

The *tert*-butyl chloride–lithium naphthalene radical anion and *tert*-butyllithium–naphthalene systems. Mechanism of metallation¹

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Abstract

A mechanism of lithiation of aromatics has been inferred from a comparative study of the systems *tert*-butyl chloride–lithium naphthalene radical anion and *tert*-butyllithium–naphthalene. Both systems give *tert*-butyldihydronaphthyllithiums, naphthyllithiums and *tert*-butylnaphthalenes. Although *tert*-butyllithium is a reaction product in the former system, it has been shown not to be involved in the formation of the products. In the system *tert*-butyllithium–naphthalene the distribution of products is markedly dependent upon the strength of the catalyzing Lewis base. Weak Lewis bases favor formation of *tert*-butylnaphthalene (mainly the 2-isomer) as well as *tert*-butyldihydronaphthyllithiums, whereas strong Lewis bases favor metallation. Mechanisms are proposed which postulate the involvement of a *tert*-butyl radical–naphthalene donor–acceptor complex in the fundamental elementary reaction. © 1997 Elsevier Science S.A.

Keywords: Lithium; Radical anions; Naphthalene; Mechanism

1. Introduction

Reactions between organic molecules containing carbon-to-heteroatom bonds and alkali metal aromatic hydrocarbon radical anions may lead to the formation of carbanionic products. As such, these reactions are of pertinence to main group organometallic chemistry. Indeed, Grignard reagents have been generated by reacting sodium naphthalene radical anion and alkyl iodides in tetrahydrofuran (THF) containing magnesium bromide [1]. Organolithium reagents have been prepared from lithium naphthalene radical anion and simple alkyl halides [2], functionally substituted alkyl halides [3] or chlorobenzenes [4], as well as by reacting alkyl phenyl ethers [5] and thioethers [6] with lithium naphthalene, or 1-dimethylaminonaphthalene, radical anion. In the above-mentioned reaction the alkali metal aromatic hydrocarbon radical anions function as homogeneous sources of alkali metals [7,8], i.e. as ‘solutions’ of alkali

metals in THF, which is the solvent of choice for preparing radical anions. Important advantages in using these ‘solutions’ over their heterogeneous counterparts are: (a) the very short reaction times, (b) their ease of handling as standard solutions, and (c) their paramagnetic nature which permits measurements of equilibria and kinetics (for recent applications of the method see Ref. [9]). Of course, there are also serious disadvantages. Alkylolithiums or alkyl derivatives of heavier alkali metals are unstable in tetrahydrofuran [10], and for their preparation one has either to employ low temperatures and immediately derivatize the alkyl alkali reagent or generate them in the presence of magnesium 2-ethoxyethoxide [11], with which they form a complex exhibiting normal organometallic activity but with a markedly reduced tendency to cleave THF. Another serious limitation is that *sec*- and *tert*-alkyl halides and the corresponding phenylsulfides react in a complicated manner with alkali metal aromatic hydrocarbon radical anions, giving rise to alkyldihydroarene carbanions as well as the desired alkyl alkali metal [12]. This problem seems to have been satisfactorily resolved by employing lithium di-*tert*-butylnaphthalenes or 4,4'-di-*tert*-butyl biphenyl radical anions [7]. Particularly clean reactions were obtained with lithium 4,4'-di-*tert*-butylbiphenyl

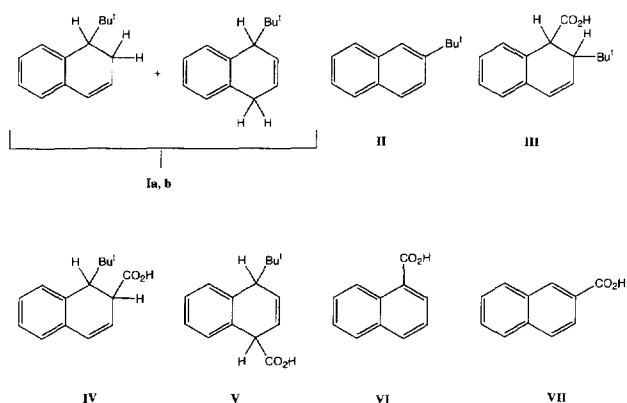
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¹ Dedicated to the memory of Professor Yu.T. Struchkov in recognition of his outstanding contributions to structural organometallic chemistry.

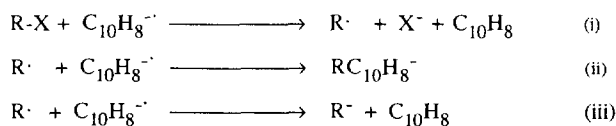
(LiDBB) [7], leading almost exclusively to pure organolithium product.

According to the proposed mechanism shown in Scheme 1 for the reaction between naphthalene radical anion and an alkyl halide [13], the formation of the alkylation product is presumed to arise from combination of an alkyl radical with naphthalene radical anion, step (ii). The overall reaction has the stoichiometry 2:1 for $(C_{10}H_8)^{\cdot-}/RX$, as has been shown by titration [14] in analogous reactions.

There is very little information concerning the structure of the carbanion $RC_{10}H_8^-$ in the literature [13]. However, one would expect on the basis of simple arguments that, of the two possible structures **1** and **2**, the most probable one should be **1**, because it appears to be stabilized by a combination of allylic as well as benzylic type resonances. Thus one would tend to depict the monoalkylated products as **3** and **4**, resulting from protonation of **1**, rather than as **5** which would result from the protonation of **2** [13]. Scheme 1 requires that naphthalene radical anion reacts with an alkyl halide partly by an electron transfer and partly by a radical combination mechanism. This is in contrast to the behavior of lithium 4,4'-di-*tert*-butylbiphenyl radical anion, which even with *tert*-alkyl halides reacts exclusively by an electron transfer mechanism, judging from the almost quantitative yields of *tert*-alkyllithium products [7]. An explanation [7] for this contrasting behavior based on stereochemical considerations is being challenged in this work.



One of the possible origins of the alkyldihydro-naphthyl carbanions in the reaction between naphtha-



Scheme 1.

lene radical anions and alkyl halides could be addition of the alkyllithium product to naphthalene and, therefore, we decided to make a comparative study of the reactions ${}^tBuX + (C_{10}H_8)^{\cdot-}Li^+$ and ${}^tBuLi + C_{10}H_8$. The two systems are closely analogous. Namely, they both may lead to *tert*-butyl-dihydronaphthyllithiums. Specifically we sought answers to the following questions.

(a) Why does lithium naphthalene radical anion react with primary alkyl halides or sulfides to give almost exclusively the organolithium product, whereas with *tert*-alkyl halides or sulfides mainly *tert*-alkyl-dihydronaphthyllithiums are produced?

(b) Why do lithium 4,4'-di-*tert*-butyl-biphenyl radical anion and *n*-butyl chloride or *tert*-butyl chloride give, respectively, *n*-butyllithium or *tert*-butyllithium as the sole product, whereas a radical anion of an aromatic hydrocarbon of great electron affinity, such as lithium anthracene radical anion, gives exclusively *n*- (or *tert*-) butyl-dihydroanthracenyllithium?

(c) Why do *n*-butyllithium and naphthalene lead to naphthyllithiums, whereas the same organolithium reagent and anthracene give almost exclusively 9-lithio-10-*n*-butyl-9,10-dihydroanthracene?

We selected to work with lithium rather than with sodium in anticipation that the alkyllithium products would be considerably more stable than the corresponding organosodiums, thus keeping to a minimum the possibility of alkylation from side or secondary reactions. It should be mentioned that a study of naphthalene alkylation by *tert*-butyllithium has been reported [15] at temperatures above 70 °C and in a hydrocarbon medium, i.e. under conditions markedly different from those which must be used in the reaction between an alkyl halide and any alkali metal aromatic hydrocarbon radical anion. Of pertinence to the present study is a report concerning the metallation of naphthalene [16]. It could be of interest also to mention a study of pyridine alkylation by both preformed unsolvated *n*-butylmagnesium iodide and by magnesium or lithium and *n*-butyl halides, in which an in situ generated pyridine radical anion could be involved [17].

2. Results and discussion

2.1. *tert*-Butyl chloride and lithium naphthalene radical anion

We began with the determination of the stoichiometry of the reaction between lithium naphthalene radical anion and *tert*-butyl chloride. Fig. 1, which is a magnetic titration plot, exhibits a sharp break at a ratio [*tert*-butyl chloride]/[lithium naphthalene radical anion] of 0.5, i.e. the stoichiometry is 1:2. When *tert*-butyl chloride was reacted with two equivalents of lithium

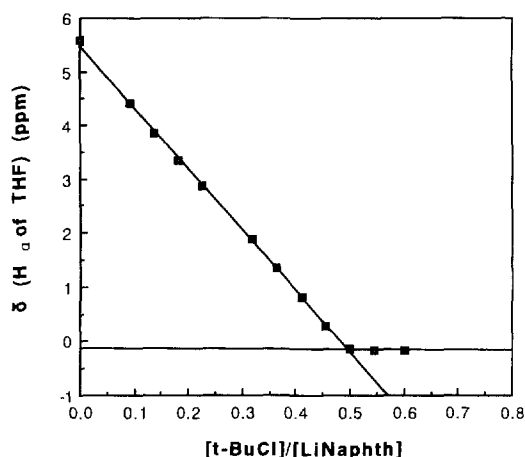


Fig. 1. Magnetic titration of lithium naphthalene against *tert*-butyl chloride.

naphthalene radical anion in THF and at temperatures of -50°C or lower, a brownish solution was produced. Carboxylation of this solution immediately after completion of the reaction afforded a mixture of pivalic acid (25%) and three isomeric *tert*-butyldihydronaphthoic acids containing detectable amounts of 1- and 2-naphthoic acids (45%). The total yield based on $^1\text{BuCl}$ was 70%. In the neutral fraction of the carboxylation mixture the presence of 2-*tert*-butylnaphthalene was established by gas chromatography and NMR spectroscopy. In another experiment *tert*-butyl chloride was reacted with two equivalents of lithium naphthalene radical anion at ca. -70°C . The reaction mixture was then stirred at $26 \pm 2^{\circ}\text{C}$ for 6.5 h and subsequently carboxylated. The neutral fraction from the carboxylation mixture was a 3.72:1.0 mixture of naphthalene and 2-*tert*-butylnaphthalene, the latter having been formed in 27% yield. The acidic fraction from the carboxylation mixture was mainly 1-*tert*-butyl-1,2-dihydro-2-naphthoic and 4-*tert*-butyl-1,4-dihydro-1-naphthoic acid (50% yield); total yield 77%. Replacing the THF solvent from a low temperature reaction by dry decalin and subsequent pyrolysis at $160\text{--}170^{\circ}\text{C}$ gave a mixture of 1-*tert*-butylnaphthalene and 2-*tert*-butylnaphthalene in a 1:1.2 ratio. Hydrolysis immediately after completion of the reaction mixture of a low temperature run and analysis of the hydrocarbons by gas chromatography indicated, besides naphthalene, a mixture of 1-*tert*-butyl-1,4-dihydronaphthalene and 1-*tert*-butyl-1,2-dihydronaphthalene (18%), 2-*tert*-1,2-dihydrobutylnaphthalene (27.8%), 1-*tert*-butylnaphthalene, (0.25%) and 2-*tert*-butylnaphthalene (0.56%). From these numbers, a ratio of 1.0:1.55 can be calculated for alkylation of naphthalene in the 1- and 2-positions respectively. The presence of 2-*tert*-butylnaphthalene in the carboxylation as well as in the hydrolysis mixture suggested that the precursor of this hydrocarbon was thermally unstable with respect to aromatization, obviously by loss of lithium hydride. It

appeared reasonable to expect that the structure of the precursor of 2-*tert*-butylnaphthalene was **2**, with the components of lithium hydride on adjacent carbon atoms. In order then to confirm the instability of **2** and to facilitate the identification of the two gas chromatographic peaks, we made a rough kinetic study. The mixture from a low temperature reaction was thermostated at $26 \pm 2^{\circ}\text{C}$ and aliquots were withdrawn at time intervals of ca. 0.5 h and, after hydrolysis, subjected to gas chromatographic analysis. In this way we followed the increase of the 2-*tert*-butylnaphthalene peak relative to the sum of the two peaks corresponding to the *tert*-butyldihydronaphthalene derivatives. In Fig. 2, the ratio 2-*tert*-butylnaphthalene over the sum of the two peaks corresponding to the two isomeric dihydronaphthalene derivatives is plotted against time. It was noted that the increase of the 2-*tert*-butylnaphthalene peak is accompanied by a corresponding decrease of the peak of the 2-*tert*-butyldihydronaphthalene, i.e. the component with the longer retention time, which was the main reaction product. We therefore assigned structure **2** to the main reaction product and structure **1** to the minor product. The sum of the 2-*tert*-butylnaphthalene plus the dihydro derivative **5** corresponding to its precursor was in a 1.3:1.0 ratio with the dihydro derivative corresponding to **1**. It could be of interest to notice in Fig. 2 that (a) the precursor of 2-*tert*-butylnaphthalene decays according to zero-order kinetics and (b) the same precursor had decayed completely after about 3 h at $26 \pm 2^{\circ}\text{C}$. In order to have some additional confirmation of the relative isomer distribution in the alkylation products, the mixture of hydrocarbons formed on hydrolysis of the mixture of a low temperature reaction was subjected to aromatization with Pd/C to give a mixture of 1-*tert*-butyl-naphthalene and 2-*tert*-butyl-naphthalene in a ratio of 1:1.3, which agrees with the ratio estimated from the gas chromatographic analysis of the mixture of

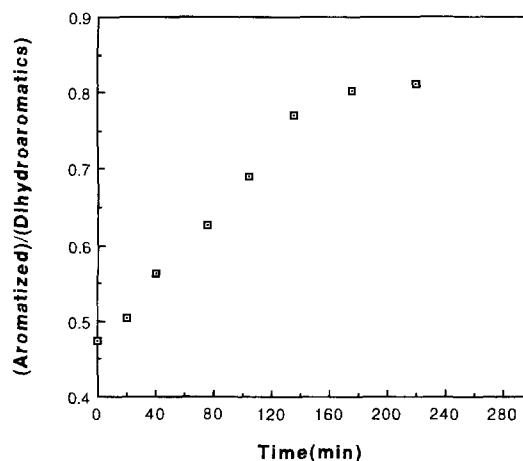


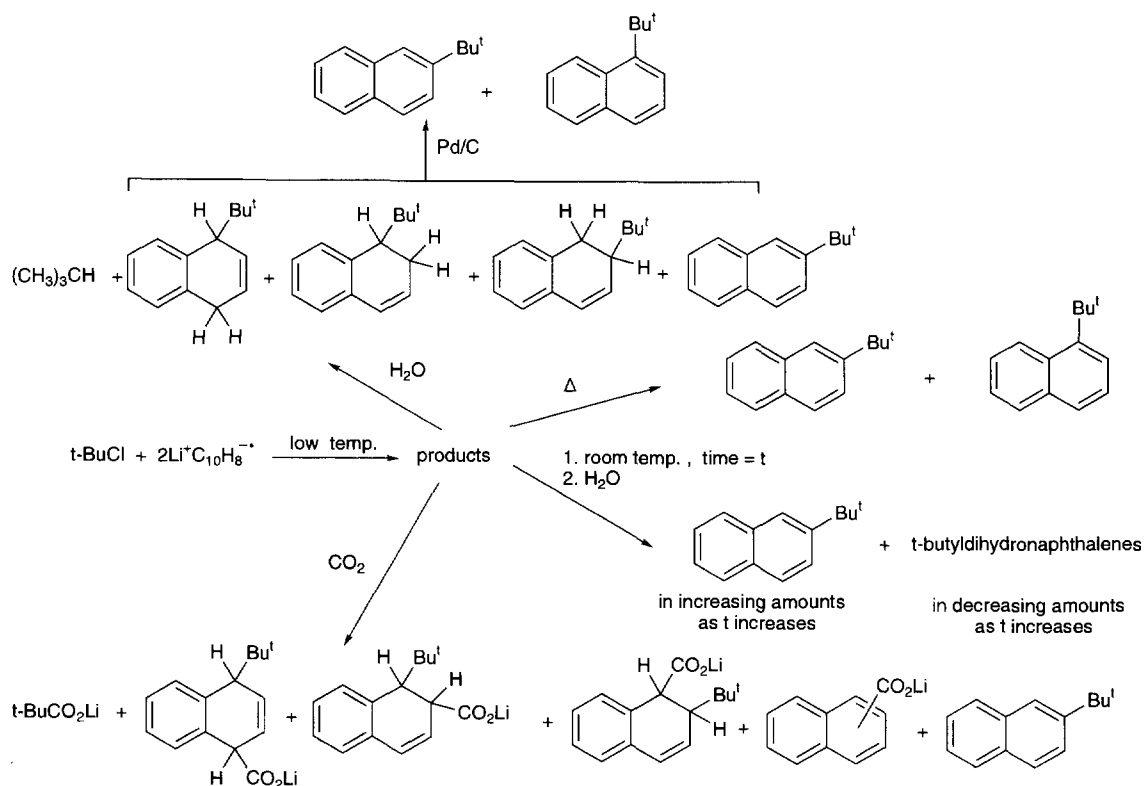
Fig. 2. Raw kinetic data for the formation of 2-*tert*-butyl-naphthalene and the decay of **2**.

the *tert*-butyldihydronaphthalene products. The experimental results clearly indicate that alkylation at the 2-position occurs preferentially and that the reasoning that a combination of allylic and benzylic type resonances should make structure **1** more favorable does not bear out.

Carboxylation of **1** should lead to 4-*tert*-butyl-1,4-dihydro-1-naphthoic acid or 1-*tert*-butyl-1,2-dihydro-2-naphthoic acid, whereas carboxylation of **2** should lead to 2-*tert*-butyl-1,2-dihydro-1-naphthoic acid. Indeed, GC/MS analysis of the methyl esters of the mixture of the acids derived from naphthalene indicated the presence of, besides 1-naphthoic acid and 2-naphthoic acid, three components with a molecular weight of 244, which corresponds to methyl *tert*-butyl-dihydro-naphthoates. The fact that the GC analysis gave just three peaks indicates that each acid is produced in one of the two possible geometric isomers.

An important question that has to be answered is whether or not the primary reaction product is *tert*-butyllithium. If it were, alkylation could arise via addition of ^tBuLi to naphthalene. Of course, it appears reasonable to assume that *tert*-butyllithium generated in situ in THF solution should be quite different from the tetrameric [18] material that exists in hydrocarbon solutions. In order to obtain an answer to the above question, we carried out a reaction between *tert*-butyl chloride and lithium naphthalene radical anion in the presence of magnesium 2-ethoxyethoxide [10]. We reasoned

that if ^tBuLi were the primary product, it would complex immediately with the magnesium alkoxide, forming a markedly less reactive organometallic reagent, incapable of adding to or metallating naphthalene (see, in the experimental section, the attempted reaction of preformed *tert*-butyllithium with naphthalene in the presence of magnesium 2-ethoxyethoxide). The latter reagent, unlike magnesium halides, resists reduction by alkali metal aromatic hydrocarbon radical anion in THF and combines with alkyl alkali reagents to form a bimetallic compound. This compound exhibits normal organometallic behavior but with a markedly diminished reactivity in comparison with the corresponding organoalkali reagent. Thus a solution of *tert*-butyl chloride in THF containing more than one equivalent of magnesium alkoxide was added to a solution of lithium naphthalene radical anion. Subsequent carboxylation gave 26.8% of 2-*tert*-butyl-1,2-dihydro-1-naphthoic acid, 3.6% of 1-*tert*-butyl-1,2-dihydro-2-naphthoic acid, 10.4% of 4-*tert*-butyl-1,4-dihydro-1-naphthoic acid, 19% of pivalic acid and 6.7% of 1-naphthoic acid, i.e. one of the two possible metallation products of naphthalene! The presence of 2-*tert*-butylnaphthalene in the neutral fraction of the carboxylation mixture was also confirmed. These results are a strong indication that alkylation of naphthalene occurs without the involvement of *tert*-butyllithium and, most importantly, provide valuable hints as to the mechanism of metallation of aromatics by alkyl lithium reagents. Additional information

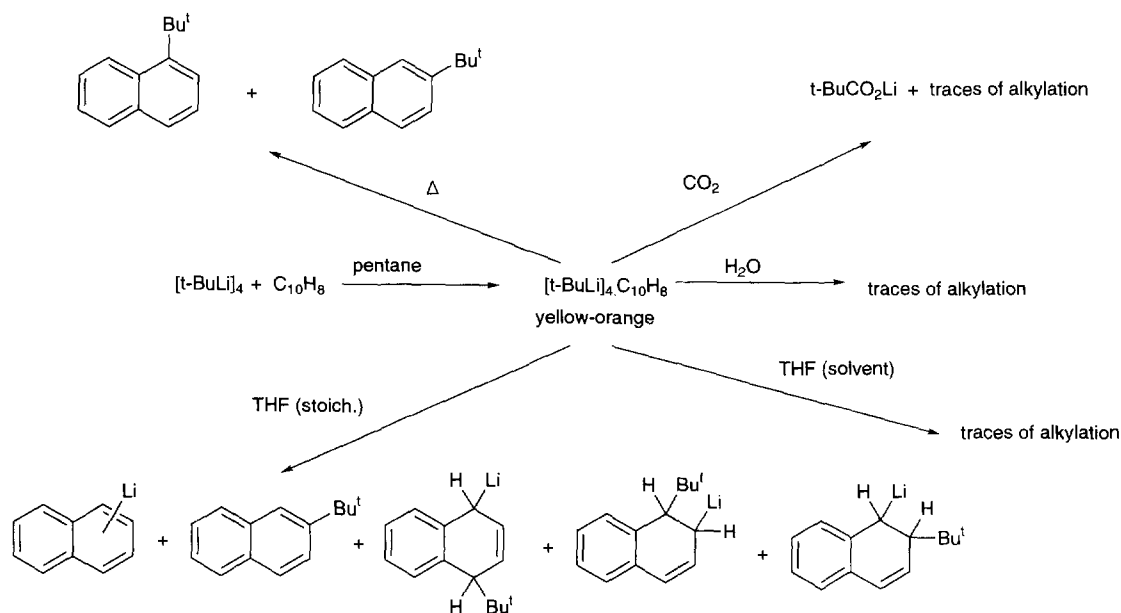


comes from a comparative study of naphthalene and preformed *tert*-butyllithium under conditions corresponding to those employed for the *tert*-butyl chloride–lithium naphthalene radical anion reaction. Scheme 2 summarizes the results described above.

2.2. *tert*-Butyllithium and naphthalene

All our early attempts to add preformed ^tBuLi to naphthalene under conditions approaching those used in the ^tBuCl + Li⁺C₁₀H₈[−] reaction met with failure. Even prolonged reaction times and temperatures higher than those employed for the lithium naphthalene radical anion and *tert*-butyl chloride reaction led only to traces of addition or alkylation products, although the reaction mixture exhibited a light brownish-red color. Obviously, the reagent was destroyed by THF cleavage. In pentane, *tert*-butyllithium and naphthalene form a yellow–orange complex which, on the basis of the reported (360 ± 14) cryoscopic molecular weight [15], we believe has the composition (^tBuLi)₄ · C₁₀H₈, theory 384, rather than the originally proposed [15] composition of (^tBuLi)₂(C₁₀H₈)₂, theory 384. Carboxylation of the complex afforded pivalic acid and only traces of alkylation products. Direct hydrolysis of the complex gave comparable results. When the complex was dissolved in THF at about −50 °C and the resulting solution stirred at that temperature for 2.5 h, again only traces of addition or alkylation products were observed. Eventually it was discovered that alkylation, addition and metallation products could be obtained by addition of one equivalent of THF per ^tBuLi to the preformed complex. Scheme 3 summarizes these reactions.

Unlike THF, triethylamine, whether as a catalyzing [19] Lewis base used in stoichiometric amounts or as a co-solvent, was found to be effective in bringing about addition, alkylation and metallation in the ^tBuLi + C₁₀H₈ system. The efficacy of triethylamine in this particular reaction can be understood on the basis of the following considerations. Triethylamine exhibits low basicity towards the Lewis acid (^tBuLi)₄ [20]. Thus naphthalene can compete with triethylamine for ^tBuLi by virtue of its π-basicity [15]. In addition, *tert*-butyllithium can survive for some time in the presence of triethylamine even at 73 °C [15], whereas THF as a co-solvent destroys it very rapidly at room temperature. In fact, the low Lewis basicity of triethylamine with respect to *tert*-butyllithium and the stability of the latter in triethylamine solutions are not unrelated phenomena. It is felt that a necessary condition for reaction of ^tBuLi with naphthalene, to give alkylation, addition and metallation products, is the intimate contact, i.e. complexation, of the unsolvated organolithium reagent with naphthalene and the interaction of the Lewis base with this ‘complex’. That such a ternary complexation does occur is borne out by the observation referred to previously that THF, a strong Lewis base, destroys the ^tBuLi when used as a co-solvent, whereas when added in stoichiometric amounts to the preformed ^tBuLi–naphthalene complex it does catalyze the addition, alkylation and metallation reactions. *N,N,N',N'*-tetramethylethylenediamine (TMEDA) catalyzes almost exclusively the metallation of naphthalene by ^tBuLi, with small amounts of alkylation or addition by-products. The results are summarized in Table 1 and Fig. 3. The trend emerging from the above experiments for the system

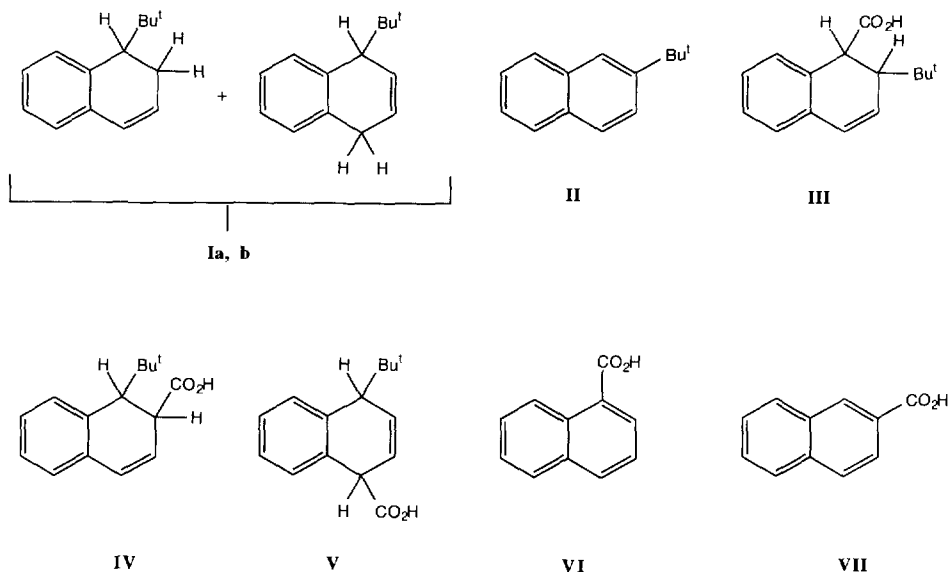


Scheme 3.

Table 1

Individual product and total yields after carboxylation (%) of the reaction between naphthalene and *tert*-butyllithium in pentane, catalyzed by Lewis bases

Lewis base	Product							Total yield (%)
	Ia,b	II	III	IV	V	VI	VII	
Et ₃ N	2.0	27.0	0.06	10.5	2.9	8.6	0.5	51.6
THF	0.5	7.0	9.5	0.0	2.0	9.7	9.2	37.9
TMEDA	0.1	2.9	2.6	0.0	0.3	35.9	24.9	60.8



tert-butyllithium–naphthalene–Lewis base is that alkylation plus addition increases with decreasing Lewis basicity, at the expense of metallation. Therefore, if one wishes to metallate naphthalene with fewer side products, one should employ ^tBuLi and a strong Lewis base such as TMEDA with a selectivity of ca. 58% metallation at the 1-position. Even better is the combination of *n*-butyllithium and TMEDA which gives exclusively metallation products with a selectivity of ca. 65% at the 1-position and yields of up to 72%. The selectivities

have been determined by reaction of the mixtures of 1- and 2-naphthyllithiums with an excess of paraformaldehyde. Thus a mixture of 1- and 2-hydroxymethyl-naphthalenes was obtained in ca. 60% yield and the composition was determined by NMR analysis.

3. Reaction mechanisms

We now examine a number of possible mechanistic schemes.

3.1. Alkyl radical–naphthalene radical anion combination mechanism, Scheme 1

Having established the structure of the alkylation products and having determined their relative isomer distribution in the reaction between *tert*-butyl chloride and lithium naphthalene radical anion, it remains to be examined whether these results agree with the proposed mechanism [13] for the formation of the alkyldihydronaphthyllithiums. If the mechanism depicted in Scheme 1 is operable, it appears reasonable to expect that in step (ii) of Scheme 1 the alkyl radical R[•] should combine with the carbon atom bearing the highest spin density, namely the carbon atom at position 1 of the naphthalene radical anion [21]. Thus alkylation at position 1 should be favored, which, however, is not the case. Moreover, if one takes as a model the reaction $\text{PhCH}_2^{\bullet} + \text{R}^{\bullet} =$

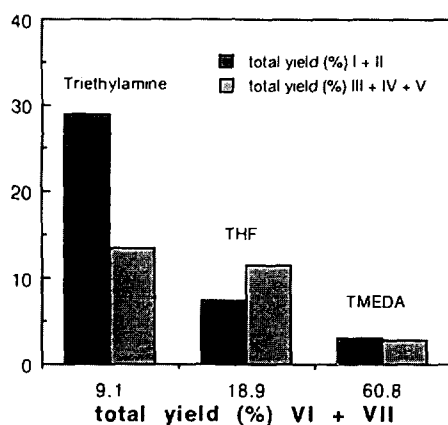
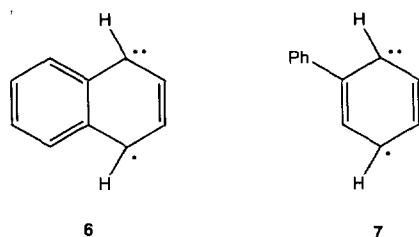


Fig. 3. Histogram of total yield, after carboxylation, of (1-*tert*-butyl-1,2(1,4)-dihydronaphthalenes + 2-*tert*-butylnaphthalene) and total yield of *tert*-butyl-dihydronaphthoic acids against total yield of naphthoic acids in the reaction between *tert*-butyllithium and naphthalene, catalyzed by the Lewis bases triethylamine, THF and TMEDA.

PhCH₂R for step (ii) of Scheme 1, it can readily be seen that the activation energy increases in the order primary < secondary < tertiary alkyl (inferred from the opposite reaction PhCH₂R → PhCH₂· + R· [22]; although the series of data for the dissociation reaction is not complete, the missing entries could be estimated from the linear correlation between energies of activation and the corresponding gas phase ionization potentials of R·'s, see Ref. [23]). This means that ease of alkylation should increase in the opposite direction, provided that the three types of free radical have comparable electron affinities so that the energetics of the competing reaction leading to the formation of the corresponding carbanion R⁻, i.e. reaction (iii) in Scheme 1, factor out. This indeed appears to be the case [electron affinity changes rather slowly with variation of the structure of negative ions; for example EA(Et⁻) = 0.9–1.0 eV, EA(^tPr⁻) = 0.7 eV [24]]. In other words, the mechanism predicts more alkyldihydronaphthyllithium formation with normal alkyl halides than with tertiary ones, whereas the experimental facts indicate exactly the opposite. In addition, the mechanism does not account for the formation of the metallation products and is not of general applicability to the system aromatic hydrocarbon radical anion–alkyl halide. It cannot explain, for example, the fact that the reaction between lithium biphenyl radical anion and a *tert*-alkyl chloride leads mainly to alkyllithium product [7], whereas lithium anthracene radical anion and an alkyl halide give exclusively alkyldihydroanthracenyllithiums. On the contrary, a radical anion such as **6** should be more reactive than **7**, and consequently combination with an alkyl radical should lead to alkylation products to a greater extent than that observed in the case of naphthalene. Therefore, from these considerations, the experimental results do not seem to agree with a mechanism involving combination between an alkyl radical and an aromatic hydrocarbon radical anion.



3.2. Alkylation of naphthalene by the alkyllithium product

Bearing in mind the relative reactivity in solution of alkyllithiums, which increases from primary to sec-

ondary to tertiary, one might anticipate that alkylation could take place via addition of an alkyllithium reagent to naphthalene [15]. However, it has already been noted that attempted reaction of naphthalene with *tert*-butyllithium in THF solvent under conditions approaching those of the reaction between *tert*-butyl chloride and lithium naphthalene radical anion was unsuccessful. Moreover, the evidence, put forward in the previous discussion, that *tert*-butyllithium is not a primary reaction product makes this alternative mechanism less attractive.

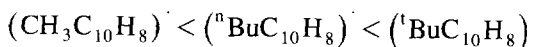
3.3. Radical attack on naphthalene, Scheme 4

There is no doubt that, in the reaction between a radical anion with an alkyl halide, alkyl radicals are formed by an electron transfer step from the radical anion to the alkyl halide. In order then to understand the elementary steps of the reaction, we must bear in mind that the aromatic hydrocarbon which is derived from the radical anion after electron donation could function as a more or less efficient free radical scavenger. The ability of an aromatic hydrocarbon 'to accommodate' a free radical can be expressed quantitatively by the corresponding 'methyl affinity' parameter [25]. The latter parameter is defined as the ratio of the rate constants for hydrogen atom abstraction from isooctane by CH₃· and the rate for addition of methyl radical to the aromatic compound A, CH₃A, in a competition experiment. The methyl affinities of biphenyl, naphthalene, phenanthrene, chrysene, pyrene, stilbene, 1,2-benzanthracene, anthracene and naphthacene (tetracene) are 5; 22; 27; 57.5; 125; 183; 468; 820 and 9250 respectively [25]. It is instructive to compare the latter numbers with the respective half-wave reduction potentials (taken from Ref. [26]), which are -2.70; -2.50; -2.46; -2.30; -2.11; -2.16; -2.00; -1.96 and -1.58 V vs. SCE. In fact, the logarithms of the methyl affinities, MeAs, correlate well with the corresponding half-wave reduction potentials, Eq. (1). This in turn means that they also correlate with the corresponding electron affinities and, therefore, the interaction between the radical and the aromatic hydrocarbon is of the donor–acceptor type.

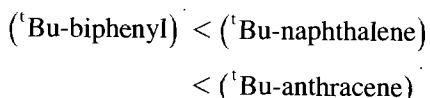
$$\ln(\text{MeA}) = 6.603_5 \varepsilon_{1/2} + 19.403; r^2 = 0.985, n = 9 \quad (1)$$

As a measure of the donor ability of the free radical, we may take the corresponding gas phase ionization potential, namely the enthalpy change for the gas phase process at 298.15 K, R· → R⁺ + e⁻. The lower the ionization energy of the free radical, the greater is the donor ability and, for example, the ionization potentials *IP* of the free radicals methyl, *n*-butyl and *tert*-butyl are 9.84, 8.02 and 6.7 eV [24] respectively, showing that

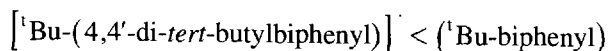
there is a marked dependence of the donor ability of the alkyl radical on its structure. The methyl affinities of the aromatic hydrocarbons and the IP s of alkyl radicals allow us to evaluate the stabilities of the adducts (RA). Thus, considering the stabilities of the adducts of methyl, *n*-butyl and *tert*-butyl radicals to naphthalene, the corresponding stabilities should vary as follows:



whereas the stability of the adduct of a given free radical, e.g. *tert*-butyl, and a series of aromatic hydrocarbons, e.g. biphenyl, naphthalene and anthracene, should vary as follows:



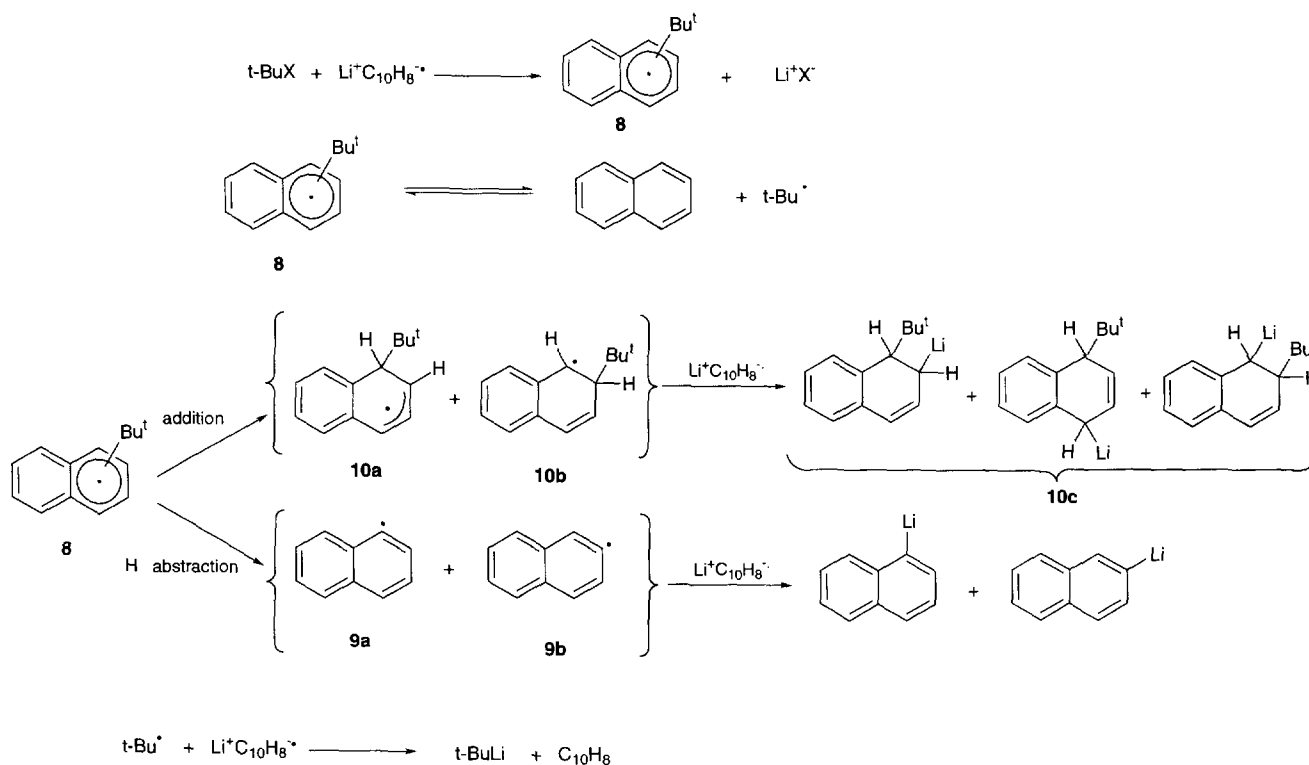
The correlation in Eq. (1) implies that, a decreasing electron affinity corresponds to a decreasing radical affinity. Since an alkyl substituted aromatic hydrocarbon, e.g. 4,4'-di-*tert*-butylbiphenyl, should exhibit a lower electron affinity than biphenyl itself, the stabilities of the adducts with, for example, *tert*-butyl radical should vary as follows:



With the above considerations in mind, we can now develop a mechanistic scheme, Scheme 4, for the *tert*-butyl chloride and lithium naphthalene radical anion

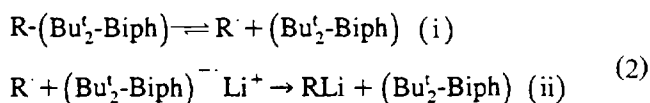
system in particular, and for the alkyl halide–radical anion systems in general. Thus, in the first step, ${}^t\text{BuCl}$ reacts with one equivalent of lithium naphthalene radical anion to produce a *tert*-butyl radical, a chloride anion and naphthalene. However, the *tert*-butyl radical, by virtue of its pronounced donor ability and naphthalene by its substantial radical affinity, could form an adduct, **8**. The proposed odd-electron species **8** is closely analogous, albeit with inverse polarity, to the intermediate proposed by Russell for the free radical chlorination of aromatic compounds [27]. Species **8** can either accept a second electron and give the carbanion **1** or **2**, or dissociate into naphthalene and the free alkyl radical. The latter is converted to the corresponding 'carbanion' by accepting a second electron from naphthalene radical anion. The formation of some naphthyllithium in the reaction between *tert*-butyl chloride and lithium naphthalene radical anion, both in the absence and presence of magnesium 2-ethoxyethoxide, see above, prompted us to consider a third possibility, namely abstraction of a hydrogen atom by the associated radical from the α - or β -position of naphthalene leading to the formation of the corresponding naphthyl radicals. The naphthyl radicals in turn, on further reduction, are converted to the corresponding naphthyllithiums.

Scheme 4 is of general applicability to the system aromatic hydrocarbon radical anion–alkyl halide. It is the stability of the (RA) that is the main factor determining the course of the reaction.



3.3.1. Case (a)

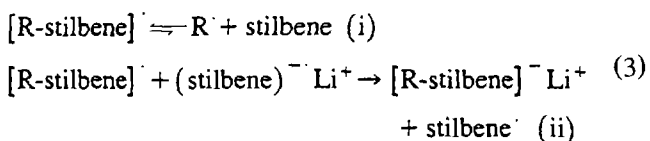
Involvement of an (RA)[·] adduct of low stability, i.e. reaction of ^tBuCl with the lithium salt of a radical anion derived from an aromatic hydrocarbon of low electron affinity, e.g. 4,4'-di-*tert*-butylbiphenyl. The very low radical affinity of the latter hydrocarbon will result in the virtually complete dissociation of the intermediate R-(Bu₂^t-Biph)[·], thus leading ultimately to almost exclusive RLi formation:



Indeed, we confirmed this experimentally. The reaction between *tert*-butyl chloride and lithium 4,4'-di-*tert*-butylbiphenyl radical anion (LiDBB) in THF at -75 to -70 °C gave, after carboxylation, an 80% yield of pivalic acid of purity almost 100%. In the analogous case of the reaction between lithium di-*tert*-butyl-naphthalene radical anion and *tert*-butyl chloride, an 83% yield of pivalic acid, ca. 90% pure, was obtained. The latter result should be compared with the 25% yield of pivalic acid in the reaction between lithium naphthalene radical anion and *tert*-butyl chloride, after carboxylation.

3.3.2. Case (b)

Involvement of an (RA)[·] adduct of marked stability, i.e. reaction between *tert*-butyl chloride and the lithium salt of an aromatic hydrocarbon of high electron affinity, e.g. stilbene. In this case the marked radical affinity of stilbene will make the dissociation process (i), Eq. (3), energetically unfavorable, thus leaving as the only possibility the formation of the carbanions (R-Stilbene)⁻ by further reduction of the radical-stilbene adduct, step (ii), Eq. (3).



The fundamental difference between the mechanisms depicted in Schemes 1 and 4 is that the former requires that a radical anion reacts only partly by electron transfer steps, whereas our mechanism, Scheme 4, postulates that a radical anion functions solely as an electron donor.

It should be noted that our interpretation of the lack of formation of alkyldihydroarene carbanionic products in the reaction of lithium 4,4'-*tert*-butylbiphenyl radical anion and *tert*-alkyl halides differs markedly from the one given by Freeman and Hutchinson [7]. They assume

a mechanism analogous to the one depicted in Scheme 1, and consider that the *tert*-butyl groups on the biphenyl skeleton hinder the alkyl radical from combining with the radical anion. This interpretation, of course, cannot explain the fact that lithium biphenyl radical anion and *tert*-butyl chloride lead mainly to alkyllithium product, although it is devoid of any bulky substituents.

3.4. Mechanism of the reaction between preformed *tert*-butyllithium and naphthalene, Scheme 5

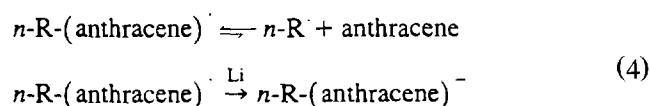
The accelerating effect of triethylamine and its kinetic involvement in the reaction between *tert*-butyllithium and naphthalene at 73 °C have been reported [15]. Also, the influence of the catalyzing Lewis base on the orientation, i.e. metallation at 1- or 2-position, of naphthalene has been recorded in the literature [16]. However, the marked dependence of the direction of the reaction, i.e. alkylation and formation of *tert*-butyldihydronaphthyllithiums versus naphthalene metallation, in the reaction between *tert*-butyllithium and naphthalene on the strength of the catalyzing Lewis base is an important finding of the present work.

There is no doubt that there is a close analogy between the systems ^tBuX + Li⁺C₁₀H₈⁻ and ^tBuLi and C₁₀H₈. Indeed, both systems lead to the formation of the same products, albeit with different distributions. This analogy prompted us to propose a mechanistic scheme involving the intermediate **8**. Obviously, formation of **8** should have as a prerequisite a *tert*-butyl radical forming step which has to arise either via single electron transfer (SET) or a homolytic reaction. An intermediate like **8** could react by a number of possible pathways, leading to products via different intermediates: (a) abstraction of a proton from the 1- or 2-position of naphthalene to form 1- and 2-naphthyl radicals respectively, **9a,b**; (b) addition to naphthalene and formation of isomeric *tert*-butyl-dihydronaphthyl radicals, **10a,b**; and (c) dissociation back to naphthalene and a 'free' *tert*-butyl radical. If one invokes a SET step, the electron acceptor can only be the naphthalene, thereby forming a radical anion. In such a case, alkylation could arise from the combination of the *tert*-butyl radical and the naphthalene radical anion. However, this alternative has been dismissed above on the basis of arguments developed in discussing the mechanism of the reaction between *tert*-butyl chloride and lithium naphthalene radical anion. It would be even more difficult to explain the formation of metallated products by postulating the involvement of a naphthalene radical anion intermediate. Indeed, one has either to invoke isobutane elimination from **10c** in order to explain the formation of metallation products or hydrogen atom abstraction from naphthalene radical anion by *tert*-butyl radical [16]. If the latter alternative were a feasibility, then a slow

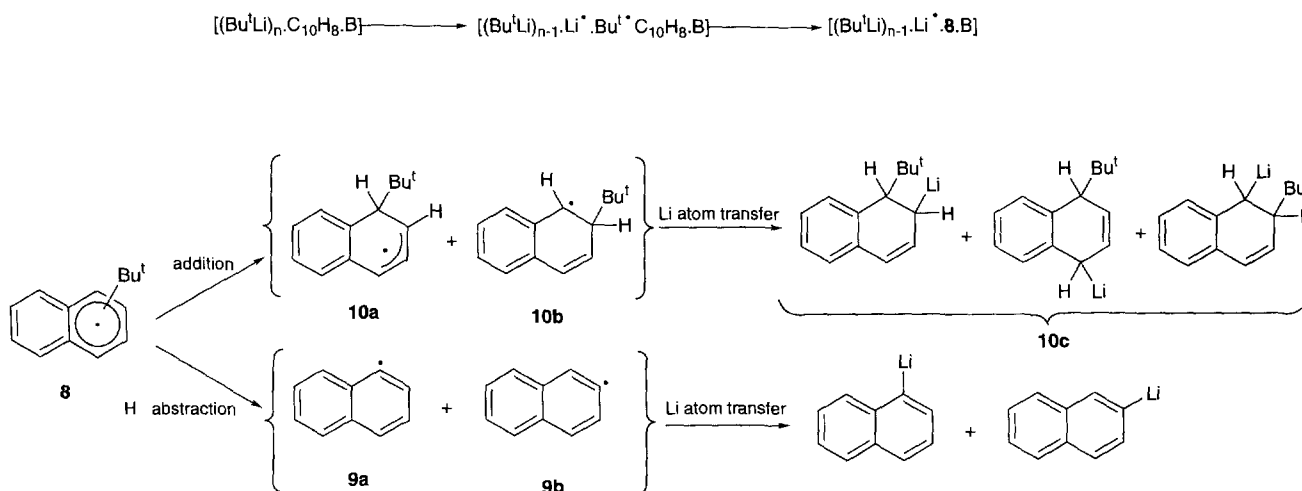
addition of *tert*-butyl chloride to a solution of lithium naphthalene radical anion should lead mainly to naphthyllithiums, simply because the originally formed *tert*-butyl radical should abstract a hydrogen atom from the unconsumed radical anion, which of course is not the case. Therefore, we favor a homolytic elementary step as the radical forming reaction. Of course, all the elementary steps, namely homolysis, the formation of **8** and its transformation to other intermediates, have to take place within a reaction cage. This is necessary because formation of final products can occur by combination of a lithium atom with the intermediates **9** and **10**.

It remains now to justify the possibility of the involvement of a homolytic step. The electron deficient character of organolithiums arises from their existence in the form of oligomers, a tetramer for *tert*-butyllithium, i.e. in the alkylolithium oligomer there are more bonds than electrons to form ordinary bonds [28]. Upon coordination of the Lewis base with the oligomer, however, the electron deficiency of the organolithium oligomer is satisfied, at least partly. Therefore, some of the multicenter bonds of the oligomer may now undergo fission. Indeed, recent studies [29] indicate that in the case of *n*-butyllithium its hexameric structure which exists in hydrocarbon media may break down to tetrameric and even dimeric species by coordinating with Lewis bases such as TMEDA. Naphthalene, by virtue of its π basicity, may interact further with the solvated alkylolithium–Lewis base adduct and form a ternary complex. It is postulated that the RLi oligomer within the ternary complex undergoes homolysis which leads to formation of the alkyl radical–naphthalene adduct **8** and that all these transformations take place within a cage. As has already been stated in discussing mechanism 4, it is the stability of the (RA) \cdot adduct which will determine the direction of the reaction. A stable (RA) \cdot

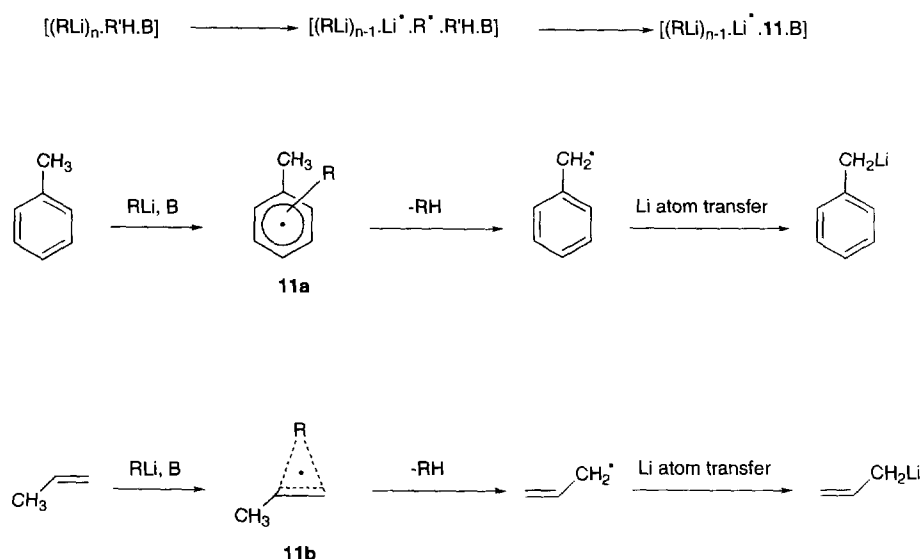
adduct may be derived from a radical of relatively high ionization energy, i.e. of low ‘donicity’, and an aromatic hydrocarbon of very high methyl affinity. For example, a primary alkyl radical such as Et \cdot or n Bu \cdot could form a stable adduct with anthracene, whose methyl affinity is 4.5 times the methyl affinity of stilbene, 37 times the methyl affinity of naphthalene and 164 times the methyl affinity of biphenyl. Thus one may explain why the reaction between, for example, ethyllithium and anthracene leads to the exclusive formation of 9-lithio-10-ethyl-9,10-dihydroanthracene [30]:



The above mechanism is depicted in Scheme 5. It is felt that this mechanistic scheme can be consistently applicable to metallation at benzylic and allylic sites. In these particular cases, the neutral substrate-free radical adducts are transformed into the benzyl and allyl radicals respectively via hydrogen atom abstraction by the coordinated alkyl radical. Benzyllithium and allyllithium are then produced by combination of these radicals with the lithium atom. This mechanism is exemplified in Scheme 6 for the metallation of toluene and propene. As a supporting argument for the hydrogen atom abstraction step by a radical in metallation at benzylic sites, we may cite [31] the linear dependence of activation energies, or their proportional $\ln k_r$, for benzylic hydrogen atom abstraction by CCl_3 from the series of carbon acids toluene, 2-methylnaphthalene, 1-methylnaphthalene, 2-methylantracene, 1-methylpyrene and 9-methylantracene on the respective $\text{p}K_a$ s, Eq. (5). A similar correlation holds between $\ln k_r$ and $\text{p}K_a$ for benzylic hydrogen atom abstraction by



Scheme 5.



Scheme 6.

trichloromethyl radical from the carbon acids toluene, cumene, diphenylmethane, triphenylmethane and fluorene, Eq. (6).

$$\ln(10^2 k_r) = -0.671(\text{p}K_a) + 30.00; \quad r^2 = 0.978, n = 6 \quad (5)$$

$$\ln(10^2 k_r) = -0.263_5(\text{p}K_a) + 9.943; \quad r^2 = 0.990, n = 5 \quad (6)$$

4. Conclusions

It has been shown that reaction between *tert*-butyl chloride and two equivalents of lithium naphthalene radical anion in THF, i.e. under stoichiometric conditions and in the absence or presence of magnesium 2-ethoxyethoxide, leads to the formation of 2-*tert*-butyl-1-lithio-1,2-dihydronaphthalene, 1-*tert*-butyl-2-lithio-1,2-dihydronaphthalene and 1-*tert*-butyl-4-lithio-1,4-dihydronaphthalene along with *tert*-butyllithium and a detectable amount of 1- and 2-naphthyllithiums. 2-*tert*-Butyl-1-lithio-1,2-dihydronaphthalene, which is the main product, undergoes a facile aromatization to 2-*tert*-butylnaphthalene by lithium hydride elimination. Alkylation products do not arise from the reaction between naphthalene and *tert*-butyllithium. The factor that determines the course of the reaction between *tert*-butyl chloride and a given lithium aromatic hydrocarbon radical anion is the radical affinity or the correlated reduction potential of the neutral hydrocarbon. The radical anion with lithium counterion of an aromatic hydrocarbon with a large negative reduction potential, i.e. an aromatic hydrocarbon of low enough electron or radical affinity, on reaction with *tert*-butyl chloride may lead

exclusively to the formation of *tert*-butyllithium, whereas the radical anion of an aromatic hydrocarbon of high enough electron or radical affinity may lead solely to *tert*-butyl-dihydroarene carbanions.

Preformed *tert*-butyllithium and naphthalene react in a manner which is markedly dependent upon the strength of the catalyzing Lewis base, and the products formed are presumed to arise from the same intermediates as in the system lithium naphthalene radical anion and *tert*-butyl chloride. A compound of low Lewis basicity, such as triethylamine, favors formation of 2-*tert*-butyl-naphthalene and *tert*-butyl-dihydronaphthyllithiums, whereas a strong Lewis base such as TMEDA leads almost exclusively to naphthyllithiums. When the reaction between *tert*-butyllithium and naphthalene is carried out in the presence of magnesium 2-ethoxyethoxide, there is no formation of addition or metallation products.

5. Experimental

Proton and carbon-13 NMR spectra were recorded with a Bruker AC 300 MHz NMR instrument. For mass spectrometric analysis a Varian SATURN GC/MS instrument was employed. Gas chromatographic analyses were performed with a Pye Unicam GCV chromatograph equipped with a Varian, Vista series, CDS 401 recorder-integrator. Column: 10% Apiezon L on Chromosorb GAWBMCS, 6' × 18', carrier gas argon, 42.85 ml min⁻¹, $T_{\text{col}} = 130^\circ\text{C}$ for hydrocarbons and 190°C for the methyl esters, $T_{\text{det}} = 230^\circ\text{C}$, $T_{\text{inj}} = 230^\circ\text{C}$. Naphthalene and stilbene were commercial products 98% or better and were recrystallized from isopropanol. Di-*tert*-butyl naphthalene [32] and 4,4'-di-*tert*-butyl-biphenyl [33] were synthesized by literature procedures.

Tetrahydrofuran was doubly distilled from LiAlH_4 under argon shortly before use. *tert*-Butyl chloride was purchased from Ferak Berlin and was distilled under argon before use. Triethylamine and *N,N,N',N'*-tetramethylethylenediamine (TMEDA) were distilled from barium oxide, under argon. *tert*-Butyllithium was prepared from high-sodium lithium dispersion and *tert*-butyl chloride containing ca. 1% *n*-butyl chloride, in pentane. Also *tert*-butyllithium has been prepared from lithium dispersion and *tert*-butyl chloride in THF at -60°C or lower and used immediately after the completion of the preparation. Radical anion solutions were prepared usually in 20 mmol quantities and in concentrations of ca. 1 M under an atmosphere of argon by stirring equivalent quantities of lithium and the aromatic hydrocarbon in THF overnight. The concentration of the radical anion was determined by reacting an aliquot of the radical anion solution with ethylene bromide under argon and titrating the liberated Br^- and/or by total alkalinity on hydrolyzed aliquots.

5.1. Product analysis

The characterization of the reaction products was made by a combination of analytical and preparative GC, GC/MS and NMR techniques. For the 1- and 2-*tert*-butyl-naphthalenes as well as for methyl 1- and 2-naphthoates authentic samples were employed. The 2-*tert*-butyl-naphthalene derivatives exhibited longer retention times on the above mentioned column. 1-*tert*-Butyl-1,2-dihydronaphthalene and 1-*tert*-butyl-1,4-dihydronaphthalene gave a single GC peak and 2-*tert*-butyl-1,2-dihydronaphthalene exhibited a longer retention time. The assignment of the latter was based also on a kinetic measurement, see the relevant paragraph in Section 2. The mixture of the acids derived from naphthalene was analysed after converting to the corresponding methyl esters with an excess of diazomethane. There were three components with retention times (A) 30.8; (B) 34.0 and (C) 51.1 min, and all exhibited $m/e = 244$. The latter corresponds to the parent ion of the isomeric methyl *tert*-butyl-dihydronaphthoates. Component A. ^1H NMR: δ (ppm) 0.85, s (9H, *tert*-butyl); 2.64, d (1H, methinic); 3.61, s (3H, methyl); 3.89, s (1H, methinic); 5.95, dif. m (1H, olefinic); 6.53, d (1H, olefinic); 7.02–7.16, m (4H, aromatic). ^{13}C NMR: 27.12, $(\text{CH}_3)_3\text{C}$; 35.58, $(\text{CH}_3)_3\text{C}$; 44.76, $\text{CH}-\text{COO}$; 46.24, $\text{CH}-^1\text{Bu}$; 52.21, CH_3-O ; 127.45, C(3); 128.15, C(4); 126.07, 127.29, 127.52, 129.05, 131.82, 133.06, aromatic; 174.53, $-\text{COO}$. The assignment was made on the basis of 2D COSY, C–H correlation and NOESY NMR spectra and is consistent with the hydrolysis experiment. Component A is assigned the structure methyl 2-*tert*-butyl-1,2-dihydro-1-naphthoate. Component B. ^1H NMR: δ ppm 0.89, s (9H, *tert*-butyl); 3.07, s (1H, methinic); 3.51, d (1H, methinic); 3.59, s (3H, methyl); 5.93, dif. m (1H, olefinic); 6.47, d (1H, olefinic);

7.01–7.12, m (4H, aromatic). Component B is assigned the structure 1-*tert*-butyl-1,2-dihydro-2-naphthoate, Component C. ^1H NMR: δ ppm 0.88, s (9H, *tert*-butyl); 3.18, s (1H, methinic); 3.68, s (3H, methyl); 4.37, asym. d (1H, methinic); 6.18, s (2H, olefinic); 7.19–7.31, m (4H, aromatic). Component C is assigned the structure methyl 4-*tert*-butyl-1,4-dihydro-1-naphthoate.

5.2. Lithium naphthalene radical anion and *tert*-butyl chloride

5.2.1. Normal addition and hydrolysis

To a solution of lithium naphthalene radical anion, from 2.7 g, 21 mmol of naphthalene, 0.140 g, 20 mg atom of lithium chips and 24 ml of THF, was added 1.10 ml, 10 mmol of *tert*-butyl chloride in 5 ml of THF at -70 to -60°C . The resulting brown solution was stirred for 1.5 h while the temperature rose gradually to -5°C . A 5 ml aliquot was withdrawn and hydrolyzed. THF and part of the hydrolysis water were removed in a thin film evaporator and the organics were taken up in methylene chloride. GC analysis of the solution gave: 1-*tert*-butyl-1,4-dihydronaphthalene and 1-*tert*-butyl-1,2-dihydronaphthalene (18.0%), 2-*tert*-butyl-1,2-dihydronaphthalene (27.8%), 1-*tert*-butyl-naphthalene (0.25%), 2-*tert*-butyl-naphthalene (0.56%), naphthalene (49.4%). Material balance 96%. Ratio of (1-*tert*-butyl-1,4- (or 1,2-) dihydronaphthalene + 1-*tert*-butyl-naphthalene) over (2-*tert*-butyl-1,2-dihydronaphthalene + 2-*tert*-butyl-naphthalene) 1.0:1.55.

5.2.2. Inverse addition and hydrolysis

A solution of lithium naphthalene radical anion, from 2.7 g, 21 mmol of naphthalene, 0.140 g, 20 mg atom of lithium metal chips and 20 ml of THF, was added via a pressure equalizing dropping funnel to 1.10 ml, 10 mmol of *tert*-butyl chloride in 10 ml of THF at -60 to -55°C during a period of 0.25 h. The resulting brown solution was stirred at -70°C for 0.5 h more, and then hydrolyzed. GC analysis of the product indicated: 1-*tert*-butyl-1,4-dihydronaphthalene and 1-*tert*-butyl-1,2-dihydronaphthalene (23.4%), 2-*tert*-butyl-1,2-dihydronaphthalene (28.9%), 1-*tert*-butyl-naphthalene (0.0%), 2-*tert*-butyl-naphthalene (2.1%), naphthalene (44.2%). Material balance 98.6%. Ratio of (1-*tert*-butyl-1,4-dihydronaphthalene + 1-*tert*-butyl-naphthalene) over (2-*tert*-butyl-1,2-dihydronaphthalene + 2-*tert*-butyl-naphthalene) 1.0:1.32.

5.2.3. Kinetic run

To a solution of 0.10 mol of lithium naphthalene in 110 ml of THF was added 0.05 mol of *tert*-butyl chloride at -60 to -35°C and the resulting mixture was stirred at -65°C for 0.25 h. The mixture was thermostated at $26 \pm 2^\circ\text{C}$ and aliquots were withdrawn every ca. 0.5 h for gas chromatographic analysis. The raw kinetic data are plotted in Fig. 2 as the ratio of

aromatized product to total *tert*-butyl-dihydronaphthalenes versus time in minutes. The relative alkylation of naphthalene at the 1- and 2-position, determined at time 0, was 1:1.35 respectively.

5.2.4. Immediate carboxylation

(i) To a solution of lithium naphthalene radical anion, prepared from 13 g, ca. 0.10 mol of naphthalene, 0.70 g, 0.10 g atom of lithium metal chips and 120 ml of THF, was added 5.50 ml, ca. 50 mmol of *tert*-butyl chloride at -55 to -50 °C. The resulting brownish solution was stirred at -70 °C for 0.25 h and then carboxylated. From the carboxylation mixture was isolated 6.6 g of acid products with strong pivalic acid odor. Steam distillation of the acids afforded 1.4 g of pivalic acid (25%), whereas the non-volatile in-steam fraction weighed 5.2 g, 45% as *tert*-butyldihydronaphthoic acids and based on *tert*-butyl chloride.

(ii) To a solution of lithium naphthalene radical anion, from 6.8 g of naphthalene, 53 mmol, 0.35 g, 50 mg atom of lithium metal chips and 80 ml of THF was added 2.8 ml, 25 mmol of *tert*-butyl chloride via syringe at -70 ± 3 °C. The resulting mixture was stirred for 0.5 h at -75 °C and then carboxylated. From the carboxylation mixture was isolated 4.5 g of an acidic fraction with strong pivalic acid odor. A small portion of this product was converted to methyl esters by reacting with a large excess of diazomethane, and it was analyzed for acids other than pivalic by gas chromatography with the following results: methyl 2-*tert*-butyl-1,2-dihydro-1-naphthoate (51.4%), methyl 1-*tert*-butyl-1,2-dihydro-2-naphthoate (7.1%), methyl-1-naphthoate (3.9%), methyl 2-naphthoate (3.4%) and methyl 4-*tert*-butyl-1,4-dihydro-1-naphthoate (32.6%).

5.2.5. Delayed carboxylation

To a solution of lithium naphthalene radical anion, prepared from 13 g, ca. 0.1 mol of naphthalene, 0.70 g, 0.1 g equiv. of lithium metal chips and 140 ml of THF, was added at -70 ± 3 °C a solution of 4.6 g, 50 mmol of *tert*-butyl chloride in 10 ml of THF. The resulting brownish solution was stirred at 26 ± 2 °C for 6.5 h and then carboxylated. From the carboxylation mixture was isolated a neutral fraction, 9.0 g and an acid fraction, a viscous product, 5.7 g. GC and NMR analysis of the neutral fraction indicated a 3.7:1.0 mixture of naphthalene and 2-*tert*-butylnaphthalene respectively. Thus the yield of 2-*tert*-butylnaphthalene was 27%, whereas the yield of acid was 50%, as *tert*-butyldihydronaphthoic acids. Total yield 77%, based on the *tert*-butylchloride.

5.2.6. Pyrolysis

To a solution of lithium naphthalene radical anion, prepared from 13 g, ca. 0.10 mol of naphthalene, 0.70 g, 0.10 g atom of lithium metal chips and 120 ml of THF, was added 5.50 ml, 50 mmol of *tert*-butyl chloride at -50 to -30 °C. Dry decalin, 60 ml, was added to the

reaction mixture, which was then stirred at room temperature for 4 h. THF solvent was distilled off under vacuum and then the decalin solution of the products heated under an atmosphere of argon at 160 – 170 °C for 24 h. The mixture was filtered, the filtrate was washed with water, dried over anhydrous magnesium sulfate and fractionated under vacuum. The fraction boiling at 80 °C (0.05 mm Hg) weighed 2.8 g, 30% based on *tert*-butyl chloride, and was found to be a 1.0:1.20 mixture of 1- and 2-*tert*-butylnaphthalenes.

5.2.7. In the presence of magnesium 2-ethoxyethoxide and subsequent carboxylation

A solution of lithium naphthalene radical anion was prepared by stirring overnight 7.0 g of naphthalene, 54.7 mmol, 0.36 g, 51.4 mg atom of lithium metal chips and 70 ml of THF. To the radical anion solution, cooled to -70 °C, was added during a period of ca. 10 min a solution of 2.9 ml, 26 mmol of *tert*-butyl chloride in 40 ml of THF containing 7.7 g, 38 mmol of magnesium 2-ethoxyethoxide at -65 to -60 °C. The resulting brown solution was stirred for 10 min longer while cooling to -78 °C and then carboxylated with a slurry of crushed dry ice in ether. Solvents from the carboxylation mixture were removed under vacuum in a thin film evaporator. To the residue was added water, 50 ml and methylene chloride, 100 ml and after shaking the mixture was filtered to separate the precipitated magnesium compounds. The neutral fraction isolated from the methylene chloride layer was found by GC analysis to contain traces of *tert*-butyldihydronaphthalenes and *tert*-butylnaphthalene. The air-dried precipitate was suspended in ca. 20 ml of water and acidified with 20% sulfuric acid. Some solid acid was liberated while the odor of pivalic acid became noticeable. The water layer from the carboxylation mixture was acidified with 20% sulfuric acid, combined with the acidified precipitate and extracted with 3×50 ml of methylene chloride. Evaporation of the combined extracts to constant weight afforded 4.25 g of a viscous product. 4 g of this material was subjected to steam distillation. Extraction of the distillate with methylene chloride gave 0.5 g of pivalic acid. The non-volatile in-steam product was taken up in methylene chloride, from which 2.9 g of a very viscous product was isolated. A small portion of this material was esterified with diazomethane and subjected to GC/MS analysis: methyl 2-*tert*-butyl-1,2-dihydro-1-naphthoate (58.0%), methyl 1-*tert*-butyl-1,2-dihydro-2-naphthoate (7.7%), methyl-1-naphthoate (10.10%), methyl 4-*tert*-butyl-1,4-dihydro-1-naphthoate (22.5%). Material balance 98.2%.

5.3. Lithium 4,4'-di-*tert*-butylbiphenyl radical anion and *tert*-butyl chloride

4,4'-Di-*tert*-butyl-biphenyl, 5.4 g, ca. 20 mmol, lithium chips, 0.140 g, 20 mg atom and THF, 50 ml were

stirred at 0 °C for ca. 8 h. *tert*-Butyl chloride, 1.10 ml, ca. 10 mmol was added to the LiDBB solution at –75 to –70 °C during a period of ca. 0.25 h. The resulting red solution was stirred at –78 °C for 0.75 h and then carboxylated. The acid fraction of the carboxylation mixture was isolated from the acidified with 20% sulfuric acid water layer with 5 × 100 ml methylene chloride, to give 0.82 (80%) of pure pivalic acid (NMR), which solidified immediately after being freed from the extraction solvent.

5.4. Lithium stilbene radical anion and *tert*-butyl chloride

Stilbene, 3.7 g, ca. 20 mmol, lithium chips, 0.140 g, 20 mg atom and THF, 30 ml were stirred for ca. 6 h at room temperature and the resulting solution was diluted with 20 ml of THF. *tert*-Butyl chloride, 1.10 ml, 10 mmol was added to the stirred solution of the stilbene radical anion at –75 to –65 °C. Reaction was completed by allowing the temperature to rise to –45 °C, and after stirring for ca. 1 h at ca. –60 °C the mixture was carboxylated. From the carboxylation mixture 1.9 g of a very viscous acidic product was isolated in which the odor of pivalic acid was absent. The NMR spectrum of the acidic product exhibited three signals due to *tert*-butyl groups, indicating, most probably, that it was a mixture of isomeric monoalkylated stilbene derivatives.

5.5. *tert*-Butyllithium and naphthalene

5.5.1. In the presence of triethylamine

To naphthalene, 1.3 g, ca. 10 mmol in 10 ml of dry argon saturated pentane was added *tert*-butyllithium, 6.7 ml, 1.50 M, 10 mmol in pentane and the resulting mixture stirred for ca. 16 h at room temperature. During this period of time the originally light yellow solution turned dark yellow–orange. The reaction flask was immersed in a dry ice and acetone bath and 5.0 ml of triethylamine, ca. 35 mmol, was added to the mixture via a syringe. Cooling was discontinued and the reaction mixture on stirring at room temperature for 4.5 h turned into a brownish-red solution. Stirring was continued for a total of 26 h. More triethylamine, 5 ml, was added, and after stirring for 1.5 h more the mixture was carboxylated. Usual work-up of the carboxylation mixture afforded a neutral fraction, 1.30 g and an acid fraction, 0.50 g. GC analysis of the neutral fraction indicated: naphthalene (58.7%), a mixture of 1-*tert*-butyl-1,4-dihydronaphthalene and 1-*tert*-butyl-1,2-dihydronaphthalene (2.8%) and 2-*tert*-butylnaphthalene (38.2%). Material balance 99.7%. The acid fraction was esterified with diazomethane and analyzed by gas chromatography: methyl 2-*tert*-butyl-1,2-dihydronaphthoate-1 (0.3%), methyl 1-*tert*-butyl-1,2-dihydronaphthoate-2 (51.1%), methyl 1-naphthoate (31.6%), methyl 2-naph-

thoate (2.4%), methyl 4-*tert*-butyl-1,4-dihydronaphthoate-1 (14.0%).

5.5.2. In the presence of *N,N,N',N'*-tetramethylethylenediamine

The experiment described in Section 5.5.1 was repeated with the exception that triethylamine was replaced by 2.0 ml, ca. 13 mmol of TMEDA. From the carboxylation mixture was isolated a neutral fraction, 0.35 g and an acid fraction, 1.2 g. The neutral fraction was found to be a mixture of naphthalene (84%), 2-*tert*-butylnaphthalene (15%) and 1-*tert*-butyl-1,4-dihydronaphthalene (0.7%). GC analysis of the methyl esters of the acids indicated: methyl 1-*tert*-butyl-1,2-dihydronaphthoate-2 (5.2%), methyl 1-naphthoate (55.4%), methyl 2-naphthoate (38.4%), methyl 1-*tert*-butyl-1,4-dihydronaphthoate (0.6%).

5.5.3. In the presence of tetrahydrofuran

The experiment described in Section 5.5.1 was repeated with the exception that triethylamine was replaced by 0.9 ml, ca. 10 mmol of THF. From the carboxylation mixture was isolated a neutral fraction, 0.5 g and an acid fraction, 0.6 g. The neutral fraction was a mixture of naphthalene (71%), 2-*tert*-butylnaphthalenes (26%) and 1-*tert*-butyl-1,4-dihydronaphthalene plus the corresponding 1,2-dihydro-isomer (2%). Acid fraction as methyl esters: methyl 2-*tert*-butyl-1,2-dihydronaphthoate (14.8%), methyl 1-naphthoate (39.1%), methyl 2-naphthoate (37.1%), methyl 1-*tert*-butyl-1,4-dihydronaphthoate (8.3%).

5.5.4. In the presence of magnesium 2-ethoxyethoxide

Magnesium 2-ethoxyethoxide, 4.0 g, ca. 20 mmol was dissolved in 20 ml of THF by warming and stirring under an atmosphere of argon. To the resulting solution was added at ca. –70 °C, 15 ml of 1.5 M, 22.5 mmol *tert*-butyllithium in pentane, followed by a solution of 5.2 g, 40 mmol of naphthalene in 10 ml of THF. Cooling was discontinued, the reaction mixture was stirred for 20 h at room temperature and then carboxylated. The neutral fraction from the carboxylation mixture was shown by GC analysis to be pure naphthalene, whereas the acid fraction, 1.6 g (70%) was pivalic acid.

5.5.5. 1-, 2-Hydroxymethylnaphthalenes

(a) An excess of naphthalene, 6.0 g, ca. 47 mmol in 10 ml of methylcyclohexane was metallated by *tert*-butyllithium, 21 ml, 1.5 M, 31.5 mmol in pentane by adding 3.1 ml, ca. 20 mmol of TMEDA at dry ice and acetone bath temperature. After stirring at room temperature for ca. 70 h, paraformaldehyde, 1.2 g, 40 mmol was added and the resulting mixture was stirred for ca. 48 h more. Excess naphthalene was removed by steam distillation and the non-volatile product was taken up in methylene chloride. Removal of the extraction solvent

under vacuum left 3.2 g, 61% of a 1.34:1.0 mixture of 1- and 2-hydroxymethylnaphthalenes respectively, as determined by NMR analysis.

(b) Naphthalene, 6.0 g, ca. 47 mmol, 10 ml of methylcyclohexane and 16.5 ml, 1.85 M, 30.5 mmol of *n*-butyllithium in methylcyclohexane were mixed and then cooled with a dry ice/acetone bath. TMEDA, 3.1 ml, ca. 20 mmol was added, cooling was discontinued and the mixture stirred at room temperature for 24 h. After adding 1.2 g, ca. 40 mmol of paraformaldehyde, the mixture was stirred for ca. 48 h and the product isolated as described in the previous paragraph. Yield 2.75 g, 58% of a 1.80:1.0 mixture of 1- and 2-hydroxymethylnaphthalenes respectively.

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