On the Mechanism of Arene-Catalyzed Lithiation: The Role of Arene Dianions—Naphthalene Radical Anion versus Naphthalene Dianion

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Dedicated to Professor Lutz F. Tietze on the occasion of his 60th birthday

Abstract: The use of lithium and a catalytic amount of an arene is a well-established methodology for the preparation of organolithium reagents that manifest greater reactivity than the classical lithium–arene solutions. In order to rationalize this conduct, the participation of a highly reduced species, the dianion, is proposed and its reactivity explored. Studies of kinetics and of distribution of products reveal that the electron-transfer (ET) reactivity profile of dilithium naphthalenide in its reaction with organic chlorides excludes alternative mechanisms of halogen–lithium exchange. The process generates organolithium compounds. The dianion thus emerges along with the radical anion as a suitable candidate for catalytic cycles in certain processes. Endowed with a higher redox potential than its radical anion counterpart, dilithium naphthalene displays a broader spectrum of reactivity and so increases the range of substrates suitable for lithiation. The reaction of dilithium naphthalene with THF is one example of the divergent reactivity of the radical anion and the dianion, which has been the source of apparent misinterpretation of results in the past and has now been appropriately addressed.

Keywords: arene ligands · electron transfer · lithiation · radical ions · reduction

Introduction

The use of lithium and a catalytic amount of an arene as electron carrier has become a well-established and widely used protocol for the preparation of organolithium compounds.[1] It represents an important improvement over the former stoichiometric version, that is the use of lithium radical anion solutions,[2] since only small amounts of arene need to be removed in the purification steps, but, even more importantly, because the newer system has higher lithiation reactivity in some processes, to the extent of being the only system reactive enough to perform certain transformations.[3] It appears that different species might be playing an active part in the catalytic version of the process along with the lithium radical anion, at least when the latter is not reactive enough to perform a specific transformation alone. However, so far no systematic studies have been reported confirming these facts.[4] The electron carrier plays a central role in the reaction, acting as a homogeneous catalytic species. Among electron carriers, naphthalene and 4,4′-di-*tert*-butylbiphenyl (DTBB) are the most frequently used catalysts. Former interpretations of the mechanism of arene-catalyzed lithiations posited arene radical anions as the very active species performing redox catalytic cycles. These radical anions, including lithium salts $LiC_{10}H_8$ or LiDTBB, are well-known species; their physical and spectroscopic properties as well as chemical reactivity have been widely reported.[5] They act as powerful electron-transfer (ET) reagents versus a number of organic halides, generating high yields of organolithium compounds.[6] Overreduction of these paramagnetic species to give the dianion has been achieved in several ways. These highly reduced species have received far less attention, perhaps owing to their elusiveness, in spite of the manifest interest concerning electronic configuration–reactivity and structure–reactivity relationships. Dipotassium naphthalene has apparently been obtained by condensation of potassium and naphthalene vapors, even though no electronic spectra of the dianion could be recorded.[7] Solutions containing an unknown amount of dianion were apparently obtained by prolonged exposure of naphthalene to an excess of lithium metal in THF at room temperature.[8] However, unequivocal preparation of the naphthalene dianion is achieved through an entirely different approach. Double deprotonation of 1,4-dihydronaphthalene using butyllithium and two equivalents of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA) in hex-

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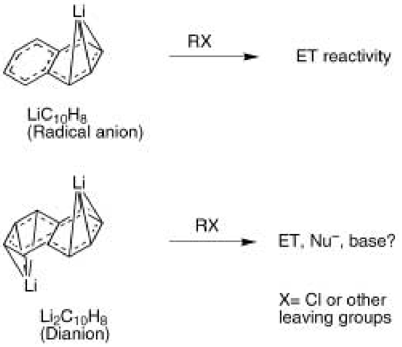
ane affords $Li_2C_{10}H_8 \cdot 2TMEDA$ as purple crystals, for which structural data in the solid state could be obtained.[9] To date, the spectrum of reactivity of these highly reduced diamagnetic species remains mostly unexplored. Potentially they could act as: a) bisallylbenzyllithium reagents, predicted to be reactive as strong bases or nucleophiles;[10] b) ET reagents, imitating their radical anion counterparts; or c) perhaps as both,[11] drawing attention to the long-standing issue of the mechanistic dichotomy between ET and nucleophilic substitution (Scheme 1).



Scheme 1. Likely mechanisms in reactions of naphthalene radical anion and naphthalene dianion.

In this work we undertake the beginning of an extensive study that will cover the reactivity displayed by dianions derived from high-reduction-potential arenes and their role in the arene-catalyzed lithiation reactions, focusing on naphthalene as a starting point.

Results and Discussion

Reactivity profiles: A reactivity profile for both kinds of reagents, radical anion and dianion lithium salts, has been constructed with organic chlorides as substrates and naphthalene as arene. Competitive kinetic techniques[12] allow accurate measurement of the relative rates of reaction of the radical anion (**I**) and dianion (**III**, and presumably **II** and **IV**, see below) as they react simultaneously with two organic chlorides. As substrates we include primary, secondary, and tertiary alkyl and aryl chlorides (1- and 2-chlorooctane, 2-chloro-2-methylheptane and chlorobenzene; for simplicity, the former three will also be referred to as *n*- or 1-, *sec*- or 2-, and *tert*-octyl chloride in this paper). In a representative example, a solution of **I** ($LiC_{10}H_8$) in THF at 0 °C was added in small fractions to a mixture of 1-chlorooctane, 2-chlorooctane, and a carefully weighed amount of dodecane as internal standard (ca. 1:1:0.5, 0.01 M in THF at 0 °C). A sample of the reacting mixture was obtained after every addition, these aliquots being immediately hydrolyzed (ice-cold 0.5 M phosphate buffer/pentane) and submitted to quantitative GLC analysis. The simultaneous determination of the remaining concentration of these two organic chlorides in solution that react with **I** permits the evaluation of their relative reaction rates,[13] $k_{2\text{-octylCl}}/k_{1\text{-octylCl}} = 0.91$ in this case. The same procedure was repeated for all pairs of organic chlorides submitted to test, the resulting relative rates being arbitrarily referred to 1-octyl chloride. Reactivity profiles were constructed in this way for **I** (radical anion, Li + $C_{10}H_8$ 1:1.1, green solution), **II** (Li excess + $C_{10}H_8$ ca. 5:1, purple solution when fresh), **III** ($Li_2C_{10}H_8 \cdot 2TMEDA$, synthesized from 1,4-dihydronaphthalene, purple when fresh), and **IV** (Li excess + $C_{10}H_8$ + 2TMEDA, i.e. **II** + 2TMEDA, purple when fresh). Only clear solutions of **I**–**IV** (in the absence of Li metal) were used, all the determinations being carried out in THF at 0 °C. The results are collected and represented in Figure 1.

Reactivity profiles for all four reagents are essentially identical, and to a great extent so is the distribution of major and most minor products obtained.[14] According to this data, dilithium naphthalenide behaves as an ET reagent in its reaction with organic chlorides in that it becomes indistinguishable from lithium naphthalenide as far as reactivity profiles are concerned. Regarding the mechanism of the lithiation, there is no selectivity for the structure of the organic halide in the process, as would be expected from an outer-sphere ET in the determining step of the reaction.[13] This is the mechanism of reaction for most radical anions, such as **I**, with organic halides. The resulting flat profiles displayed rule out other possible metalation mechanistic pathways for the dianion, such as a back approach to the halide in an S_N2-like transition state (e.g. ferrates[15] or Co^I reagents[16]) or an "ate" transition state or intermediate (e.g. alkyllithiums,[17] and perhaps dialkylmagnesium reagents[18]). These two alternative mechanisms of metallation result in totally different structure–reactivity profiles. An S_N2-like transition state would display rates of reaction following the pattern *primary > secondary ≫ tertiary alkyl* or *aryl* chlorides, whereas an "ate" transition state would be of the type *aryl ≫ primary > secondary > tertiary alkyl* chlorides, none of them matching the observed reactivity profile. Tentative structures for these high-energy transition states/intermediates can be easily drawn with the aid of canonical forms.

Abstract in Spanish: *La utilización de litio y una cantidad catalítica de un areno es una metodología ampliamente establecida para la preparación de compuestos organolíticos, presentando una mayor reactividad que las correspondientes soluciones de litio-arenos. Para explicar este comportamiento se propone la participación de especies altamente reducidas, como son los correspondientes dianiones, estudiándose su reactividad. Estudios cinéticos y de distribución de productos indican que el dilitionaftaleno muestra un perfil de reacción típico correspondiente a un agente de transferencia electrónica en su reacción con derivados clorados, pudiendo excluirse mecanismos alternativos para el intercambio cloro-litio, generándose compuestos organolíticos. Debido al mayor potencial redox de esta especie, comparado con el correspondiente radical-anión, se amplía su reactividad frente a un mayor conjunto de sustratos a litiar. Un ejemplo de esta reactividad divergente es el comportamiento de ambos agentes de litiación, radical-anión y dianión, frente a THF, que ha sido objeto de aparente debate en el pasado y que en este artículo se clarifica definitivamente.*

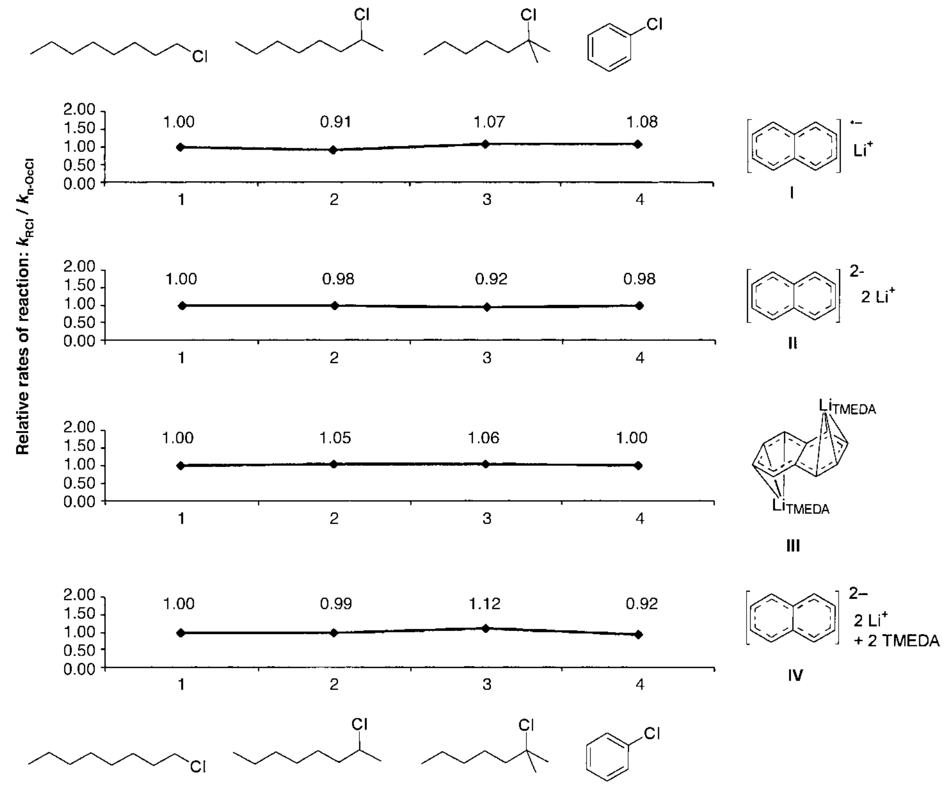


Figure 1. Reactivity profiles of naphthalene radical anion (**I**) and dianions (**III** and presumably **II** and **IV**) in their reactions with organic chlorides. Each relative rate has been obtained by evaluation of the slope by linear regression analysis of plots representing the decay of the concentration of both chlorides (refs. [12, 13]) and is arbitrarily referred to 1-chlorooctane. Each of these plots contained 5–8 points and were linear to greater than 90% consumption of the reacting chlorides (first-order reactions with respect to the alkyl chloride), the regression coefficients being >0.995 in all cases. Species **III** and **IV** have been drawn differently simply with the purpose of emphasizing that only the structure of $Li_2C_{10}H_8\cdot 2TMEDA$ obtained by deprotonation has been elucidated.

It is not likely that the radical anion present in the reaction media can compete with the dianion for RCl when both are present in similar concentrations,[19] because of both a) less favorable reduction potentials[20] and b) dissimilar electronic configurations of reactants.[21] As long as the former assumption holds, the generally accepted mechanism for the reaction of arene radical anions (e.g. $C_{10}H_8^{\bullet-}$) with RX applies, in principle, to the naphthalene dianion [Eqs. (1)–(3)]. Nucleophilic attack of the naphthalene dianion on RCl does not

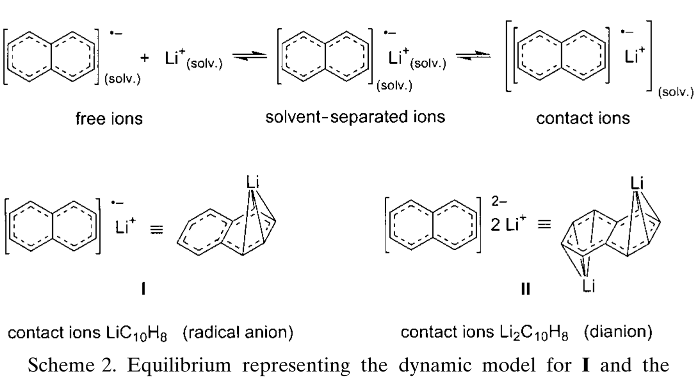
$$C_{10}H_8^{2-} + RX \begin{cases} \xrightarrow[/\!/]{k_{S_N2}} RC_{10}H_8^- + X^- \\ \xrightarrow{k_{ET}} R^\bullet + X^- + C_{10}H_8^{\bullet-} \\ \xrightarrow[/\!/]{k_{base}} R_{dehydro} + C_{10}H_9^- + X^- \end{cases} \qquad (1)$$

$$R^\bullet + C_{10}H_8^{\bullet-\,(\text{or } 2-)} \xrightarrow{k_2} R^- + C_{10}H_8^{(\text{or } \bullet-)} \qquad (2)$$

$$R^\bullet + C_{10}H_8^{\bullet-} \xrightarrow{k_3} RC_{10}H_8^- \qquad (3)$$

represent a competitive pathway for ET, as can be inferred from the reactivity profiles [Eq. (1)]. Neither does the reactivity as a base of the dianion versus RCl. Even in the case of *tert*-octyl chloride, more prone to act as a source of protons, the elimination products (isooctenes) are hardly detectable.[22] In the subsequent step, both reducing agents can in principle participate [Eq. (2)], the coupling of $R^\bullet$ and the radical anion being most likely the source of coupling by-products (mostly isomeric $RC_{10}H_9$, see below, but also $R_2C_{10}H_8$ and alkylated naphthalene, from GC-MS) [Eq. (3)]. The k_2/k_3 ratio [also expressed as the dimensionless competition parameter $k_2/(k_2+k_3)$][23] is a key parameter of the process when the aim is to maximize the formation of R^-. For radical anions, the k_2/k_3 ratio seems to be dependent on the standard reduction potential of the arene, the more negative ones having the higher k_2/k_3 ratios, resulting in higher yields of carbanionic species.[24] This trend is manifested by the dianion as slightly but reproducibly better yields in the lithiation process using **II** compared to that with **I**.

Ion pairing and electron transfer (ET) rates: Depending on the nature of the solvent, the counterion, and the temperature, radical anions and dianions of arenes may exist as different entities that differ in the degree of association between the anionic and cationic part of the molecule.[25] The nature of these species in solution has been better described as a dynamic model, an equilibrium consisting of contact (or *tight*) ion pairs and solvent-separated (or *loose*) ion pairs, the occurrence of free ions being rather unusual in ethereal solvents (Scheme 2). The thermodynamics of these equilibria in general follows uniform trends governed by solvating effects. While generally $\Delta H^\circ_{(\mathrm{solv})}$ is positive as we move toward the right of the equilibrium (due to loss of



Scheme 2. Equilibrium representing the dynamic model for **I** and the structure of the contact ion pairs **I** (calculated) and **II** (from X-ray structure and calculated).

enthalpy of solvation), so is $\Delta S^{\circ}_{(\mathrm{solv})}$, which sees its value become more positive as an increased number of solvent molecules are released from their coordination sites. The overall effect is a temperature-dependent equilibrium that shifts toward contact ion pairs as the temperature is increased and shifts toward free or loose ion pairs at low temperatures. The naphthalene radical anion is no exception to this general scenario. As for the cation, lithium has higher coordinating ability with the solvent than other alkaline cations, favoring loose ion pairs in the ion-pairing equilibrium.[26] Lithium naphthalene (**I**) in THF at room temperature has about 60–80 % solvent-separated ion pair in equilibrium with 40–20 % of contact ion pairs, as seen by UV/Vis spectroscopy.[25] As expected, the amount of solvent-separated ion pairing increases with decreasing temperature. In contrast, dianion (**II**) is expected to be a robust contact ion triple in ether solvents even at temperatures as low as −78 °C, as the result of strengthened coulombic interactions.[27] The structures of the contact ion pairs or triples for **I** and **II** are represented in Scheme 2. The structure of **I** was calculated;[28] **II** is part of a structure determined by X-ray crystallography,[9] and has also been calculated.[27, 28] Each one of these ion-pair species in the dynamic model differs to some extent from the others in their properties and reactivity. In the case of arene radical anions, this has been confirmed in a large number of experiments dealing with conductivity,[7] line widening,[29] and hyperfine constants in ESR,[30] hyperfine splittings in NMR,[31] and UV/Vis spectroscopy.[25] For ET reactions of naphthalene radical anions, in self-exchange ET[29] and reductive cleavage of alkyl halides,[32] loose ion pairs react about 1–2 orders of magnitude faster than tight ion pairs. This trend is maintained as we move toward less associated ions in the equilibrium of Scheme 2, in other words the smaller the association between ions, the faster the ET rates observed. Another important piece of information emerging from these studies is that the structures of ion pairs of hydrocarbon anions are relatively insensitive to the concentration. The formation of higher aggregates does not seem to be important for alkali metal naphthalene radical anions[31] and dianions[33] in coordinating ethereal solvents.

Distribution of products: According to the profiles displayed in Figure 1, the determining step of the reaction of **II** with organic chlorides is an ET process [Eq. (1)]. Strictly, this does not necessarily mean that **II** will carry out Cl–Li exchange and generate organolithium reagents [Eq. (2)], since the radical generated ($R^{\bullet}$) could react in a variety of ways. At this stage, a study of the distribution of products was undertaken to obtain information about the fate of the radical species resulting from the ET step [Eqs. (2) and (3)]. As expected, further reduction of $R^{\bullet}$ to afford organolithium compounds is the main reaction outcome for dianions as well as for the radical anion when primary alkyl chlorides are used as substrates. To demonstrate this, the reactions of **I**–**IV** with 1-chlorooctane were carried out in THF at −60 °C, the temperature at which solubility of crystalline **III** is adequate. Yields of the organolithium reagent formed, 1-octyllithium, were determined after the reaction with trimethylchlorosilane and pivalaldehyde as electrophilic reagents. The first step was carried out with an excess of the lithiating reagent (4:1 molar ratio) and was monitored until the concentration of the starting material dropped below detection limits (< 0.01 %), then an excess of the electrophilic reagent was added, and the reaction was allowed to warm up slowly to 0 °C and was hydrolyzed as before. Quantitative analysis of the reaction products showed a similar distribution of major products for **I** and **II** (reactions in the absence of TMEDA), with **II** invariably giving slightly better yields than **I**. In the case of **III** and **IV** (reactions in the presence of TMEDA) the distribution of main products obtained was nearly identical (Table 1). These last results confirm the similarity among the species generated after exposure of naphthalene to an excess of lithium, and pure dilithium naphthalene.

Table 1. Distribution of products corresponding to the reaction of 1-chlorooctane with the lithiating reagents **I**–**IV** and capture of 1-octyllithium with a) TMSCl or b) *t*BuCHO.

a) E^{+} = TMSCl	Products [%][a]		
Lithiating agent	*n*-Octyl-$SiMe_3$	*n*-Octane	*n*-OctylCl
I ($LiC_{10}H_8$)[b]	75	9.8	< 0.01
II ($Li_2C_{10}H_8$)[b]	81	9.8	< 0.01
III ($Li_2C_{10}H_8 \cdot 2TMEDA$)[c]	62	22	< 0.01
IV($Li_2C_{10}H_8 \cdot 2TMEDA$)[b]	59	20	< 0.01

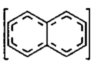
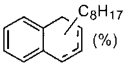
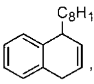
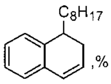
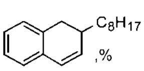
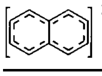
b) E^{+} = *t*BuCHO	Products [%][a]		
Lithiating agent	*n*-Octyl-CHOH*t*Bu	*n*-Octane	*n*-OctylCl
I ($LiC_{10}H_8$)[b]	41	45	< 0.01
II ($Li_2C_{10}H_8$)[b]	52	41	< 0.01
III ($Li_2C_{10}H_8 \cdot 2TMEDA$)[c]	52	23	< 0.01
IV ($Li_2C_{10}H_8 \cdot 2TMEDA$)[b]	53	24	< 0.01

[a] Yields of the products were determined by quantitative GLC using pure isolated products in the determination of response factors, and were averaged for 4–5 runs, $\sigma_{sd} = \pm 3\%$. [b] From $Li_{(s)}$ + $C_{10}H_8$ in THF. [c] Crystals obtained by double deprotonation of 1,4-dihydronaphthalene ($C_{10}H_{10}$) with 2 equiv *n*BuLi.

The scenario is slightly different for other alkyl chlorides. The reaction of lithium naphthalene radical anion with a variety of structurally different alkyl chlorides in THF has been described elsewhere.[34] We have re-examined this reaction in order to compare any differences in the distribution of products obtained when dilithium naphthalene, $Li_2C_{10}H_8$ (**II**), is used instead of the classical $LiC_{10}H_8$ (**I**) reducing agent. We have also attempted to isolate by-products (i.e., coupling products) originating in the reactions of lithium naphthalene and dilithium naphthalene with a primary, a secondary, and a tertiary alkyl chloride, followed by hydrolysis with water. These products have been largely overlooked because of the difficulty of their separation from the reaction crude and their readiness to decay. In some instances, silica gel impregnated with $AgNO_3$ proved to be the stationary phase of choice for the chromatographic purification of isomeric mixtures of alkyldihydronaphthalenes when ordinary flash chromatography failed.[35] To minimize polymerization/oxidation during handling and storage, 5–10 % of hydroquinone was added to the crude mixtures and purified compounds. Even with these precautions, some of the reaction products turned into intractable mixtures shortly after their isolation. In particular, 1-octyl-1,2-dihydronaphthalenes (**6b**, **8b**) slowly evolve towards intractable mixtures, while the 2-octyl-1,2-dihydronaphthalenes (**8c**) mainly rearomatize to 2-octylnaphthalenes. 1-Octyl-1,4-dihydronaphthalenes (**6a**, **8a**) are apparently slightly more stable species that can be rearomatized using chloranyl. By means of these chromatographic techniques, separation of the isomers was achieved in the reactions of 1-chlorooctane and 2-chloro-2-methylheptane. Quantification of all these compounds was carried out using pure isolated samples for the determination of the response factors with a FID detector, the results gathered in Table 2 being the average of 4–6 determinations. Unfortunately, in the case of 2-chlorooctane, complex mixtures of regioisomers and diastereoisomers (**7**) prevented adequate separation and identification of the coupling products other than by GC-MS. For the overall quantification of these 2-octyldihydronaphthalene derivatives, all regio and diastereoisomers were supposed to have the same response factor. Products account for ≈90% of the starting material in most cases except in the reaction of **II** with *tert*-octyl chloride (71%). What constitutes the remaining 29% is uncertain. A number of potential by-products including R_2, $R_2C_{10}H_8$, or isooctenes were sought but not found in significant amounts in the reaction mixture. The extremely basic/ET character of **II** might have initiated an anionic or radical polymerization of initially formed **8b**; however, this hypothesis was not verified.

Several points should be noticed from the results in Table 2. First, while both lithium naphthalene and dilithium naphthalene react with *n*-octyl chloride to afford high yields of octyllithium, the reaction is not likewise effective for *sec*- or *tert*-octyl chloride (i.e., 2-chloro-2-methylheptane in our study). Yields for the corresponding secondary or tertiary organolithium reagents drop, whereas the proportion of coupling derivatives of the type $RC_{10}H_9$ increases, becoming quite abundant or even dominant.[36] The origin of this behavior probably lies in the relative readiness of $R^{\bullet}$ to be further reduced to R^- (primary, secondary, or tertiary $R^{\bullet}$, originated after electron transfer to the halide from **I** or **II**). In cyclic voltammetry, a simple two-electron wave is obtained for the reduction of *n*-butyl iodide, but for *tert*- and *sec*-butyl iodides a second peak has been observed which enables the determination of an effective reduction potential for tertiary and secondary alkyl radicals. In the latter two cases, the radical is not reduced at the potential at which the reductive cleavage of the halide occurs; $R^{\bullet}$ is reduced at a more negative potential than the halide, giving rise to a second wave and setting a relative experimental order for the ease of reduction of alkyl radicals as $n\text{-R} > sec\text{-R} > tert\text{-R}^{\bullet}$.[37] In our case, the more negative reduction potential of $R^{\bullet}$ is manifested as a closer competition of coupling reactions [Eq. (3)] with reduction [Eq. (2)] and therefore a drop in RLi yields (Table 2). Secondly, it should be noticed in Table 2 that the yield of octanes (directly related to octyllithium yields) increases only slightly when $Li_2C_{10}H_8$ is used, even though it is a much stronger reducing agent that $LiC_{10}H_8$. This may be for several reasons: a) We may have reached the "flat" or even the "Marcus inverted region" where activation free energy and the driving force for an ET process no longer move together.[38] Since, to the best of our knowledge, no thermodynamic or electrochemical values corresponding to a double-electron reduction of naphthalene are available,[39] the weight of this hypothesis cannot be evaluated and remains uncertain. b) Interaction of configurations might be favored for the radical/radical-anion pair ($^{\text{doublet}}R^{\bullet}/^{\text{doublet}}Ar^{\bullet-}$) rather than for the radical/dianion pair ($^{\text{doublet}}R^{\bullet}/^{\text{singlet}}Ar^{-2}$). If this was the case, most of the second electron transfer (responsible for the process $R^{\bullet} + e^- \rightarrow R^-$ and subsequent generation of the alkyllithium reagent) would be carried out by the naphthalene radical anion **I** instead of **II**. If this were the case, no improved yields would be observed. An experiment designed to clarify this point is currently under consideration. Definitive evidence should be obtained from the reduction rates of $R^{\bullet}$ when **II** is compared with **I** as a reducing agent. A priori, these rates should be available through kinetic experiments using suitable radical clocks.[40] c) Finally, another factor should be kept in mind if we try to compare reactivities for both species: as we mentioned before, the nature of the ion pairing in **I** (and likewise in **II**) significantly affects the corresponding rates of ET to substrates. Dianions are expected to be contact ion triples even at −78 °C. Instead, at low temperatures lithium naphthalene in THF is in an equilibrium shifted towards loose ion pairs, which have lower activation barriers in the ET process than tight ion pairs. The ion pairing nature of **I** and **II** should affect ET rates to a lesser extent than reduction potentials, but this is only true if we are far from the Marcus

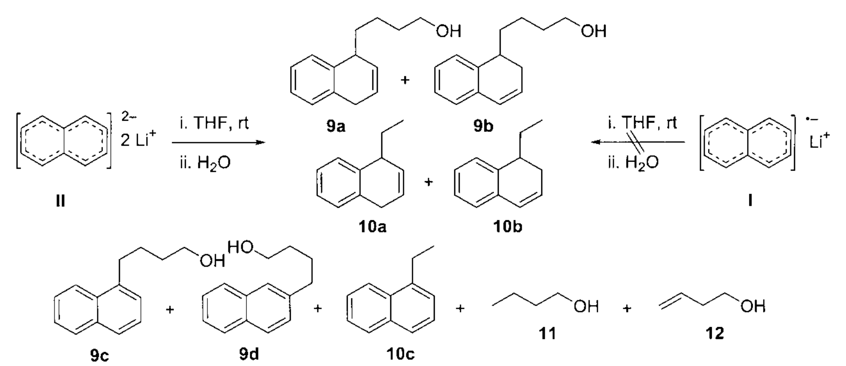
Table 2. Reaction of **I** and **II** with structurally different octyl chlorides, and analysis of the by-products.

 Li^+ (I)	$C_{18}H_{18}$ [%]	overall  (%)	% total quantified	 ,%	 ,%	 ,%
n-$C_8H_{17}Cl$	82	6	88	**6a**, 3.7	**6b**, 2.3	–
s-$C_8H_{17}Cl$	55	38 (7)	93	–	–	–
t-$C_8H_{17}Cl$	37	61	98	**8a**, 29	**8b**, 36	**8c**, 1.6[b]
 2– 2 Li^+ (II)						
n-$C_8H_{17}Cl$	89	7	96	**6a**, 4.1	**6b**, 2.9	–
s-$C_8H_{17}Cl$	57	32 (7)	89	–	–	–
t-$C_8H_{17}Cl$	41	30	71	**8a**, 20	**8b**, 7.0	**8c**, 3.0[b]

[a] Reactions performed by addition of the halide to a 0.4 M solution of **I** or **II** in THF at −78 °C and subsequent hydrolysis with water. Molar ratio: halide/(**I** or **II**) = 1/4. Yields determined by quantitative GLC using pure isolated products and decane/dodecane as internal standard, corresponding to the average of 4–6 experiments, $\sigma_{sd} = \pm 5\%$. *tert*-Octyl chloride = 2-chloro-2-methylheptane. [b] Isolated as the corresponding aromatized compound, i.e., 2-(1,1-dimethylhexyl)naphthalene (**8d**).

flat region. In the proximity of the Marcus flat region, an increased exergonicity of the ET reaction does not bring about enlarged ET reaction rates any more. For the aforesaid reasons, this cannot be rigorously evaluated here.

The lithium salts of naphthalene radical anion or dianion are not the reagents of choice for the preparation of secondary and especially tertiary alkyllithium reagents. This is a well-known drawback of lithium naphthalene solution as a lithiation agent. In an effort to overcome this problem from a synthetic point of view, sterically hindered electron carriers endowed with more negative reduction potentials than naphthalene were introduced.[41] These arenes settled the problem of extensive coupling of secondary and tertiary halides most satisfactorily;[34a] 4,4′-di-*tert*-butylbiphenyl (DTBB) is the most representative arene electron carrier used for this purpose. We can state now that the success of these reagents is based mainly on steric factors rather than reduction potentials, regardless of the fact that both factors cooperate in the final goal.[42]



Scheme 3. The reaction of dilithium naphthalene with THF at room temperature affords the products **9a–c** and **10a–c** along with **11**, while lithium naphthalene is essentially unreactive. Under THF reflux, dilithium naphthalene yields only aromatized products **9c**,**d** and **10c**.

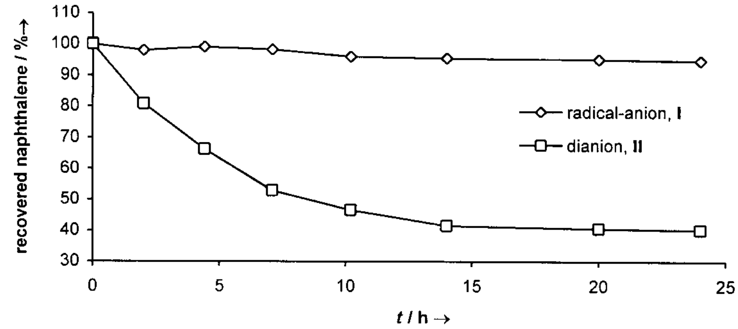


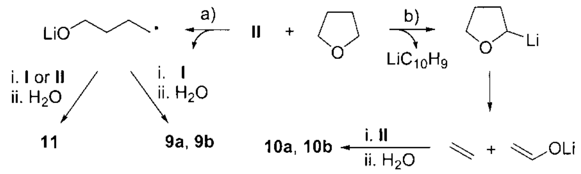
Figure 2. Plot of the reactions of lithium naphthalene (**I**, 0.5 M) and dilithium naphthalene (**II**, 0.5 M) with THF at 25 °C. The advance of the reaction was monitored as the decrease in the total amount of naphthalene + dihydronaphthalenes = "recovered naphthalene". For the reaction of **II**, a half-life of 2.8 h in the activity of the mixture was measured, whereas for **I**, the concentration of recovered naphthalene remained almost constant after 24 h.

The advantages of arene dianions versus arene radical anions in lithiation processes inevitably come from the higher reduction potential of the corresponding redox pairs. We expect that this will broaden the scope of current lithiating agents to include functional groups reducible only with difficulty. A number of studies implementing this suggestion are currently underway. In connection with these studies, a case that deserves special attention is the reaction of dilithium naphthalene (**II**) with unstrained cyclic ethers. In particular we have focused our attention on the reactions of tetrahydrofuran (THF) and tetrahydropyran (THP) with lithium naphthalene (**I**) and dilithium naphthalene (**II**). The first set of results is quite revealing (Scheme 3, Figure 2).

We quantitatively monitored the stability of the lithium naphthalene radical anion (**I**) and dianion (**II**) in THF at room temperature for 24 h by GLC. The advance of the reaction is represented in Figure 2 as the decrease in the overall concentration of naphthalene (**1**) and 1,2- and 1,4-dihydronaphthalenes (**3** and **2**) (these are the products that would be obtained by hydrolysis of **I** and **II**, provided that no reaction with the solvent has taken place, i.e., at time = 0).[43] Plots in Figure 2 display a significant difference in the rate of reaction of lithium naphthalene (**I**) and dilithium naphthalene (**II**) with THF at 25 °C. While a solution of $LiC_{10}H_8$ (**I**, 0.5 M) is fairly stable in THF at room temperature (>96 % **1**–**3** recovered after 24 h), the dilithium naphthalene solution (**II**, 0.5 M) slowly reacts with THF affording mixtures of 4-(1,4-dihydronaphthyl)-1-butanol (**9a**, 24 %), 4-(1,2-dihydronaphthyl)-1-butanol (**9b**, 11 %), 1-ethyl-1,4-dihydronaphthalene (**10a**, 4 %) and 1-ethyl-1,2-dihydronaphthalene (**10b**, 5 %), accompanied by small amounts of the corresponding aromatized products (**9c**, 9 %; **10c**, 2 %, which have arisen in the course of the reaction) and 8 % of *n*-butanol (**11**). The structures were elucidated by 500 MHz ^1H NMR on the basis of HMBC and NOESY experiments. HMBC turned out to be decisive in rejecting isomeric 2-substituted dihydronaphthalenes as major products. The plateau is reached when approximately 60 % of the starting dilithium naphthalene has given rise to coupled products **9** and **10** in its reaction with the solvent. An approximate half-life of 2.8 h is obtained by applying pseudo-first-order kinetics to this decay. The remaining 40 % of naphthalene-reduced products probably originated from accumulated dihydronaphthalenyllithium ($LiC_{10}H_9$), an apparently unreactive species towards THF under these experimental conditions. Again, addition of hydroquinone is critical in order to preserve intact the reaction crudes for further analysis and quantification, and to isolate the corresponding reaction products, which readily polymerize upon exposure to air.

Cleavage of THF mediated by lithium naphthalene has been the cause of some widespread misleading results found in the literature. Fujita and co-workers reported a photochemical reaction of naphthalene radical anion with THF at room temperature under a mercury arc lamp, which gave mixtures of **9a** (30%) and apparently **9e** [4-(1,2-dihydro-2-naphthyl)-1-butanol, 5%].[44] Thermal decomposition of lithium naphthalenide in THF at 65 °C was later reported by the same authors to afford mixtures of **9a** and **9e** (4% and 46% yield, respectively).[45] The relative amount of products seems to be reversed depending on the kind of activation used. Interestingly, while the authors refer to the reagent as "lithium naphthalenide" or "lithium naphthalene", these reagents were prepared from a 2:1 mixture of lithium and naphthalene in the thermal case. No mention of the stoichiometry of the reagents was made in the earlier communication.[44] Later in a full paper the experiment was described as using Li/naphthalene in a 2:1 molar ratio.[46] We have repeated the photochemical experiment using lithium naphthalene 1:1 (**I**, green) in THF in a thermostatted quartz cell at 25 °C under a 400 W high-pressure Hg lamp. After 8 h of irradiation, 97% of the original naphthalene was recovered as mixtures of naphthalene and dihydronaphthalenes (**1**–**3**). Increasing the temperature to 65 °C in two new experiments with **I**, neither the photochemical process nor the dark (thermal) one changed the composition of the crude mixture noticeably. Interestingly, the reaction we carried out at 65 °C in THF using dilithium naphthalene (**II**) afforded the regioisomers **9c** and **9d** in 71% and 7% yield, respectively, along with 6% **10c**. No mention of the ethylated products **10** was made in these papers. On the other hand, the formation of the ethylated products **10** has been described previously, where alcohols **9** were overlooked.[47]

The former set of reactions is an example of a process in which different reactivity is found for the dianion and radical anion of naphthalene. Among the isolated products, some can be explained by considering $Li_2C_{10}H_8$ (**II**) as a strong base capable of THF deprotonation followed by THF cleavage, incorporation of the ethylene released, and hydrolysis. This is the case for products **10a** and **10b**, this reactivity being reminiscent of THF cleavage promoted by alkyllithium reagents (α cleavage).[48] Other products are better viewed as the result of reductive cleavage of the solvent promoted by **II** and subsequent coupling with **I** followed by hydrolysis (**9a**, **9b**). On paper, nucleophilic substitution on THF would afford the same kind of products. Since little is known about the reactivity of the naphthalene dianion (**II**), we cannot rule out this (from intuition apparently) rather less likely reaction pathway, for now. Finally, 1-butanol (**11**) is satisfactorily accounted for as the result of an ET process (reductive cleavage followed by further reduction of the n-butoxy ω-radical thus formed and protonation). 3-Butenol (**12**, from β-cleavage of THF) was not detected in the reaction mixture. The occurrence of **11**, and probably **9a** and **9b**, is evidence of a unique high-energy reaction pathway for naphthalene dianion that is *not* accessible to naphthalene radical anion under identical reaction conditions (Scheme 4).

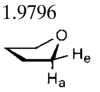
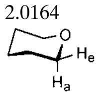


Scheme 4. Proposed mechanism for the cleavage of THF mediated by dilithium naphthalene (**II**) a) reacting as a ET reagent; b) reacting as a base.

Unlike THF, THP showed almost no signs of reaction after one day at room temperature in the presence of **II** (>94% of naphthalene, dihydronaphthalenes, and dihydronaphthalene dimers recovered after four days at room temperature; no traces of 1-pentanol were detected). As expected, **I** is also unreactive with THP. An explanation for the underlying differences in reactivity between THF and THP has to be sought on several fronts: firstly, in their action as the very reagents in the reaction, and secondly as the solvents in which the reaction takes place. Considered as reagents, the compounds only undergo reductive cleavage at a reasonable rate at room or higher temperatures, where the conformational equilibrium is open to more conformations. The THF framework has little preference for any particular conformation. Besides the half-chair conformation, which is less than 1.0 kcal mol^{-1} above the envelope, there are a number of additional conformations of nearly the same energy, the barriers being also very low (e.g. 1.3 kcal mol^{-1} between C_s and C_2, nearly free pseudorotation of 0.14 kcal mol^{-1}). Occupancy of these fairly accessible states should be significant at room or higher temperatures. Some of them are expected to be reactive. Instead, for THP, the chair is located in a deep energy well, reminiscent of the cyclohexane conformation. The chair is ≈5 kcal mol^{-1} below the next energy minimum, the energy barrier being more than 10 kcal mol^{-1}. It appears to us that the origins of the difference in reactivity should be sought in these differences in the conformational equilibria of the ethers themselves.[49]

Focusing on the absolute minimum conformations of these cyclic ethers alone, that is the THF envelope and the THP chair, we have calculated a number of parameters in connection to the ET and basic reaction pathways (Scheme 4, Table 3). The vertical electron affinity (VEA) is the energy difference between the radical anion and the neutral molecule at the fixed geometry of the neutral molecule. The adiabatic electron affinity (AEA) is the energy difference between the two in their most stable states. In the gas phase, the most stable state of the radical anion entails bond breaking and corresponds to the extended conformation of the alkoxy ω-radical ($^{-}$O-CH$_2$-CH$_2$-CH$_2$-CH$_2$$^{\bullet}$). By convention, negative

Table 3. Comparison of some physical and calculated properties of THF and THP.

Physical constants	THF	THP	Ref.
μ [D][a]	1.75	1.74	[50]
ε_s[b]	7.56	5.66	[51]
ε_{op}[c]	1.9796	2.0164	[52]
calcd minimum[d]			[e]
VEA[d, f]	– 96.1	– 97.3	[e]
AEA[d, g]	– 56.4	– 62.2	[e]
Mulliken charges on α-H	0.102 (H$_e$) 0.083 (H$_a$)	0.099 (H$_e$) 0.075 (H$_a$)	[e]

[a] Dipole moment in the gas phase from MW spectroscopy. [b] Static dielectric constant at 20 °C. [c] Optical dielectric constant at 20 °C, $\varepsilon_{op} = n^2$ (squared refractive index). [d] UB3LYP 6–31G(d, p), isolated molecule. [e] This work. [f] Vertical electron affinity [kcal mol^{-1}]. [g] Adiabatic electron affinity [kcal mol^{-1}].

EA indicates that the reaction $(CH_2)_nO + e^- \rightarrow [(CH_2)_nO]^{\bullet -}$ is endoergic. Little difference is found between the VEA values for the two ethers in their conformational minima (Table 3). We think that this would probably not be the case if other accessible conformations of the THF were to be considered. Such states are numerous and an exhaustive study is not being considered here. As expected, the AEA does show some difference in magnitude, $\approx 5.8\,\text{kcal}\,\text{mol}^{-1}$, which is consistent with the release of ring strain.[53] Alternatively, interaction of THF or THP with a base might result in deprotonation and subsequent α-cleavage (Scheme 4). Again, when only the envelope and the chair conformations are considered, the differences in the Mulliken charges on the α-hydrogens are negligible ($\approx +0.10$ for both H_e in THF and THP). Apparently the origins of the reactivity difference are more likely to be found in the differences in the type of conformational equilibrium rather than in the reactivity of the most representative conformation of THF and THP.

As solvents, THF and THP also have slightly different properties that may affect the ET rates of **I** and **II**. A rough approach to this complex problem can be made from the Marcus treatment of the outer-sphere ET reactions. According to this theory, the activation energy $\Delta G^{\neq}$ in an ET reaction depends quadratically on the standard free energy ΔG° and linearly on the reorganization energy, λ [Eq. (4)]. The reorganization energy λ can be divided into two contributions, the solvent-independent inner term, λ_{in}, which arises from structural differences between the equilibrium configuration of the reactant and product states (or bond contribution), and the outer term, λ_{out}, also called *solvent reorganization energy*, because it arises from differences between orientation and polarization of solvent molecules through the transition state (solvent contribution) [Eq. (5)]. Considering the surrounding solvent as a dielectric continuum and applying any suitable model for the reagents (e.g. the spherical reagent model) it can be demonstrated that the effect of the solvent can be approximated by a term depending on ε_{op} and ε_s, that is, the optical and static dielectric constants of the solvent, parameters depending on the solvent alone [Eq. (6)].[54] We find that $\lambda_{out}(\text{THF})/\lambda_{out}(\text{THP}) = 1.17$, slightly favoring the reaction in THP. The effect is quite small and other factors such as larger coordinating stabilization of the products by THF presumably prevails.[55]

$$\Delta G^{\neq} = \frac{(\lambda + \Delta G^{\circ})^2}{\lambda} \tag{4}$$

$$\lambda = \lambda_{in} + \lambda_{out} \tag{5}$$

$$\lambda_{out} \propto \left(\frac{1}{\varepsilon_{op}} - \frac{1}{\varepsilon_s}\right) \tag{6}$$

Application of Equation (4) would certainly be of the highest interest for the evaluation of ET reaction rates in our system. Unfortunately, obtaining accurate values for the driving force of the reaction is not trivial, particularly if we are dealing with irreversible steps. ΔG° is the difference in free energy between the successor complex (donor$^+\cdot$acceptor$^-$) and the precursor complex (donor$\cdot$acceptor) in an outer-sphere ET reaction. In other comparable reaction systems, such as the reaction of arene radical anions with alkyl halides, estimated ΔG° and λ values have been obtained from experimental electrochemical methods and other techniques. The irreversible nature of these reactions makes it a difficult task to obtain reliable thermodynamic data such as a standard reduction potential, E°. Our ET to alkyl ethers is in this sense comparable to the dissociative ET to alkyl halides, which presumably also passes through an irreversible ET bond-breaking concerted step.[56] An added difficulty that appears at this point is the lack of experimental electrochemical data on reduction potentials for alkyl ethers. This information is, however, available for alkyl halides, owing to their accessible reduction potentials in solution, from which a rough estimate of free energies can be made. Of somewhat limited reliability, calculations may emerge at this point as another resort to obtain a rough estimate of the thermodynamics of the process. From the adiabatic electron affinities of THF and THP (Table 3), in principle, it appears that the reaction will be faster for THF than for THP on thermodynamic grounds and straightforward (and nonrigorous) application of the Marcus equation [Eq. (4), Table 3],[57] reproducing at least qualitatively the experimental results.

Conclusion

A number of conclusions can be drawn from the present work. The original question as to whether dianions do or do not play an active part in the mechanism of the lithiation catalyzed by arenes for which organic chlorides are the natural substrates is now answered. Dilithium naphthalene arises as a formal lithiating agent in its reaction with organic chlorides, and presumably with other functional groups,[1, 58] displaying an outer-sphere ET reactivity profile in its interaction with these acceptors. Since it is endowed with a higher redox potential than its radical anion counterpart, its reactivity spectrum is broadened and so is the range of substrates suitable for lithiation. That is the case for the reaction of dilithium naphthalene with THF, which has been the source of apparent misinterpretation of results in the past and which has now been re-examined and unambiguously addressed. The study of the dianions of high-reduction-potential arenes is still a barely explored area, which will certainly afford significant fruits, not only in the synthetic field but also conceptually and mechanistically.

Experimental Section

General aspects: All reactions were carried out under an atmosphere of nitrogen in oven-dried glassware. THF was distilled from sodium/benzophenone. THP was distilled from Na/K. IR spectra were measured with a Nicolet Impact 400 D-FT spectrometer. NMR spectra were recorded with a Bruker AC-300 or a Bruker Avance-500 at room temperature and with TMS as the reference. LRMS and HRMS were measured with Shimadzu GC/HS QP-5000 and Finnigan MAT 95 S spectrometers, respectively. Gas-chromatographic analyses (GLC) were determined with a Hewlett–Packard HP-5890 instrument equipped with a flame ionization detector and a 12 m capillary column (0.2 mm diam, 0.33 µm film thickness), nitrogen ($2\,\text{mL}\,\text{min}^{-1}$) as carrier gas, $T_{injector} = 275\,^{\circ}\text{C}$, $T_{detector} = 300\,^{\circ}\text{C}$, $T_{column} = 80\,^{\circ}\text{C}$ (3 min) and $80-270\,^{\circ}\text{C}$ ($15\,^{\circ}\text{C}\,\text{min}^{-1}$), $p = 40$ kPa, as routine working conditions. Lithium naphthalene and dilithium naphthalene were prepared by standard methods of manipulation under Ar atmosphere from naphthalene and a stoichiometric amount or an excess of mechanically activated lithium powder at 0 °C. The lithium granules (Aldrich) were mechanically activated by milling under mineral oil in a rotary mill. Activated lithium in the form of thin powder was necessary to obtain solutions of **II** at 0 °C fast enough to ensure that decomposition of the solvent did not occur extensively and the kinetics studies could be carried out thereafter.

1,4-Dihydronaphthalene (2):[59] A mixture of naphthalene (38 g, 0.3 mol) and Na (28 g, 1.2 mol) was stirred for 2 h at 140–145 °C. After cooling down to 90–100 °C, benzene (100 mL) was added and reflux was maintained for three hours while ethanol (150 mL) was slowly added at the same temperature. Then benzene (150 mL) and ethanol (150 mL) were added and the resulting reaction crude was dropped into a stirred mixture of HCl (12 M, 130 mL) and ice (100 g). The organic phase was extracted with benzene (3×50 mL), washed with sat. $NaHCO_3$ (50 mL), and dried over Na_2SO_4, and the solvents were evaporated in vacuo. A solution of $Hg(AcO)_2$ (64 g, 200 mmol) in water (200 mL) and Et_2O (200 mL) was added to the resulting oil with stirring at room temperature. The mixture was allowed to stand for one day, and gave a mass of crystals. The crystals were filtered and dissolved in a mixture of HCl (12 N, 25 mL) and hexane (100 mL). The resulting solution was extracted with hexane (3×50 mL), the organic phase dried over Na_2SO_4, the solvents evaporated in vacuo, and the remaining oil distilled under vacuum (15 Torr). The portion that distilled at 120 °C consisted of pure 1,4-dihydronaphthalene (25.7 g, 66% yield). $R_f = 0.53$ (hexane); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 3.40$ (apparent d, $J = 1.2$ Hz, 4H, $2\times CH_2$), 5.93 (apparent t, $J = 1.5$ Hz, 2H, CH=CH), 7.05–7.20 (m, 4H, $4\times H_{arom}$); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 29.75$ ($2\times CH_2$), 124.75, 125.85 ($4\times CH_{arom}$), 128.4 (CH=CH), 134.2 ($2\times C_{arom}$); IR (film): $\tilde{\nu} = 3062, 3030, 1666, 1496, 1456, 745\ cm^{-1}$ (C=CH); MS (70 eV, EI): m/z (%): 132 (<1) $[M+2]^+$, 131 (11) $[M+2]^+$, 130 (100) $[M]^+$, 129 (99), 128 (61), 127 (28), 115 (53), 77 (12), 65 (10), 64 (41), 63 (26), 51 (34), 50 (15).

2-Chlorooctane:[60] PPh_3 (40 g, 150 mmol) was added to a solution of 2-octanol (16 mL, 100 mmol) in CCl_4 (200 mL), and the mixture was refluxed for 4 days. The resulting solution was filtered and the residue washed with hexane at 0 °C. The solvents were evaporated in vacuo and the residue was distilled (60 °C, 15 Torr) yielding pure 2-chlorooctane (12.5 g, 85%). $R_f = 0.92$ (hexane); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.89$ (t, $J = 6.7$ Hz, 3H, CH_3CH_2), 1.20–1.35 (m, 8H, $4\times CH_2$), 1.50 (d, $J = 6.7$ Hz, 3H, CH_3CHCl), 1.62–1.78 (m, 2H, CH_2CHCl), 4.03 (sextet, $J = 6.7$, 1H, CHCl); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.05$ (CH_3CH_2), 22.55, 26.6, 28.8, 31.7, 40.4 ($5\times CH_2$), 25.35 (CH_3CHCl), 58.95 (CHCl); IR (film): $\tilde{\nu} = 673\ cm^{-1}$ (CCl); MS (70 eV, EI): m/z (%): 113 (<1) $[M-Cl]^+$, 112 (5) $[M-HCl]^+$, 84 (21), 83 (39), 82 (11), 71 (11), 70 (61), 69 (32), 57 (30), 56 (59), 55 (73), 43 (84), 42 (57), 41 (100).

2-Chloro-2-methylheptane:[61] 2-Heptanone (14 mL, 100 mmol) in Et_2O (20 mL) was added to a solution of methylmagnesium bromide (85 mL of a 1.4 M toluene/THF (75/25) solution, 120 mmol) in Et_2O (70 mL), and the mixture was stirred for 1 h at 0 °C. The resulting mixture was hydrolyzed with water (40 mL), extracted with hexane (3×30 mL) and shaken with HCl (12 M, 100 mL) for 5 min. It was then extracted with hexane (3×30 mL), the organic phase was dried over $CaCl_2$, and the solvent was evaporated in vacuo. The resulting residue was purified by distillation at reduced pressure (50 °C, 15 Torr) to yield pure 2-chloro-2-methylheptane (13.3 g, 90%). $R_f = 0.70$ (hexane); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.90$ (t, $J = 6.7$ Hz, 3H, CH_3CH_2), 1.22–1.40 (m, 4H, $CH_3CH_2CH_2$), 1.41–1.52 (m, 2H, CH_2CH_2CCl), 1.57 (s, 6H, $(CH_3)_2CCl$), 1.69–1.79 (m, 2H, CH_2CCl); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.0$ (CH_3CH_2), 22.55, 24.8, 31.9 ($3\times CH_2$), 32.4 ($2\times CH_3C$), 46.05 (CH_2CCl), 71.35 (CCl); IR (film): $\tilde{\nu} = 630\ cm^{-1}$ (CCl); MS (70 eV, EI): m/z (%): 133 (<1) $[M-CH_3]^+$, 97 (10), 84 (16), 79 (10), 77 (32), 76 (18), 71 (20), 70 (19), 69 (40), 57 (62), 56 (100), 55 (62), 43 (64), 42 (14), 41 (94).

Trimethyloctylsilane (4):[62] 1-Chlorooctane (1.7 mL, 10 mmol) was added dropwise at −78 °C to a blue suspension of lithium powder (210 mg, 30 mmol) and 4,4′-di-*tert*-butylbiphenyl (DTBB, 270 mg, 1 mmol) in THF (10 mL) previously stirred for 15 min at room temperature. Once the solution recovered the blue color, trimethylchlorosilane (2 mL, 16 mmol) was added and the temperature was allowed to rise to room temperature. The resulting mixture was hydrolyzed with water (5 mL) and was extracted with hexane (3×20 mL). The organic phase was dried over Na_2SO_4, the solvents were evaporated in vacuo, and the remaining oil was distilled under reduced pressure (50 °C, 15 Torr) in a Kugelrohr, yielding pure trimethyloctylsilane (1.4 g, 75%). ^1H NMR (300 MHz, $CDCl_3$): $\delta = -0.03$ (s, 9H, $3\times SiCH_3$), 0.43–0.53 (m, 2H, CH_2Si), 0.88 (t, $J = 6.7$ Hz, 3H, CH_3CH_2), 1.20–1.40 (m, 12H, $6\times CH_2$); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = -1.65$ ($3\times SiCH_3$), 14.1 (CH_2Si), 16.7 (CH_3CH_2), 22.7, 23.9, 29.3, 29.35, 31.95, 33.65 ($6\times CH_2$); IR (film): $\tilde{\nu} = 1248, 836, 756\ cm^{-1}$ ($SiCH_3$); MS (70 eV, EI): m/z (%): 186 (<1) $[M]^+$, 171 (23), 74 (11), 73 (100), 59 (53), 45 (17), 43 (14), 41 (11).

2,2-Dimethyl-3-undecanol (5):[63] The procedure is identical to that described for **4**, except that pivalaldehyde (1.5 mL, 14 mmol) was used as electrophile. The reaction crude was extracted with Et_2O (3×20 mL) and the purification of the compound was carried out by column chromatography (silica gel, hexane/ethyl acetate) yielding pure 2,2-dimethyl-3-undecanol (1.3 g, 65% yield). $R_f = 0.56$ (hexane/ethyl acetate 8:2); ^1H NMR (300 MHz, $CDCl_3$): $\delta = 0.88$ (apparent t, $J = 6.7$ Hz, 3H, CH_3CH_2), 0.89 (s, 9H, $3\times CH_3C$), 1.28–1.30 (m, 12H, $6\times CH_2$), 1.45–1.60 (m, 2H, CH_2CHOH), 3.18 (dd, $J = 9.8$, 5.5 Hz, 1H, CHOH); ^{13}C NMR (75 MHz, $CDCl_3$): $\delta = 14.1$ (CH_3CH_2), 22.65 (CH_2), 25.7 ($3\times CH_3C$), 27.1, 29.3, 29.65, 29.75, 31.55, 31.9 ($6\times CH_2$), 34.95 (CH_3C), 80.0 (COH); IR (film): $\tilde{\nu} = 3383$ (OH), 1078 cm^{-1} (C–O); MS (70 eV, EI): m/z (%): 185 (<1) $[M-CH_3]^+$, 87 (16), 83 (41), 70 (10), 69 (100), 57 (61), 56 (15), 55 (48), 44 (10), 43 (37), 41 (61).

Competitive kinetics of species I, II, and IV: A suspension of lithium (**I**: 7.5 mg, of $LiC_{10}H_8$, ≈1 mmol; **II**: 70 mg, 10 mmol) and naphthalene (**I**: 192 mg, 1.5 mmol; **II**: 128 mg, 1 mmol) was prepared by stirring in THF (10 mL) at 0 °C for 1 h under an Ar atmosphere. For the preparation of **IV**, dry TMEDA (0.450 mL, 3 mmol; previously distilled over Na) was added to **II**. The resulting suspension was centrifuged at 0 °C and aliquots of 0.2 mL were added to a stirred solution containing a mixture of the two organic chlorides submitted to test (0.1 mmol each) and dodecane (8.25 mg, 0.05 mmol) as internal standard in THF (10 mL) at 0 °C. After every addition, when the color disappeared a sample was taken and hydrolyzed with 0.5 M phosphate buffer at 0 °C, extracted with pentane, and submitted to GLC analysis. Immediately, another aliquot of **I**–**IV** was added and the same procedure repeated until the reaction was completed (5–8 samples, <10 min overall reaction time). The concentration of the remaining organic chlorides was quantified for every sample against the internal standard and the calibration lines previously obtained for each reagent for that purpose.

Competitive kinetics using III; preparation of III: To a mixture of 1,4-dihydronaphthalene (**2**, 260 mg, 2.0 mmol) and dry TMEDA (0.75 mL, 5.0 mmol, previously distilled over Na) in dry hexane (10 mL, previously distilled over Na/K alloy), *n*BuLi (1.6 M in hexane, 3.1 mL, 5 mmol) was added and the mixture was allowed to stand for 12 h. The supernatant solvent was cannulated off and the purple crystals obtained were washed with dry hexane (2×5 mL) in the same way. The crystals were dissolved/suspended in dry benzene (10 mL; previously distilled over Na/K alloy,) and cooled down to 0 °C. Aliquots of **III** were used as described for **I**–**IV**.

Lithiation of 1-chlorooctane with I–IV and reaction with electrophiles: Solutions of **I**–**IV** were obtained as before, with the amount of the reagents increased appropriately to obtain a 0.4 M solution of **I**–**IV** (fourfold). The solutions were cooled down to −60 °C and a mixture of 1-chlorooctane (148 mg, 1.0 mmol in 1 mL THF), dodecane (170.3 mg, 1.0 mmol), and THF (1 mL) was added dropwise. After 20 min, an excess of trimethylchlorosilane (1.3 mL, 10 mmol) or pivalaldehyde (1.3 mL, 12 mmol) was added and the temperature was allowed to rise to room temperature overnight. The resulting crude mixture was hydrolyzed with 2 M phosphate buffer (5 mL) and the organic phase was analyzed by quantitative GLC using pure **4** and **5** and commercially available reagents.

Lithiation and hydrolysis of 1-chlorooctane, 2-chlorooctane, and 2-chloro-2-methylheptane with I and II; isolation/preparation of 6a–b and 8a–c: Solutions of **I** and **II** were obtained as before, with the amount of the reagents increased appropriately to obtain a 0.4 M solution (fourfold). The solutions were cooled down to −78 °C and the appropriate alkyl chlorides (1.0 mmol) and dodecane (170.3 mg, 1.0 mmol) dissolved in THF (1 mL) were added dropwise. After 30 min, the mixture was hydrolyzed with 2 M phosphate buffer (5 mL), hydroquinone (10 mg) was added, and the organic phase was analyzed by GLC. The reaction products **8a–c** were isolated by combining the crudes of a number of identical reactions (ca. 5), extracting with $\mathrm{Et_2O}$ (3 × 20 mL), drying over $\mathrm{Na_2SO_4}$, removing the solvents in vacuo and purifying the resulting residue by column chromatography (silica gel/10% $\mathrm{AgNO_3}$, hexane/diethyl ether). 10% of hydroquinone was added to the purified products. Pure **6a–b** was prepared from the reaction of **II** with 1-fluorooctane (yields: 47% for **6a** and 36% for **6b**) by the same purification techniques.

1-Octyl-1,4-dihydronaphthalene (6a): $R_f = 0.62$ (hexane); ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): $\delta = 0.86$ (t, $J = 6.4$ Hz, 3H, $\mathrm{CH_3}$), 1.10–1.48 (m, 12H, 6 × $\mathrm{CH_2}$), 1.58–1.79 (m, 2H, $\mathrm{CH_2}\mathit{CH_2}\mathrm{CH}$), 3.23–3.49 (m, 3H, $\mathit{CH_2}\mathrm{CH{=}CHC}\mathit{H}$), 5.87–6.0 (m, 2H, $\mathrm{C}\mathit{H}\mathrm{{=}C}\mathit{H}\mathrm{CH_2}$), 7.05–7.30 (m, 4H, 4 × $\mathrm{H_{arom}}$); ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$): $\delta = 14.1$ ($\mathrm{CH_3}$), 22.65, 26.0, 29.3, 29.55, 29.85, 30.0, 31.85 (7 × $\mathrm{CH_2}$), 38.2 ($\mathit{C}\mathrm{H_2CH{=}CH}$), 39.35 ($\mathrm{CH_2}\mathit{C}\mathrm{HCH{=}}$), 124.55, 125.5, 125.85, 127.9, 128.15, 129.8 (4 × $\mathrm{CH_{arom}}$, CH=CH), 134.6, 139.15 (2 × $\mathrm{C_{arom}}$); IR (film): $\tilde{\nu} = 3031, 781, 756, 747\ \mathrm{cm^{-1}}$ (C=CH); MS (70 eV, EI): m/z (%): 243 (<1) $[M+\mathrm{H}]^+$, 242 (2) $[M]^+$, 130 (11), 129 (100), 128 (31), 41 (10); HRMS: calcd for $\mathrm{C_{18}H_{26}}$ 242.2035; found 242.2034.

1-Octyl-1,2-dihydronaphthalene (6b): $R_f = 0.62$ (hexane); ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): $\delta = 0.87$ (t, $J = 6.7$ Hz, 3H, $\mathit{CH_3}\mathrm{CH_2}$), 1.15–1.40 (m, 12H, 6 × $\mathrm{CH_2}$), 1.50–1.60 (m, 2H, $\mathrm{CH_2}\mathit{CH_2}\mathrm{CH}$), 2.24 (apparent dt, $J = 17.4$, 4.6 Hz, 1H, $\mathrm{C{=}CHC}\mathit{H}\mathrm{H}$), 2.50 (apparent ddt, $J = 17.4$, 7.0, 3.1 Hz, 1H, $\mathrm{C{=}CHCH}\mathit{H}$), 2.65–2.76 (m, 1H, $\mathrm{CH_2C}\mathit{H}\mathrm{CH_2}$), 5.86–5.95 (m, 1H, $\mathrm{CH{=}C}\mathit{H}\mathrm{CH_2}$), 6.42 (apparent dd, $J = 9.2$ Hz, 2.4 Hz, 1H, $\mathrm{C}\mathit{H}\mathrm{{=}CHCH_2}$), 6.98–7.18 (m, 4H, 4 × $\mathrm{H_{arom}}$); ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$): $\delta = 14.1$ ($\mathrm{CH_3}$), 22.65, 27.4, 28.4, 29.6, 29.75, 29.85, 31.85 (7 × $\mathrm{CH_2}$), 34.1 ($\mathrm{CH_2}\mathit{C}\mathrm{HCH_2}$), 37.05 ($\mathit{C}\mathrm{H_2CH{=}CH}$), 126.15, 126.3, 126.75, 126.9, 127.3, 127.4 (4 × $\mathrm{CH_{arom}}$, CH=CH), 133.3, 139.7 (2 × $\mathrm{C_{arom}}$); IR (film): $\tilde{\nu} = 3032, 3015, 783, 756, 745\ \mathrm{cm^{-1}}$(C=CH); MS (70 eV, EI): m/z (%): 244 (<1) $[M+2\mathrm{H}]^+$, 243 (2) $[M+\mathrm{H}]^+$, 242 (11) $[M]^+$, 130 (23), 129 (100), 128 (46), 127(11), 41 (13); HRMS: calcd for $\mathrm{C_{18}H_{26}}$ 242.2035; found 242.2039.

1-(1,1-Dimethylhexyl)-1,4-dihydronaphthalene (8a): $R_f = 0.70$ (hexane); ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): $\delta = 0.76$, 0.85 (2s, 6H, 2 × $\mathit{CH_3}\mathrm{CH}$), 0.90 (apparent t, $J = 6.7$ Hz, 3H, $\mathit{CH_3}\mathrm{CH_2}$), 1.12–1.39 (m, 8H, 4 × $\mathrm{CH_2}$), 3.15–3.42 [m, 3H, $\mathit{CH_2}\mathrm{CH{=}C}$, $\mathrm{C(CH_3)_2C}\mathit{H}$], 5.98–6.15 (m, 2H, $\mathrm{C}\mathit{H}\mathrm{{=}C}\mathit{H}\mathrm{CH_2}$), 7.08–7.20 (m, 4H, 4 × $\mathrm{H_{arom}}$); ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$): $\delta = 14.15$ ($\mathit{C}\mathrm{H_3CH_2}$), 22.8, 25.15, 31.6 (3 × $\mathrm{CH_2}$), 23.7, 24.2 (2 × $\mathrm{CH_3}$), 32.9 ($\mathrm{CH_2}\mathit{C}\mathrm{H{=}C}$), 39.95 ($\mathrm{CH_2C{=}C}$), 41.45 ($\mathrm{CH_3}\mathit{C}$), 49.05 ($\mathit{C}\mathrm{HCH{=}C}$), 124.7, 125.45, 126.7, 127.9, 129.4, 130.1 (4 × $\mathrm{CH_{arom}}$, CH=CH), 137.15, 137.25 (2 × $\mathrm{C_{arom}}$); IR (film): $\tilde{\nu} = 3032, 1381, 1362, 746\ \mathrm{cm^{-1}}$ [$\mathrm{C(CH)_3}$, C=CH); MS (70 eV, EI): m/z (%): 242 (<1) $[M]^+$, 130 (56), 129 (100), 128 (91), 127 (14), 71 (44), 57 (59), 43 (55), 41 (40); HRMS: calcd for $\mathrm{C_{18}H_{26}}$ 242.2035; found 242.2079.

1-(1,1-Dimethylhexyl)-1,2-dihydronaphthalene (8b): $R_f = 0.70$ (hexane); ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): $\delta = 0.80$ (s, 6H, 2 × $\mathrm{CH_3}$), 0.89 (t, $J = 7$ Hz, 3H, $\mathit{CH_3}\mathrm{CH_2}$), 1.16–1.40 (m, 8H, 4 × $\mathrm{CH_2}$), 2.42–2.64 [m, 3H, $\mathit{CH_2}\mathrm{CH{=}C}$, $\mathrm{CHC(CH_3)_2}$], 5.86–5.97 (m, 1H, $\mathrm{CH{=}C}\mathit{H}\mathrm{CH_2}$), 6.34 (apparent dd, $J = 9.8$, 3.05 Hz, 1H, $\mathrm{C}\mathit{H}\mathrm{{=}CHCH_2}$), 6.95–7.21 (m, 4H, 4 × $\mathrm{H_{arom}}$); ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$): $\delta = 14.15$ ($\mathit{C}\mathrm{H_3CH_2}$), 22.75, 25.9, 32.9 (3 × $\mathrm{CH_2}$), 23.75 ($\mathrm{CH_2}\mathit{C}\mathrm{H{=}C}$), 24.7, 25.55 (2 × $\mathrm{CH_3}$), 38.15 ($\mathit{C}\mathrm{CH_3}$), 40.45 ($\mathit{C}\mathrm{H_2C}$), 44.05 [$\mathit{C}\mathrm{HC(CH_3)_2}$], 125.6, 125.7, 126.45, 127.8, 128.4, 130.95 (4 × $\mathrm{CH_{arom}}$, CH=CH), 135.3, 135.55 (2 × $\mathrm{C_{arom}}$); IR (film): $\tilde{\nu} = 3049, 3017, 1755, 1723, 1467, 1386, 1366, 746\ \mathrm{cm^{-1}}$ [$\mathrm{C(CH)_3}$, C=CH]; MS (70 eV, EI): m/z (%): 243 (<1) $[M+\mathrm{H}]^+$, 242 (1) $[M]^+$, 130 (52), 129 (100), 128 (69), 127 (12), 71 (31), 57 (54), 43 (43), 41 (30); HRMS: calcd for $\mathrm{C_{18}H_{26}}$ 242.2035; found 242.2036.

2-(1,1-Dimethylhexyl)naphthalene (8c): $R_f = 0.67$ (hexane); ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): $\delta = 0.80$ (t, $J = 6.7$ Hz, 3H, $\mathit{CH_3}\mathrm{CH_2}$), 0.99–1.28 (m, 6H, 3 × $\mathrm{CH_2}$), 1.39 (s, 6H, 2 × $\mathrm{CH_3}$), 1.68 (apparent t, $J = 8.2$ Hz, 2H, $\mathrm{CH_2C(CH_3)_2}$), 7.38–7.88 (m, 7H, 7 × $\mathrm{H_{arom}}$); ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$): $\delta = 14.05$ ($\mathit{C}\mathrm{H_3CH_2}$), 22.55, 24.45 (2 × $\mathrm{CH_2}$), 29.0 (2 × $\mathrm{CH_3}$), 32.55 ($\mathrm{CH_2}$), 37.85 ($\mathit{C}\mathrm{CH_3}$), 44.3 ($\mathrm{C}\mathit{C}\mathrm{H_2}$), 123.85, 125, 125.15, 125.7, 127.3, 127.45, 127.9 (7 × $\mathrm{CH_{arom}}$), 131.55, 133.35, 147.2 (3 × $\mathrm{C_{arom}}$); IR (film): $\tilde{\nu} = 3056, 1383, 1372, 745\ \mathrm{cm^{-1}}$ ($\mathrm{C(CH)_3}$, C=CH); MS (70 eV, EI): m/z (%): 242 (<1) $[M+2\mathrm{H}]^+$, 241 (2) $[M+\mathrm{H}]^+$, 240 (11) $[M]^+$, 170 (14), 169 (100), 141 (24), 41 (18); HRMS: calcd for $\mathrm{C_{18}H_{24}}$ 240.1878; found 240.1879.

Reaction of I and II with THF under thermal conditions; isolation/preparation of products 9a–d and 10a–c: A suspension of lithium (**I**: 70 mg, 10 mmol; **II**: 165 mg, 23.5 mmol), naphthalene (**I**: 1.408 g, 11 mmol; **II**: 1.28 g, 10 mmol) and decane (0.030 mL) in THF (20 mL) was stirred for 24 h at room temperature or heated under reflux (65 °C) for 8 h under an Ar atmosphere. Eight duplicated samples were taken during this time and were submitted to GLC analysis after hydrolysis; every sample was hydrolyzed by the same procedure as for the reaction crude. The reaction crude was hydrolyzed with 2 M phosphate buffer (10 mL) at 0 °C, 100 mg of hydroquinone was added, and was extracted with $\mathrm{Et_2O}$ (3 × 20 mL). The organic phase was dried over $\mathrm{Na_2SO_4}$ and the solvents were removed in vacuo. Quantitative GLC and NMR analysis of the reaction crudes revealed that only **II** afforded significant amounts of **9a–d** and **10a–c**. The resulting crude was purified by flash chromatography (silica gel, hexane/AcOEt) affording **9a,b** from the reaction at room temperature (10% of hydroquinone was added to the purified products), and **9c,d** from the reaction at reflux. Pure **10a,b** was prepared by bubbling ethylene overnight into a 0.5 M THP solution of **II** (yields: 26% of **10a** and 28% of **10b**), **10c** being commercially available. Hydrolysis with 2 M phosphate buffer, drying over $\mathrm{Na_2SO_4}$, evaporation of solvents in vacuo, and addition of a 10% of hydroquinone before and after chromatographic purification (flash silica gel, hexane) gave **10a,b** as mixtures of regioisomers, which was found to be identical to that obtained from the reaction with THF. The dihydronaphthalene derivatives **10a,b** were also aromatized to **10c** with DDQ under $\mathrm{CCl_4}$ reflux.

4-[1-(1,4-Dihydronaphthyl)]-1-butanol (9a):[64] $R_f = 0.76$ (AcOEt); ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): $\delta = 1.18$–1.76 (m, 6H, 3 × $\mathrm{CH_2}$), 3.30–3.41 (m, 3H, $\mathit{CH_2}\mathrm{CH{=}C}$, $\mathrm{C}\mathit{H}\mathrm{CH{=}C}$), 3.60 (apparent t, $J = 7$ Hz, 2H, $\mathit{CH_2}\mathrm{OH}$), 5.87–6.02 (m, 2H, CH=CH), 7.06–7.22 (m, 4H, 4 × $\mathrm{H_{arom}}$); ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$): $\delta = 22.05$, 30.0, 33.0, 33.85, 37.85 (5 × $\mathrm{CH_2}$), 39.25 ($\mathit{C}\mathrm{HCH_2}$), 62.95 ($\mathit{C}\mathrm{H_2OH}$), 124.90, 125.65, 125.95, 127.85, 128.20, 129.45 (4 × $\mathrm{CH_{arom}}$, CH=CH), 134.65, 138.70 (2 × $\mathrm{C_{arom}}$); HRMS: calcd for $\mathrm{C_{14}H_{18}O}$ 202.1358; found 202.1368.

4-[1-(1,2-Dihydronaphthyl)]-1-butanol (9b):[64] $R_f = 0.76$ (AcOEt); ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): $\delta = 1.15$–1.70 (m, 6H, 3 × $\mathrm{CH_2}$), 2.24 (apparent dt, $J = 17.1$, 4.9 Hz, 1H, $\mathrm{C}\mathit{H}\mathrm{HCH{=}C}$), 2.52 (apparent ddt, $J = 17.7$, 6.7, 3.1 Hz, 1H, $\mathrm{CH}\mathit{H}\mathrm{CH{=}C}$), 2.66–2.78 (m, 1H, $\mathrm{CH_2C}\mathit{H}\mathrm{CH_2}$), 3.59 (apparent t, $J = 6.1$ Hz, 2H, $\mathrm{C}\mathit{H_2}\mathrm{OH}$), 5.85–5.97 (m, 1H, $\mathrm{CH{=}C}\mathit{H}\mathrm{CH_2}$), 6.42 (apparent dd, $J = 9.2$, 2.4 Hz, 1H, $\mathrm{C}\mathit{H}\mathrm{{=}CHCH_2}$), 6.90–7.20 (m, 4H, 4 × $\mathrm{H_{arom}}$); ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$): $\delta = 23.50$, 28.40 (2 × $\mathrm{CH_2}$), 32.80 ($\mathrm{CH_2}\mathit{C}\mathrm{HCH_2}$), 33.85 ($\mathrm{CH_2}$), 37.0 ($\mathit{C}\mathrm{H_2CH{=}C}$), 62.81 ($\mathit{C}\mathrm{H_2OH}$), 126.15, 126.35, 126.40, 126.75, 127.3, 127.40 (4 × $\mathrm{CH_{arom}}$, CH=CH), 133.20, 139.25 (2 × $\mathrm{C_{arom}}$); HRMS: calcd for $\mathrm{C_{14}H_{18}O}$ 202.1358; found 202.1340.

4-(1-Naphthyl)-1-butanol (9c):[64] $R_f = 0.75$ (AcOEt); ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): $\delta = 1.63$–1.95 (m, 4H, 2 × $\mathrm{CH_2}$), 3.11 (t, $J = 7.3$ Hz, 2H, $\mathrm{CH_2C}$), 3.7 (apparent t, $J = 6.4$ Hz, 2H, $\mathit{CH_2}\mathrm{OH}$), 7.34–7.53 (m, 4H, 4 × $\mathrm{H_{arom}}$), 7.71 (apparent d, $J = 7.3$ Hz, 1H, $\mathrm{H_{arom}}$), 7.85 (apparent d, $J = 7.2$ Hz, 1H, $\mathrm{H_{arom}}$), 8.04 (apparent d, $J = 8.5$ Hz, 1H, $\mathrm{H_{arom}}$); ^{13}C NMR (75 MHz, $\mathrm{CDCl_3}$): $\delta = 26.85$, 32.65, 32.70 (3 × $\mathrm{CH_2}$), 62.70 ($\mathrm{CH_2OH}$), 123.75, 125.35, 125.45, 125.65, 125.90, 126.55, 128.7 (7 × $\mathrm{CH_{arom}}$), 131.80, 133.85, 138.35 (3 × $\mathrm{C_{arom}}$); IR (film): $\tilde{\nu} = 3343$ (OH), 3044, 1596, 777 (C=CH), 1058, 1030 $\mathrm{cm^{-1}}$ (CO); MS (70 eV, EI): m/z (%): 202 (<1) $[M+2\mathrm{H}]^+$, 201 (4) $[M+\mathrm{H}]^+$, 200 (27) $[M]^+$, 154 (22), 153 (12), 142 (16), 141 (100), 115 (28); HRMS: calcd for $\mathrm{C_{14}H_{16}O}$ 200.1201; found 200.1190.

4-(2-Naphthyl)-1-butanol (9d):[65] $R_f = 0.75$ (AcOEt); ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): $\delta = 1.61$–1.95 (m, 4H, 2 × $\mathrm{CH_2}$), 2.81 (t, $J = 7.3$ Hz, 2H, $\mathrm{CH_2C}$), 3.68 (apparent t, $J = 6.1$ Hz, 2H, $\mathit{CH_2}\mathrm{OH}$), 7.30–7.90 (m, 7H, 7 × $\mathrm{H_{arom}}$).

1-Ethyl-1,4-dihydronaphthalene (10a):[66] $R_f = 0.72$ (hexane); ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): $\delta = 0.81$ (t, $J = 7.3$ Hz, 3H, $\mathit{CH_3}\mathrm{CH_2}$), 1.60–1.80 (m, 2H, $\mathrm{CH_3}\mathit{CH_2}$), 3.29–3.48 (m, 3H, $\mathit{CH_2}\mathrm{CH{=}C}$, $\mathrm{C}\mathit{H}\mathrm{CH{=}C}$), 5.80–6.07 (m, 2H, CH=CH), 6.80–7.30 (m, 4H, 4 × $\mathrm{H_{arom}}$); MS (70 eV, EI): m/z (%): 159 (2) $[M+\mathrm{H}]^+$, 158 (13) $[M]^+$, 130 (12), 129 (100), 128 (56), 127 (19), 51 (12).

1-Ethyl-1,2-dihydronaphthalene (10b):[67] $R_f = 0.72$ (hexane); ^{1}H NMR (300 MHz, $\mathrm{CDCl_3}$): $\delta = 0.88$ (t, $J = 7.3$ Hz, 3H,$\mathit{CH_3}\mathrm{CH_2}$), 1.60–1.80 (m, 2H, $\mathrm{CH_3}\mathit{CH_2}$), 2.25 (apparent dt, $J = 17.1$, 4.6 Hz, 1H, $\mathrm{CH}\mathit{H}\mathrm{CH{=}C}$), 2.51 (apparent ddt, $J = 17.1$, 6.7, 3.1 Hz, 1H, $\mathrm{C}\mathit{H}\mathrm{HCH{=}C}$), 2.58–2.68 (m, 1H, $\mathrm{CH_2C}\mathit{H}\mathrm{CH_2}$), 5.80–6.07 (m, 1H, $\mathrm{CH{=}C}\mathit{H}\mathrm{CH_2}$), 6.42 (apparent dd, $J = 9.8$, 2.0 Hz, 1H, $\mathrm{C}\mathit{H}\mathrm{{=}CHCH_2}$), 6.80–7.30 (m, 4H, 4 × $\mathrm{H_{arom}}$); MS (70 eV, EI): m/z (%): 160 (<1) $[M+2\mathrm{H}]^+$, 159 (2) $[M+\mathrm{H}]^+$, 158 (19) $[M]^+$, 130 (12), 129 (100), 128 (55), 127 (19), 51 (12).

Reaction of I and II with THF under photochemical conditions: Suspensions of **I** and **II** were prepared as before (thermal reaction), and were placed in a quartz photochemical reactor thermostatted at 25 °C under Ar atmosphere. They were irradiated for 8 h with a 400 W high-pressure Hg lamp. The crudes were analyzed as before (thermal case) by comparison with pure isolated compounds.

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