), 260 (31), 156 (19), 141 (15), 131 (31), 130 (100), 129 (70), 128 (53), 115 (20), 104 (20), 91 (15); ^1H NMR (CCl_4) δ 7.0 (m, 8 H), 6.3 (s, 1 H), 3.2–1.0 (m, 11 H).

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Registry No. **1**, 91-20-3; **2**, 612-17-9; **3**, 447-53-0; **4**, 119-64-2; **5**, 100334-83-6; **6**, 23405-30-3.

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