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Organolithium and organomagnesium compounds of the naphthalene series in organic synthesis

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Abstract. The review summarises procedures for the synthesis of organolithium and organomagnesium compounds of the naphthalene series, including binaphthyls, the properties of these compounds and their use in organic synthesis. The bibliography includes 283 references.

I. Introduction

Organometallic, primarily, lithium and magnesium, derivatives of naphthalene play an exceptionally important role in organic synthesis. In recent years, these compounds have been widely used in the synthesis of chiral binaphthyl catalysts and complex natural compounds. Of special note are various 1,8-disubstituted naphthalenes necessary for studying the *peri* effects. However, reviews of a vast literature on the synthesis of organometallic derivatives of naphthalene are lacking. Scarce data are available in monographs.[1–6] The main aim of the present review is to close this gap as regards Li and Mg derivatives of naphthalene. The review summarises data published predominantly in the last two decades. An earlier literature is cited if the corresponding data remain to be important and are of principal significance.

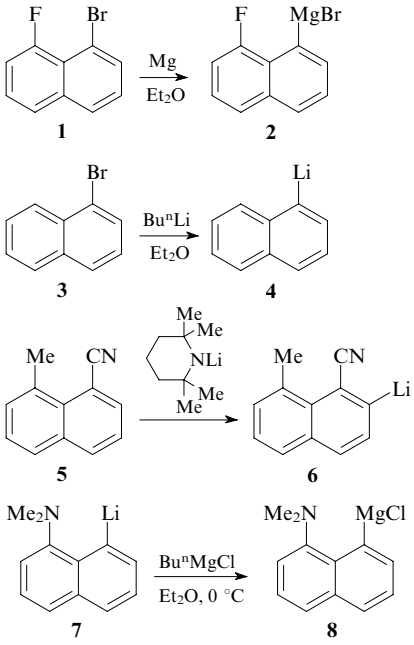
II. General features

1. Synthesis

There are four main methods for the synthesis of organolithium and -magnesium compounds of the naphthalene series: (i) the reactions of the corresponding metal with naphthyl halides, (ii) the reactions of commercial organolithium or -magnesium compounds with naphthyl halides, (iii) direct deprotonation of aromatic C–H bonds and the formation of C–M bonds (CH-metallation) and (iv) transmetallation. Examples of the reactions are presented in Scheme 1.

The first of the above-mentioned procedures is most often used for the synthesis of organomagnesium compounds (Grignard reagents), for example, **1** → **2**.[7] It was proposed to use chemical activation of magnesium with the aim of increasing the product yield.† Of various methods for magnesium activation, the method of auxiliary reagents is the most widely used procedure. This method is based on an increase in the reactivity of inert aryl halides by adding more active alkyl halide, which rapidly reacts with magnesium and activates its surface. 1,2-Dibromoethane has gained wide acceptance as an auxiliary reagent, in the presence of which even chloronaphthalenes are involved in the Grignard reaction.[8] Rieke magnesium prepared by reduction of anhydrous $MgBr_2$ or $MgCl_2$ with sodium or potassium in THF is an efficient reagent.[8,9]

Scheme 1



The synthesis of 1- and 2-lithium-substituted naphthalenes by the reactions of metallic lithium with halonaphthalenes also gives good results, although this method is nowadays rarely used and only if the presence of another stronger base, for example, of butyllithium, in the mixture is undesirable.[10]

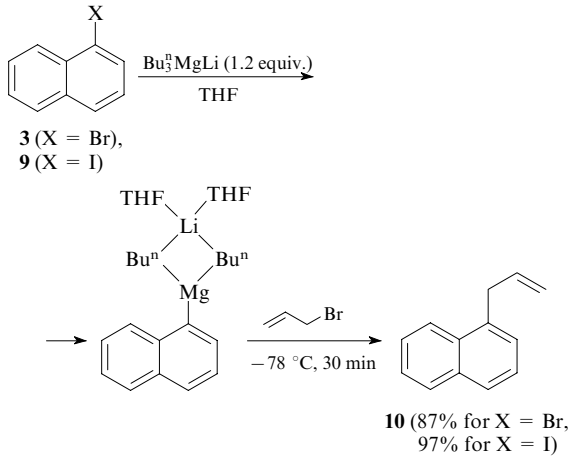
The second procedure presented in Scheme 1 (**3** → **4**) is used primarily for the synthesis of organolithium compounds. This method has gained wide acceptance due to the pioneering studies by Gilman.[11] Commercial lithium alkyls (n-, *sec*- or *tert*-butyl-

† Methods for magnesium activation were covered in detail in the review.[8]

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lithium) are generally used as organometallic reagents. In this connection, it should be kept in mind that the synthesis of lithium-substituted naphthalenes from commercial reagents used after a long storage can be accompanied by side reactions.[12] Metal–halogen exchange reactions of aryl halides can be performed with the so-called *ate*-complexes R_3MgLi instead of lithium alkyls.[13] In this case, the exchange of the bromine and iodine atoms occurs at 0 and −78 °C, respectively. Mild conditions of the exchange reactions and their high rate allow one to perform these reactions with substrates containing functional groups active toward lithium alkyls (CN, $CONR_2$, CO_2R, *etc.*). Most studies of metal–halogen exchange in aryl halides dealt with metallation of substituted phenyl halides. However, the results of the reactions with halides **3** and **9** giving rise to 1-allylnaphthalene (**10**) in high yield show that this method is also applicable to naphthyl halides.

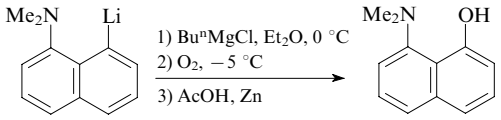


Iodine atoms are most readily involved in exchange with metals; bromine atoms are the second in activity (see, the example with compounds **3** and **9**). Attempts to perform metal–halogen exchange reactions with 1-chloronaphthalene failed.[11] Fluorine is virtually not replaced with metal.‡

Metallation based on direct ionisation of C−H bonds gives good results in two cases: (i) if the naphthalene ring contains a strong electron-withdrawing substituent, for example, the cyano group (see the synthesis of 2-naphthyllithium **6** from cyanide **5**[14,15]) and (ii) if the ring contains the so-called directing groups, which coordinate the organometallic reagent, thus lowering the activation energy of metallation (see numerous examples in Sections II.4 and III.3–III.11). Ionisation of C−H bonds is most often performed with the use of Bu^{n}Li,[16] Bu^{s}Li[17,18] or Bu^{t}Li[16] (selected references are given). Examples of the use of MeMgI,[18] MeLi,[16,18] n-C_5H_{11}Li,[19] PhLi[17,20] and a Bu^{n}Li–Bu^{t}OK mixture (the superbasic reagent LICKOR)[21–24] for this purpose were documented. Lithium amides, such as lithium tetramethylpiperidide (LTMP)[14,25–27] or lithium diisopropylamide (LDA),[18] are particularly useful when the strength of the base should be combined with its low nucleophilicity as in the transformation **5** → **6** (see Scheme 1). Compounds of the naphthyloxazoline series were subjected to metallation with ethoxyvinyllithium (EVL)[28] (reactions with other bases afforded addition products to the aromatic system, see Section III.11).[22,29,30]

Unsubstituted naphthalene is subjected to metallation with difficulty and non-selectively. For example, prolonged reflux of this compound with an excess of Bu^{n}Li in diethyl ether afforded 1- and 2-lithium-substituted naphthalenes in a ratio of 7 : 3 in a total yield of as low as 20%.[31] The use of the LICKOR system (as a stronger base) led to an increase in the total yield;[21] however, after the addition of CO_2, the reaction products contained considerable amounts of isomeric dicarboxylic acids along with small amounts of tricarboxylic acids. The reactions in high-boiling solvents, for example, in decalin (see Section II.5), lead to the addition of organometallic reagents to the naphthalene system.

Transmetallation is widely used for the introduction of heavy metals (see examples in Section III.1). In addition, this reaction is used for the transformations of organolithium compounds into their magnesium-containing analogue (**7** → **8**, Scheme 1).[32,33] In particular, the oxidative synthesis of naphthols (for example, of **11**)[34] and Kumada cross-coupling involve this reaction (see Section IV.1).



On the whole, the mechanism of formation of metal naphthalenes is analogous to that for other lithium and magnesium arenes.[5] It should be noted that the one-electron transfer plays a considerable role in metal–halogen exchange,[35] and the surface factors are of importance in the synthesis of Grignard reagents.[36]

2. Influence of solvents and coordinating additives

Diethyl ether, THF (more rarely, 2-methyltetrahydrofuran[37]), anisol, toluene, hexane, tertiary amines and their mixtures generally serve as solvents in the synthesis of organomagnesium[3] and -lithium[2,4,5] compounds of the naphthalene series.[4] The choice of the solvent is mainly determined by the ability of the metallating agents to undergo aggregation. On the whole, a decrease in aggregation leads to smaller dispersion of the negative charge in the alkyl carbanion, which increases its activity in metallation reactions. It is also important that a decrease in aggregation leads to an increase in coordinative unsaturation of the lithium ion, whose typical coordination number, like that of the magnesium ion, is four. Due to this fact, metal can interact with the adjacent groups, including C−H σ-bonds (agostic interactions),[30] thus decreasing the activation barrier to the reaction and resulting in its higher selectivity.

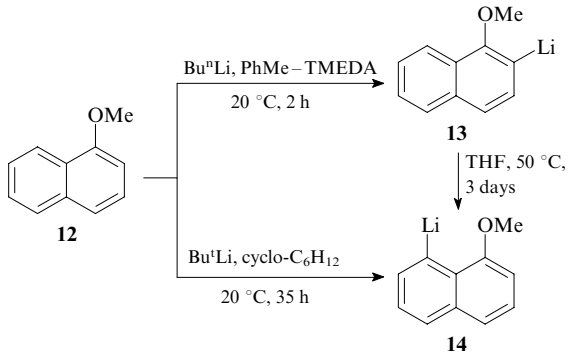
For example, Bu^{n}Li exists in a hydrocarbon medium as a hexamer, whereas it forms tetramers in diethyl ether and THF.[2,5,20,25,38] A further decrease in aggregation of Bu^{n}Li is achieved by the addition of the following coordinating additives to the reaction mixture: diazabicyclo[2.2.2]octane (DABCO),[4] hexamethylphosphoramide (HMPA),[28,39,40] *N*,*N*,*N*′,*N*′,*N*″-pentamethyldiethylenetriamine (PMDTA)[20] or tetramethylethylenediamine (TMEDA),[21,41,42] TMEDA being most widely used. The latter compound promotes the transformation of n-butyllithium into the dimeric form.[20,41,43,44] Attempts to transform Bu^{n}Li into the monomeric form failed even in THF in the presence of 1 equiv. of PMDTA.[20] In this connection, it is clear why, for example, metallation of 1-methoxynaphthalene occurs slowly and in low yield in hydrocarbons, whereas this reactions readily proceeds in the presence of TMEDA[40] or with the use of Et_2O and THF.[45,46]

3. Kinetic and thermodynamic control

The direction of metallation of naphthalenes can be influenced by the temperature. For example, the reaction of Bu^{n}Li with 1-methoxynaphthalene (**12**) in Et_2O, THF or a PhMe–TMEDA mixture at room temperature or lower temperatures produces predominantly 1-methoxy-2-naphthyllithium (**13**) (Scheme 2).[41,45] Heating of compound **13** leads to its isomerisation into more stable 1-methoxy-8-naphthyllithium (**14**). Calorimetric measurements demonstrated that the energy difference between the 1,2- and 1,8-isomers is 1.9 kcal mol^{-1} (Ref. 47) (this difference estimated by PM3 calculations[41] is twice larger, 3.95 kcal mol^{-1}). Presumably, the Li···O distance in derivative

‡ Under particular conditions, chloro- and fluoronaphthalenes can react with phenyllithium and other strong bases to form dehydronaphthalenes (see Section III.14); the reactions of metallic lithium with chloro- and fluoronaphthalenes are accompanied by reductive processes giving rise to radical anions and dianions and elimination of halogen.[2]

Scheme 2

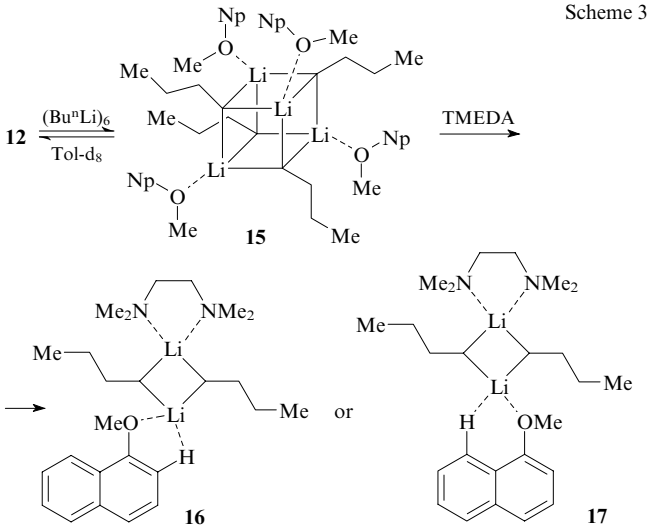


14 is shorter than that in compound **13**, which provides its higher stability.

The direction of metallation of 1-methoxynaphthalene (1-MeONp) depends also on the nature of the metallating agent and the solvent. For example, the addition of Bu^{n}Li to 1-methoxynaphthalene in toluene-d$_8$ (Tol-d$_8$) at −65 °C (or at room temperature) does not lead to lithiation;[41] instead, the reaction affords, apparently, complex **15**, in which the methoxy oxygen atom of substrate **12** is coordinated to the lithium ion (Scheme 3). This assumption is supported by downfield shifts of the protons of the MeO group ($\Delta\delta$ = 0.05 ppm) and the H-2 proton of naphthalene ($\Delta\delta$ = 0.11 ppm) in the ^{1}H NMR spectra. The addition of one equivalent of TMEDA to this complex causes reorganisation of the latter to form aggregates **16** or **17**. The latter serve as models of transition states for abstraction of the H-2 and H-8 protons, respectively. Quantum-mechanical calculations[41] demonstrated that transition state **16** lies substantially lower than transition state **17**, metallation rather than complexation being the rate-determining step of the process. These conditions are referred to as the kinetic control.[41]

Metallation of 1-methoxynaphthalene with *tert*-butyllithium proceeds more slowly and affords exclusively 8-lithium derivative **14** (see Scheme 2). In this case, the NMR spectra did not reveal complexation. Nevertheless, it is hypothesised that the formation of *peri*-complex **17** does occur but very slowly, and this complex is present in solution at an insignificant equilibrium concentration. It is the formation of complex **17** that is the rate-determining step, whereas metallation of the C−H bond occurs rather rapidly. This assumption is evidenced by the fact that the kinetic isotope effect was not observed in the reaction of Bu^{t}Li with a mixture of 8-D- and 8-H-methoxynaphthalenes, whereas the isotope effect in 2-metallation of a mixture of 2-D- and 2-H-methoxynaphthalenes

Scheme 3



Np is 1-naphthyl.

in the Bu^{n}Li – TMEDA system is as high as 15±3. These conditions were classified as the thermodynamic control conditions. In the reaction with 1-methoxynaphthalene, *sec*-butyllithium behaves as Bu^{n}Li.[41]

4. Influence of directing groups

As a rule, substituents in the naphthalene ring, particularly, those containing heteroatoms direct metallation to the *ortho* or *peri* position or, more commonly, simultaneously to both positions. These substituents are called directing groups. The methoxy group in compound **12** provides a classical example. Data on other directing groups are summarised in Table 1. The directing effect of the group is determined by the following two main factors: (i) the ease of coordination of this group to the organometallic reagent determining its orientation for deprotonation, and (ii) the electron-withdrawing properties of this group resulting in an increase in CH-acidity of the adjacent protons.

Only a few directing groups promote selective *peri*-lithiation. Among them are primarily dialkylamino and dialkylaminomethyl groups. This is not surprising taking into account the relatively low electronegativity of the nitrogen atom and a weak 'acidifying' ability of such groups (see also selective *peri*-lithiation of 1-naphthyllithium, Section II.8). To the contrary, due to a high electronegativity, substituents containing the carbonyl group (OCONR$_2$ or CONR$_2$) facilitate the replacement with metal primarily of the

Table 1. Yields of the *peri* and *ortho* isomers produced in the reactions of electrophiles with lithiated 1-R-naphthalenes.

R	Metallation conditions	Electrophile	Yield (%)		Ref.
			peri	*ortho*	
OH	Bu^{t}Li, tetrahydropyran (THP), 20 °C	Me_2S_2	50	19	48
OMe	Bu^{n}Li, Et$_2$O – n-C$_6$H$_{14}$, 20 °C	CO_2	8	20	45, 49
OMe	Bu^{n}Li, Et$_2$O – n-C$_6$H$_{14}$ – TMEDA, 20 °C	CO_2	0.4	60	45
OMe	Bu^{t}Li, n-C$_5$H$_{12}$ – cyclo-C$_6$H$_{12}$, 20 °C	CO_2	19.4	0.6	45
OMe	LICKOR, THF, −78 °C	D_2O	0	92	22
OCH_2OMe	LICKOR, THF, −78 °C	D_2O	0	95	22
$(OCH_2)_2CH_2SiMe_3$	Bu^{n}Li, Et$_2$O, 20 °C	Me_3SiCl	0	87	50
$OCONEt_2$	Bu^{s}Li, TMEDA – THF, −78 °C	MeI	0	90	51
NH_2	Bu^{n}Li, Et$_2$O	CO_2	20	0	52
NMe_2	Bu^{n}Li, Et$_2$O, 20 °C	DMF	76	0	34
CH_2NMe_2	Bu^{n}Li, Et$_2$O – n-C$_6$H$_{14}$, 20 °C	Ph_2CO	60	6	53
$CH(OMe)_2$	Bu^{t}Li, Et$_2$O, −78 to 0 °C	MeI	27	13	54
CH(NEt$_2$)OLi	Bu^{n}Li, C$_6$H$_6$, refluxing	MeI	2	33	54
$CONEt_2$	Bu^{s}Li, TMEDA – THF, −78 °C	Me_3SiCl	0	80	25
$CONPr^i_2$	Bu^{s}Li, THF, −78 °C	D_2O	0	93	16

ortho-protons. Changes in the reaction conditions can substantially influence the direction of metallation. For example, the reaction of Bu^nLi or Bu^tLi with 1-methoxynaphthalene in the presence of TMEDA affords predominantly the 2-Li derivative, whereas the reaction of compound **12** with Bu^tLi in a purely hydrocarbon medium (n-pentane – cyclohexane) produces a mixture of the 8-Li and 2-Li isomers in a ratio of 97 : 3, although the total yield of the products is at most 20% (see Table 1).

The hierarchy of the directing groups taking into account, in particular, their relative directing ability and stability to organometallic reagents was discussed in the review [25] for compounds of the benzene series.

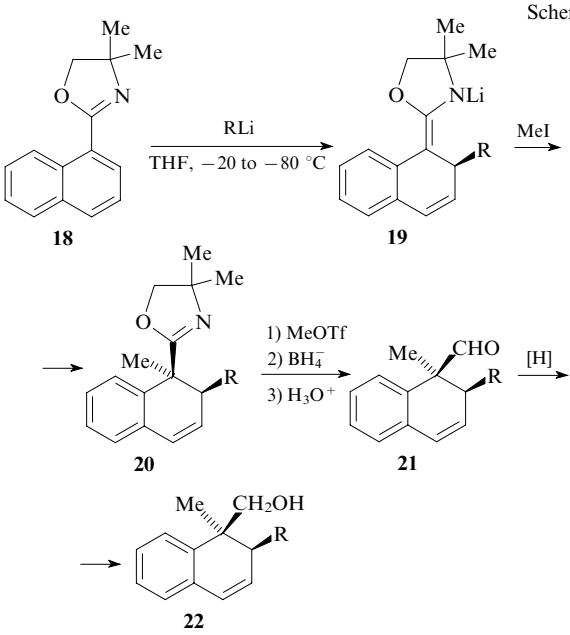
5. Side reactions

The character of side reactions substantially depends on the procedure for the synthesis of organometallic compounds. For example, CH-metallation of naphthalenes containing electron-withdrawing substituents in the naphthalene moiety leads predominantly to the addition of the metallating agent to the aromatic system. Naphthyloxazolines provide a typical example.[12, 19, 55] For instance, (1-naphthyl)oxazoline **18** reacts with lithium alkyls in THF at low temperature to form azaenolates **19**, which give oxazoline derivatives of 1,2-dihydronaphthalene **20** (generally, as the only diastereomer) in 60% – 99% yields after the addition of iodomethane.[12] This reaction can be used for the stereospecific synthesis of optically active derivatives of hydrogenated naphthalenes, in particular, of aldehydes **21** and alcohols **22** (Scheme 4).

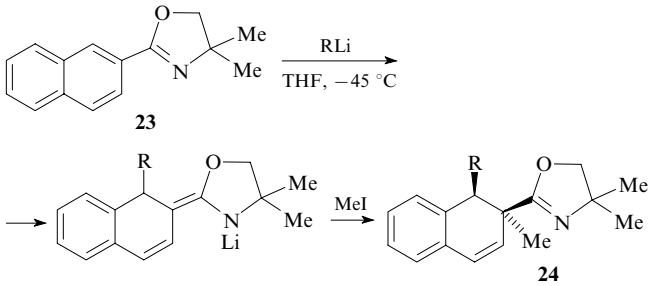
The procedure for the preparation of lithium alkyls is responsible for whether or not these transformations occur successfully. For example, the addition of commercial or long-stored RLi occurs slowly and ambiguously. The best results were obtained in the reactions with lithium alkyls prepared *in situ* by treatment of methyllithium with the corresponding stannanes R_4Sn. Apparently, this is associated with the formation of the *ate*-complex $R_4Sn \cdot MeLi$, in which the nucleophilicity of alkyl anions is substantially higher. In these transformations, lithium dialkylamides,[56, 57] lithiosilane ($PhMe_2SiLi$) [58] or vinyllithium [59] can be used instead of lithium alkyls.

(2-Naphthyl)oxazoline **23** behaves analogously to the 1-isomer, the attack of the nucleophile occurring exclusively on position 1 of the naphthalene ring. Methylation of intermediate azaenolate affords the oxazoline derivative of dihydronaphthalene **24**.[12, 55, 56]

Scheme 4

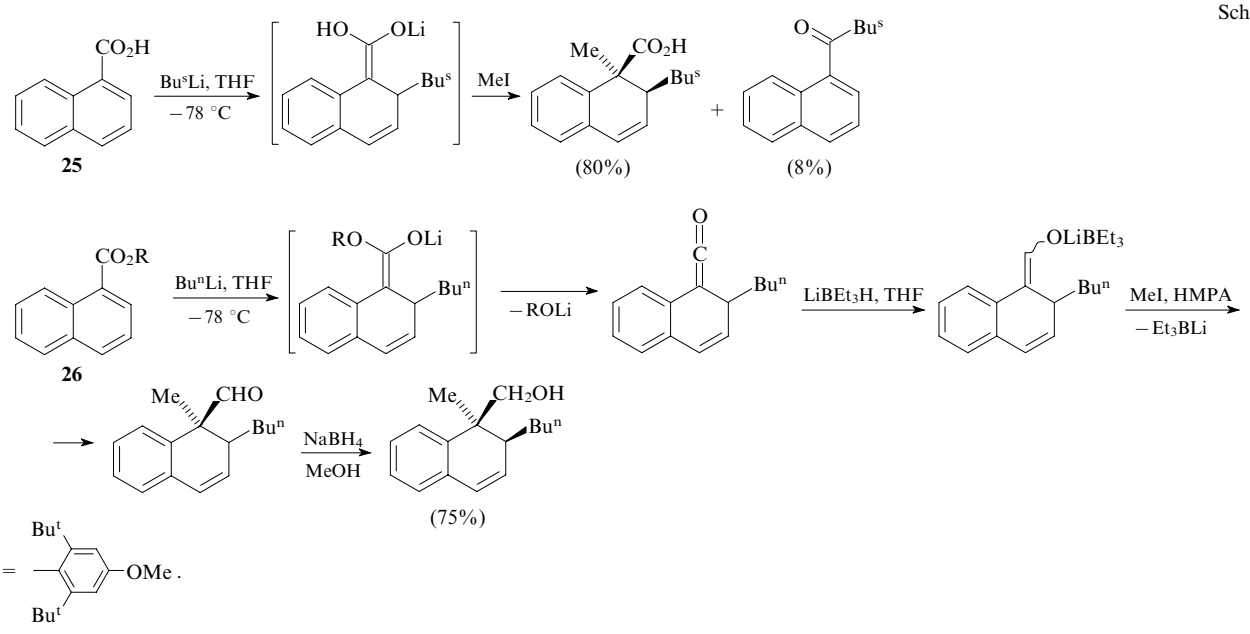


R = Me, Bu^n, Bu^s, Bu^t, $CH_2{=}CHCH_2$, $CH_2{=}CMe$, $PhCH_2$, $PhC{\equiv}CCH_2$.

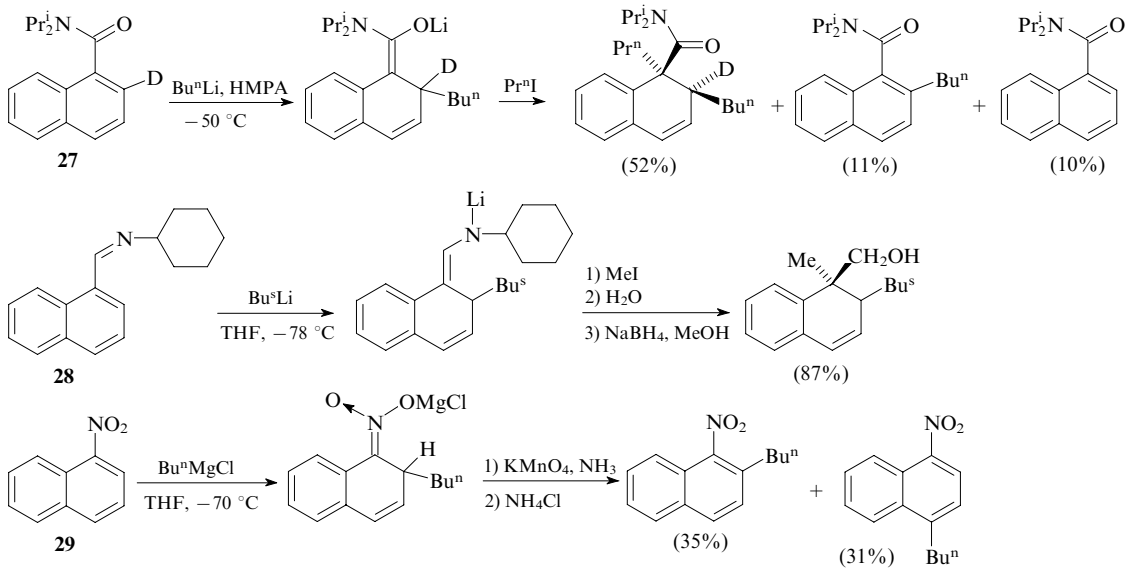


The CO_2H,[60] CO_2R, COR,[61–64] $CONR_2$,[12, 16] $CH{=}NR$,[65–67] NO_2,[68–70] SO_2R [71] and BR_2 groups [72] also promote the addition of metallating agents to the naphthalene π-system. Selected examples of the addition of metallating agents to naphthalene derivatives **25** – **29** are shown in Scheme 5. In essence, the carboxamide group is the only electron-withdrawing

Scheme 5



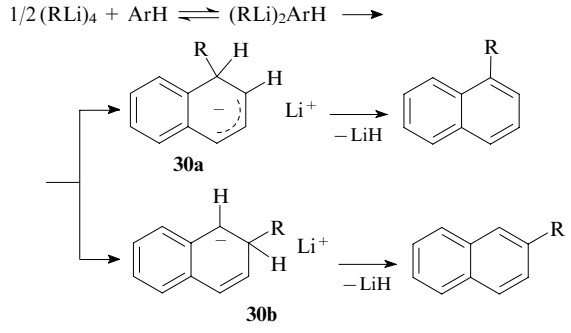
Scheme 5 (continued)



substituent providing a rather high percentage of metallation (for more details, see Section III.10).[16, 25, 73, 74]

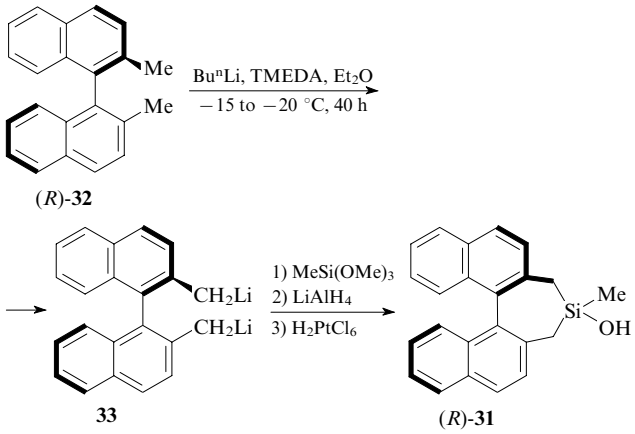
At high temperature, alkyllithium reagents can add to unsubstituted naphthalene.[75–77] For example, heating of a mixture of equimolar amounts of naphthalene and Bu^nLi, Bu^sLi or Bu^tLi (decalin, 20 h) at 165 °C afforded the corresponding monoalkylnaphthalenes in 15%, 20% or 30%–45% yields, respectively, the replacement occurring predominantly (> 90%) at the α position. The reaction with Bu^tLi additionally produces di(*tert*-butyl)naphthalene (30%–50%). Kinetic measurements led to the conclusion that alkylation is preceded by the rapid formation of the $(RLi)_2ArH$ complex, which is slowly transformed into adducts **30a** and **30b**. At high temperature, the latter undergo fast aromatisation accompanied by elimination of lithium hydride to form 1- and 2-alkylnaphthalenes (Scheme 6).

Scheme 6

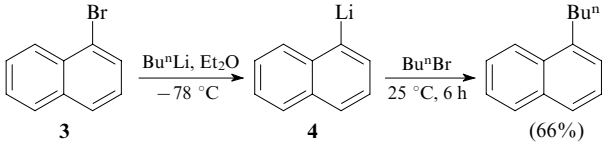


Let us mention other side reactions, which will be considered below. For example, the activated MeO and Me_2N groups in naphthalene derivatives can be replaced with a metallating agent (see Sections III.8 and III.11).[78, 79] In the presence of a halogen atom (Br[27, 80] or F[81]) in the *ortho* position with respect to the metal atom, the corresponding aryne can be formed (see Section III.14). In addition, when preparing organometallic compounds, it should be remembered that these compounds can undergo protolysis under the action of the solvent or the reagent (for example, of acetone[82]).

Metallation of alkylnaphthalenes can give also benzyl-type anions, many of which are of interest on their own. For example, organosilicon compound **31** was prepared from 2,2′-dimethyl-1,1′-binaphthyl (**32**) through the intermediate formation of dilithium derivative **33**.[25, 83–85]



In the synthesis of lithium-substituted naphthalenes by metal–halogen exchange, the products can undergo alkylation with the resulting alkyl halide.[86–88] For example, 1-naphthyllithium (**4**), which was prepared by treatment of 1-bromonaphthalene with butyllithium at low temperature, is transformed at room temperature into 1-butylnaphthalene in good yield.[87]



The Schlenk equilibrium is characteristic of the Grignard reagents:[3]

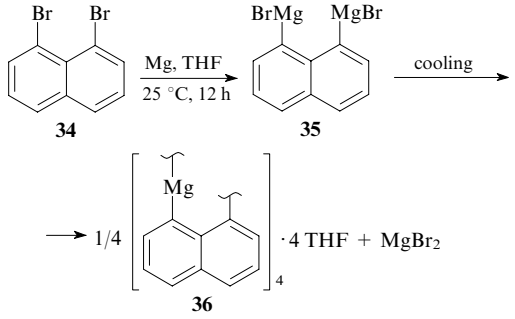
$$2\,RMgX \rightleftharpoons R_2Mg + MgX_2.$$

For example, the reaction of 1,8-dibromonaphthalene (**34**) with magnesium in THF produces 1,8-di(bromomagnesio)naphthalene (**35**), which is transformed into tetramer **36** upon cooling of the solution. The structure of the latter compound was established by ^1H and ^{13}C NMR spectroscopy and X-ray diffraction.[37] The reaction of compound **35** with D_2O produces 1,8-D_2-naphthalene in a quantitative yield, and the reaction of this compound with an excess of Me_3SnCl gives mono- and 1,8-bis(trimethylstannyl)naphthalenes.[37, 89]

Table 2. Selected geometric parameters of lithium-substituted naphthalenes and comparison with lithium-substituted benzenes (X-ray diffraction data).

Compound	Substituents in the aromatic moiety	Ligand	CSD refcode	Bond lengths and distances /Å		Angle /deg		Ref.
				d (see [a])	δ (see [b])	Li–C–Li	α (see [c])	
4	1-Li	TMEDA	HIGQUJ	2.206; 2.246	0.578; 1.845	71	83	
7	8-Li, 1-NMe_2	THF	QOYZOT	2.207; 2.223	0.373; 1.052	64	39	91
7	8-Li, 1-NMe_2	Et_2O	–	2.224; 2.232	–	–	–	92
12	8-Li, 1-OMe	THF	QESQUA	2.162; 2.231	0.284; 1.689	66	63	28
37	2-Li, 1-$CONPr^i_2$	THF	QOGBET	2.162; 2.389	0.032; 1.870	70	54	93
38	–	–	GIBTOA	2.216; 2.247	0.249; 0.527	74	15	94
39b	–	–	PUDLUV	2.322; 2.242	1.022; 1.366	63	90	95
40	2-$CONPr^i_2$	Et_2O	QOGBAP	2.176; 2.303	0.371; 1.604	67	57	93

[a] *d* Are the C–Li bond lengths; [b] δ is the deviation of the lithium atom from the plane of the aromatic ring; [c] α is the angle between the plane of C_2Li_2 and the plane of the naphthalene (or benzene) ring.

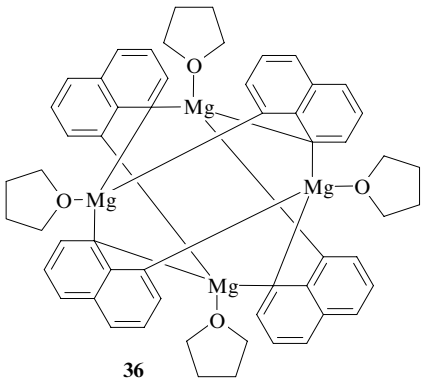


Gilman and Brannen [90] found that treatment of 1-naphthyllithium or 1-naphthylmagnesium bromide with various electrophiles, for example, with $SiCl_4$ or CO_2, often affords 1,1′-binaphthyl and perylene as by-products in low yields (< 3%). Presumably, naphthalene–naphthalene coupling occurs according to the free-radical mechanism and is associated with one-electron oxidation of metal naphthalenes.

There are many other specific side transformations, which depend on the nature of the substrate, the metallating agent and the reaction conditions. These transformations are considered below as needed.

6. Crystal structures of organometallic compounds

The Cambridge Structural Database (CSD, February 2005 release) contains data on one organomagnesium derivative of naphthalene **36** (PEFXIH) and four lithium-naphthalenes (Table 2, Fig. 1). Compound **36** is a tetranuclear cluster with the symmetry S_4. The magnesium atoms form a distorted tetrahedron.



Each naphthalene fragment is located above one of the tetrahedron faces and is bound to three Mg atoms by two *peri*-carbon atoms. One carbon atom forms a σ-bond with the Mg atom, and another carbon atom forms a three-centre two-electron bond with two other Mg atoms. Each Mg atom is additionally coordinated by one THF molecule (standard Grignard reagents are coordinated by two solvent molecules). The crystals are stabilised by a large number of disordered solvent molecules. In the absence of the latter (for example, upon evacuation), crystals are destroyed.

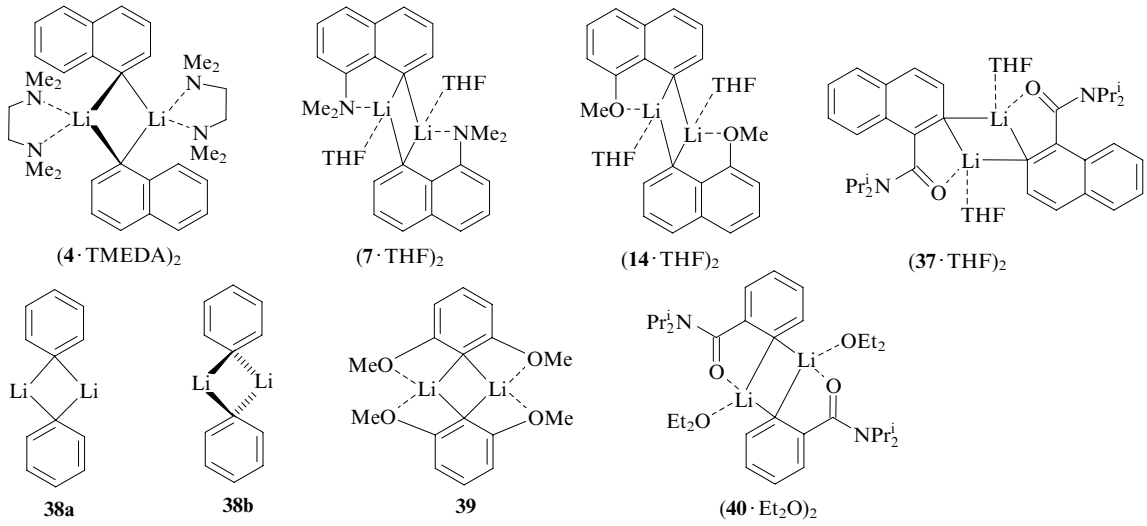


Figure 1. Schematic representation of dimeric lithium-substituted naphthalenes and benzenes.

In crystals, all lithium-substituted naphthalenes have a dimeric structure (see Fig. 1). Dimerisation occurs due to coordination of the Li atoms by two *ipso*-carbon atoms, resulting in the formation of the rhomboid quasi-ring C_2Li_2. Both solvent molecules (THF, Et_2O or TMEDA) and the chelating groups present in the ring [NMe_2 (**7**), MeO (**14**) or $CONR_2$ (**37**)] can serve as two other ligands for Li. In the dimer $(\mathbf{4}\cdot TMEDA)_2$, whose naphthalene ring contains no chelating groups, the α angle is nearly equal to 90 degrees (83°). Intramolecular chelation leads to a substantial decrease in this angle (see the data for dimers **7**, **14** and **37**, Table 2) and a decrease in the deviation of the Li atoms from the plane of the aromatic rings. In each dimer, the naphthalene fragments are virtually coplanar. In all lithium-substituted naphthalenes, the C—Li bond length varies only slightly (2.2–2.3 Å). These tendencies are typical also of phenyllithium (**38**) and its derivatives **39** and **40**. However, it should be noted that calculations (MNDO)[96] performed for the nonsolvated dimer $(PhLi)_2$ in the gas phase demonstrated that 'planar' structure **38a** is more favourable than 'perpendicular' structure **38b**.[97]

7. NMR spectra

One-dimensional ^1H, ^{13}C and ^6Li NMR spectra and two-dimensional ^1H-^1H (COSY), ^{13}C-^1H and ^6Li-^1H (HOESY) spectra were measured for a number of lithium-substituted naphthalenes.[20,41,98] All signals were unambiguously assigned based on the analysis of cross-peaks. As can be seen from Table 3, in the ^1H NMR spectra of complex $\mathbf{4}\cdot TMEDA$, the H-2 (8.57 ppm) and H-8 (8.47 ppm) protons are the most deshielded because of their close proximity to the electropositive substituent (the lithium atom). This tendency persists in the ^1H NMR spectra of 1-methoxy-2-naphthyllithium (**13**) and 1-methoxy-8-naphthyllithium (**14**), in which the H-3 (in **13**) and H-2 (in **14**) protons are the most deshielded. Analogous conclusions can be drawn based on ^{13}C NMR spectra (Table 4), the metallated carbon atom resonating at the lowest field. The ^1H and ^{13}C NMR spectroscopic data were used for the determination of the degree of aggregation of lithium-substituted naphthalenes in solution and for the elucidation of the mechanism of lithiation. For example, the ^{13}C NMR spectrum of 1-methoxy-8-naphthyllithium (**14**) in THF-d_8 at −100 °C shows a signal for C-8 as a septet with the spin–spin coupling constant $^1J(^{13}C, ^7Li) = 19.3$ Hz. Taking into account the nuclear spin of the ^7Li isotope ($I = 3/2$), this is evidence that the dimeric structure $(\mathbf{14}\cdot THF)_2$ observed in the crystals is retained in solution.

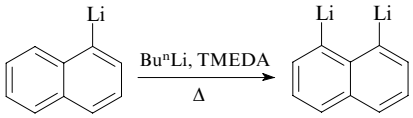
The NMR method was successfully used for the explanation of the direction of metallation of 1-methoxynaphthalene (**12**) and 1-naphthyllithium (**4**) giving rise to naphthylene-1,8-dilithium. The ^1H NMR spectrum of the complex $\mathbf{4}\cdot MeLi$ is indicative of a stronger deshielding of the H-8 proton compared to H-2 (unlike the free 1-naphthyllithium molecule).[98]

8. Quantum-mechanical calculations

Almost all quantum-mechanical calculations for Li and Mg derivatives of naphthalene were performed with the aim of explaining the regioselectivity of lithiation of naphthalenes.[29,30,98–101] The optimal structures and the energies of isomeric lithium-substituted naphthalenes, primary substrate–metallating agent complexes and the corresponding transition states were calculated. Calculations were performed predominantly with the use of the semiempirical MNDO method.

Schleyer and co-workers[98] came up with one of the most fruitful ideas. They postulated the existence of agostic interactions between the coordinatively unsaturated lithium atom and σ electrons of the adjacent C—H bonds in the transition state of lithiation.[30] These interactions should lead to an elongation of the C—H bond and an increase in the positive charge on the hydrogen atom that is replaced. These parameters can easily be calculated and serve as an indication of the direction of metallation.

Let us consider lithiation of 1-naphthyllithium (**4**) giving rise exclusively to naphthylene-1,8-dilithium (**41**) as an example.[98]



4 **41**

An analysis of the optimised structure of the complex $(\mathbf{4}\cdot EDA)_2$ (EDA is ethylenediamine) did not explain the pathway of this reaction and even, on the contrary, provided evidence that 2-metallation is preferable. Quantum-chemical calculations combined with experimental observations were used to resolve these contradictions. It was found that the addition of Bu^{n}Li to the dimer $(\mathbf{4}\cdot TMEDA)_2$ is accompanied by heat evolution but does not lead to the immediate formation of dilithium derivative **41**. For this purpose, it is necessary to perform subsequent prolonged heating of the reaction mixture. This suggests that repeated lithiation occurs inside the complex between 1-naphthyllithium

Table 3. ^1H NMR spectra of selected lithium-substituted naphthalenes.

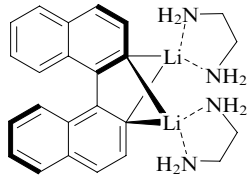
Compound	Solvent	T /°C	δ (multiplicity of the signal, J /Hz)							Ref.
			H-2	H-3	H-4	H-5	H-6	H-7	H-8	
4·TMEDA	C_6D_6	22	8.57 (d, 5.8)	7.56 (dd, 8.0; 5.8)	7.81 (d, 8.0)	7.93 (d, 8.0)	7.47 (ddd, 8.0; 6.8; 1.2)	7.57 (ddd, 8.0; 6.8; 1.2)	8.47 (d, 8.0)	98
13	THF-d_8	32	4.05 (s)	8.12 (d, 7.3)	7.39 (d, 7.3)	7.73 (d, 8.0)	7.24 (dd, 7.3; 8.5)	7.33 (dd, 8.2; 8.5)	8.08 (dd, 8.2)	41
14	THF-d_8	32	8.15 (d, 5.8)	7.18 (dd, −)	7.35 (d, 7.7)	7.27 (d, 8.1)	7.12 (dd, −)	6.68 (d, 7.6)	3.85 (s)	41

Table 4. ^{13}C NMR spectra of selected lithium-substituted naphthalenes.

Compound	Solvent	T /°C	δ										Ref.
			C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10	OMe	
4·TMEDA	C_6D_6	24	195.0	140.4	124.4	124.2	129.2	123.8	122.7	138.3	148.7	133.8	–	98
13	THF-d_8	32	163.0	163.0	141.0	119.3	126.3	121.6	122.3	120.1	124.0	133.7	58.1	41
14	THF-d_8	32	185.2	139.1	125.1	122.9	128.8	123.2	101.4	161.0	139.6	139.4	55.2	41

and the metallating agent (the role of such complexes in metallation reactions was discussed in the review [102]). The structure of the complex with MeLi optimised by the MNDO method actually confirmed that the C-8 – H-8 bond in this compound is activated toward metallation to a greater extent than the C-2 – H-2 bond.

These calculations demonstrated that lithiation of 1-naphthol occurs predominantly at position 8; of 2-naphthol, predominantly at position 3; of 1,3-, 1,4- and 1,5-binaphthols and 1,4,5-trinaphthol, exclusively at the *peri* position adjacent to the OH group (for the reaction conditions, see Section III.3).[29,30] As mentioned above, 1-methoxynaphthalene (**12**) is lithiated predominantly at the C-2 atom under kinetically controlled conditions, whereas lithiation occurs at the C-8 atom under the thermodynamically controlled conditions. In the former case, this is due to the fact that the transition state corresponding to metallation at the C-2 atom is energetically more favourable (by $\sim$6 kcal mol^{-1}). The latter case is attributed to higher stability of the 8-lithium derivative (by $\sim$4 kcal mol^{-1}).[41] The energies of the 2- and 8-lithium derivatives of 1-aminonaphthalene were estimated by the *ab initio* method.[101] The relative stabilities of the structures of **42** · EDA_2 with the perpendicular and parallel orientation of the naphthalene moieties and the rotation barrier about the C-1 – C-1′ bond were evaluated by the MNDO method.[99,100]



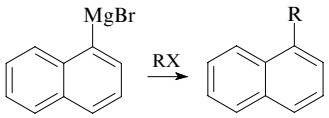
42 · EDA_2

III. Synthesis and reactions of naphthylmetals

Organomagnesium compounds of the naphthalene series have found use immediately after the historical discovery by Grignard. As early as 1903, Gattermann [103] synthesised 1-naphthaldehyde by the reaction of ethyl formate with α-naphthylmagnesium bromide. Beginning in 1930s, lithium-substituted naphthalenes came into use along with Grignard reagents. In the present review, a vast literature on these compouns is systematised according to the type of additional substituents in the ring. As a rule, these substituents have a strong effect not only on the synthesis of organometallic derivatives but also on their reactivity. All reactions of magnesium- and lithium-substituted naphthalenes can, in essence, be classified into four main types: (1) reactions with C-electrophiles, (2) reactions with heteroelectrophiles, (3) oxidation reactions and (4) cross-coupling reactions. Since the latter reactions are of particular importance, they are considered in the special section (Section IV). As for the difference in the reactivity, there are no general rules, which allow one to decide whether lithium or magnesium naphthalenes are reagents of choice. In many cases, both these types of naphthylmetals give comparable results. However, there are also many examples when the reactions better proceed with either magnesium or lithium derivatives.

1. Naphthylmetals based on naphthalene and alkylnaphthalenes

General feautures of the procedures for the synthesis of Li and Mg derivatives of naphthalene were considered in Section II.1. The reactions of these derivatives with various alkylating and carbonyl-containing reagents are the most abundant. For example, the reaction of 8-methyl-1-naphthyllithium with dimethyl sulfate produces 1,8-dimethylnaphthalene in 90% yield.[104] Analogously, 1-naphthylmagnesium bromide (**43**) is smoothly alkylated with dialkyl sulfates and S_N1-active reagents to form compounds **44a** – **f**.



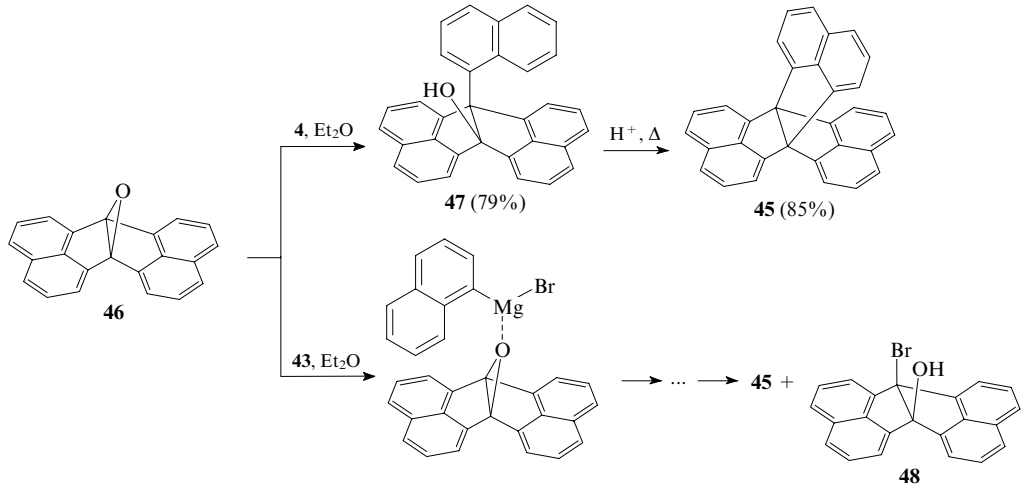
43 **44a** – **f**

RX	Product **44**	R	Yield (%)	Ref.
Me_2SO_4	**a**	Me	68	105
Et_2SO_4	**b**	Et	60	105
CH_2=C(Me)CH_2Cl	**c**	CH_2=C(Me)CH_2	85	105
1-NpCH_2Br	**d**	1-NpCH_2	–	106
1-Fc$CH_2N^+Me_2EtBr^-$	**e**	1-FcCH_2	51	107
1-AdBr	**f**	1-Ad	2	108

The reaction of 2-methyl-1-naphthyllithium with ethylene oxide produces 1-(2-hydroxyethyl)-2-methylnaphthalene (67%).[109] Trisnaphtho[3.3.3]propellane (**45**) was synthesised by the reaction of 1-naphthyllithium (**4**) with epoxide **46** (Scheme 7).[110] This reaction proceeds through the intermediate formation of alcohol **47**. The reaction with 1-naphthylmagnesium bromide (**43**) instead of the Li derivative affords a mixture of products **45** and **48** in a ratio of 1 : 1.8.

The reactions of CO_2 with 1-MgBr-, 2-MgBr- or 1,5-$(MgBr)_2$-containing naphthalenes produce the corresponding naphthalenecarboxylic or -dicarboxylic acids in good yields.[111] The reactions with lithium-substituted naphthalenes instead of Mg derivatives give comparable results.[11,112]

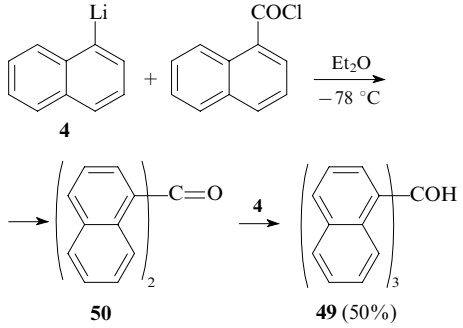
Scheme 7



Considerable study was given to formylation of magnesium- and lithium-substituted naphthalenes (data were briefly summarised in the review [113]). 2-(*N*-Methyl-*N*-formyl)pyridine,[114] *N*-methylformanilide,[46, 115] *N*-formylpiperidine,[116] *N*-formylmorpholine [117] and DMF [118–120] are generally employed as formylating agents. As a rule, the reactions proceed rapidly and under mild conditions. However, in the reactions performed with a deficiency of a formylating agent, the resulting aldehyde can react with the starting organometallic compound to give the corresponding dinaphthylmethanol. The latter fact was used in the synthesis of 1,1′- and 2,2′-dinaphthylmethanols by treatment of 1- and 2-naphthylmagnesium bromides with 0.4–1.0 equiv. of ethyl formate.[106, 121, 122]

Secondary and tertiary alcohols were synthesised by the reactions of 1-naphthylmagnesium bromides with propionic aldehyde,[105] aromatic aldehydes,[123] acetone, diethyl ketone, ethyl methyl ketone, di(1,1′-naphthyl) ketone [124] and acenaphthenequinone.[125] Analogous reactions were documented also for 2-naphthylmagnesium bromide [126] and lithium-substituted naphthalenes.[123]

Tris(1-naphthyl)methanol (**49**) was prepared by the slow addition of 1-naphthoyl chloride to an ethereal solution of 1-naphthyllithium (**4**) at −78 °C.[10]



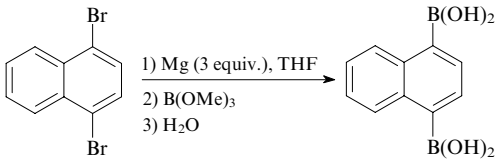
50 **49** (50%)

Tris(2-naphthyl)methanol was synthesised analogously from 2-naphthyllithium and 2-naphthoyl chloride in 56% yield.[10] Evidently, both reactions proceed through the intermediate formation of binaphthyl ketone (for example, **50**), which rapidly reacts with the starting naphthyllithium. This hinders the use of this method for the synthesis of ketones of the naphthalene series. Earlier, Blicke [121] has synthesised ketone **50** (in 40% yield) by the reaction of 1-naphthoyl chloride with 1-naphthylmagnesium bromdie.§ However, in Blicke's opinion, a procedure of choice for the synthesis of ketones is based on the reactions of organometallic compounds with an appropriate nitrile. For example, the reaction of 1-naphthylmagnesium bromide with 1-naphthonitrile produces ketone **50** in 75% yield.

The synthesis of naphthonitriles by electrophilic cyanation of lithium-substituted naphthalenes with 1-cyanobenzotriazole was documented.[127]

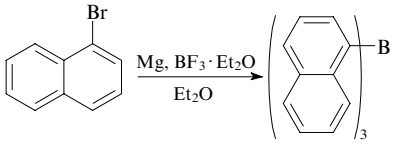
In recent years, the reactions of lithium and magnesium naphthalenes with heteroorganic compounds as electrophiles have acquired great importance. In particular, of special interest (due to the wide use of cross-coupling reactions) are naphthylboronic acids and trialkylnaphthyl stannanes, which can be prepared by the reactions with lithium or magnesium naphthalenes. For example, 1- and 2-naphthylboronic acids are generated in good yields in the reactions of triisopropyl borate with 1- and 2-lithium-substituted naphthalenes, respectively.[128] Organomagnesium compounds can also be used, for example, in the synthesis of naphthalene-1,4- (**51**) [129] and naphthalene-1,5-diboronic acids [130] from the corresponding dibromonaphthalenes.

§ Blicke failed to reproduce the earlier procedure proposed by Schmidlin and Massini [106] due, presumably, to the presence of an intolerable impurity of unconsumed magnesium.



51 (56%)

A convenient procedure was developed for the synthesis of tris(1-naphthyl)borane (**52**) by stirring a mixture of α-naphthyl bromide, magnesium and boron trifluoride etherate,[131] which does not require the special preparation of α-$C_{10}H_7MgBr$. The reaction is completed within 24 h. The ultrasonic treatment of the reaction mixture leads to a decrease in the reaction time to 30 min.[131]

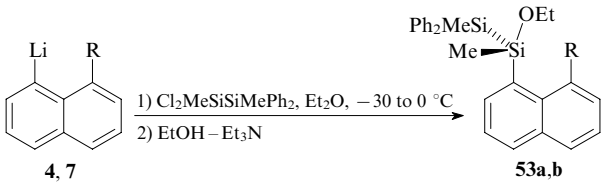


52 (91%)

Noyori and co-workers [132] used the Grignard reagent, which was prepared from 2,2′-dibromo-1,1′-binaphthyl, for the synthesis of the well-known BINAP ligand and its analogues (see Section III.15, Scheme 16).

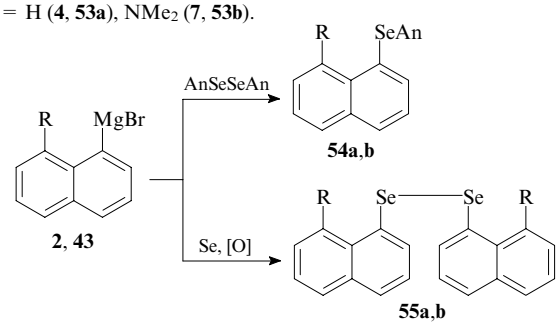
Silylation,[133, 134] selenenylation,[7, 135, 136] stannylation [37, 137] and chloromercuration [138] of lithio- and magnesionaphthalenes (Scheme 8) were documented. For example, the reaction of 1,1-dichloro-1,2-dimethyl-2,2-diphenyldisilane with 1-naphthyllithium derivatives **4** and **7** under an inert atmosphere followed by the treatment of the mixture with ethanol afforded naphthylethoxydisilanes **53a**,**b**, from which stable naphthylsilylenes were generated.[133] The reactions of naphthylmagnesium bromides **2** and **43** with di(*p*-anisyl) diselenide produce 1-(*p*-anisyl)selenylnaphthalenes **54a**,**b**.[7] The reactions with a selenium powder and oxidising agents afford dinaphthyl diselenides **55**.[7, 135] The reaction of 1,8-di(bromomagnesio)naphthalene (**35**) with an excess of trimethylchlorostannane produce a mixture of mono- (**56**) and

Scheme 8

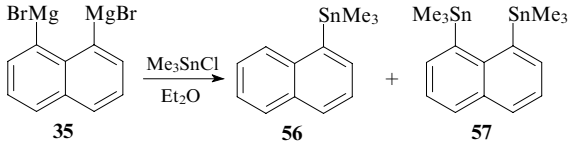


4, **7** **53a**,**b**

R = H (**4**, **53a**), NMe_2 (**7**, **53b**).

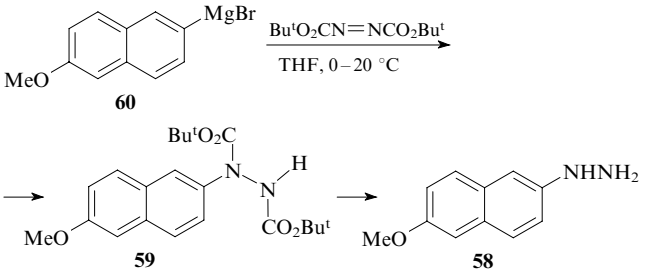


R = F (**2**, **54a**, **55a**), H (**43**, **54b**, **55b**); An = C_6H_4OMe-4.



1,8-bis(trimethylstannyl)naphthalenes (**57**) in 67% and 22% yields, respectively.[37]

There is evidence for the possibility of electrophilic amination[139] and hydrazination[140] of lithium and magnesium naphthalenes. For example, 2-hydrazino-6-methoxynaphthalene (**58**) and its precursor **59** were prepared by the reaction of Grignard reagent **60** with di-*tert*-butyl azodicarboxylate.

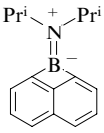
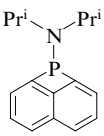
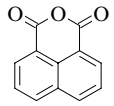
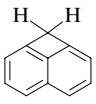
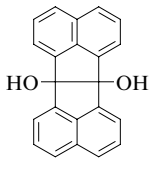
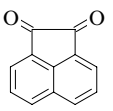
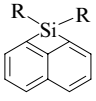
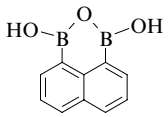
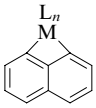
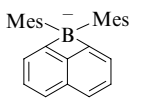


Undoubtedly, naphthalene-1,8-dilithium (**41**) is the most important reagent. This compound is regularly used in the synthesis of various 1,8-disubstituted naphthalenes and *peri*-fused heterosystems. This compound was synthesised for the first time by Letsinger[141,142] in 1962 by the reaction of butyllithium with 1,8-dibromonaphthalene (**34**) in diethyl ether at room temperature. Katz[143,144] recommended to perform the synthesis of naphthalene-1,8-dilithium with the available reagent diiodonaphthalene. Metallation of 1-bromonaphthalene or unsubstituted naphthalene with an excess of butyllithium is also a convenient procedure for the synthesis of compound **41**.[98,145–147]

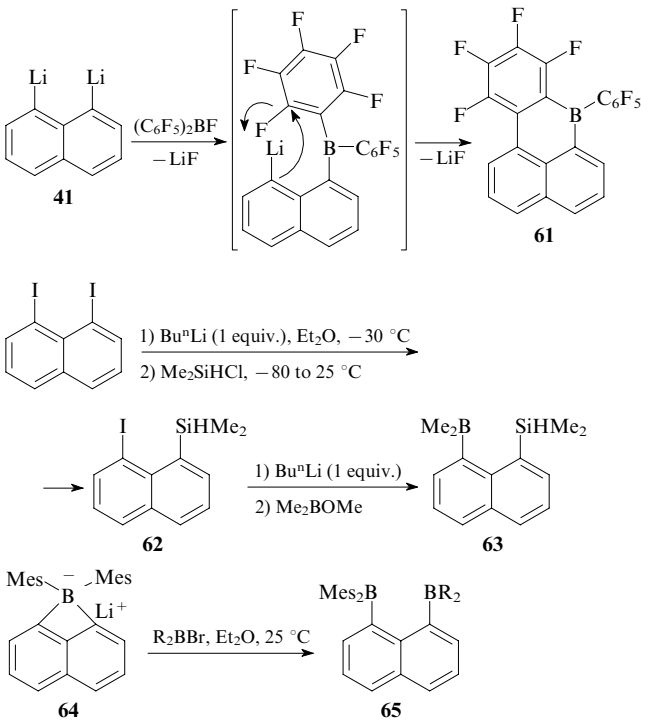
Main types of compounds prepared by the reactions of various electrophiles with naphthalene-1,8-dilithium are listed in Table 5. As can be seen from this table, all structures are symmetrical and are either 1,8-disubstituted naphthalenes or *peri*-cyclic systems. Asymmetrical compounds of this series can be synthesised by the stepwise replacement of the Li atoms in compound **41** (synthesis of unsymmetrical *peri*-cyclic compound **61**, Scheme 9),[163] stepwise lithiation–replacement of 1,8-dihalonaphthalenes (synthesis of compounds **62** and **63**)[164] or cleavage of the anionic borate ring in *peri*-fused system **64** with dialkylboryl bromides. The last original approach to the synthesis of unsymmetrical 1,8-diborylnaphthalenes **65** was developed by Gabbaï and Hoefelmeyer.[156]

Four-membered *peri*-metallacycles can be synthesised with the use of both naphthalene-1,8-dilithium and its magnesium analogue **35**. This approach was applied in the synthesis of the (1,8-Np)ML$_n$ complexes (see Table 5).[162] In this connection, it should be noted that 1,8-bis(trimethylstannyl)naphthalene (**57**) is

Table 5. Types of naphthalene derivatives prepared by the reactions of various electrophiles with naphthyl-1,8-dilithium (**41**).

Compound	Electrophile	Yield (%)	Ref.	Compound	Electrophile	Yield (%)	Ref.
					$Pr^i_2NBCl_2$	89	157
X = CPh_2OH	Ph_2CO	58	141				
$C(C_6H_4OMe\text{-}4)_2OH$	$(4\text{-}MeOC_6H_4)_2CO$	43	148		$Pr^i_2NPCl_2$	75	158
$C(C_6H_4Cl\text{-}4)_2OH$	$(4\text{-}ClC_6H_4)_2CO$	–	149				
HgCl	$HgCl_2$	89	150				
$SiMe_3$	Me_3SiCl	83	89				
$SnMe_3$	Me_3SnCl	70	89				
BMe_2	Me_2BOEt	47	143, 144				
BPh_2	Ph_2BBr	–	150				
$B(NR_2)_2$ (R = Me, Et, Pr^i)	$(R_2N)_2BBr$ (R = Me, Et, Pr^i)	–	151				
PPh_2	Ph_2PCl	–	152	X = S	S_8	35–40	159
$P(NMe_2)_2$	$(Me_2N)_2PCl$	44	153	Se	Se	18–20	159
$P(NEt_2)_2$	$(Et_2N)_2PCl$	60	154	Te	Te	8–12	159
				PPh	$PhPCl_2$	59	158
	CO_2	85	141, 145		CH_2Cl_2	18–21	160
		14	155		R_2SiCl_2 (R = CH_2SiMe_3, Bu^s)	44–70	161
				R = CH_2SiMe_3, Bu^s			
	$B(OBu^n)_3$	71	141				
	$B(OBu^n)_3$	60	142		L_nMCl_2	–	162
	Mes_2BF	39	156	L_nM = Cp_2Ti, $(Et_3P)_2Pt$, $(C_5Me_5)(Ph_3P)Ir$, $(C_5Me_5)_2Zr$			
$Li^+(THF)_4$							

Scheme 9

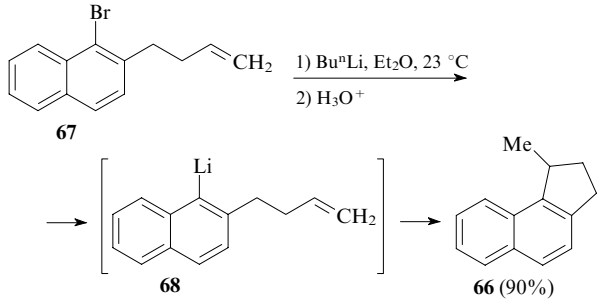


R = Me (71%), Et (91%).

more easily produced from naphthalene-1,8-dilithium (**41**)[89] than from 1,8-di(bromomagnesio)naphthalene (**35**),[37] whereas the yield of 1*H*-cyclobuta[*de*]naphthalene increases to 30% (*cf.* 18%–21%, Table 5) in the reaction starting from 1,8-di(iodomagnesio)naphthalene with the use of methylene ditoluenesulfonate as the electrophile.[160] Additional data on the use of naphthalene-1,8-dilithium in the synthesis of heteroorganic *peri*-disubstituted naphthalenes were reported in the review.[165]

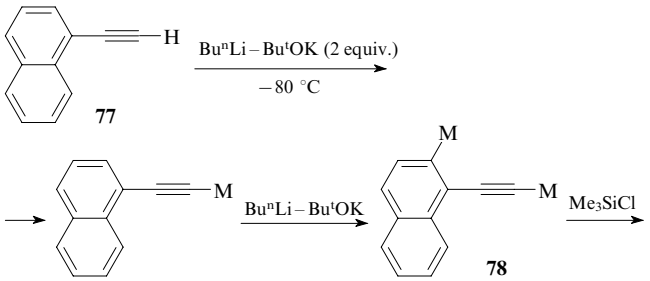
2. Naphthylmetals containing alkenyl and alkynyl groups

Lithium and magnesium derivatives of naphthalene containing alkenyl or alkynyl substituents in the naphthalene ring are scarce. The intramolecular addition of the carbanionic centre to a multiple bond is very typical of compounds containing an unsaturated group adjacent to the Li atom. The formation of benz[*e*]indane **66** in high yield from bromide **67** is a typical example.[166] The intramolecular addition in intermediate **68** occurs according to Markovnikov's rule.

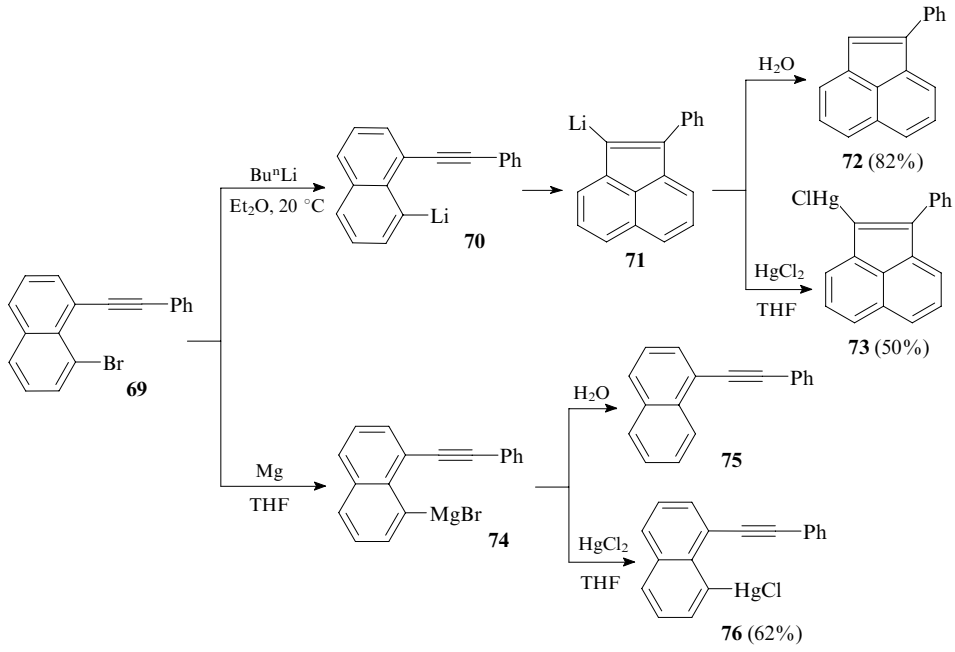


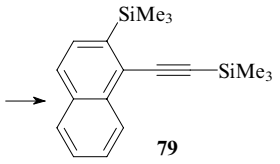
The reaction of butyllithium with 1-bromo-8-phenylethynylnaphthalene (**69**) produced 8-lithio-derivative **70**, which was isomerised to give lithium acenaphthylene **71** (Scheme 10). This reaction can be applied in the synthesis of various acenaphthylene derivatives, for example, of compounds **72** and **73**. Magnesium analogue **74** does not undergo the above isomerisation and gives compounds of the naphthalene series, for example, derivatives **75** and **76**, under the actions of electrophiles (see Scheme 10).[167]

Direct CH-metallation of ethynylnaphthalenes was studied along with metal–halogen exchange. Metallation of unsubstituted 1-naphthylacetylene (**77**) with 2 equiv. of LICKOR in a THF–hexane mixture (1 : 1) occurs exclusively at position 2 (compound **78**), as evidenced by the formation of bis(trimethylsilyl) derivative **79** in high yield after the addition of Me_3SiCl to the reaction mixture.[23]



Scheme 10

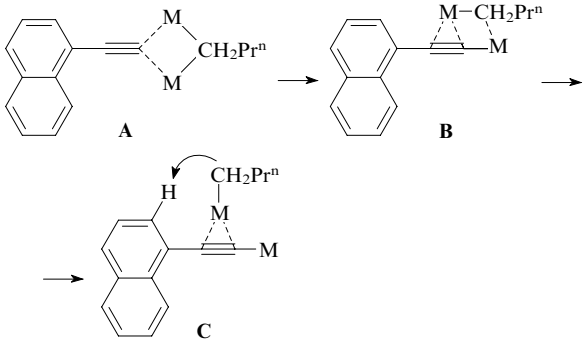




79

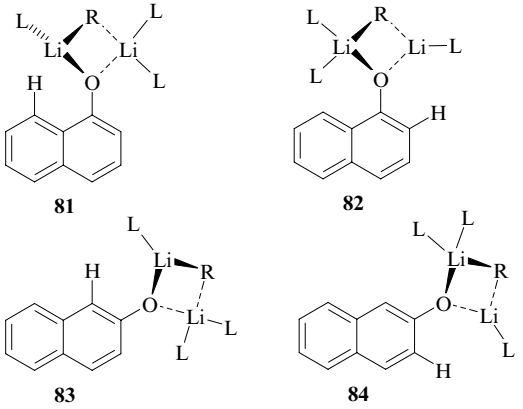
M = Li, K.

Under analogous conditions, 1-(3,3-dimethylbut-1-yn-1-yl)naphthalene (**80**) gives a mixture of metallation products, among which the 3-M derivative prevails (51%). Other isomers are distributed as follows: 4- and 5-M-substituted derivatives (in a total yield of 35%), 6- and 7-M-substituted derivatives (13%) and 2-metal derivative (1%). Interestingly, *peri*-lithiation products are absent in both cases, which is surprising in the light of the data on CH-metallation of other 1-R-naphthalenes.[23] The factors responsible for the difference in the behaviour of acetylenes **77** and **80** (as well as their benzene analogues) were studied in detail, including by theoretical methods. The *ortho*-directing effect of the metallated acetylenic group in the further metallation reaction was attributed to 'gliding' of the metallating agent along the triple bond toward the H-2 atom (**A** → **B** → **C**). It is assumed that the analogous motion toward the H-8 atom is sterically less favourable.

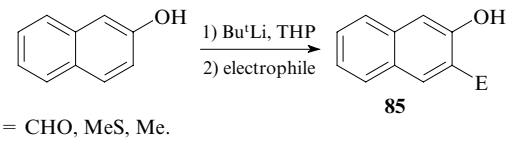


3. Naphthylmetals based on naphthols

Lithiation of naphthols with Bu^{n}Li or Bu^{t}Li occurs with different degrees of regioselectivity.[29, 30, 48] Although the precise structures of metallated species are unknown, they have presumably the structures of complex lithium naphtholates **81** – **84**.



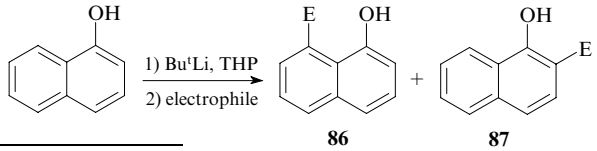
The highest selectivity is achieved in metallation of 2-naphthol, which gives only the corresponding 3-substituted derivative **85** in good yield after the subsequent treatment with *tert*-butyllithium in tetrahydropyran and an electrophile (Me_2NCHO, Me_2S_2 or MeI).[29, 48]



85

E = CHO, MeS, Me.

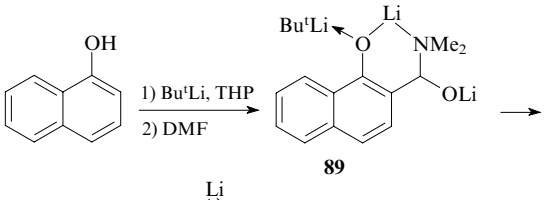
Under the same conditions, 1-naphthol gives a mixture of *peri*- (**86**) and *ortho*-lithiation products (**87**), with the former generally predominating.[48]



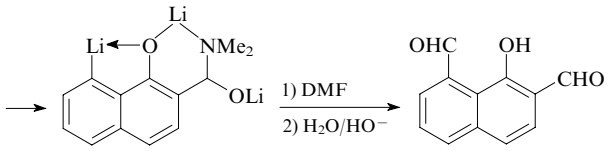
86 **87**

E	Yield (%)	
	86	**87**
CHO	40	20
MeS	50	19
Me	8	38

After metallation of 1-naphthol with a Bu^{n}Li – TMEDA system followed by the reaction with DMF, only 8-hydroxy-1-naphthaldehyde was found in 43% yield.[30] Metallation with a Bu^{t}Li – THP mixture followed by the addition of dimethylformamide afforded dialdehyde **88** (20% – 43%), which is presumably generated from intermediate α-aminoalkoxide **89** as a result of lithiation.[48]



89

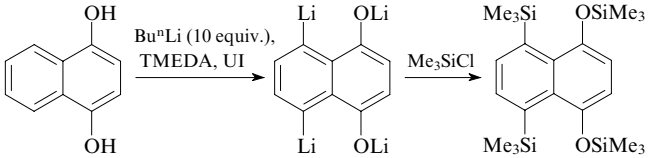


88 (20% – 43%)

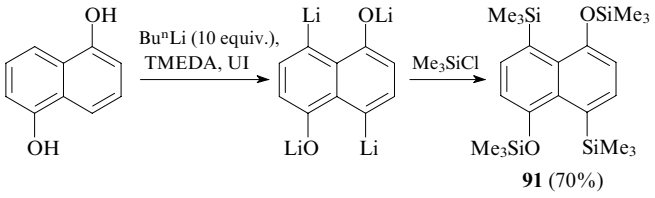
It is worthy of note that 2-naphthol does not react with n-butyllithium in TMEDA,[30] whereas the corresponding reaction in diethyl ether produces (after the addition of CO_2) 3-hydroxy-2-naphthoic acid (7%) and the starting compound (62%).[168]

The yields of substituted naphthols strongly depend on the reaction conditions. The best results were obtained in the case of the fast addition of a 2 M Bu^{t}Li solution in pentane to the concentrated naphthol solution. The theoretical interpretation of the direction of metallation of 1- and 2-naphthols is considered in Section II.8.

Lithiation of 1,3-, 1,4-, 1,5- and 1,6-dihydroxynaphthalenes and 1,4,5-trihydroxynaphthalene with a Bu^{n}Li – TMEDA system occurs exclusively at the *peri* position with respect to the 1-OH group, which was confirmed by the synthesis of the corresponding monoaldehydes in high yields. When the reaction is initiated with ultrasonic irradiation (UI), 1,4- and 1,5-dinaphthols are subjected to dilithiation, as evidenced by isolation of compounds **90** and **91** after the treatment of the reaction mixture with trimethylchlorosilane.

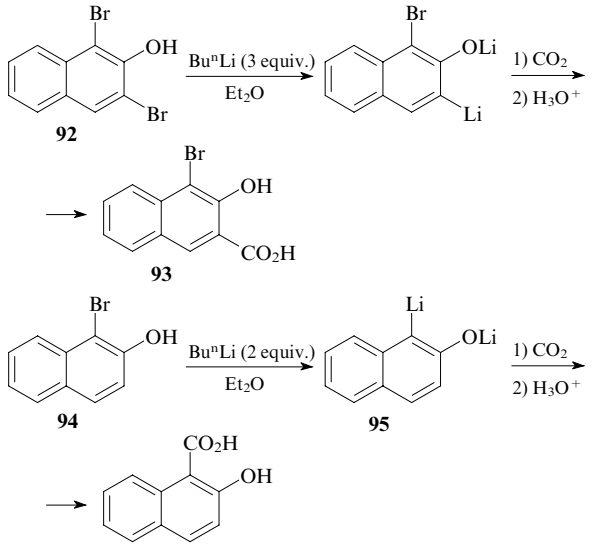


90 (75%)



91 (70%)

Metal–halogen exchange is also used for the preparation of lithium naphthols. For example, bromine at position 3 in 1,3-dibromo-2-naphthol (**92**) is replaced with lithium under the action of Bu^{n}Li, as evidenced by isolation of acid **93** after the treatment of the reaction mixture with CO_2.[169] In this case, the direction of metallation is identical to that for unsubstituted 2-naphthol. In 1-bromo-2-naphthol (**94**), metal–halogen exchange is also more preferable than metallation of the C—H bond at position 3. This allows one to prepare 1-lithium derivative **95**, which is difficult to synthesise according to other procedures (see also Ref. 170).

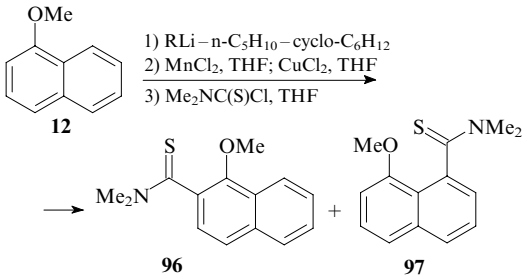


92 **93** **94** **95**

Analogous results were obtained by metallation of 4-bromo-1-naphthol and 4-, 6- and 8-bromo-2-naphthols.[169, 171] Metallation of their derivatives containing the protected OH group provides additional possibilities for the synthesis of substituted naphthols (see Section III.4).

4. Metallation of alkoxy derivatives of naphthalene

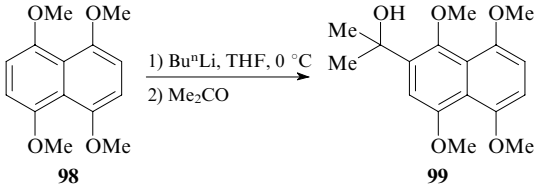
The factors determining the direction of lithiation of 1-methoxynaphthalene (**12**) were discussed in Sections II.3 and II.8. In the general case, the reaction with Bu^{n}Li or a Bu^{n}Li–Bu^{t}OK mixture occurs predominantly at position 2, whereas the reaction with *tert*-butyllithium occurs at position 8. There are contradictory data on the degree of regioselectivity of the reaction and the total yield of metallation products. For example, Shirley and co-workers [45, 49] prepared a mixture of 1-methoxy-2-naphthalene- and 1-methoxy-8-naphthalenecarboxylic acids by the reaction of 1-methoxynaphthalene with Bu^{n}Li–TMEDA–Et$_2$O–n-C$_6$H$_{14}$ and Bu^{t}Li–n-C$_5$H$_{12}$–n-C$_6$H$_{14}$ systems followed by the treatment of the reaction mixture with CO_2 in total yields of 60% and 20% in a ratio of 99:1 and 1:9, respectively. However, more recent studies [41, 170] demonstrated that the total yield of the acids in such reactions is substantially higher, whereas the regioselectivity is, on the contrary, somewhat lower. In addition to the synthesis of alkoxynaphthalenecarboxylic acids,[16, 33, 41, 169] lithium derivatives of 1-alkoxynaphthalenes were involved in H/D exchange,[41, 67] alkylation,[16] acylation,[33] trimethylsilylation,[50, 67] trimethylstannylation,[67] iodination [172] and the reactions with aldehydes.[173, 174] In some cases, when the reactions of lithium derivatives **13** and **14** with electrophiles give unsatisfactory results, good results can be obtained by transforming lithium derivatives into manganese- or copper-containing compounds. For example, the synthesis of thiocarbamoyl derivatives **96** and **97** was documented.[175]



12 → **96** + **97**

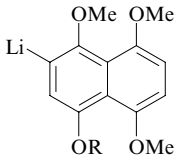
RLi	Yield (%)	
	96	**97**
Bu^{t}Li	29	60
Bu^{n}Li	79	13

The reaction of Bu^{t}Li with 1,4-dimethoxynaphthalene afforded *peri*- and *ortho*-lithiation products in a ratio of 2:1 (products were detected by transforming them into the corresponding aldehydes).[176] Lithiation of 1,4,5,8-tetramethoxynaphthalene (**98**) produced the 2-lithium derivative, which gave alcohol **99** after the treatment with acetone.



98 **99**

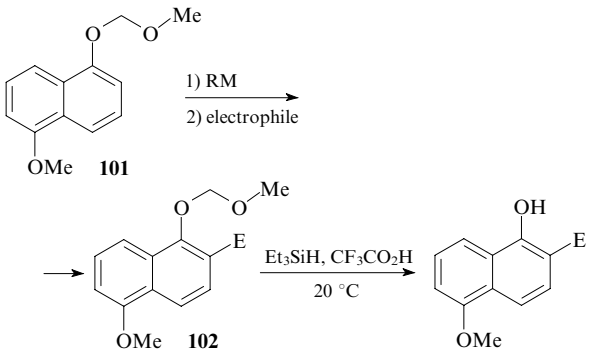
Interestingly, 2-lithium derivatives **100**, which were derived from the corresponding bromides, undergo protolysis in the presence of acetone.[82] Apparently, the protolysis rate in this case is substantially higher than the rate of formation of the corresponding alcohols due to steric effects.



100

R = PhCH$_2$, PhCH$_2$OCH$_2$, Me$_3$SiCH$_2$CH$_2$OCH$_2$ (SEM).

Unlike 1-methoxynaphthalene, methoxymethyl ether of 1-naphthol (1-MOMO-Np) is lithiated exclusively at the *ortho* position.[173] The directing effect of the 1-MOMO group is stronger than the effect of the methoxy group, as exemplified by compound **101** [67, 177] (see also Ref. 178). After completion of the reaction, the methoxymethyl group can be removed by the reaction with triethylsilane in an acidic medium.[177]



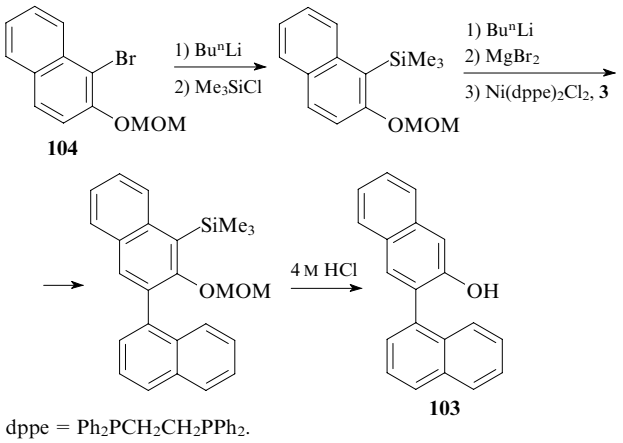
101 → **102**

RM	Reaction conditions	Electrophile	E	Yield of **102** (%)	Ref.
Bu^nLi-Bu^tOK	THF, −78 °C	D_2O	D	95	67
		Me_3SiCl	Me_3Si	93	67
		Me_3SnCl	Me_3Sn	98	67
Bu^nLi– TMEDA	THF, 20 °C	Me_2NCHO	CHO	73	177
		Me_2SO_4	Me	45	177
		Bu^nCHO	$Bu^nCH(OH)$	77	177

In the presence of 2-(trimethylsilyl)ethoxymethoxy (OSEM) and carbamoyloxy groups at position 1, lithiation of the ring occurs exclusively at position 2.[50]

2-Methoxy-[169,179] and 2-ethoxynaphthalenes[168] are metallated with high selectivity at position 3. By contrast, lithiation of 2-MOMO-Np affords a mixture of 1- and 3-lithium isomers in a ratio of 3 : 4.[180] A substituent can be introduced at position 3 of this compound and the corresponding product can be prepared in good yield after the protection of the more active position 1. This strategy was successfully applied in the synthesis of 3′-hydroxy-1,2′-binaphthyl (**103**) from bromide **104** (Scheme 11).[32]

Scheme 11

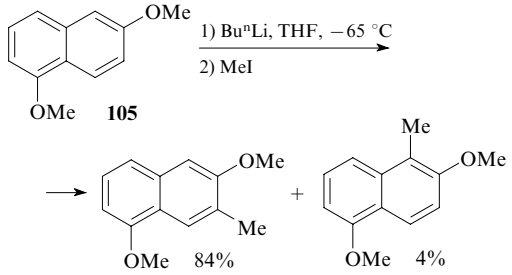


dppe = $Ph_2PCH_2CH_2PPh_2$.

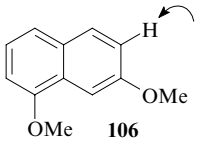
Metallation of 2-(trimethylsilyl)ethoxymethoxynaphthalene affords a mixture of 1- and 3-isomers in a ratio of 1 : 1 in a total yield of 80%.[50]

In the reaction with Bu^nLi, 2,7-dimethoxynaphthalene, unlike 2-methoxynaphthalene, gives not only the 3-lithium-substituted derivative but also the 1-isomer (15%). In the presence of an excess of butyllithium, dilithiation can occur at positions 3 and 6.[169,181,182]

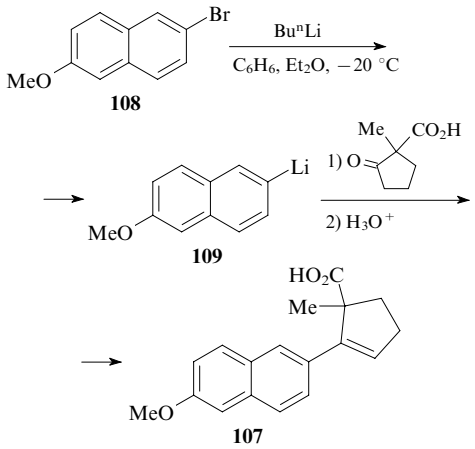
Study of the reaction of 1,6-dimethoxynaphthalene (**105**) demonstrated that the 6-methoxy group exerts the stronger directing effect than the 1-methoxy group.



This conclusion is also true for 1,7-dimethoxynaphthalene (**106**), which undergo metallation at position 6 (the yield of the product was 98%).[49,181,183]

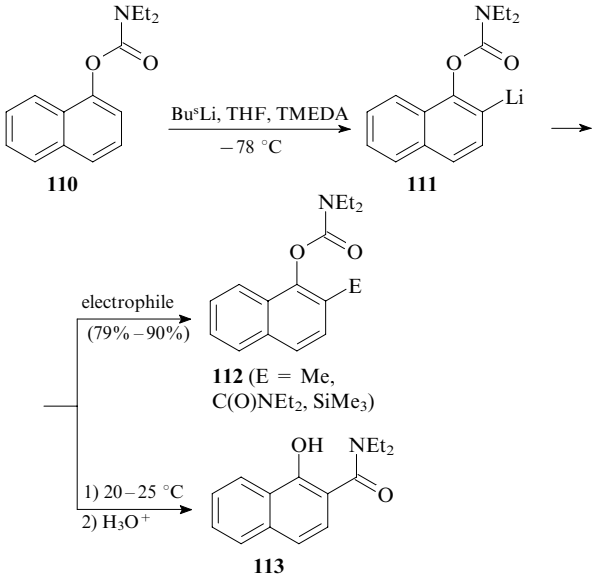


Metal derivatives of alkoxynaphthalenes, which cannot be prepared by direct metallation of the C—H bond in alkoxynaphthalenes, are generated from the corresponding bromonaphthalenes. The synthesis of compound **107** from 2-bromo-6-methoxynaphthalene (**108**) through lithium derivative **109** is a typical example.[184]



Additional data on metal–halogen exchange in halogen-substituted alkoxynaphthalenes are given in Table 6.

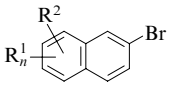
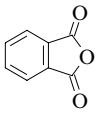
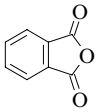
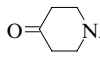
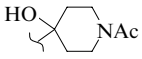
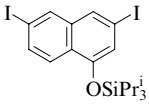
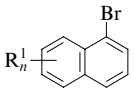
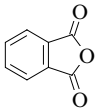
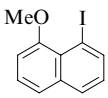
1-Naphthyl-*N*,*N*-diethylcarbamate (**110**) is metallated at −78 °C to form 2-Li derivative **111**, whose treatment with electrophiles affords compounds **112** in high yield.[25]



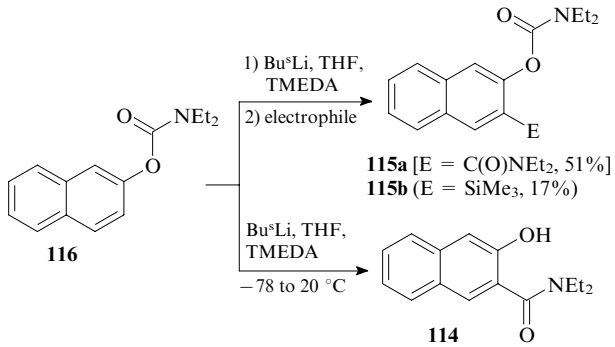
Since the nucleophilic site in the amide group is located on the carbonyl oxygen atom, such a high regioselectivity, apparently, indicates that carbamate **110** subjected to metallation has a conformation, in which the C=O bond is directed toward the C-2 rather than C-8 atom. At room temperature, naphthyllithium **111** is isomerised to give α-naphthol derivative **113**.

This rearrangement giving rise to β-naphthol **114** is typical also of the 3-lithium derivative of 2-naphthyl-*N*,*N*-diethylcarbamate. However, taking into account low yields of compounds **115**, metallation of derivative **116** is less regioselective.[25]

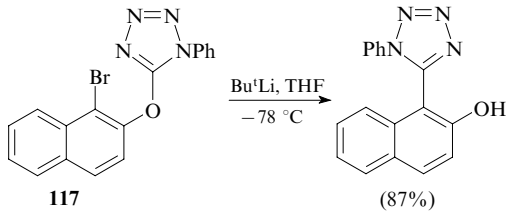
Table 6. Reactions based on metal – halogen exchange in alkoxynaphthalenes.

Substrate	R^1	R^2	Metallating agent	Electrophile	Product [a]	Yield (%)	Ref.
	1,4-$(OMe)_2$	5-OCH_2Ph	Bu^nLi	$B(OMe)_3$	$B(OH)_2$	–	185
	1,4-$(OMe)_2$	5-OMe	Bu^tLi	PhCHO	CH(OH)Ph	82	186
	1-OCH_2Ph	5-OMe	Mg	$Me_3SiC{\equiv}CCH_2Br$	$Me_3SiC{\equiv}CCH_2$	77	186
	1,4-$(OMe)_2$	H	Bu^tLi		2-$HO_2CC_6H_4CO$	56	187
	1,4-$(OMe)_2$	3-Me	Bu^nLi	$ClCO_2Et$	CO_2Et	86	188
	6-OMe	H	Mg		2-$HO_2CC_6H_4CO$	69	189
	6-OMe	H	Mg	CO_2, DMF, EtCN	CO_2H, CHO, C(O)Et	70, 80, 50	119
	6-OEt	H	Mg			50	190
	–	–	Bu^nLi	AcN(Me)OMe	2,7-Ac_2	52, 66	191
	3-OMe	–	Mg		2-$HO_2CC_6H_4CO$	80	192
	2-OMe	–	Bu^nLi	CO_2	CO_2H	70	169
	2-OMe	–	Bu^nLi	$B(OPr^i)_3$	$B(OH)_2$	63	193
	4-OCH_2Ph-5-OMe 7-CH_2OMe	–	Bu^nLi	HC(O)N(Me)OMe	CHO	89	194
	–	–	Mg	D_2O	D	70	49

[a] Substituents introduced instead of the halogen atom are given.



An analogous rearrangement was observed in the reaction of *tert*-butyllithium with 1-bromo-2-(1-phenyltetrazol-5-yloxy)-naphthalene (**117**).[195]



The behaviour of organometallic derivatives of naphthyl triflates and naphthyl tosylates is considered in Section III.14.

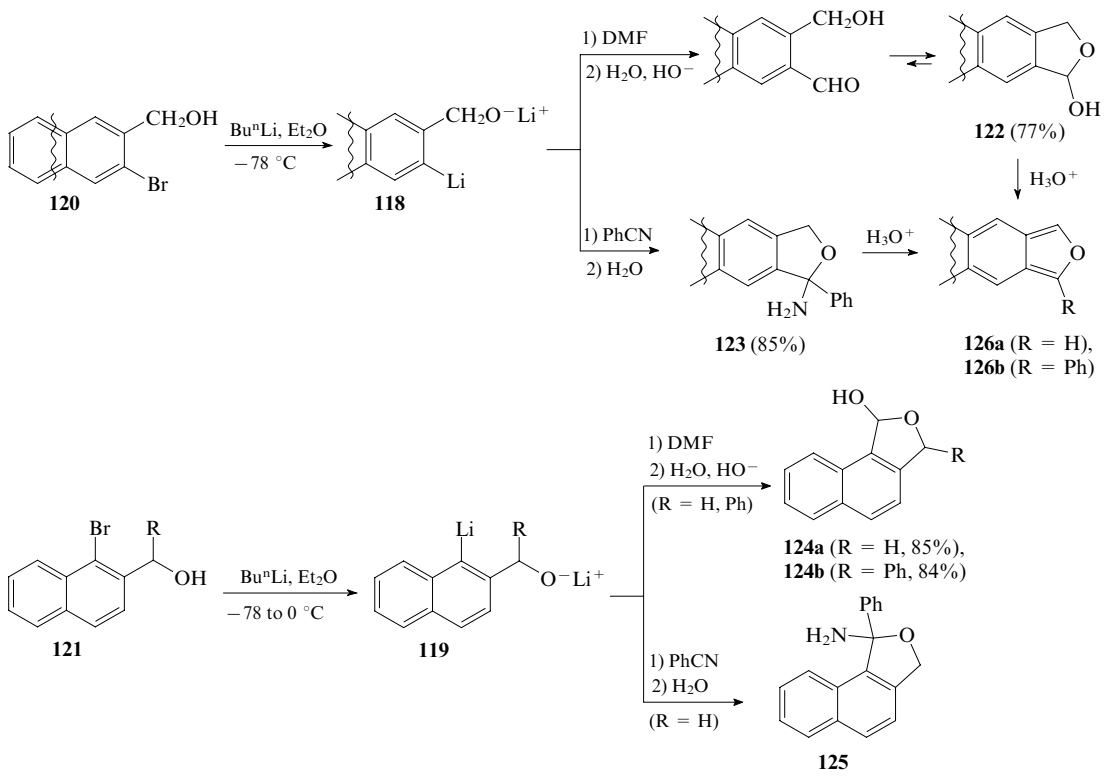
5. Metallation of hydroxymethylnaphthalenes

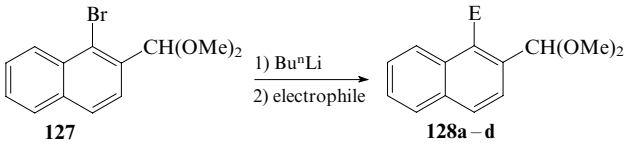
Data on direct CH-metallation of hydroxymethylnaphthalenes are lacking. The corresponding lithium-substituted naphthalenes **118** and **119** were prepared from bromides **120** and **121** by metal – halogen exchange. Lithiated derivatives were used for the generation of partially hydrogenated naphthofurans **122** – **125**, which, in turn, were used for the preparation of *ortho*-quinonoid naphthofurans, for example, **126a**,**b**, the latter being highly active as dienes (Scheme 12).[196 – 198]

6. Metallation of naphthaldehydes and their latent forms

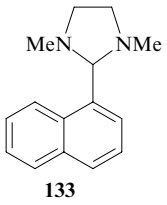
The synthesis of organometallic derivatives of naphthaldehydes requires the pre-protection of the aldehyde group. Good results were obtained with the use of metal – halogen exchange, for example, in acetals. The successive treatment of bromide **127** with butyllithium and dimethylformamide affords aldehyde **128a** in almost quantitative yield. The reactions with benzaldehyde and 2-naphthaldehyde as electrophiles[196] produce alcohols **128b**,**c**, whereas the reactions with aryl isopropyl sulfenates, $ArS(O)OPr^i$, afford diaryl sulfoxides **128d**.[199]

Scheme 12

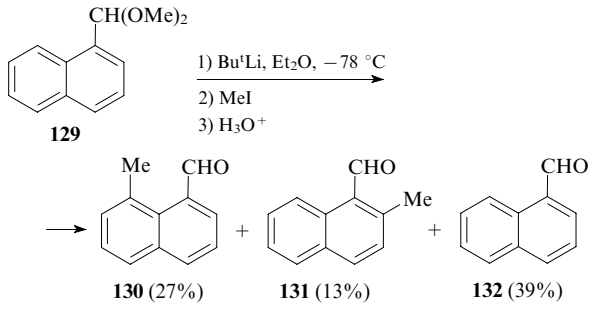




E = CHO (**a**), PhCH(OH) (**b**), 2-NpCH(OH) (**c**), S(O)Ar (**d**).



CH-Metallation of naphthaldehyde acetals gives less satisfactory results. For example, the successive treatment of 1-dimethoxymethylnaphthalene (**129**) with *tert*-butyllithium and iodomethane followed by hydrolytic cleavage of the acetal afforded a mixture of aldehydes **130**–**132**.[54]



It is worthy of note that *peri*-metallation dominates over *ortho*-metallation by a factor of more than two. The use of aminals (for example, compounds **133**) instead of acetals leads to a decrease in the yield of compounds **130**–**132** to 6%, 12% and 15%, respectively.

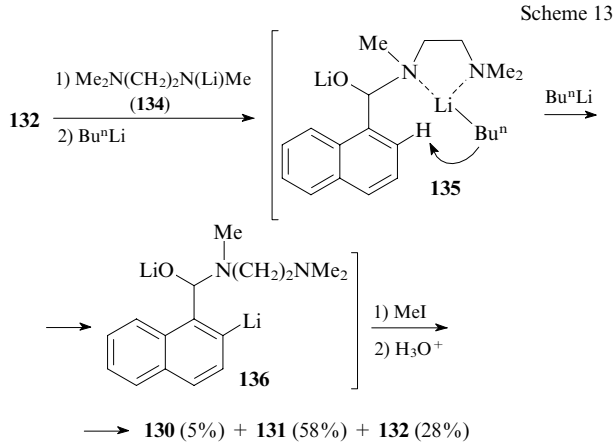
Similar results were obtained by metallation of 2-substituted analogues of compounds **129** and **133**.[54]

Metallation of Schiff bases (for example, of compound **28**, see Section II.5) leads primarily to the addition of the metallating agent rather than to metallation.[54]

An original procedure for metallation of naphthaldehydes is based on the preliminary transformation of these compounds into the corresponding α-amino alkoxides by treatment with lithium (dimethylaminoethyl)methylamide (**134**).[54, 200, 201] For example, metallation of amino alkoxide **135** derived from 1-naphthaldehyde (**132**) with an excess of butyllithium occurs predominantly at position 2 to form dilithium derivative **136**, whose methylation followed by hydrolysis affords a mixture of naphthaldehydes **130**–**132**, with compound **131** predominating (Scheme 13). The method is based on the fact that amino alkoxide **135** contains the 'built-in' chelating group, whose action is analogous to that of TMEDA. The transformation of lithium derivative **136** into boronic ester followed by oxidation with oxygen or hydrogen peroxide afforded 2-hydroxy-1-naphthaldehyde in 12%–17% yield.[200]

Metallation of 2-naphthaldehyde according to this procedure gave a mixture of the 3-Li and 1-Li derivatives in a ratio of ~3 : 1. The reaction of this mixture with iodomethane produces the corresponding methyl derivatives, whereas the treatment of this

Scheme 13

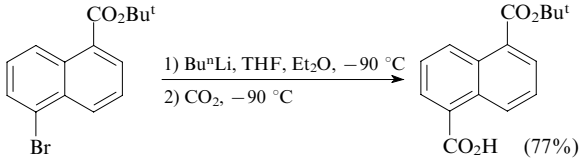


mixture with sulfur affords 3-thio-2-naphthaldehyde in 94% yield.[201]

The use of lithium diethylamide, pyrrolidide, piperidide or *N*-methylpiperazide instead of compound **134** gives worse results.[54]

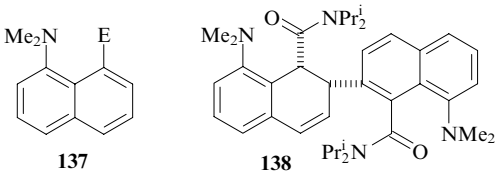
7. Metallation of naphthalenecarboxylic acids and their esters

Since the reactions of metallating agents with naphthalenecarboxylic acids or their esters afford addition products to the naphthalene ring (see Scheme 5), the corresponding metal derivatives are prepared by metal–halogen exchange at low temperature.[202]



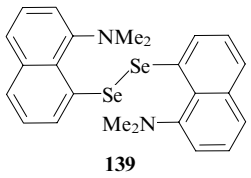
8. Metallation of aminonaphthalenes

The most pronounced directing effect of the amino groups on metallation is observed for 1-dimethylaminonaphthalene. The treatment of this compound with Bu^nLi or Bu^tLi [16, 173] in diethyl ether affords exclusively 8-lithium derivative **7**,[203] whose structure was established by X-ray diffraction. The reactions of compound **7** with different electrophiles, including CD_3OD, CO_2, Ph_2CO, Ac_2O, DMF, BF_3,[34] Me_2AlCl,[204] $MnCl_2$,[175] MeNCS,[175] Me_3SnCl, Me_3SiCl, R_2SnBr_2,[203] $(p\text{-Tol})_2SbBr$,[205] Pr^i_2NCOCl,[16] $Cl_2MeSiSiMePh_2$ [133] or $F_2MeSi-SiMePh_2$,[206] produce the corresponding 1-NMe_2-8-E-naphthalenes **137**. In the synthesis of 8-carbamoylnaphthalenes, it is necessary to add a suspension of compound **7** to carbamoyl chloride because the addition in the reverse order leads to the formation of binaphthyl derivative **138**.[16]

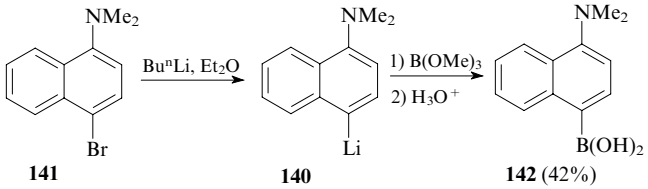


E = D, CO_2H, CHO, C(O)Me, $C(O)NPr^i_2$, $Ph_2C(OH)$, BBu^n_2, C(S)NHMe, $SiMe_3$, $SnMe_3$, *etc.*

The treatment of compound **7** with selenium followed by oxidation of the reaction mixture affords diselenide **139**.[136]

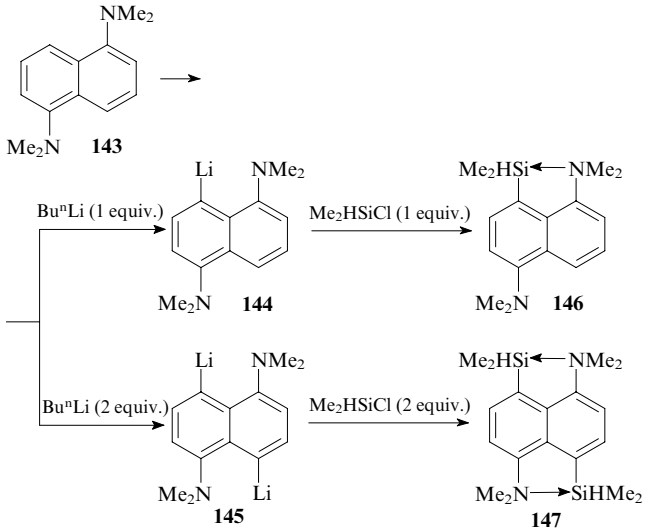


The synthesis of other lithium derivatives of 1-dimethylaminonaphthalene (for example, **140**) is based on metal–halogen exchange. This procedure was applied in the synthesis of boronic acid **142** from 4-bromo-1-dimethylaminonaphthalene (**141**).[207]

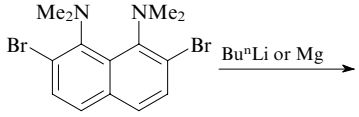


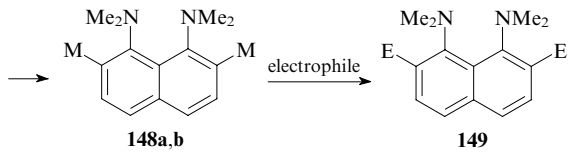
2-Bromomagnesio-6-dimethylaminonaphthalene was prepared from 2-bromo-6-dimethylaminonaphthalene by metal–halogen exchange. Taking into account low activity of the latter, the Grignard reaction was carried out in the presence of the auxiliary reagent, dibromoethane.[8]

The reaction of 1,5-bis(dimethylamino)naphthalene (**143**) with n-butyllithium produces either 4-lithium (**144**) or 4,8-dilithium derivatives (**145**) depending on the amount of n-butyllithium. The reactions of compounds **144** and **145** with halosilanes [$Si(OMe)_3Cl$, Ph_2SiHCl, Me_2SiHCl, *etc.*] were used for the synthesis of *peri*-substituted derivatives of naphthalenes **146** and **147** containing N→Si bonds.[208]



1,8-Bis(dimethylamino)naphthalene ('proton sponge') is not metallated by butyllithium.[209] However, its 4-lithium,[210] 2-lithium and 2,7-dilithium derivatives [88, 211] and their MgBr analogues can easily be prepared by metal–halogen exchange. Compounds **148a**,**b** are of particular importance. The reactions of the latter compounds with electrophiles produce 2,7-disubstituted proton sponges **149**, which are difficult to synthesise according to other procedures and which are of fundamental importance.[88, 211]

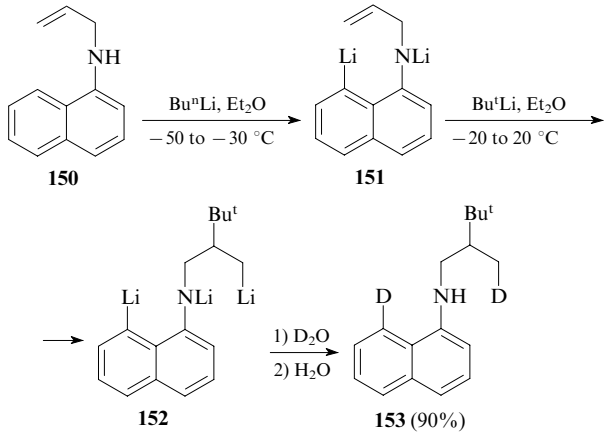




148a,b **149**

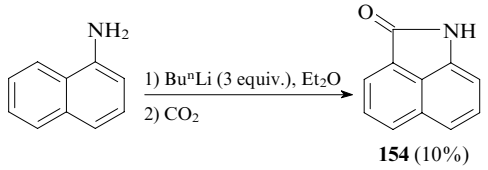
M = Li (**148a**), MgBr (**148b**); E = D, Me, CO_2Et, $Ph_2C(OH)$, $SiMe_3$, I, SMe, *etc*.

Metallation of naphthalenes containing a secondary or primary amino group as a substituent is complicated because of the initial formation of N-anions. Nevertheless, these compounds also generally undergo lithiation at the *peri* position.[102,212] For example, the reaction of 1-allylaminonaphthalene **150** with an excess of Bu^nLi produces dianion **151**, whose treatment with *tert*-butyllithium affords trianion **152**, and the latter is transformed into compound **153** under the action of D_2O.[212]



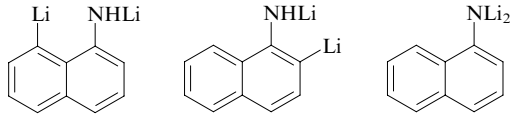
150 **151** **152** **153** (90%)

The reaction of 1-aminonaphthalene with Bu^nLi followed by the treatment with CO_2 gives rise to naphtholactam **154** in low yield.[52]



154 (10%)

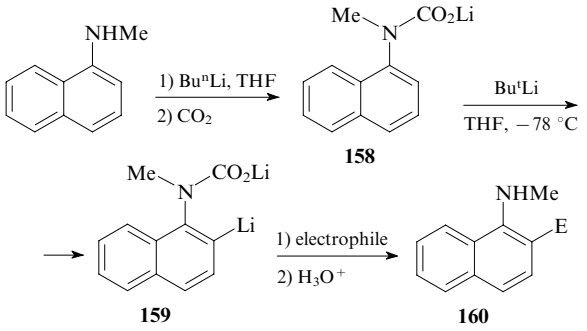
According to *ab initio* calculations, *peri*-lithiated dianion **155** is 14.4 kcal mol^{-1} more stable than *ortho* isomer **156** and 27.3 kcal mol^{-1} more stable than dilithium naphthylamide (**157**).[101]



155 **156** **157**

Katritzky *et al*.[213] developed a general one-pot procedure for *ortho*-lithiation of aminonaphthalenes (Scheme 14) providing great scope for their functionalisation. According to the proposed procedure, 1-methylaminonaphthalene is initially lithiated with n-butyllithium and then transformed into lithium carbamate **158** by the reaction with CO_2. Lithiation of the latter with *tert*-butyllithium occurs selectively at position 2 to form compound **159**, whose treatment with various electrophiles gives 2-substituted 1-naphthylamines **160** in a total yield of 48% – 61%.

Scheme 14

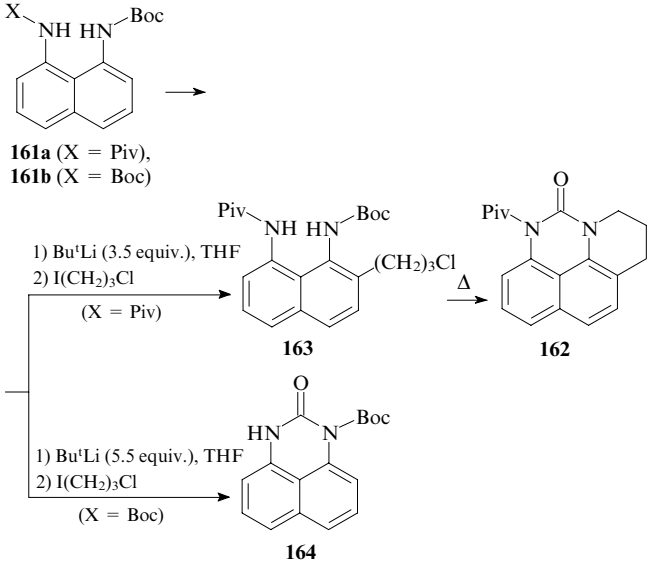


158 **159** **160**

E = $PhCH_2$, $Ph_2C(OH)$, $Pr^iCH(OH)$, Bu^tNHCO.

Analogously, 2-methylaminonaphthalene can be transformed into 3-substituted derivatives but in lower yields.

The transformation of *peri*-diamine **161a** into urea derivative **162** by the successive treatment with butyllithium and 3-chloro-1-iodopropane is yet another example of *ortho*-lithiation.[214] Evidently, intermediate chloride **163** is generated by alkylation of the corresponding 2-lithium derivative. It is worthy of note that if both amino groups in *peri*-diamine contain the *tert*-butoxycarbonyl substituents (compound **161b**), cyclisation of diamine **161b** giving rise to 1-Boc-perimidone **164** occurs instead of metallation of the naphthalene moiety.



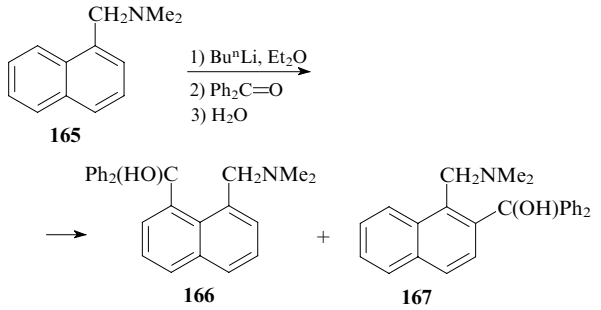
161a (X = Piv), **161b** (X = Boc) **163** **162** **164**

9. Nitronaphthalenes

Data on Li and Mg derivatives of nitronaphthalenes are lacking. As a rule, the reactions of organomagnesium reagents with nitronaphthalenes afford addition products to the naphthalene ring (see Scheme 5).[68–70,215–217] The treatment of the latter with dichlorodicyanobenzoquinone (DDQ)[68] or $KMnO_4$[70] gives alkylnitronaphthalenes.

10. Dialkylaminomethyl- and dialkylaminocarbonylnaphthalenes

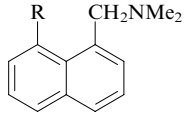
Metallation of 1-dimethylaminomethylnaphthalene (**165**) with butyllithium followed by the reaction of the resulting 8-lithium derivative with benzophenone afforded alcohol **166** in 58% yield. In addition, *ortho* isomer **167** was found in the reaction mixture, but attempts to isolate this isomer in pure form failed (presumably, the ratio of the *peri*- to *ortho*-lithiation products is 91 : 9).[53]



The same alcohols were prepared in good yields from bromides through metal – halogen exchange.[53]

Analogous experiments with 2-dimethylaminomethylnaphthalene demonstrated low selectivity of metallation (the ratio of the 3- to 1-substitution products was 55 : 45).

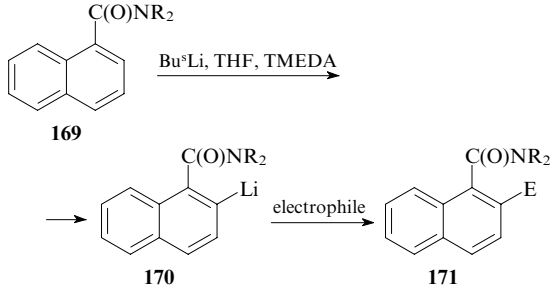
Clayden *et al.*[16] used 1-dimethylaminomethyl-8-naphthyllithium in the synthesis of 8-carbamoyl-1-dimethylaminomethylnaphthalenes **168a**,**b**.¶ The lithium derivative was prepared by the reaction of compound **165** with *tert*-butyllithium.[16] The synthesis of compound **168c** was documented.[205]



168a – c

R = C(O)NEt$_2$ (**a**), C(O)NPr$^i_2$ (**b**), (*p*-Tol)$_2$Sb (**c**).

As mentioned above (see Section II.4), the carboxamide group is one of few electron-withdrawing groups, which promote the efficient metallation of the naphthalene moiety. For example, the reactions of 1-naphthamides **169** with *sec*-butyllithium produce 2-lithium derivatives **170**; its treatment with electrophiles gives 2-substituted 1-naphthamides **171** generally in good yields (Table 7).



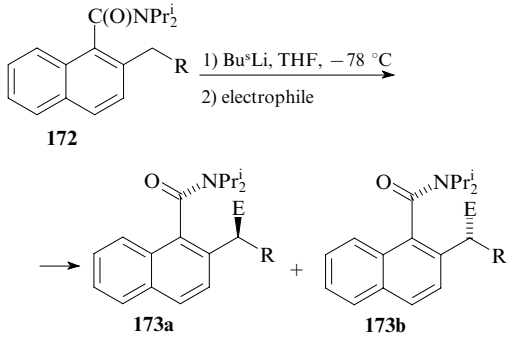
ortho-Lithiation is particularly favoured by low temperature (to -100 °C) and the reverse order of mixing of the reactants (a solution of the substrate is added to the metallating agent).[224]

Based on the existence of atropoisomerism in the series of *N*,*N*-dialkyl-2-R-1-naphthamides, Beak and co-workers[223] studied asymmetric deprotonation of *N*,*N*-dihexyl-1-naphthamide under the action of Bu^{s}Li in the presence of chiral diamine, *viz*., (−)-sparteine. Subsequent methylation and ethylation of the 2-lithium derivative obtained after lithiation afforded atropoisomers of *N*,*N*-dihexyl-2-alkyl-1-naphthamides with 50% and 55% *ee*, respectively.[223]

It is worthy of note that under the above-mentioned conditions, position 8 is not subjected to lithiation and no indication of the nucleophilic addition at the aromatic ring is observed. To achieve *peri*-metallation, various 2-substituted 1-naphthamides were tested as substrates. However, in none of the experiments, did *peri*-metallation occur. Lithiation of 2-ethyl- and 2-propyl-1-carboxamides **172** afforded solely the corresponding benzyl anion; its treatment with electrophiles gave rise to a mixture of stereoisomers **173a** and **173b**, with one of them substantially predominating.[85] High stereoselectivity of metallation is attributed to the almost perpendicular orientation of the carboxamide fragment relative to the naphthalene moiety, resulting in stereochemical induction.

Table 7. Reactions of 2-lithio-1-naphthamides **170** with electrophiles.

R	Electrophile	E	Yield of **171** (%)	Ref.
Et	1)TosN$_3$, 2) NaBH$_4$	NH$_2$	74	218, 219
Et	1) O$_2$, 2) H$_3$O$^+$	OH	34	220
Et	1) LiCu(CN)NMePh, 2) O$_2$	NMePh	61	221
Et	Me$_3$SiCl	Me$_3$Si	80	25
Pr^i	D$_2$O	D	93	16
Pr^i	EtI	Et	82	85
Pr^i	Pr^{n}I	Pr^n	78	85
Pr^i	MeCHO	MeCH(OH)	92	74, 222
CH(Pr^n)Bu^n	MeCHO	MeCH(OH)	35	74
n-C$_6$H$_{13}$	MeI	Me	30	223

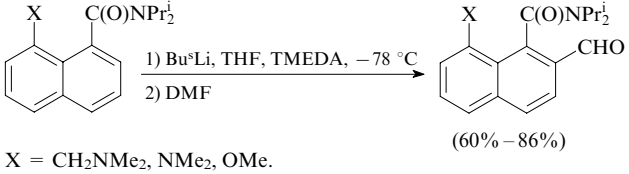


R = Me, Et; E = D, Alk, Me$_3$Si, Me$_3$Sn, *etc.*

Due to a high kinetic isotope effect in metallation reactions of naphthalene derivatives ($k_H/k_D > 80$ at -78 °C), *N*,*N*-diisopropyl-2-D-1-carboxamide (**27**) would be expected to undergo *peri*-metallation. However, the reaction of this compound with Bu^{n}Li or Bu^{s}Li led only to the addition of the nucleophile at position 2 (see Scheme 5).[16, 73] In the presence of the Bu^t or Bn substituents at the nitrogen atom, the α-proton abstraction from the *N*-benzyl group was observed.[73, 225]

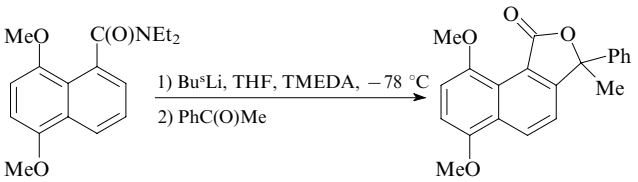
Nowadays, the only procedure for the preparation of thermodynamically less stable 8-lithio-1-naphthamides is based on bromine – lithium exchange in 8-bromo-1-naphthamides.[226] Recall also that the carboxamide group can be introduced at the *peri* position with respect to the already present substituent by the reaction of the corresponding carbamoyl chloride with 1-R-8-naphthyllithium.[16]

The 1-carboxamide group is superior to other groups,[16] including the methoxy group,[226, 227] in the directing ability.

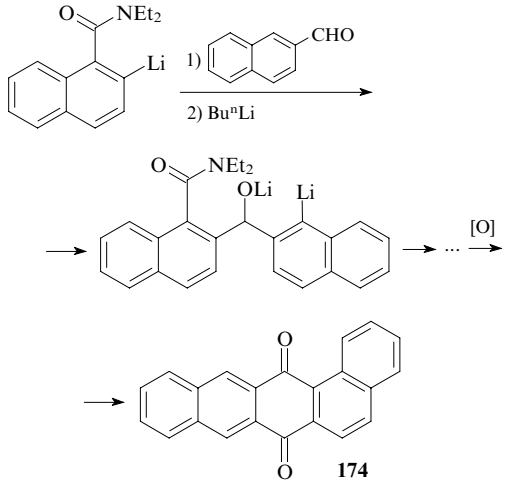


X = CH$_2$NMe$_2$, NMe$_2$, OMe.

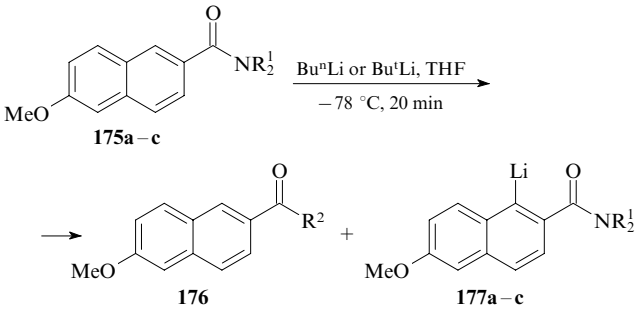
¶ According to the IUPAC nomenclature, these compounds are called *N*,*N*-dialkyl-8-(*N*,*N*-dimethylaminomethyl)-1-naphthamides.



The distinguishing feature of the carboxamide group is that it is stable to the action of organolithium compounds only at lowered temperature. At high temperature, the carboxamide group can be subjected to the nucleophilic attack. This fact was used in the synthesis of isomeric benzanthraquinones (for example, of compound **174**,[228] dibenzanthracenes[226] and cholanthrenes[224]) and a series of other polynuclear arenes[219] (see also the review[25]).

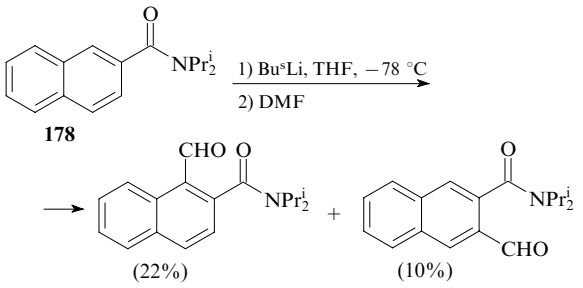


Metallation of 2-naphthamides is very sensitive to the reaction conditions and steric factors. For example, compounds containing methyl groups at the amide nitrogen atom (compound **175a**) do not undergo metallation, and the reaction affords ketone **176** as virtually the only product regardless of the nature of the metallating agent (BunLi or ButLi). Metallation of compounds containing the *N*-isopropyl group (**175c**) gives only Li derivative **177c**, whereas diethylamide **175b** can form both ketone (in the reaction with BunLi) and the Li derivative (in the reaction with ButLi).[229]



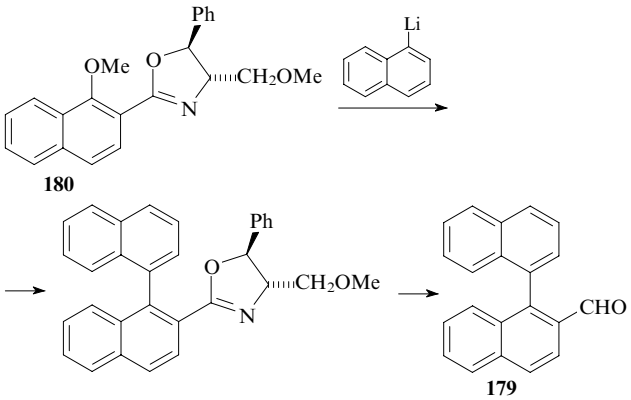
R^1 = Me (**a**), Et (**b**), Pr^i (**c**); R^2 = Bu^n or Bu^t.

N,*N*-Diethyl-2-naphthamide containing the unsubstituted naphthalene ring reacts with ButLi at −45 °C to form a mixture of products, *viz*., the product of the addition of the nucleophile to the naphthalene ring (50%), the 1-lithium derivative (30%) and *tert*-butyl 2-naphthyl ketone (10%).[12,25] Approximately the same ratio of metallation products was observed in the reaction with *N*,*N*-diisopropyl-2-naphthamide (**178**) with the only difference that the reaction occurs at positions 1 and 3.[230]

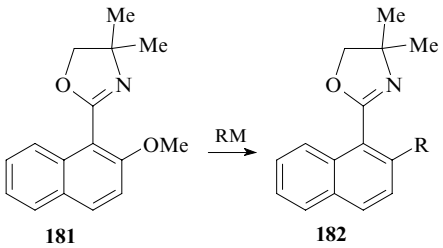


11. Naphthyloxazolines

As mentioned above, the oxazoline substituent promotes the addition of various metallating agents to the naphthalene ring (see Section II.5). In some cases, the oxazoline substituent activates the adjacent group (for example, the methoxy group) toward the nucleophilic substitution (Meyers's reaction).[78,231] In particular, this reaction was used for the preparation of 1,1′-binaphthyl-2-carbaldehyde (**179**) starting from (1-methoxy-2-naphthyl)oxazoline **180**.[232]

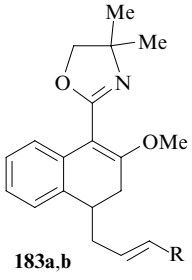


In the reactions with C- and N-nucleophiles, the methoxy group in (2-methoxy-1-naphthyl)oxazoline **181** is replaced to give compounds **182**.[12]



RM = MeLi, BunLi, BusLi, ButLi (94% – 98%), *syn*-MeCH=CHLi (60%), Me_2NLi, Pr^i_2NLi, PhMgBr (98% – 100%).

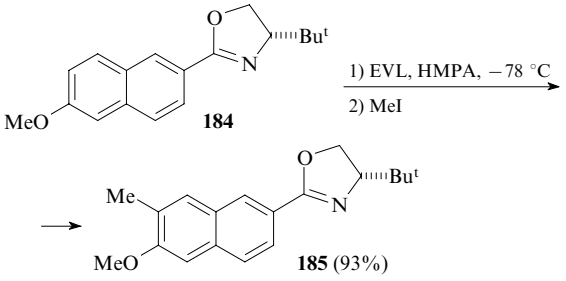
It is interesting that the reaction of compound **181** with allyllithium leads to the addition of the nucleophile at position 4 to give 3,4-dihydronaphthalenes **183a**,**b**. The latter can be subjected to aromatisation with DDQ.[66,78]



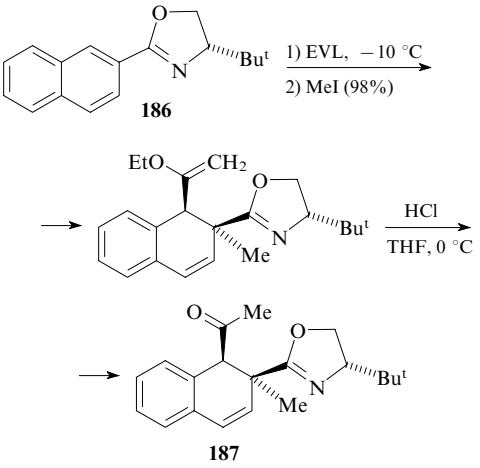
R = H (**a**), $SiMe_3$ (**b**).

The replacement of the NMe_2 group in (2-dimethylamino-1-naphthyl)oxazolines with Bu^sLi was documented.[78, 79]

The only example of successful metallation of naphthyloxazolines by the reaction of compound **184** with ethoxyvinyllithium (EVL) in the presence of hexamethylphosphoramide was documented. Contrary to expectation, the reaction occurs at the *ortho* position with respect to the 6-methoxy group, and the addition of iodomethane to the reaction mixture affords 7-methyl derivative **185**.[28, 233]

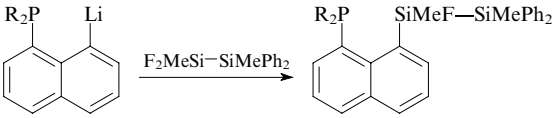


This anomalous situation remains to be explained. However, in the absence of HMPA and at higher temperature (−10 °C), ethoxyvinyllithium also adds to the naphthalene moiety of compound **186** at positions 1 and 2, and the treatment of the resulting compound with MeI and a hydrochloric acid solution yields 1,2-dihydronaphthalene **187**.[234]



12. Metallation of phosphorylated naphthalenes

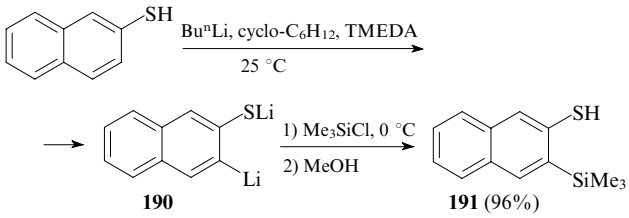
Data on organometallic derivatives of phosphorylated naphthalenes are scarce. For example, the use of 1-lithium-substituted 8-phosphinonaphthalenes **188** in the synthesis of pentacoordinate phosphodisilanes **189** was documented,[206] however experimental details were not reported.



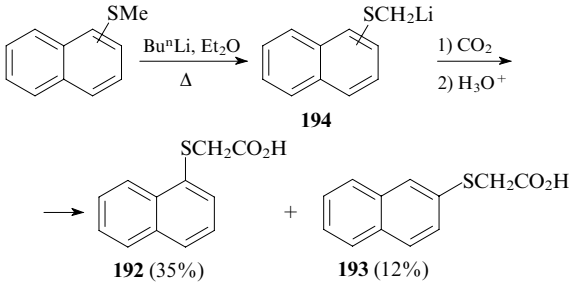
R = Et, Ph.

13. Sulfur-containing naphthalenes

Metallation of naphthalene-2-thiol with n-butyllithium affords solely 3-lithium derivative **190**, which was detected as compound **191**.[235]

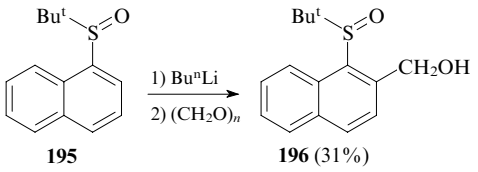


Metallation of 1- and 2-methylthionaphthalenes occurs at the methyl group, whereas the naphthalene ring remains intact, as evidenced by isolation of acids **192** and **193** after carbonisation of the reaction mixture. This is quite understandable because the sulfur atom better stabilises the adjacent carbanionic centre in compound **194** through the unoccupied 3d orbitals.

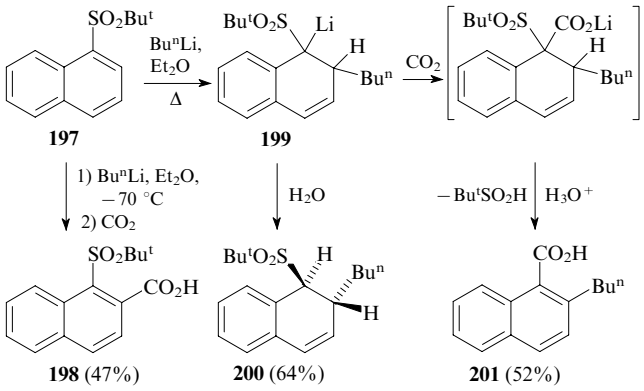


Nevertheless, 2-ethylthionaphthalene undergoes metallation at the ring, and carbonisation of the resulting compound affords 3-ethylthio-2-naphthoic acid.[236]

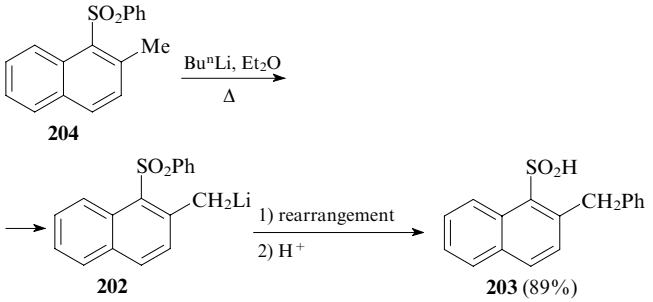
tert-Butyl 1-naphthyl sulfoxide (**195**) is metallated with n-butyllithium at the *ortho* position, which is confirmed by the isolation of alcohol **196** after the treatment of the mixture with paraformaldehyde.[199]



At −70 °C, *tert*-butyl 1-naphthyl sulfone (**197**) is metallated with Bu^nLi or MeLi to form the 2-lithium derivative, whose carbonisation affords carboxylic acid **198**.[71] At high temperature, the reaction with MeLi proceeds analogously, whereas the reaction with Bu^nLi gives addition product **199**, which is transformed into either *trans*-1-*tert*-butylsulfonyl-2-butyl-1,2-dihydronaphthalene (**200**) or 2-butyl-1-naphthoic acid (**201**) depending on the subsequent treatment of the mixture (with H_2O or CO_2).



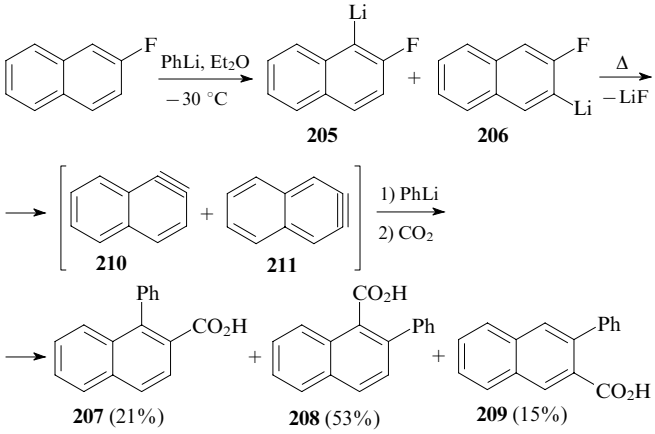
In the presence of the methyl group adjacent to the arylsulfonyl group, the initially formed benzyl-type anion **202** is rearranged into the corresponding benzylnaphthalenesulfinic acid **203**.[237]



In addition to sulfone **204**, the reaction was performed with 2-SO_2Ph-1-Me-, 2-SO_2Ph-3-Me and 1-SO_2Ph-8-Me-naphthalenes. Naphthalene-1-sulfamides undergo metallation at position 2.[238]

14. Halogen-containing naphthylmetals. Formation of dehydronaphthalenes

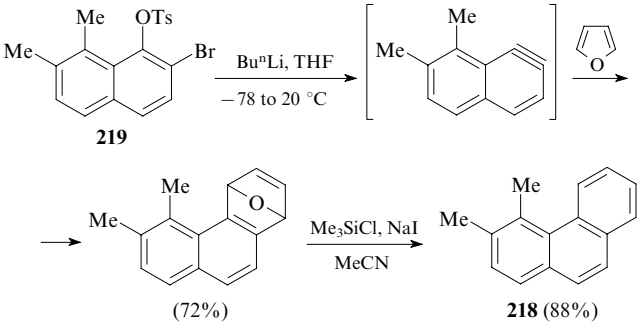
The following two types of halogen-containing naphthylmetals should be distinguished: compounds containing the metal and halogen atoms in the *ortho* positions with respect to each other and compounds in which these atoms are more distant from one another. In the former case, metallation giving rise to metal *o*-halonaphthalenes can be followed by elimination of metal halide to form 1,2- and 2,3-dehydronaphthalenes, which is facilitated by heating. Naphthynes can add a metallating agent at the triple bond. These compounds can also be trapped by special scavengers of the furan type. For example, the reaction of 2-fluoronaphthalene with phenyllithium produces a mixture of 1- (**205**) and 3-lithium derivatives (**206**), whose heating followed by treatment with CO_2 affords a mixture of naphthalenecarboxylic acids **207**–**209**.[239]



Evidently, acids **207** and **208** are derived from 1,2-naphthyne (**210**), whereas their isomer **209** is generated from 2,3-naphthyne (**211**). Under these conditions 1-fluoronaphthalene, as well as 1- and 2-chloronaphthalenes, behave analogously (although the reaction time in the case of the chlorides is substantially longer).[239] Lithium alkyls[81,239] and lithium amides[27,240] can be used as metallating agents instead of phenyllithium although the specific features of each reagent should be taken into account. For example, the reaction of 2,3-dibromonaphthalene (**212**) with lithium tetramethylpiperidide results in CH-metallation giving rise to 1-lithium derivative **213**. After elimination of the LiBr molecule, the latter compound is transformed into 3-bromo-1,2-naphthyne, which gives compound **215** after the addition of isobenzofuran **214**. By contrast, the treatment of dibromide **212** with butyllithium affords 2-lithium 3-bromonaphthalene (**216**) as a result of metal–halogen exchange. In the presence of isobenzofuran **214**, the latter compound is transformed into tetracene derivative **217** through 2,3-naphthyne (**211**) (Scheme 15).

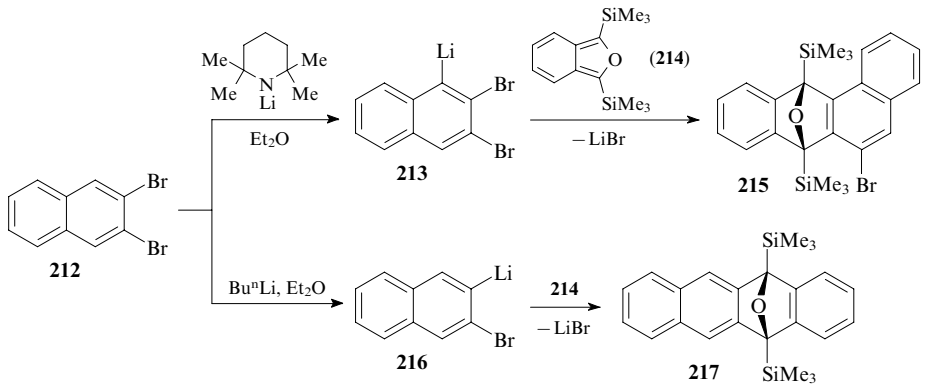
An analogous approach was successfully applied in the synthesis of 5,6,11,12-tetraphenylnaphthacene (rubrene) and its analogues starting from 2,3-dibromo-1,4-diphenylnaphthalene.[80]

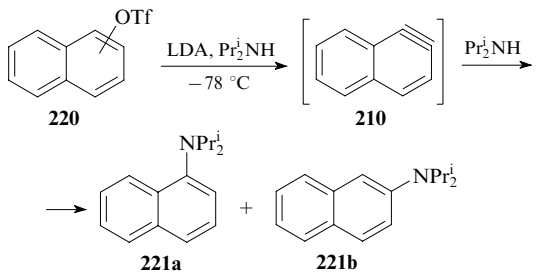
The introduction of the lithium atom at the *ortho* position with respect to good leaving groups, such as OTf or OTs, also leads to the formation of naphthynes.[241,242] The synthesis of 1,2-dimethylphenanthrene (**218**) from *o*-bromotoluenesulfonate **219** is a typical example.



To generate naphthynes from naphthyl triflates through CH-metallation, it is necessary to use strong low-nucleophilic bases (such as LDA). For example, the reactions of 1- and 2-naphthyl triflates (**220**) with LDA in an excess of diisopropylamine produce exclusively 1,2-naphthyne (**210**), which adds diisopropylamine to form 1- and 2-diisopropylaminonaphthalenes **221a** and **221b** in a total yield of 86 % in a ratio of 8 : 92.

Scheme 15





This reaction gives naphthalene as a by-product (7% – 8%).[243]

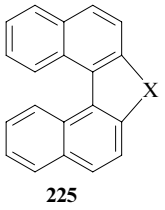
At rather low temperature (below −45 °C), metal *o*-halonaphthalenes are quite stable and can be used in various standard transformations, for example, in the synthesis of 2-bromo-1-fluoronaphthalene from 1-fluoronaphthalene.[81]

Halogen-containing metal naphthalenes, in which the metal and halogen atoms are distant from each other (including *peri*-substituted compounds), have no specific features (see the reactions involving 1-MgBr-4-Br-,[111] 1-MgBr-6-Br-,[1] 1-MgBr-8-Br-,[7,123] 1-MgBr-8-Cl-[123] and 1-Li-4,5-F_2-naphthalenes[244]).

15. Metal derivatives of binaphthyls

Organolithium and -magnesium derivatives are widely used for the synthesis of binaphthyls (see Section IV) and their functionalisation. The synthesis of 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl (BINAP, **222a**) is a prominent example. This chiral ligand was used for the design of efficient metal complex catalysts for asymmetric hydrogenation.[245,246] Racemic or optically active dihalides **223** serve as the starting compounds in the synthesis of BINAP. These reagents are lithiated with Bu^tLi or Bu^nLi at low temperature,[99,247] and then the resulting dilithium derivative **42** is treated with diphenylchlorophosphine. The Grignard reagents can also be used. The latter are transformed into diarylphosphinyl derivatives **224**, which are reduced to the target compounds **222a**–**c** (Scheme 16).[132] In the reactions of dihalides **223** with one equivalent of a metallating agent [Bu^nLi (see Ref. 247) or Mg (see Ref. 132)] followed by the treatment with an electrophile, only one-half of the molecule is subjected to functionalisation, which provides a route to unsymmetrically substituted 1,1′-binaphthyls.

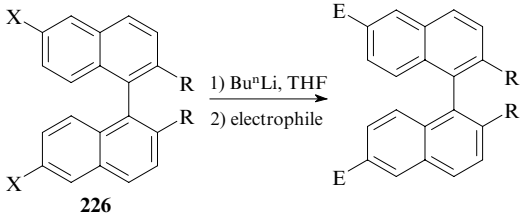
Dinapthoheterols **225** were synthesised by the reactions of dichlorosilanes, dichlorogermanes and other 1,1-bifunctional reagents with dilithium derivative **42**.[248]



225

X = $SiMe_2$, $GeMe_2$, PPh, AsPh, *etc*.

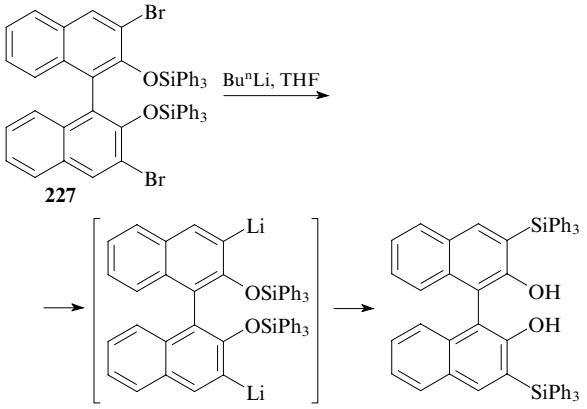
Other positions in 1,1′-binaphthyls are most often functionalised by metal – halogen exchange (for example, in the case of 6,6′-dihalides **226**[249–253] or isomeric 4,4′-dihalides[254]).



226

X = Br, I; R = H, OMe, OEt, $OC_{12}H_{25}$-n, OMOM;
E = I, CHO, CF_3, Me_3Si, $B(OH)_2$, *etc*.

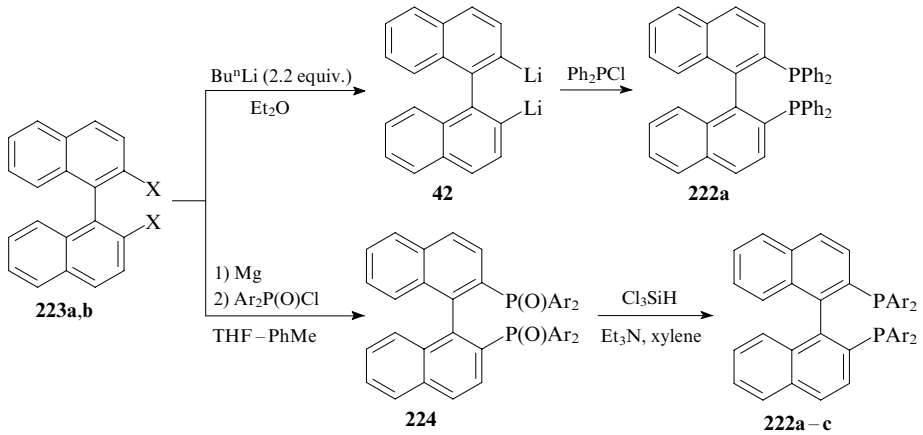
Lithiation of 2,2′-bis(triphenylsilyloxy)-3,3′-dibromobinaphthyl (**227**) is accompanied by the migration of the Ph_3Si groups to positions 3 and 3′ to form compound **228**.[255]



227

228 (80% – 95%)

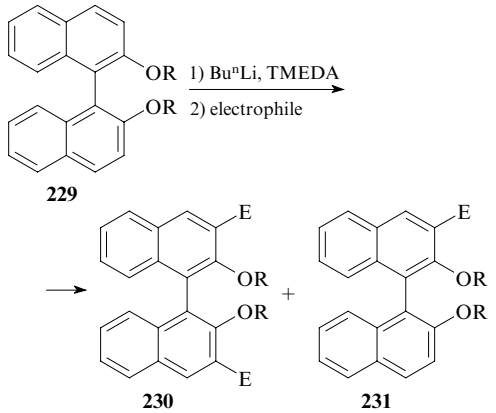
Scheme 16



223a,**b** **42** **222a** **224** **222a**–**c**

X = Br (**223a**), I (**223b**); Ar = Ph (**222a**), 4-MeC_6H_4 (**222b**), 4-$Bu^nC_6H_4$ (**222c**).

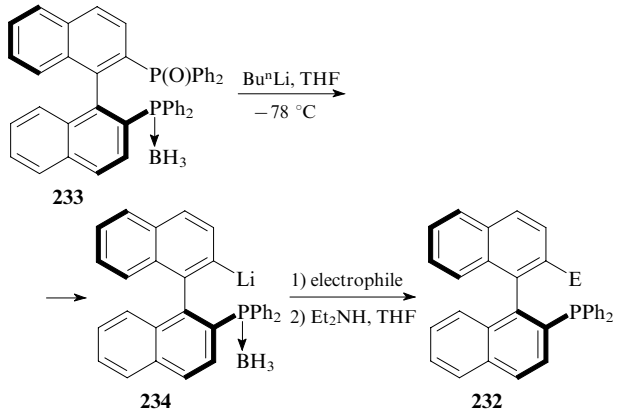
Direct CH-lithiation of 2,2′-dialkoxy-1,1′-binaphthyls **229** was documented. Metallation occurs at positions 3 and 3′, and the addition of an electrophile to the resulting compound affords compounds **230** (sometimes, with an impurity of monosubstitution product **231**).[250,256–264]



R = Me, Et, n-$C_{12}H_{25}$, MOM, C(O)NEt_2;
E = Hal, CHO, CO_2H, C(OH)Ph_2, $B(OH)_2$, *etc.*

It is interesting that lithiation of 2′-methoxy-1,1′-binaphthyl-2-carboxylic acid with Bu^nLi occurs at the *ortho* position with respect to the carboxy group.[265]

Hayashi and co-workers[266] developed a procedure for the synthesis of optically pure 2′-substituted 2-diphenylphosphino-1,1′-binaphthyls **232**. This method is based on the treatment of the phosphine borane complex **233** with an excess of Bu^nLi giving rise to monolithium derivative **234**, whose treatment with electrophiles affords binaphthyls **232** in good yields.



E = D, I, $SiMe_3$, $SnMe_3$, *etc.*

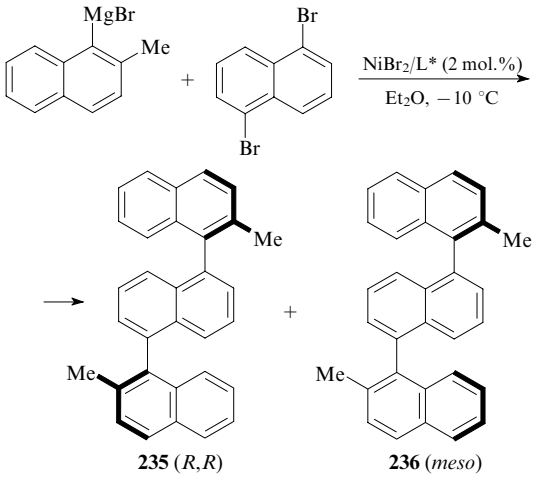
The use of compounds containing the PPh_2 or P(O)Ph_2 groups instead of $PPh_2 \cdot BH_3$ as the starting reagents give worse results.

IV. Naphthylmetals in cross-coupling reactions

In recent years, organolithium and -magnesium compounds of the naphthalene series have been widely used in cross-coupling reactions, primarily, for the synthesis of binaphthyls, polynaphthyls and arylnaphthalenes. There are several general approaches to these reactions. These approaches are based on catalytic, non-catalytic and oxidative cross-coupling of metal naphthalenes. The main catalytic methods are based on (1) Kumada cross-coupling,[267] in which aryl halides (including naphthylmagnesium halides) are used, (2) Negishi cross-coupling (recent publications were summarised in the study [268]), (3) Stille cross-coupling [269] and (4) Suzuki cross-coupling.[270] In the last three methods, organozinc, organotin and organoboron compounds of the aromatic series are used, respectively, as the starting compounds. Although only the Kumada method is within the scope of the present review, it should be remembered that the synthesis of Zn, Sn and B derivatives of naphthalene generally involve the use of lithium-substituted naphthalenes in earlier steps.

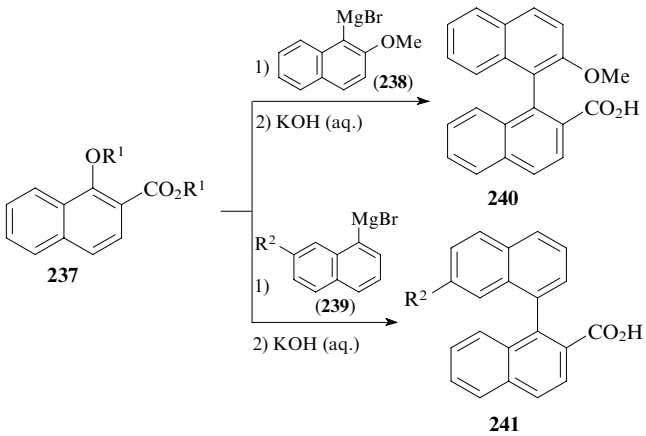
1. Catalytic reactions

The application of the Kumada reaction in the synthesis of binaphthyls was described above (see Scheme 11). In the presence of the chiral ferrocenylphosphine nickel catalyst, which was prepared *in situ* from nickel bromide and (*S*)-1-[(*R*)-2-(diphenylphosphino)ferrocenyl]ethyl methyl ether (L*), this reaction proceeds with high enantioselectivity (95% – 98% *ee*) and produces chiral binaphthyls,[271,272] ternaphthalenes [273] and arylnaphthalenes.[274] For example, the reaction of 2-methyl-1-naphthylmagnesium bromide with 1,5-dibromonaphthalene gives ternaphthalene **235** and its *meso* isomer **236** in a ratio of 84 : 16 in a total yield of 89%. (Similar results were obtained for 1,4-dibromonaphthalene.[273])



2. Non-catalytic reactions

The synthesis of 1,1′-binaphthyls by Meyers's reaction (see Section III.11, the synthesis of compound **179**) is a typical example of non-catalytic transformations. The Japanese chemists successfully used 1-alkoxy-2-naphthalenecarboxylates **237** as the substrates.[275–277] It was demonstrated that if the group R^1 in compound **237** is rather bulky (for example, Pr^i), organometallic reagents **238** or **239** do not virtually attack the ester group; instead, 1,1′-binaphthyls **240** or **241** are generated in high yield.



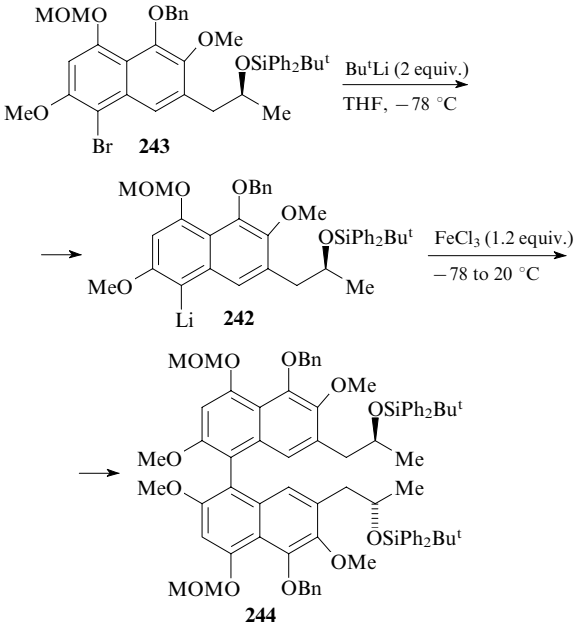
R^1 = Alk, Ar; R^2 = H, OMe.

If the substituent R^1 is chiral (for example, menthyl), stereochemical induction takes place, and the reaction affords

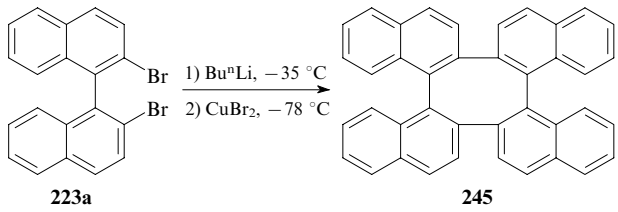
binaphthyl with high optical purity. Other modifications of these reactions were described in the publications.[278, 279]

3. Oxidative coupling

Several procedures were developed for oxidative cross-coupling of naphthalenes with the aim of preparing binaphthyls. One of these methods is based on the direct reaction of oxidising agents with naphthylmetals. The advantage of this method is high activity of the latter compounds, which allows one to perform the synthesis at low temperature, thus preventing racemisation and retaining labile substituents in the substrate. For example, naphthyllithium **242**, which was prepared from bromide **243**, was transformed into binaphthyl **244** under the action of $FeCl_3$, and compound **244** was used for the synthesis of the phytotoxic plant pigment phleichrome.[280]

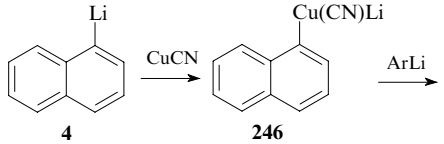


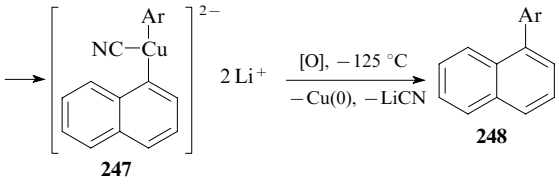
In addition to $FeCl_3$, cobalt and copper chlorides were tested as oxidising agents but with less success. It should be noted that 2,2′-dilithio-1,1′-binaphthyl (**42**), which was prepared from dibromide (*R*)-(+)-**223a**, was oxidised with $CuBr_2$ to form cyclooctatetraene derivative (*R*)-(+)-**245** in 16% yield with 90% *ee*.[281]



An efficient procedure for the synthesis of biaryls (including arylnaphthalenes and binaphthyls) is based on the transformation of lithium-substituted naphthalenes into cuprates followed by their oxidation.[282, 283]

For example, the reaction of 1-naphthyllithium (**4**) with monovalent copper cyanide produces cuprate **246** (lower order cuprate). The reaction of the latter with another lithium aryl affords higher order cuprate **247**, whose oxidation with oxygen at low temperature gives the target compounds **248** generally in good yield.





Ar = 2,6-$Me_2C_6H_3$ (72%), 3-F-4-MeC_6H_3 (76%), 1-$C_{10}H_7$ (82%), 2-MeO-1-$C_{10}H_6$ (80%).

A considerable advantage of this reaction is that it is insensitive to steric factors and can be used for the preparation of highly functionalised compounds. It is interesting that the best results were obtained with the use *tert*-butyllithium for the synthesis of 1-naphthyllithium from 1-bromonaphthalene.

V. Conclusion

The above discussion demonstrated that organolithium and organomagnesium compounds of the naphthalene series find increasing application in organic synthesis. This refers to both rather simple functionalisations and the synthesis of various compounds with very complex structures. In many cases, the synthetic methods based on the reactions of lithium and magnesium naphthalenes provide the only route to the targer compounds as, for example, in the synthesis of naphthylboronic acids, substituted binaphthyls, numerous *peri*-disubstituted naphthalenes and, particularly, polyfused systems containing small *peri*-rings. It should be noted that a search for new directing groups with the aim of increasing the selectivity of CH-metallation of the naphthalene ring, the development of convenient procedures for metal–halogen exchange in chloronaphthalenes, investigation of the structures of organometallic compounds and, in particular, of the nature of the so-called 'agostic interactions' and the further development of cross-coupling reactions of these compounds are still of importance in this field of science.

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