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NMR and Calculational Studies on the Regioselective Lithiation of 1-Methoxynaphthalene

Jürgen Betz and Walter Bauer*

Contribution from the Universität Erlangen-Nürnberg, Institut für Organische Chemie, Henkestrasse 42, D-91054 Erlangen, Germany

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Abstract: 1-Methoxynaphthalene (**1**) undergoes regioselective lithiation in position 2 (*n*-BuLi/TMEDA) or in position 8 (*t*-BuLi), respectively. The detected formation of a *n*-BuLi/**1** complex (1:1 *n*-BuLi/**1** mixture) appears to have only minor influence on the regioselectivity (both products are obtained). The exchange of hydrogen atom H2 by deuterium results in a remarkably reduced reaction rate for the lithiation with *n*-BuLi in THF-d_8. This isotope effect and the formation of the thermodynamically less favorable 2-lithio compound suggest a kinetically controlled mechanism. The lack of an isotope effect for the reaction of 8-deuterio-1-methoxynaphthalene with *t*-BuLi and the formation of the thermodynamically preferred 8-lithiated product indicate a thermodynamically controlled mechanism. Slow conversion of the 2- into the 8-lithiated species (at higher temperatures) gives further evidence that *n*-BuLi and *t*-BuLi afford the kinetically and thermodynamically preferred products, respectively.

Introduction

In the 1930's Gilman[1] and Wittig[2] were the first who observed the regioselective introduction of lithium into (hetero)substituted arenes. This was an important step in the development of modern organic synthesis: electrophilic aromatic substitutions were possible without getting mixtures of regioisomeric products. Due to its synthetical power this hydrogen/metal interconversion (also termed ortho-lithiation), facilitated by substituents with free electron pairs, was investigated intensively.[3] The magnitude of this effect depends on the nature of the substituent and decreases in the order[4] $CONEt_2 > CH_2NMe_2 > OCH_3 > F$. An interesting aspect arises for the regioselective metalation of arenes carrying two different directing metalation groups (DMGs). In this context Schlosser[5,6] et al. as well as Meyers[7] reported "optional site selectivity" in metalation. They were able to change the position of the ortho-lithiation of para-substituted benzenes from the "stronger" DMGs to the weaker directing group. These changes were mainly achieved by addition of chelating ligands such as *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (PMDTA) or hexamethylphosphoric triamide (HMPA) to the metalation agents.[5,7]

Another interesting regioselective reaction is the lithiation of 1-methoxynaphthalene (**1**). Treatment of **1** with *n*-butyllithium (*n*-BuLi) in hydrocarbon solvents and subsequent quench with CO_2 is reported to release a mixture of 1-methoxy-2-naphthoic acid (**2b**) and 1-methoxy-8-naphthoic acid (**3b**).[8−11] The ratio of the product composition depends on the reaction conditions: in diethyl ether/hexane 73% **2b** and 27% **3b**, respectively, are obtained (overall yield 28%).[11] The regiochemistry of this reaction can be controlled very effectively. Thus, the reaction of **1** with *n*-BuLi and 1 equiv of TMEDA results in more than 99% 2-lithiation (yield 60%). However, investigations by Mannschreck et al.,[12] Schlosser et al.[13] and our group revealed a distinctly smaller regioselectivity (8:1 to 9:1 for lithiation with *n*-BuLi/TMEDA), questioning the excellent selectivity reported by Shirley. Treatment of **1** with *tert*-butyllithium yields more than 98% of the species lithiated in position 8 (20−35% yield)[11] (Scheme 1).

Results and Discussion

^{1}H NMR spectra of 1-methoxynaphthalene and anisole show significant changes when *n*-BuLi is added to their solutions in hexane.[10,14] Such shifts are attributed to the formation of an aryl ether/*n*-BuLi complex. ^{1}H NMR measurements of a 1:1

* Corresponding author. E-mail: bauer@organik.uni-erlangen.de.

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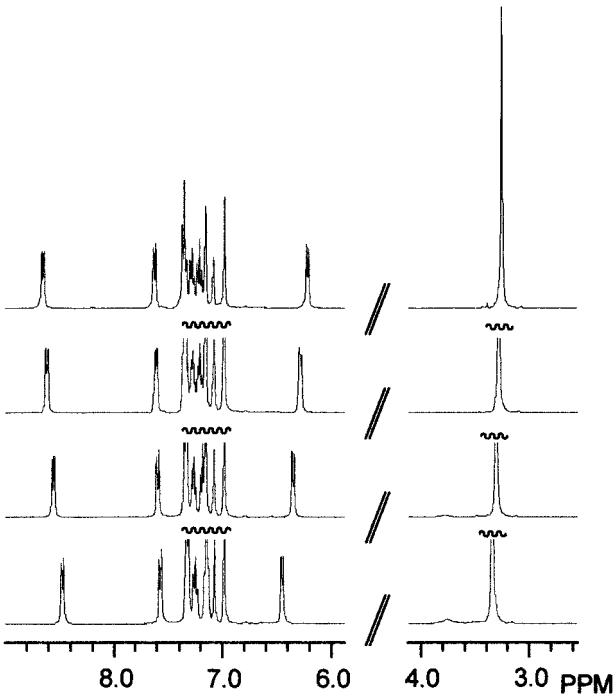
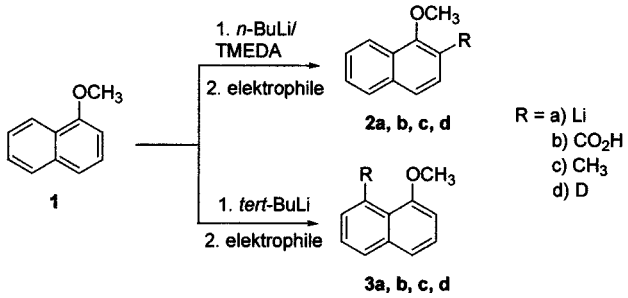


Figure 1. ^{1}H NMR (toluene-d_8, −65 °C) spectra of (a; top row) 1-methoxynaphthalene (**1**), (b) **1** + 0.85 equiv of *n*-BuLi, (c) **1** + 1 equiv of *n*-BuLi, (d) **1** + 2 equiv of *n*-BuLi. Only the signals of 1-methoxynaphthalene are reproduced.

Scheme 1



mixture of anisole/*n*-BuLi (toluene-d_8, −64 °C)[15] show a significant downfield shift for the methoxy-hydrogen and *o*-hydrogen atoms whereas the meta- and para-proton resonances undergo an upfield shift.

Addition of 1 equiv of *n*-butyllithium to a 0.8 M solution of **1** in toluene-d_8 at −65 °C generates analogous shifts for the ^{1}H resonances. The signals of the methoxy protons and H2 are shifted downfield by 0.05 and 0.11 ppm, respectively (Figure 1). These downfield shifts appear to be typical for organolithium compounds (e.g. phenyllithium,[16] mesityllithium,[17] and 1-naphthyllithium[18]). Note, however, that the aromatic ring is not yet lithiated under the above conditions. The remaining signals are shifted upfield only slightly, except for H8 with a significant 0.08 ppm upfield shift. These results are compatible with the formation of a **1**/*n*-BuLi complex where the oxygen is coordinated to the lithium atoms.

As is shown in Figure 1 and Figure 2a the chemical shift of the OCH_3-hydrogen atoms increases continuously upon the addition of *n*-BuLi. This concentration dependence suggests the existence of an equilibrium between the educts (*n*-BuLi and **1**) and the detected **1**/*n*-BuLi complex. Since the concentration of **1** varied in the different **1**/*n*-BuLi samples, concentration effects might be attributed for these shifts.[12] However, as shown in Figure 2b, variation of the concentration of pure **1** has only a negligible influence on the OCH_3 chemical shift. Therefore, the increasing downfield shift must be due to the addition of *n*-BuLi.

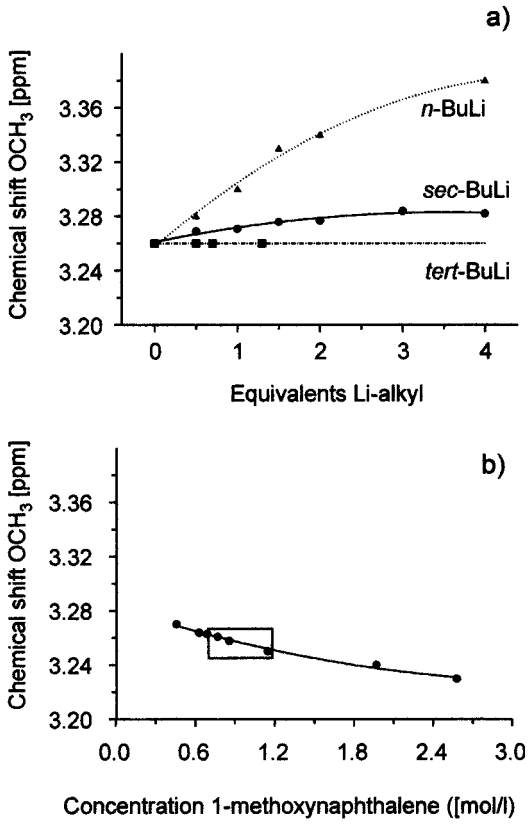


Figure 2. Chemical shifts of the methoxy hydrogen resonances of 1-methoxynaphthalene (**1**) due to (a) addition of *n*-, *sec*-, and *t*-BuLi (0.8−1.2 M solutions of **1** in toluene-d_8, at −65 °C) and (b) the variation of the concentration of **1** (toluene-d_8 at −65 °C). The rectangle in b) represents the range of the concentrations employed for the samples in a).

Further evidence for complexation can be gained from the aggregation level of *n*-BuLi. In principle, the aggregation number can be determined by NMR spectroscopy from the ^{13}C,^{6,7}Li coupling constants and/or the multiplicity of the α-carbon signal.[19,20] However, no resolved line splitting is observable for a 1:1 **1**/*n*-BuLi mixture even at low temperature. As is summarized in Table 1 the ^{13}C chemical shifts of dimeric, tetrameric, and hexameric *n*-BuLi differ significantly and may thus also be employed to characterize the degree of aggregation. The ^{13}C spectrum of the 1:1 mixture of **1**/*n*-BuLi in toluene-d_8 at −65 °C shows two different sets of ^{13}C resonances for the butyl carbon atoms (Figure 3). Comparison of these experimental data with the values from the literature indicates the existence of a hexameric and a tetrameric species (Table 1).

The intensities of the signals (Figure 3) show that the tetrameric aggregate is dominating. Thus, 1-methoxynaphthalene (**1**) must partly disrupt the *n*-BuLi aggregate (which is known

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Table 1. ^{13}C NMR Chemical Shifts of *n*-BuLi, Free and as a 1:1 *n*-BuLi/1-Methoxynaphthalene Mixture (δ, ppm)

	n-BuLi			1:1 *n*-BuLi/**1** mixture	
C	hexamer[13]	tetramer[16]	dimer[16]	hexamer	tetramer
α	12.0	10.5	12.8	11.6	9.5
β	31.9	33.9	35.8	32.0	33.1
γ	32.1	35.4	37.3	32.2	33.2
δ	14.5	14.7	14.9	14.3	14.5
solvent	toluene-d_8	THF-d_8	THF-d_8	toluene-d_8	toluene-d_8
temp,°C	−64	−96	−96	−65	−65

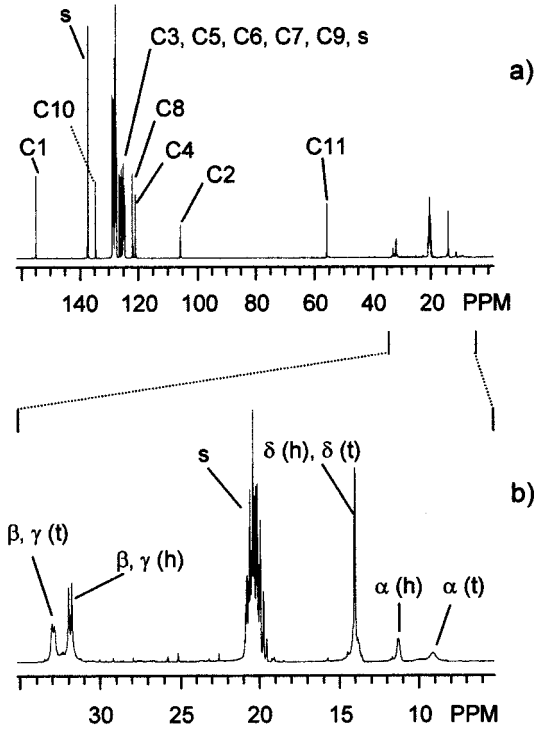


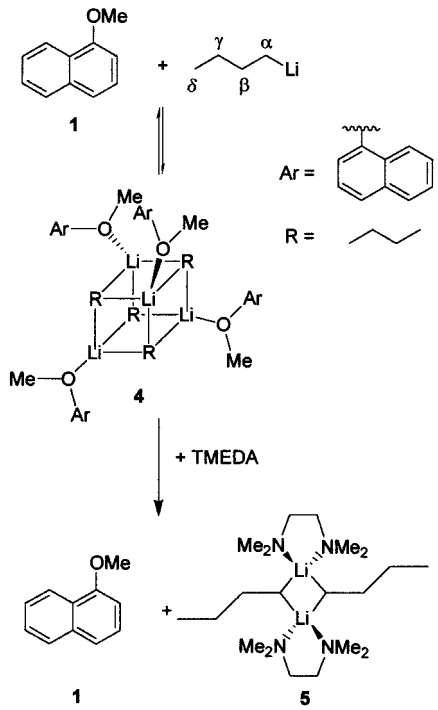
Figure 3. ^{13}C spectrum (toluene-d_8, −65 °C) of 1-methoxynaphthalene + 1 equiv of *n*-BuLi: (a) the full region and (b) the zoomed region between 5 and 45 ppm (s = solvent signal, h = hexamer, t = tetramer). Note that in spectrum a) only one set of signals for 1-methoxynaphthalene is observable.

to be hexameric in hydrocarbon solvents[21]) to give a tetramer (**4**), peripherally solvated by 1-methoxynaphthalene (**1**, Scheme 2).

The existence of two sets of ^{13}C signals shows that the intermolecular exchange of the butyl group (between two different aggregates) is slow on the NMR time scale. By contrast, 1-methoxynaphthalene (**1**) (in the 1:1 mixture of **1**/*n*-BuLi) shows only one set of ^{13}C signals, indicating fast intermolecular exchange between free **1** and the **1**/*n*-BuLi complex (Figure 3).

The close proximity of some protons to the lithium cation can also be shown by ^{6}Li,^{1}H two-dimensional heteronuclear Overhauser effect spectroscopy (HOESY).[22,23] The HOESY spectrum of an equimolar **1**/*n*-BuLi (*n*-BuLi is enriched with 96% ^{6}Li) mixture shows, apart from the expected cross-peaks between ^{6}Li and the ^{1}H *n*-butyl resonances, additional cross-peaks between ^{6}Li and the methoxy, the H2, and the H8 resonances. This confirms the short distances between ^{6}Li and these hydrogen atoms and thus confirms the formation of a **1**/*n*-BuLi complex.

Scheme 2



Despite this complexation (and the correlated proximity of the reaction centers) no facile metalation of 1-methoxynaphthalene is observed. In toluene-d_8 at −65 °C the 1:1 mixture of **1**/*n*-BuLi undergoes no NMR-detectable reaction. Even when stored at room temperature for several hours no formation of **2a** nor **3a** was observed.

Addition of 1 equiv of TMEDA to the equimolar **1**/*n*-BuLi mixture leads to entirely different results. The ^{1}H chemical shifts of 1-methoxynaphthalene (**1**) (toluene-d_8, −65 °C) are comparable to those of 1-methoxynaphthalene (**1**) without added *n*-BuLi. Similar to earlier observations on anisole,[15] TMEDA has replaced **1** as the complexing agent to *n*-BuLi and therefore **1** is now liberated. The ^{6}Li,^{1}H-HOESY spectrum again shows the expected cross-peaks between ^{6}Li and the ^{1}H resonances of the butyl group; however, no ^{6}Li interactions with the ^{1}H signals of **1** are detectable. Instead, ^{6}Li,^{1}H cross-peaks to the TMEDA protons arise. This clearly demonstrates that 1-methoxynaphthalene is now separated from the *n*-BuLi moiety, whereas TMEDA is now ligated to *n*-BuLi. The ^{13}C signals of **1** in a 1:1:1 mixture of **1** with *n*-BuLi and TMEDA are identical with those of **1** without added *n*-BuLi. This also demonstrates the "free" character of **1**. The ^{13}C resonances of the butyl group are compatible with the numbers of dimeric *n*-BuLi. Thus, addition of TMEDA causes deaggregation of the **1**/*n*-BuLi complex and leads to the formation of the dimeric TMEDA/*n*-BuLi aggregate (**5**), which is intensively investigated and well-described in the literature.[15,19,20,24]

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Chart 1

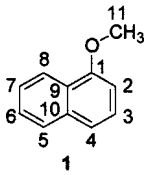

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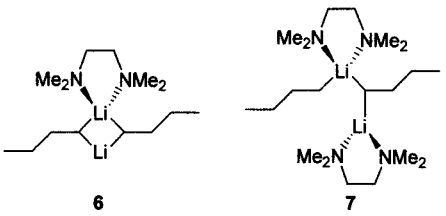
Chart 2



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When compared to the **1**/*n*-BuLi mixture, the addition of 1 equiv of TMEDA enhances the reactivity of *n*-BuLi drastically. 1-Methoxynaphthalene (**1**) is metalated by TMEDA/*n*-BuLi even at temperatures below 0 °C. Similar to the ortho-lithiation of anisole this process must involve a reactive intermediate that is nondetectable by NMR. For this reaction a *n*-BuLi dimer with only one TMEDA ligand (**6**) as the reactive species has been suggested (Chart 2).[15] Within this compound one lithium atom has two free coordinating sites, allowing coordination of the aryl ether by Li−O and by agostic Li−H interactions, respectively. Collum et al.[25] proposed, according to their NMR rate studies, an *n*-BuLi/TMEDA dimer as the effective metalating agent for the lithiation of anisole. On the basis of the importance of precomplexation Collum suggests the open dimer **7** as the active species (Chart 2). PM3 calculations on the mixed 1-methoxynaphthalene/**7** complexes **8a** and **9a** (Figure 4) which mainly differ in the orientation of **1** toward **7** reveal only a small difference in the heat of formation. Complex **8a** ($\Delta H_f^0 = -61.3$ kcal/mol), where the *n*-BuLi/TMEDA dimer is directed toward hydrogen H2, is about 0.5 kcal energetically more favorable than complex **9a** ($\Delta H_f^0 = -60.8$ kcal/mol, orientation of **7** toward hydrogen atom H8). Pronounced differences in the heat of formation occur for the transition states of the hydrogen abstraction (**8b** and **9b**, respectively, Figure 4). Here, the heat of formation for **8b** ($\Delta H_f^0 = -47.8$ kcal/mol) is about 5 kcal/mol lower than that for **9b** ($\Delta H_f^0 = -42{,}7$ kcal/mol). Considering the different ground-state energies of **8a** and **9a**, respectively, the activation energy for the lithiation in the ortho-position turns out to be 4.5 kcal/mol lower. PM3 calculations on the lithiation of **1** with the (*n*-BuLi)$_2$/TMEDA complex **6** (Figure 5) gave similar results. Although the energy differences within the ground states (**10a** and **11a**) and the transition states (**10b** and **11b**), respectively, are more pronounced, the difference in the activation energy of 4.3 kcal/mol is in the same range as that in the upper case (Figure 4). Again, abstraction of the hydrogen atom H2 turns out to be energetically favorable. According to these calculations, the pronounced regioselectivity of the lithiation with *n*-BuLi/TMEDA seems to be a *kinetically driven process*. Similar PM3 calculations on the lithiation of **1** with monomeric *n*-BuLi (without TMEDA) reveal only a small difference (0.9 kcal/mol) for the activation energies (lithiation in the ortho-position again is energetically favorable). This small

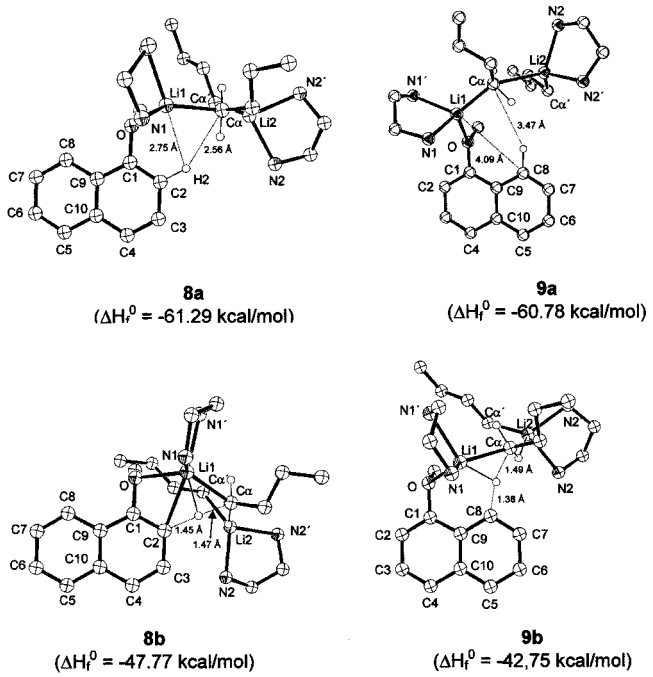

Figure 4. ORTEP-derived drawings of PM3 calculations on the reaction of 1-methoxynaphthalene with (*n*-BuLi/TMEDA)$_2$. **8a** and **9a** represent the ground states and **8b** and **9b** the transition states for the hydrogen abstraction (one negative frequency in the vibrational calculations). The numbers in brackets represent the calculated heat of formation. For clarity, most of the hydrogen atoms and the methyl groups of the TMEDA ligand are omitted.

energy difference is in agreement with the experimental results, since the actual reaction of **1** with *n*-BuLi in hydrocarbon solvents gives a 3:1 mixture of 2- and 8-lithiated product.[11]

Calorimetric measurements[26] and PM3 calculations for the metalated compounds **2a** and **3a**, respectively, show that metalation in position 8 is thermodynamically favorable. This is probably due to better lithium−oxygen interactions in **3a** (shorter Li−O distance according to the PM3 calculations), and a less distorted geometry of the 1-methoxynaphthalene skeleton (Figure 6). The exclusive formation of the energetically minor stable product (**2a**) via an energetically preferred (PM3 calculations) transition state **8b** suggests a kinetically controlled mechanism for the lithiation of **1** with *n*-BuLi in the presence of TMEDA. Attempts to determine the actual state of aggregation of the lithiated products (**2a**, **3a**) in toluene-d_8 failed. Even upon cooling to −95 °C the ^{13}C spectra show no line splitting of the lithiated carbon atom signal. Even at low temperatures the inter- and/or intramoluecular exchange processes are too fast to give resolved signals.

NMR investigations on the metalation of 1-methoxynaphthalene with 1 equiv of *t*-BuLi in toluene-d_8 at −65 °C showed no evidence for the formation of a **1**/*t*-BuLi complex. The ^{1}H and ^{13}C spectra of 1-methoxynaphthalene are essentially unchanged when 1 equiv of *t*-BuLi is added (see also Figure 2, no change in the chemical shift of H11 due to addition of *t*-BuLi). The ^{13}C signals of the *tert*-butyl group show the line splitting of a static tetramer (^{13}C−^{7}Li coupling); there is no change due to the addition of **1**. In the ^{7}Li,^{1}H-HOESY spectrum, no cross-peaks between ^{7}Li and the ^{1}H resonances of 1-meth-

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(26) Klumpp, G. W.; Sinnige, M. J. *Tetrahedron Lett.* **1986**, *27*, 20, 2247. The protonation of 8-lithio-1-methoxynaphthalene (142 ± 5 kJ/mol) is 8 kJ/mol less exothermic than the protonation of the corresponding 2-lithio compound (150 ± 4 kJ/mol)

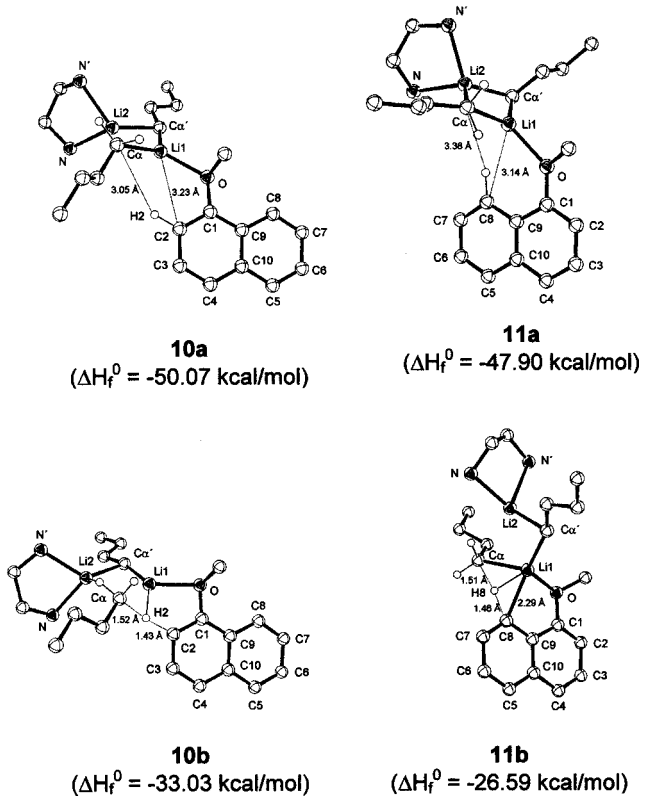

Figure 5. ORTEP-derived drawings of PM3 calculations on the reaction of 1-methoxynaphthalene with $(n\text{-BuLi})_2$/TMEDA (**6**). **10a** (lithium coordination via H2) and **11a** (lithium coordination via H8) represent the ground states and **10b** and **11b** the transition states for the hydrogen atom abstraction (one negative frequency in the vibrational calculations). The numbers in brackets represent the calculated heat of formation. For clarity, most of the hydrogen atoms and the methyl groups of the TMEDA ligand are omitted.

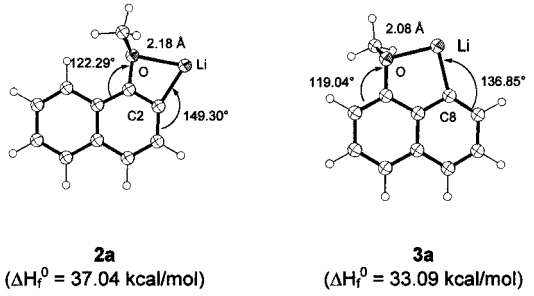

Figure 6. ORTEP-derived drawings of PM3 calculations on 1-methoxy-2-naphthyllithium (**2a**) and 1-methoxy-8-naphthyllithium (**3a**).

oxynaphthalene are detectable. Each of the four *tert*-butyl groups of the *t*-BuLi tetramer (*t*-BuLi is known to be tetrameric in hydrocarbon solvents[27−29]) is bonded to three lithium atoms of the lithium tetrahedron (four center two electron bond). This sterically demanding arrangement of the bulky *tert*-butyl groups probably prevents the approach and, therewith, the coordination of 1-methoxynaphthalene (**1**). Note that at −65 °C, where the NMR measurements were performed, no reaction is detectable. At temperatures where lithiation in position 8 takes place (e.g.

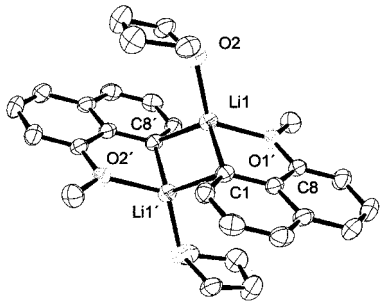

Figure 7. ORTEP drawings of the crystal structure of dimeric 1-methoxy-8-naphthyllithium·THF $(\mathbf{3a}\cdot\text{THF})_2$. Hydrogen atoms are omitted.

room temperature) *t*-BuLi undergoes fast intramolecular exchange (fluxional exchange).[29] During these rearrangements coordination of **1** to free coordination sites of lithium atoms appears to be possible. We presume a mechanism via a mixed *t*-BuLi/1-methoxynaphthalene complex with low stationary concentration nondetectable by NMR. The formation of the thermodynamically preferred product and the longer reaction times[11] compared to the reaction of **1** with *n*-BuLi/TMEDA suggest a thermodynamically controlled mechanism for the metalation of **1** with *t*-BuLi. A first series of PM3 calculations on the abstraction of the hydrogen atom (ortho- and peri-position, respectively) with monomeric *t*-BuLi revealed a kinetically facilitated metalation in the ortho-position. These theoretical results are in contrast with the experimental observations (in hydrocarbon solvents *t*-BuLi metalates 1-methoxynaphthalene exclusively in the peri-position). As mentioned above, *t*-BuLi is tetrameric in hydrocarbon solvents, thus a reaction mechanism via monomeric *t*-BuLi is unlikely. Therefore we employed dimeric *t*-BuLi as model for higher aggregated *t*-BuLi (PM3 calculations with higher aggregate *t*-BuLi were unfortunately not successful). PM3 calculations with dimeric *t*-BuLi actually show a reversed reactivity—now abstraction of the hydrogen atom H8 is favorable. This effect (reversed reactivity while going from monomeric to dimeric butyllithium) could exclusively be observed with *t*-BuLi. Comparable calculations with dimeric *n*- or *sec*-BuLi (see below) show no change in the site selectivity, here the activation energy remains favorable for lithiation in the ortho-position. Although we predict a thermodynamically controlled mechanism for the lithiation of **1** with *t*-BuLi, these calculations indicate at least a reduced reactivity for lithiation in the ortho-position.

Recently we were able to obtain crystals of 8-lithio-1-methoxynaphthalene (**3a**) from THF solution. The single-crystal diffraction reveals a centrosymmetrical dimeric structure solvated by two THF molecules $(\mathbf{3a}\cdot\text{THF})_2$ (Figure 7).[30] Unfortunately, solvent free crystals were not accessible. This is probably due to the strong stabilization of tetracoordinated lithium cations in the solid state. Solvent free monomeric, dimeric, or trimeric aggregates would possess only doubly or triply coordinated lithium atoms. The formation of a tetrameric species of **3a** (with a tetracoordinated lithium atom) is not likely due to the steric hindrance. The structure consists of two approximately planar parallel naphthyl backbones. The anionic carbon atoms (C8 and C8′, respectively) are attached to two lithium atoms (Li1 and Li1′, respectively). The C8−Li distance (2.162 Å) is about 7 pm shorter than the corresponding C8−

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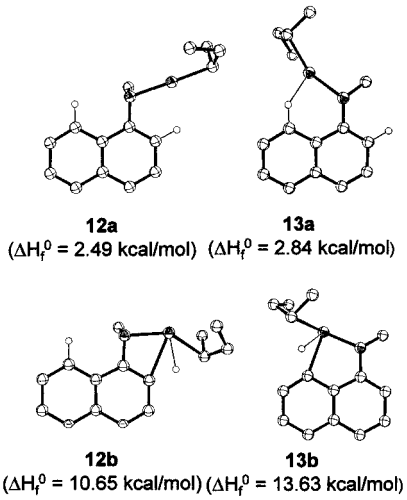

Figure 8. ORTEP-derived drawings of PM3 calculations on the reaction of 1-methoxynaphthalene with *sec*-BuLi. **12a** (lithium coordination via H2) and **13a** (lithium coordination via H8) represent the ground states and **12b** and **13b** the transition states for the hydrogen atom abstraction (one negative frequency in the vibrational calculations). The numbers in brackets represent the calculated heat of formation. For clarity, most of the hydrogen atoms and the methyl groups of the TMEDA ligand are omitted.

Li′ distance (2.232 Å). Furthermore, Li1 is connected to the oxygen atom O1 and is incorporated in a five-membered ring (C8−C9−C1−O1−Li1) that is approximately coplanar with the connected naphthyl plane. These spatial arrangements give the impression of strong developed monomeric subunits which form the dimeric structure. The ^{13}C spectrum of a solution of (**3a**·THF)$_2$ in THF-d_8 at −100 °C shows a septet for the lithiated carbon atom C8 ($^1J(^{13}C,^7Li)$ = 19.3 Hz). Since commercial *t*-BuLi was employed this line-splitting pattern arises from ^{13}C−^{7}Li coupling and indicates the existence of a dimeric aggregate of **3a** in solution.

NMR investigations on the reaction of 1-methoxynaphthalene (**1**) with *sec*-BuLi mostly show the same results as the reaction of 1-methoxynaphthalene (**1**) with *n*-BuLi. The addition of *sec*-BuLi to a 1-methoxynaphthalene (**1**) solution in toluene-d_8 at −65 °C generates a shift of the hydrogen atom resonances, indicating the formation of a *sec*-BuLi/**1** complex. As outlined for the addition of *n*-BuLi, the H2 and H11 resonances are shifted downfield whereas H8 is shifted upfield. When compared to the addition of *n*-BuLi these shifts are distinctly smaller. Again, the shifts of the remaining hydrogen signals are negligibly small. The ^{6}Li,^{1}H-HOESY spectrum of a 1:1 *sec*-BuLi/**1** mixture (the *sec*-BuLi is lithium-6 enriched) shows cross-peaks between ^{6}Li and the hydrogen atoms of the 1-methoxynaphthalene, confirming the existence of a *sec*-BuLi/**1** complex. As shown in Figure 2 the ^{1}H OCH$_3$ resonances of the 1-methoxynphthalene continuously change due to the addition of *sec*-BuLi. This indicates the existence of an equilibrium between the educts (**1** and *sec*-BuLi) and the detected complex. PM3 calculations on the lithiation of 1-methoxynaphthalene with *sec*-BuLi show a local minimum in the heat of formation for a *sec*-BuLi/**1** complex with Li−H2 interactions **12a** (ΔH_f^0 = 2.5 kcal/mol) and a second local minimum for a complex with Li−H8 interactions **13a** (ΔH_f^0 = 2.8 kcal/mol) (Figure 8). Calculations on the abstraction of the respective hydrogen atom revealed an energetically favorable transition state for lithiation in ortho-position **12b** (ΔH_f^0 = 10.7 kcal/mol, for transition state **13b** ΔH_f^0 = 13.6 kcal/mol). This means, taking the different ground-state energies into account, that the activation energy for lithiation in position 2 is 2.6 kcal/mol lower. This is in agreement with the experimental observations that lithiation in the ortho-position is preferred (the reaction of 1-methoxynaphthalene with 1 equiv of *sec*-BuLi yields a 3:1 mixture of 2-methyl-1-methoxynaphthalene (**2c**) and 8-methyl-1-methoxynaphthalene (**3c**)).

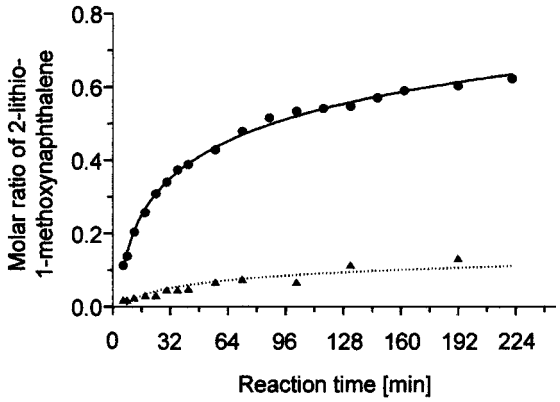

Figure 9. Time dependence of the formation of 2-lithio-1-methoxynaphthalene by the reaction of 1-methoxynaphthalene (solid curve) and 2-deuterio-1-methoxynaphthalene (dotted curve) with 1 equiv of *n*-BuLi/TMEDA (toluene-d_8, 5 °C).

The reaction of 1-methoxynaphthalene (**1**) with *sec*-BuLi in hydrocarbon solvents and subsequent quench with iodomethane yields a mixture of 2-methyl-1-methoxynaphthalene (**2c**) and the corresponding 8-methyl-1-methoxynaphthalene (**3c**) (60−64% **2c** and 36−40% **3c**, overall yield 5−10%). Addition of 1 equiv of TMEDA to a 1:1 mixture of 1-methoxynaphthalene and *sec*-BuLi leads, compared to the *n*-BuLi reaction, to a minor enhanced formation of the 2-lithiated product; however, the overall yield increases significantly (78% **2c** and 22% **3c**, overall yield 85%).

To gain a more pronounced understanding of the reaction mechanism we replaced the "reactive" hydrogen atom (H2 for the reaction with *n*-BuLi/TMEDA and H8 for the reaction with *t*-BuLi) by deuterium. This revealed insight into the kinetics of the hydrogen atom abstraction. A series of ^{1}H NMR spectra of a 1:1:1 *n*-BuLi/TMEDA/**1** mixture (toluene-d_8, 5 °C) showed a logarithmic dependence of the product formation against time. The formation of 2-lithio-1-methoxynaphthalene (**2a**) was determined by the ratio of integrals of the 1-methoxynaphthalene (**1**) and **2a** OCH$_3$ signals, respectively. A reaction temperature of 5 °C was selected to slow the reaction as compared to the preparative conditions (room temperature). A second series of ^{1}H spectra of an equimolar *n*-BuLi/TMEDA/2-deuterio-1-methoxynaphthalene mixture (comparable concentration as in the first case, toluene-d_8, 5 °C) shows likewise a logarithmic dependence of the product formation. In contrast to the undeuterated case, the reaction rate is decreased dramatically (Figure 9). The number of the isotope effect (k_H/k_D) of 15 ± 3, when compared with the isotope effect of anisole ($k_H/k_D \approx 7$)[31] and benzene (k_H/k_D = 2.0−4.5),[32] is quite high but values up to 30 and higher are reported in the literature.[33] Although the lithiation in position 2 is retarded, no noticeable competing

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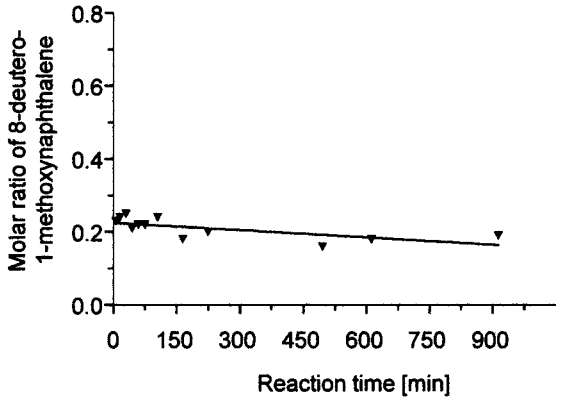

Figure 10. Reaction of a 1-methoxynaphthalene/8-deuterio-1-methoxynaphthalene mixture with *t*-BuLi (toluene-d_8, room temperature). The molar ratio of 1-methoxynaphthalene/8-deuterio-1-methoxynaphthalene remains constant over a long period.

formation of 8-lithio-1-methoxynaphthalene is observable under these conditions. However, at higher temperatures (+25 °C) some lithiation in position 8 is observed as well.

For the lithiation in position 8 we studied the reaction of *t*-BuLi with a mixture of 8-deuterio-1-methoxynaphthalene and nondeuterated material, whereupon the ratio of deuterated and nondeuterated material remains nearly constant during the reaction (Figure 10). This means there is no discrimination between deuterated and nondeuterated material. These results—pronounced isotope effect for the reaction with *n*-BuLi/TMEDA and lack of an isotope effect with *t*-BuLi—may be interpreted in the following way: in the case of *n*-BuLi or *n*-BuLi/TMEDA, the "docking" of 1-methoxynaphthalene to the lithium site is a facile process with low activation energy. The rate-determining step is the removal of H2 or H8 by the base, hence the observed isotope effect and a *kinetically controlled mechanism*. By contrast, "docking" of 1-methoxynaphthalene to *t*-BuLi (tetramer or lower aggregated) is a high activation energy process due to steric reasons. This is the rate-determining step. Once "docked", removal of H2 or H8 is a facile process much lower in energy. The activation energy difference between a protonated and a deuterated site is negligible as compared to the "docking" activation energy. Hence, an isotope effect k_H/k_D of ca. 1 is observed. Moreover, it is reasonable to assume that there is rapid exchange between lithium at the 2 and the 8 positions at the "docked" state in the case of *t*-BuLi, catalyzed by the base and leading to the preference of the thermodynamically more stable 8-lithiated species. Hence, we are dealing with an overall *thermodynamically controlled mechanism*.

The energetic preference of the 8-lithio species (**3a**) over 2-lithio-1-methoxynaphthalene (**2a**) may be demonstrated by a rearrangement reaction: a sample of 2-lithio-1-methoxynaphthalene (**2a**), prepared from **1** with *n*-BuLi in THF-d_8, shows changes of its composition upon heating. Besides formation of 1-methoxynaphthalene, additional signals for 8-lithio-1-methoxynaphthalene (**3a**) arise.

Conclusions

The one-dimensional ^{1}H and ^{13}C spectra as well as the two-dimensional ^{6}Li,^{1}H-HOESY spectra of a *n*-BuLi/**1** mixture indicate the existence of an equilibrium between free *n*-BuLi and 1-methoxynaphthalene coordinated *n*-BuLi whereas no complexation of **1** is detectable when TMEDA is added to this mixture. The predominant formation of the thermodynamically less favorable 2-lithio-1-methoxynaphthalene (**2a**) via, according to PM3 calculations, energetically favorable transition states strongly suggests a kinetically controlled mechanism. The preferred regiospecific formation of **2a** when the butyllithium is activated either due to addition of TMEDA or by using THF as solvent (both decrease the state of aggregation of *n*-BuLi[15,18−20,24,34]) confirms the kinetic aspect of the mechanism. For a 1:1 mixture of **1** with *t*-BuLi no evidence for complexation can be gained. Along with the lack of an isotope effect precomplexation is the rate-determining step in the reaction of **1** with *t*-BuLi. The slow formation of the thermodynamic product and especially the conversion of 2-lithio-1-methoxynaphthalene (**2a**) into 8-lithio-1-methoxynaphthalene (**3a**) at higher temperatures confirm the suggested thermodynamically controlled mechanism for this reaction.

Experimental Section

All one- and two-dimensional NMR measurements were recorded on a JEOL GX400 spectrometer (100.6 MHz for ^{13}C, 58.8 MHz for ^{6}Li, and 155.5 MHz for ^{7}Li). ^{1}H and ^{13}C spectra were referenced to the solvent signals: δ 6.98 (^{1}H, ortho hydrogen atom) and δ 20.4 (^{13}C, methyl carbon) for toluene-d_8 and δ 3.57 (^{1}H, −CDH−O) for THF-d_8.

All manipulations involving lithioorganic compounds were carried out in flame-dried glassware. All solvents and reagents (Aldrich or Fluka) were distilled (TMEDA from calcium hydride) or used without further purification (THF-d_8 and toluene-d_8 are dried and stored over Na/Pb-alloy).

Typical Sample Preparation for the NMR Observations. 1-Methoxynaphthalene (**1**, 0.10 mL, 0.60 mmol) is introduced into a 5-mm NMR tube fitted with a serum cap. The corresponding amount of the butyllithium agent is added and the solvent is removed in vacuo. The sample is cooled to −78 °C, and 0.70 mL of toluene-d_8 (and, if necessary, 0.10 mL TMEDA) is added. Samples for the ^{6}Li,^{1}H HOESY spectra of **1**/*n*-BuLi mixtures are prepared the same way, however, with ^{6}Li-enriched *n*-BuLi. The preparation of *n*-Bu^{6}Li in hexane was as described.[18] For the concentration dependence measurement of pure 1-methoxynaphthalene a starting sample of 0.05 mL of **1** in 0.70 mL of toluene-d_8 is prepared. After the measurement is completed additional 1-methoxynaphthalene is added stepwise to this solution.

2-Lithio-1-methoxynaphthalene (2a). 1-Methoxynaphthalene (0.10 mL, 0.70 mmol) is placed in an NMR tube and 0.35 mL of *n*-BuLi (2.02 M in hexane) is added. The solvent is removed in vacuo and 0.70 mL of THF-d_8 is added. After ca. 2 h at room temperature the metalation is complete (yield 92%; integration ^{1}H spectrum).

^{1}H NMR (400 MHz, THF-d_8, +32 °C): δ 4.05 (s, 3H, OMe), 7.24 (dd, ^3J = 7.3 Hz, ^3J = 8.5 Hz, 1H, H6), 7.33 (dd, ^3J = 8.2 Hz, ^3J = 8.5 Hz, 1H, H7), 7.39 (d, ^3J = 7.3 Hz, 1H, H4), 7.73 (d, ^3J = 8.0 Hz, 1H, H5), 8.08 (d, ^3J = 8.2 Hz, 1H, H8), 8.12 (d, ^3J = 7.3 Hz, 1H, H3). **^{13}C NMR** (100 MHz, THF-d_8, +32 °C): δ 58.1 (OMe), 119.3 (C4), 120.1 (C8), 121.6 (C6), 122.3 (C7), 124.0 (C9), 126.3 (C5), 133.7 (C10), 141.0 (C3), 163(C1/C2).

8-Lithio-1-methoxynaphthalene (3a). 1-Methoxynaphthalene (2.00 mL, 14.0 mmol) is introduced into a Schlenk flask and 10.0 mL of dry hexane and 9.30 mL of *t*-BuLi (1.5 M solution in cyclohexane) are added. The solution is stirred for 35 h at room temperature and the precipitate is filtered off. The filtration residue is washed with dry hexane and dried in vacuo (yield 1.2 g; 52%).

^{1}H NMR (400 MHz, THF-d_8, +32 °C): δ 3.85 (s, 3H, OMe), 6.68 (d, ^3J = 7.6 Hz, 1H, H2), 7.12 (dd, 1H, H3), 7.18 (dd, 1H, H6), 7.27 (d, ^3J = 8.1 Hz, 1H, H4), 7.35 (d, ^3J = 7.7 Hz, 1H, H5), 8.15 (d, ^3J = 5.8 Hz, 1H, H7). **^{13}C NMR** (100 MHz, THF-d_8, +32 °C): δ 55.2

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(OMe), 101.4 (C2), 122.8 (C4), 122.9 (C5), 123.2 (C3), 125.1 (C6), 134.4 (C10), 139.1 (C7), 139.6 (C9), 161.0 (C1), 185.2 (C8).

Isomerization of 2-Lithio-1-methoxynaphthalene. 1-Methoxynaphthalene (0.10 mL, 0.60 mmol) is introduced into a 5 mm NMR tube fitted with a serum cap and 0.25 mL of *n*-BuLi (2.5 M solution in hexane) is added. The solvent is removed in vacuo and the residue is dissolved in 0.70 mL of THF-d_8 and ca. 0.02 mL of cyclohexane as an internal standard. After 3 h at room temperature (metalation in the ortho-position) the temperature is raised to 50 °C and a series of ^{1}H spectra are recorded over a period of 3 days.

1-Methoxy-2-naphthoic Acid (2b). 1-Methoxynaphthalene (1.44 mL, 1 mmol) is introduced into a Schlenk flask and 10.0 mL of dry hexane, 4.60 mL of *n*-BuLi (1.3 M solution in cyclohexane), and 1.00 mL of TMEDA are added. The solution is stirred 2 h at room temperature and then poured on ether/solid CO_2. Diluted HCl solution is added. The organic layers are washed with Na_2CO_3 solution and concentrated HCl is added to the combined aqueous layers, whereupon the acid precipitates (yield 1.29 g; 63%, NMR pure).

^{1}H NMR (400 MHz, $CDCl_3$, +31 °C): δ 4.14 (s, 3H, H11), 7.61 (m, 2H, H6,7), 7.68 (d, 1H, H3), 8.05 (d, 1H, H4), 8.23 (d, 1H, H8). **^{13}C NMR** (100 MHz, $CDCl_3$, +31 °C): δ =64.1 (C11), 117.7−137.5 (ArC), 158.3 (C1), 168.5 (COOH).

1-Methoxy-8-naphthoic Acid (3b). 1-Methoxynaphthalene (1.44 mL, 1 mmol) is introduced into a Schlenk flask and 10.0 mL of dry hexane and 6.70 mL of *t*-BuLi (1.5 M solution in cyclohexane) are added. The solution is stirred for 35 h at room temperature and then poured on ether/solid CO_2. Diluted HCl solution is added. The organic layers are washed with Na_2CO_3 solution and concentrated HCl is added to the combined aqueous layers, whereupon the acid precipitates (yield 0.71 g; 35%, NMR pure).

^{1}H NMR (400 MHz, $CDCl_3$, +31 °C): δ 4.02 (s, 3H, H11), 6.93 (d, 1H, H2), 7.42−7.53 (m, 3H, H3,4,6), 7.58 (d, 1H, H7), 7.89 (d, 1H, H5). **^{13}C NMR** (100 MHz, $CDCl_3$, +31 °C): δ=55.9 (C11), 106.5 (C2), 120.9−134.8 (ArC), 154.6 (C1), 177.7 (s, COOH).

2-Methyl-1-methoxynaphthalene (2c) and 8-Methyl-1-methoxynaphthalene (3c). 1-Methoxynaphthalene (1.00 mL, 0.60 mmol) is introduced into a Schlenk flask and 10.0 mL of dry hexane, 4.60 mL of *n*-BuLi (1.3 M solution in cyclohexane), and, if necessary, 1.00 mL of TMEDA are added. The solution is stirred 12−14 h at room temperature and quenched with an excess of iodomethane (usually 2.00 mL). After 2 h at room temperature 10.0 mL of sodium hydroxide solution (2 M) is added. The aqueous phase is separated and washed with two 10.0 mL portions of hexane. The combined organic phases are washed with 10.0 mL of brine and dried over $MgSO_4$. The solvent is removed and the residue is dried in vacuo. The product composition is determined by ^{1}H NMR in $CDCl_3$. Standard NMR techniques have been employed for the ^{1}H and ^{13}C assignments of the mixture of regioisomers.

2-Methyl-1-methoxynaphthalene (2c). ^{1}H NMR (400 MHz, $CDCl_3$, +32 °C): δ =2.55 (s, 3H, Me), 3.98 (s, 3H, OMe), 7.37 (d, 1H, H3), 7.51 (ddd, 1H, H6), 7.58 (ddd, 1H, H7), 7.62 (d, 1H, H4), 7.88 (d, 1H, H5) 8.21 (d, ^3J = 8.5 Hz, 1H, H8). **^{13}C NMR** (100 MHz, $CDCl_3$, +32 °C): δ 15.8 (Me), 60.9 (OMe), 121.6 (C1), 123.6 (C6), 125.1 (C7), 125.6 (C8), 125.9 (C3), 127.8 (C5), 128.0 (C10), 129.3 (C4), 133.6 (C9), 153.4 (C2).

8-Methyl-1-methoxynaphthalene (2c). ^{1}H NMR (400 MHz, $CDCl_3$, +32 °C): δ =2.88 (s, 3H, Me), 3.91 (s, 3H, OMe), 6.79 (d, ^3J = 7.5 Hz, 1H, H2), 7.17 (d, ^3J = 7.1 Hz, 1H, H7), 7.29 (dd, 1H, H6), 7.32 (dd, 1H, H3), 7.38 (d, ^3J = 8.1 Hz, H4), 7.60 (d, ^3J = 8.2 Hz, 1H, H5).

2-Deuterio-1-methoxynaphthalene (2d). 1-Methoxynaphthalene (1.00 mL, 6.70 mmol) is introduced into a Schlenk flask and 10.0 mL of dry hexane, 3.80 mL of *n*-BuLi (1.6 M solution in hexane), and 1 mL of TMEDA are added. The solution is stirred for 3 h at room temperature and quenched with an excess of CH_3OD. After 10.0 mL of brine is added, the aqueous phase is separated and washed with two 10.0 mL portions of hexane. The combined organic phases are washed with 10.0 mL of brine and dried over $MgSO_4$. The solvent is removed and the residue is dried in vacuo. This raw product (0.90 g, 5.60 mmol mixture of deuterated and nondeuterated 1-methoxynaphthalene) is again introduced into a Schlenk flask and 3.50 mL of *n*-BuLi and 0.90 mL of TMEDA are added. After 0.5 h the reaction is stopped by addition of CH_3OD. Workup analogous to the first reaction yields 0.85 g (80%) of **2d**. This material contains ca. 15% of the 8-deuterated species.

^{1}H NMR (400 MHz, $CDCl_3$, +31 °C): δ 3.95 (s, 3H, H11), 7.37 (d, 1H, H3), 7.42 (d, 1H, H4), 7.48 (m, 2H, H6,7), 7.79 (d, 1H, H5), 8.28 (d, 1H, H8). **^{13}C NMR** (100 MHz, $CDCl_3$, +31 °C): δ 55.2 (C11), 103.4 (t, C2-D), 120.1 (C4), 121.8 (C8), 125−128 (C3, C5, C6, C7), 134.4 (C10), 155.3 (C1).

8-Deuterio-1-methoxynaphthalene (3d). 1-Methoxynaphthalene (1 mL, 0.6 mmol) is introduced into a Schlenk flask and 10 mL of dry hexane and 3.5 mL of *t*-BuLi (1.7 M solution in pentane) are added. The solution is stirred for 36 h at room temperature and quenched with an excess of CH_3OD. After 10 mL of brine is added, the aqueous phase is separated and washed with two 10 mL portions of hexane. The combined organic phases are washed with 10 mL of brine and dried over $MgSO_4$. The solvent is removed and the residue is dried in vacuo. Yield 0.73 g (67%, this material contains ca. 15% nondeuterated 1-methoxynaphthalene and ca. 3% of material deuterated in position 2).

^{1}H NMR (400 MHz, $CDCl_3$, +31 °C): δ 3.95 (s, 3H, H11), 6.83 (d, 1H, H2), 7.37 (d, 1H, H3), 7.42 (d, 1H, H4), 7.48 (m, 2H, H6,7), 7.79 (d, 1H, H5). **^{13}C NMR** (100 MHz, $CDCl_3$, +31 °C): δ 55.2 (C11), 103.4 (C2), 120.1 (C4), 121.8 (t, C8-D), 125−128 (C3, C5, C6, C7), 134.4 (C10), 155.3 (C1).

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Supporting Information Available: Tables of Cartesian coordinates (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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