METALATIONS BY ORGANOLITHIUM COMPOUNDS

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I. Introduction

Metalation by organolithium compounds has become increasingly important in many areas of chemistry. A table of patents listing the catalytic applications of lithium for polymerization reactions gives an idea of their industrial importance,[1] and the great impact of organolithium compounds on the synthetic rubber industry cannot be overlooked.[2-4]

Academic interest in the field of metalation by organolithium compounds has centered on three main areas: the position of metalation; the mechanism, including structure and kinetic studies; and the synthetic methods involved. In the earlier years covered by this review, the position of metalation was of primary importance; the present trends emphasize mechanistic studies. The synthetic utility remains important throughout the entire period covered.

This review is limited to the metalation of organic compounds by organolithium compounds. The term metalation is used in its broadest sense to describe a substitution reaction in which an acidic hydrogen is replaced by a metal to produce a true organometallic compound. This review covers only those reactions which utilize an organolithium reagent as the metalating agent, as illustrated for the reaction between ethyllithium (**1**) and fluorene (**2**). All references to the use of organolithium reagents as catalytic agents, as in the polymerization of olefins, and additions across the double bond, as in the azomethine linkage in pyridines, have been omitted. Also omitted are all examples where the lithium becomes attached to an atom other than a group IVA element, *i.e.*, carbon, silicon, tin, germanium, and lead.

Metalations by organolithium reagents were reviewed by Gilman[5] and covered the literature through 1952; reviews on other aspects of lithium chemistry are also available.[6-19] It is the purpose of this review to emphasize the advances made since that time, to define the present state of the art, and to indicate areas for further basic research.

The literature from 1952 through 1966 has been surveyed. A few references, in which the experimental details, procedures, and products were too obscure to be reported accurately, have been intentionally omitted.

II. History and General Scope of Metalation

A. HISTORY

Schlenk and Bergmann[20] first reported a metalation reaction in 1928 after they discovered that ethyllithium (**1**) reacts with fluorene (**2**) by replacing an acidic hydrogen to produce fluor-

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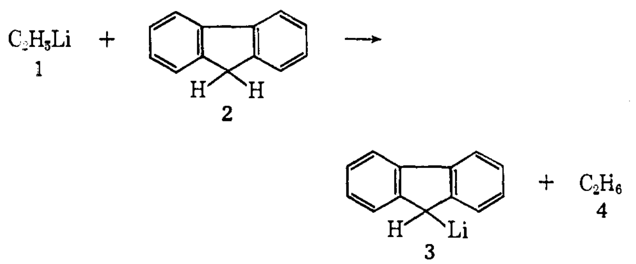
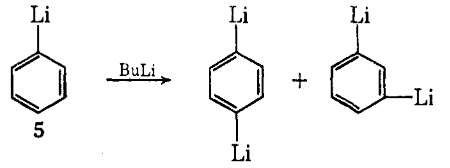


enyllithium (3) and ethane (4). This reaction has been expanded during the years to include most compounds which contain an acidic hydrogen. The reaction is not restricted to those compounds which contain a classical acidic hydrogen, since the metalation of phenyllithium (5) has been reported.[21]



Ziegler's discovery[22] that alkyl halides will react with lithium metal in ether or benzene to yield organolithium compounds has made these reagents readily available, and the work of Gilman and others has demonstrated the great synthetic utility of the metalation reaction.[5,6]

B. METALATING AGENTS

The most commonly used metalating agents are butyl- and phenyllithium. While these are not the most reactive organolithium compounds, they are the most readily available. Butyllithium is more frequently used because it is the more reactive of the two. In addition, butane, the secondary product of the metalation, escapes from the reaction medium as a gas and thus tends to drive the reaction toward completion, leading to higher yields of metalated product. The other less common organolithium compounds are considered individually in a later section.

The successful preparation of an organolithium reagent is dependent upon all the usual precautionary conditions employed in organometallic reactions.[17]

Butyllithium in ether is usually prepared in 80–95% yield from butyl chloride and lithium metal containing 0.05% sodium. Several studies have been initiated to determine the effect of a purer grade metal on the yield. When lithium containing 0.005% sodium was used, the yield decreased to about 50%, a precipitate formed, the lithium became dull instead of shiny, and the temperature was extremely difficult to control.[23] Addition of several pieces of sodium to such a reaction mixture had no effect. Several workers demonstrated that at least 0.02% sodium, intimately mixed with the lithium, was essential for the reaction to proceed normally.[23-25] In addition, retention of configuration is reported to be proportional to the amount of sodium present in the lithium.[26]

The most commonly used procedure to determine the concentration of organolithium compounds is the Gilman double titration.[5] The method has been studied extensively,[16,27-31] since there are inherent difficulties associated with any analysis where the compound under consideration cannot easily be obtained in standardized quantities. Gilman has published a study of the efficiency of various allylic halides used in the titration.[29] Certain compounds, such as alkoxides, are known to give erroneous analytical results, and some organolithium compounds, such as methyl- and phenyllithium, are particularly difficult to determine by this method. Several procedures have been reported to avoid these difficulties.[32,33]

The preparation of previously unknown organolithium compounds, either in solution or in the crystalline state, has been one of the more recent advances in this field of chemistry. Table III, including some of these new compounds and their method of preparation, appears at the end of this review.

The transmetalation reaction, as exemplified by the preparation of vinyllithium (7) from tetravinyltin (6), is used very effectively for the preparation of many of these new compounds.[34,35] The product organolithium can be filtered away from the precipitated tetraphenyltin (8), and used either in solution or further purified. Another advantage to this method of preparation is that the product organolithium is obtained free from lithium halide.

$$\underset{6}{(CH_2{=}CH)_4Sn} \xrightarrow[\text{hydrocarbon or ether}]{PhLi} \underset{7}{4CH_2{=}CHLi} + \underset{8}{Ph_4Sn}$$

Benzyllithium has been exceedingly difficult to prepare by any of the usual techniques.[36,37] For example, reaction of benzyl chloride with lithium metal results mainly in the coupling product, bibenzyl,[38] and metalation of toluene with butyllithium produces only small yields of the desired organometallic compound.[38] Gilman exploited the cleavage of benzylic ethers (9) by lithium metal in THF to provide the first practical preparation of benzyllithium (10).[37,39] Benzyllithium has also been prepared by the transmetalation reaction between tribenzyltin chloride (11) and methyllithium (12).[40]

$$\underset{9}{PhCH_2OCH_3} \xrightarrow[THF]{Li} \underset{10}{PhCH_2Li} + CH_3OLi$$

$$\underset{11}{(PhCH_2)_3SnCl} + \underset{12}{4MeLi} \xrightarrow{\text{ether}} \underset{10}{3PhCH_2Li} + Me_4Sn + LiCl$$

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Metalation of toluene by the butyllithium–TMEDA (tetramethylethylenediamine) (**16**) complex,[41,42] which results in a quantitative yield of benzyllithium–TMEDA within minutes, is currently the most efficient method to prepare benzyllithium.

Triphenylsilyllithium (**14**) can readily be prepared *via* triphenylsilyl fluoride (**13**).[43] This procedure provides easy access to this versatile metalating agent. Gilman has also shown that **14** can be prepared from triphenylsilyl chloride and lithium metal in THF.[44]

$$SiF_4 + PhMgBr \longrightarrow \underset{\mathbf{13}}{Ph_3SiF} \xrightarrow[THF]{Li} \underset{\mathbf{14}}{Ph_3SiLi}$$

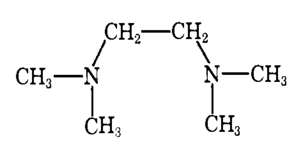
C. COMPLEXES OF METALATING AGENTS

Organolithium compounds form coordination complexes with various materials including neutral Lewis bases, ethers, amines, alkoxides, and lithium halides.[12,45–68] In this complexed form, the compounds exhibit remarkably different characteristics depending upon the complexing agent. For example, solid complexes of butyllithium–lithium halide[53,66] are inert in hydrocarbon solution, but upon addition of ether they are regenerated to conventional organolithium compounds.

Complexes are also formed with ethers and dioxanates[59,60,69,70] and may even contain lithium halide in a ternary complex, depending upon the mode of preparation. Many of these complexes have been isolated and studied.[60]

The most interesting complexes, from the synthetic standpoint, are formed from organolithium compounds and tertiary amines. The addition of triethylenediamine (DABCO), (**15**) in benzene to butyllithium in hydrocarbon produces a crystalline precipitate of the butyllithium–DABCO complex.[56,57] Many of these complexes can serve as metalating agents for compounds which are not ordinarily metalated. For example, toluene is not easily metalated by butyllithium, but is attacked quantitatively by butyllithium–TMEDA,[41,42] and in at least 85% yield by butyllithium–DABCO.[50] Even powdered lithium metal reacts with diamines to give a complex which is capable of metalating certain hydrocarbons.[71]


DABCO
15


TMEDA
16

While cyclic amines, such as DABCO (**15**), lead to crystalline precipitates, open-chain ditertiary amines, such as TMEDA (tetramethylethylenediamine) (**16**), produce stable complexes which are soluble in hydrocarbons;[41,42] thus both solid and solution forms of the complexes are available.

D. STRUCTURE OF ORGANOLITHIUM COMPOUNDS

Since the initial discovery that organolithium compounds are polymeric, many studies have been directed toward elucidating their structure. Clearly, the structure must be at least partially understood before kinetic and mechanistic studies attain much significance. The general subject of structure has been reviewed,[7] and only the more significant facts will be considered here.

All of the organolithium compounds studied so far are polymeric. The only reported exception to this, lithiomethyltrimethylsilane,[72] has been refuted by other workers.[73–75] The apparent degree of polymerization varies with both the solvent and the structure and, in general, is higher for straight-chain than for branched-chain compounds. This suggests that steric hindrance is an important factor in determining the polymeric form. It is interesting to note, then, that the *n*-alkyllithiums above *n*-propyl are liquids.[7,76] The degree of polymerization (*n*) is summarized in Table I[7,41,42,46–48,77–82] for some of the more common organolithiums. Organolith-

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Table I

Degree of Polymerization (*n*) of Some Organolithium Compounds

Compound	*Solvent*	*n*	*Ref*
Ethyllithium	Cyclohexane	6	7, 47
	Benzene	6	46, 77, 78
	Benzene	2	79
	Hydrocarbon	6	80
	Diethyl ether	2 (solvated)	48
n-Butyllithium	Cyclohexane	6	80
	Benzene	6	80
	Benzene	2	79
	Diethyl ether	6	81
n-Butyllithium–TMEDA complex	Hydrocarbon	1	41, 42
t-Butyllithium	*n*-Hexane	4	82
	Benzene	4	82
	Hydrocarbon	4	80
Phenyllithium	Diethyl ether	2	81

ium compounds are also polymeric in the vapor phase[45,54,83] and in the solid state.[84,85]

The paucity of physical measurements on organolithium compounds is largely a result of the difficulty in obtaining pure compounds and the great care which must be exercised in handling these compounds to prevent decomposition. Only recently have heat of formation,[86,87] viscosity and density,[88] and crystal structure[84,85,89] measurements been reported.

Instrumental measurements have been used extensively to determine various properties of organolithium compounds. For example, temperature dependence,[65,90–92] exchange reactions,[93–97] and complex formation[48,62] have all been studied by nmr. Bonding inferences have been obtained through nmr[98] and ir studies,[45,69,77,99–102] as well as through association data.[54,103–107] It should be carefully observed that many of the early ir frequencies reported for organolithium compounds are actually caused by alkoxide formation.[45,102,108] Other complex physical measurements have also been reported.[58,109]

The thermal stability of organolithium compounds has been the subject of several studies. Most organolithium compounds decompose on heating to lithium hydride and an unsaturated molecule. For example, butyllithium forms lithium hydride, 1-butene, *n*-butane, and resin[110] on thermal decomposition. A free-radical mechanism for this process has been excluded.[111,112] The products of pyrolysis of several organolithium compounds have also been determined,[51,52,113,114] as well as their stereochemical stability at higher temperatures.[115–117]

III. Solvents

The role of the solvent in organometallic reactions is exceedingly complex. A complete discussion of the present state of knowledge regarding solvation is well beyond the scope of this review, but some of the more salient features are included.

Ethers, such as diethyl ether and tetrahydrofuran (THF), and hydrocarbons, such as pentane and hexane, are the most commonly used solvents for organolithium reactions.[118] Dioxane and the "glymes" (ethylene glycol ethers) have occasionally been used.[119] Acetals are not usually satisfactory and have had only limited use.[120,121]

In general, organometallic reactions proceed more rapidly in ethereal solvents than in hydrocarbons.[22,27,122–126] The accelerated rate effects are attributed to the much greater solvating properties of the ethers through complex formation between the ether and the metal. Such complexes are solvated dimers[124] of higher reactivity than the original polymeric forms which exist in hydrocarbon solution. In addition, complexing tends to loosen, or ionize, the carbon–lithium bond, leading to over-all lower energy requirements in the transition state.[127,128]

In hydrocarbon solvents, where organolithium compounds are present in polymeric form, depolymerization to dimers or monomers may be required before appreciable reaction be-

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tween the organometallic compound and the substrate can commence[129] (see also ref 246).

The major disadvantage to the use of ethers as solvents is that they are readily cleaved by some organometallic reagents; thus reactions conducted in ethereal solvents can be considered as competition reactions between the ether and the reactants for the metalating agent.

Numerous studies have been conducted to evaluate the relative stabilities of organometallic reagents in ethereal solvents.[69,130–141] Generalizations derived from these studies are summarized in Table IV at the end of this review.

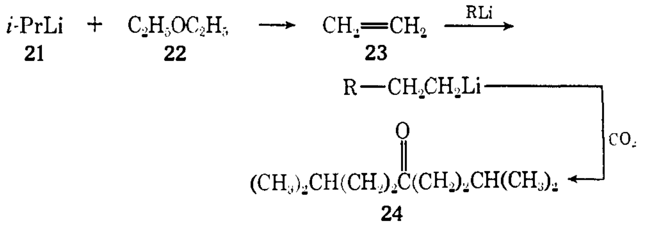
While it is well known that organolithium reagents are not indefinitely stable in ethereal solvents, insufficient work has been reported to establish the exact nature of the decomposition. Several workers have demonstrated that the solvent can be incorporated into the final product,[142–144] and, in certain cases, specific cleavage reactions by the metalating agent have been used for synthesis.[136,145–147]

Several different workers have demonstrated that the decomposition of diethyl ether (**18**) by organolithium reagents

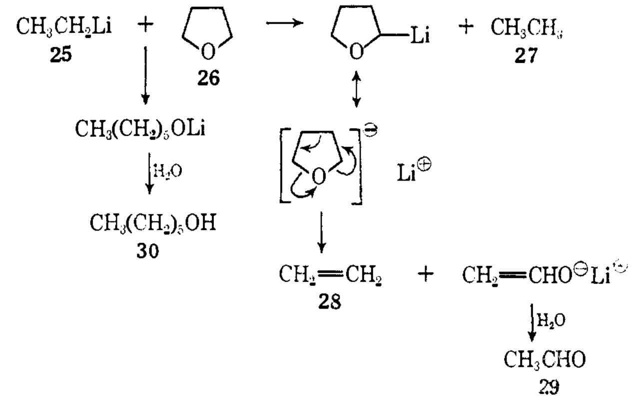
$$\underset{\mathbf{17}}{\mathrm{RLi}} + \underset{\mathbf{18}}{\mathrm{C_2H_5OC_2H_5}} \longrightarrow \mathrm{RH} + \underset{\mathbf{19}}{\mathrm{C_2H_5OLi}} + \underset{\mathbf{20}}{\mathrm{CH_2{=}CH_2}}$$

(**17**) leads to lithium ethoxide (**19**) and ethylene (**20**). Ziegler[141] showed that the hydrocarbon products were ethylene, butane, hexane, and *n*-octane. Later Gilman[134] established the presence of the ethoxide by isolating ethanol, after hydrolysis, from the reaction.

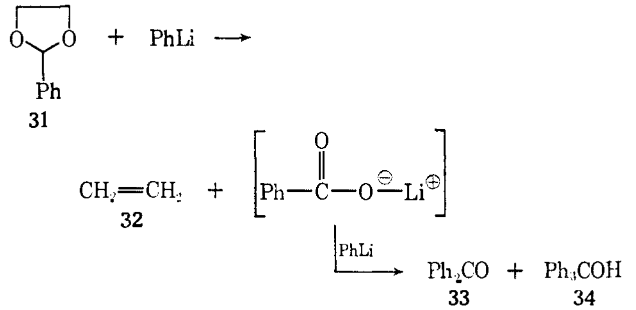
Bartlett has also demonstrated that ethylene is one of the decomposition products.[142] When a solution of isopropyllithium (**21**), prepared in diethyl ether (**22**) at −60°, was warmed to room temperature and carbonated, the product was diisoamyl ketone (**24**), which arises *via* reaction of the ethylene (**23**) formed by the decomposition of the solvent.



Several studies have been made to determine the decomposition products from tetrahydrofuran and substituted tetrahydrofurans with organolithium compounds.[133] Pure recrystallized ethyllithium (**25**) decomposes tetrahydrofuran (**26**) to produce ethane (**27**), ethylene (**28**), acetaldehyde (**29**), and 1-hexanol (**30**). These products were explained by the illustrated mechanism.[148] In a similar reaction, decomposition of 2-phenyltetrahydrofuran by propyl- or phenyllithium yields acetophenone and ethylene.[149] It has been suggested that this type of cleavage reaction should be classified as an E2 elimination.



The decomposition of 2-phenyl-1,3-dioxolane (**31**) gives an 80–94% yield of ethylene (**32**) and 85% of benzophenone (**33**) and triphenylcarbinol (**34**).[150] Since benzoic acid was not isolated, it was proposed that the phenyllithium reacted with the benzoate anion to produce benzophenone and triphenylcarbinol. Only a few studies have been reported on the stereochemistry of ether cleavages by butyllithium.[139,149,151]



In many cases the choice of either ethereal or hydrocarbon solvent can change the stereochemistry as well as the nature of the product obtained from the reaction. For example, when butadiene is polymerized by butyllithium in ether, the product is predominantly the 1,2-polybutadiene, whereas in hydrocarbon solvent the 1,4 configuration is predominant.[3,4,129,152]

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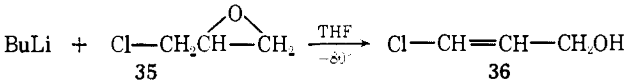
Table II

Degree of Metalation *vs.* Hydrocarbon Acidity

Compound	pK_a[161]	*% yield of acid*[a]	*Ref*
Toluene	37	24	170
Diphenylmethane	35	66	171
Triphenylmethane	33	87	170
Fluorene	25	85	172
Indene	21	93	54

[a] After carbonation.

Additionally, there is evidence that metalated compounds have greater stereochemical stability in hydrocarbons than in ethers.[122] For example, butyllithium reacts with α-chloropropylene oxide (**35**) in THF at −80° to yield only the *trans*-3-chloroallyl alcohol (**36**).[153] However, the yield of *trans* product decreases as the solvent is changed from THF to diethyl ether to hexane. At room temperature, both the *cis* and *trans* isomers are obtained, even in THF.



$$\text{BuLi} + \text{Cl—CH}_2\text{CH—CH}_2 \xrightarrow[-80°]{\text{THF}} \text{Cl—CH=CH—CH}_2\text{OH}$$

35 36

The final product can often be changed by using a different solvent. For example, butyllithium metalates phenylacetonitrile in ether on the α carbon, but in hydrocarbon the addition product predominates,[154] In the mixed solvent system THF-hexane, the α carbon is primarily attacked.[155]

Since the first demonstration of its use, THF has become increasingly popular as a solvent for organolithium reactions.[14] THF has the obvious advantage of a higher boiling point than diethyl ether, and its superior complexing characteristics greatly facilitate many reactions previously thought to be inaccessible. Compounds containing halogens can be metalated readily in THF without concomitant benzyne formation, and in many cases greater yields of a specific product can be obtained.[156,157] The major disadvantage is that many organolithium reagents are less stable in THF than in other solvents. This problem has been at least partially circumvented by employing either lower temperatures or the mixed solvent system THF-ether.[157–159]

There is no absolute rule for determining the stability of a given organolithium compound in an ethereal solvent. For example, triphenylsilyllithium is more stable in THF,[150] while pentachlorophenyllithium is more stable in ether.[138]

There is considerable evidence to show that the presence of one organolithium species in solution enhances the solubility of a second species in that same solution. For example, butyllithium increases the solubility of lithium butoxide in heptane[108] and ethyllithium is more soluble in a solution of *t*-butyllithium in benzene than in benzene alone.[65]

IV. Properties of the Compounds Metalated

A. HYDROCARBON ACIDITY

The primary prerequisite for metalation is the presence of a potentially acidic hydrogen in the molecule. The term "acidic hydrogen" relates to the natural difference in electronegativity between carbon and hydrogen, resulting in the formation of a partial positive charge on the hydrogen.

The measurement of hydrocarbon acidity has received increasing attention in recent years.[161–169] It is of particular interest in metalation chemistry since, in the absence of secondary effects, the degree of relative hydrocarbon acidity usually parallels the degree of metalation. Table II[54,170–172] illustrates this parallelism for some strictly aromatic hydrocarbons. The extent of metalation is expressed in terms of the yield of acid obtained after carbonation of the metalated compound. Undoubtedly, the actual extent of metalation is as high, or higher, than the carbonation value.

It follows then that metalation will be enhanced by those factors which tend to increase the acidity of the hydrogens. Thus the presence of electron-withdrawing groups in the molecule, such as nitrile and carboxyl, facilitate metalation. For example, both phenylacetic acid[173–182] and phenylacetonitrile[155] are readily metalated by butyllithium, whereas ethylbenzene is unaffected.

Advances made in the last several years permit metalation of compounds which previously could not be metalated. Metalation has now been accomplished in such diversified compounds as those which contain *ortho*-aromatic halogens[183]

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and benzylic halogens.[137,153,184–203] The details of these reactions are considered in their respective sections.

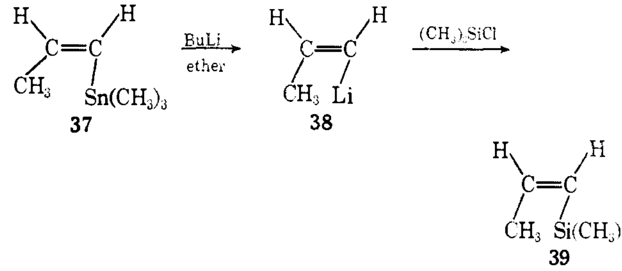
B. DERIVATIVES

After metalation, the molecule is usually further treated with an additional reagent, either to synthesize a desired compound or to determine the position, or extent, of metalation. The two most commonly used agents for preparing derivatives are carbon dioxide and trisubstituted halosilanes. The lower molecular weight halosilanes, such as trimethylchlorosilane, are frequently preferred since the products can be analyzed readily by gas phase chromatography. In this regard, it cannot be over-emphasized that when more than one pathway is available to a molecule, or when more than one organolithium derivative is present in the solution, internal competition reactions can and do occur. Thus the derivatives may not reflect accurately the precise course of the reaction.

In general, organolithium compounds react similarly to other organometallic reagents in their reactions with derivatizing agents. Very few "abnormal" reactions are reported,[204,205] and most of these result from secondary reactions. Thus carbonation of an organolithium compound frequently leads to a mixture of acids and ketones *via* further reaction of the lithium salt of the formed carboxylate[5,206]

The lithium atom in a metalated compound can be replaced by treating the molecule with suitable reagents to obtain amides or ketones,[207] sulfinates,[208] carboxylic acids,[5] and alcohols.[209–211] These reactions are summarized in Table VI.

Seyferth[212–214] has demonstrated clearly that both carbonation and silylation of propenyllithium compounds proceed with retention of configuration. Metalation of *cis*-propenyltrimethyltin (**37**) by butyllithium in ether followed by silylation produced the *cis*-trimethylsilylpropene (**39**). The final product could arise either through two consecutive inversions, from **37** to **38** and **38** to **39**, or through retention of configuration at each step. Nmr studies of all three compounds clearly demonstrated that there was retention of configuration with each transformation. It has been assumed for many years, based on indirect evidence, that these reactions proceed with retention; however, this work constitutes the first direct proof based on instrumental measurements.



C. COLOR OF METALATED COMPOUNDS

Although many organometallic compounds are highly colored in solution, there is no unequivocal correlation between the observed color and the nature of the compounds.[215,216] In fact, no rule of thumb has yet been suggested to predict the color which would result from changing either the metal ion or the organic moiety in any given compound. The visible color of a specific organolithium compound is dependent upon, among other things, the solvent,[92,127,217] temperature, concentration, mode of preparation, and probably the extent of aggregation. The colors of some organolithium compounds, as reported in the literature, have been summarized in Table V. It is interesting to note the absence of any blue organolithium compounds, even though lithium ketyls are blue. In the case of benzyldimethylamine, the colors for lithium, sodium, and potassium counterions are recorded.

D. MECHANISM AND KINETICS

The present trend in organometallic research is toward structural, mechanistic, and kinetic studies. Several general reviews on organometallic reaction mechanisms have been published,[10,11,218,219] and one specifically on organolithium mechanisms.[7] However, insufficient knowledge has been obtained to formulate to an exact degree the specific pathways utilized by organolithium reagents.

Any realistic discussion of organolithium mechanisms must take cognizance of at least the following several points.

1. Organolithium compounds exhibit varying degrees of polymerization dependent upon the solvent, concentration, and temperature.

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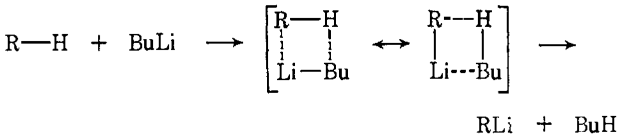
2. The same organolithium compound can exhibit different degrees of reactivity depending upon the method of preparation, *i.e.*, presence or absence of lithium halide,[63,67] as well as concentration, solvent, and degree of polymerization.

3. In a metalation reaction, a new organolithium species is generated *in situ*, which makes the kinetics very complex.

4. Organolithium compounds are easily contaminated by oxygen etc., to give undetected impurities which are often erroneously included as normal parts of the products.

The initial step in a metalation reaction is the coordination between the metal and the atom bearing the most acidic hydrogen.[5,220,221] This is followed by the rate-determining step which is the breaking of the carbon–hydrogen bond.[163,222–225] Evidence for this is found in the many hydrogen–deuterium exchange studies, all of which show the expected isotope effect.[162,163,226–229] This initial coordination step has been viewed as an acid–base exchange by some authors,[5,162,163,221,230,231] and as an electrophilic attack on the cation of the organoalkali compound on a carbon atom with increased electron density.[232] The former is presently the more accepted theory.

While the exact nature of the initial coordination step has not been clearly defined, a four-center type of coordination appears to fit the data, as illustrated with butyllithium.[218,233]



$$\mathrm{R{-}H + BuLi} \longrightarrow \left[\begin{array}{c}\mathrm{R{-}H}\\ \vdots\quad\vdots\\ \mathrm{Li{-}Bu}\end{array} \longleftrightarrow \begin{array}{c}\mathrm{R{\cdots}H}\\ |\quad|\\ \mathrm{Li{\cdots}Bu}\end{array}\right] \longrightarrow \mathrm{RLi + BuH}$$

While electron-transfer reactions have been suggested for some metalation reactions,[56,125,234,235] this has not been established as a generalization. It has been established, however, that olefins can equilibrate in the presence of their radical ion.[236] Carbenes have been proposed as intermediates in some organolithium reactions.[237–241]

The factors governing orientation in the metalation of aromatic systems have been investigated.[220–224,227,230,232,242–245] There are two general theories regarding the orientation. Bryce-Smith[230] feels that the position of metalation by organosodium compounds is influenced primarily by the thermodynamic stability of the carbon–hydrogen bond undergoing scission, while Benkeser,[223] using both organosodium and -potassium compounds, proposes that the initial attack is kinetically controlled but that the final position of metalation is a result of thermodynamic stabilities. These same conclusions have not yet been extrapolated to organolithium systems. Waack[246] has separated organolithium reagents into three broad areas on the basis of their metalating ability and has concluded that the most reactive group (benzylic and allylic lithiums) is probably the most thermodynamically unstable, so that no real correlation exists between thermodynamic stability and the rate of metalation. It has also been suggested[13] that the over-all nucleophilicity of the metalating species is the rate-controlling factor. These views support the theory that the basic mechanism involved is the nucleophilic attack on hydrogen by the metal.[221]

Kinetic studies of metalations by organolithium reagents in nonpolymerizing systems have received relatively less attention primarily because of the great difficulty in handling the organometallic compounds. However, it has been demonstrated that the rate of reaction is dependent upon the solvent.[27,68,123] Many early studies on kinetics did not consider the fact that organolithiums are polymeric and not monomeric. The rate of reaction between ethyllithium and anisole has been studied and found to be second order,[247] as has the rate of exchange between phenyllithium and deuterated phenyl bromide[233] and deuterated benzene.[55]

Most of the kinetic studies have been carried out on systems which are prototypes for polymerization reactions. The addition of organolithium compounds to 1,1-diphenylethylene and fluorene has been studied in great detail.[7,127,248–257] The reaction order for the organolithium reagent was found to be variable dependent upon the structure of the reagent.

Organolithium reagent	*Order*	*Ref*
Butyllithium	$^1/_6$	250
t-Butyllithium	$^1/_4$	248
Ethyllithium	$^1/_9$	252
Vinyllithium	$^1/_3$	255

The theory has been advanced that in hydrocarbon solution the relative rate of metalation is dependent upon dissociation

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(236) M. A. Doran and R. Waack, *ibid.*, 3, 94 (1965).

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(249) A. G. Evans and D. B. George, *Proc. Chem. Soc.*, 144 (1960).

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(252) A. G. Evans, C. R. Gore, and N. H. Rees, *ibid.*, 5110 (1965).

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(255) R. Waack and P. E. Stevenson, *J. Am. Chem. Soc.*, **87**, 1183 (1965).

(256) R. Waack, P. West, and M. A. Doran, *Chem. Ind.* (London), 1035 (1966).

(257) T. C. Wu, D. Wittenberg, and H. Gilman, *J. Org. Chem.*, **25**, 596 (1960).

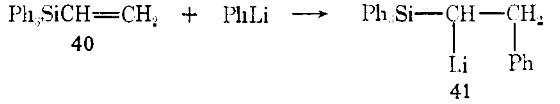
of the polymeric form to the monomeric form;[248,250] however, this has been disputed by others.[94,258] It must be remembered, however, that a new organolithium compound is generated *in situ* in all of these reactions, so the kinetic calculations cannot be based solely upon the initial reacting species. The role of the solvent in kinetic studies has been discussed,[259] and several reactions have been considered in terms of ion pairs.[97,260,261]

V. Types of Compounds Metalated

A. METALATION OF HYDROCARBONS

Those few hydrocarbons which can be metalated by uncomplexed organolithium compounds contain an activated, acidic hydrogen in the molecule.

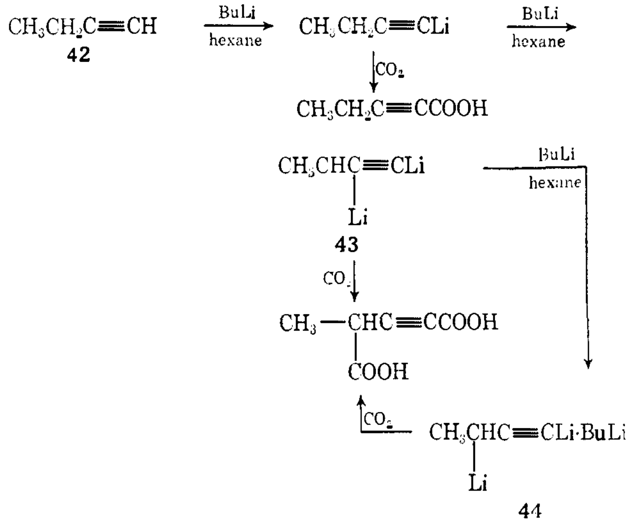
In general, unactivated saturated hydrocarbons are sufficiently inert to metalation that they can be used as solvents for the reaction. Olefins frequently add one molecule of the organolithium compound to produce the equivalent of a metalated saturated chain.[50,142,262,263] For example, phenyllithium adds to vinyltriphenylsilane (**40**) to form the metalated intermediate (**41**).[262] Butyllithium adds in a 1,4 manner to molecules such as butadiene and isoprene[3,4] to form the equivalent of allylically metalated compounds.



$$\mathrm{Ph_3SiCH{=}CH_2 + PhLi \longrightarrow Ph_3Si{-}\underset{\displaystyle Li}{CH}{-}\underset{\displaystyle Ph}{CH_2}}$$

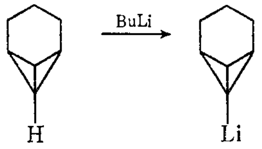
40 41

Recently some workers have shown that terminal acetylenic compounds can be polymetalated. West[264] found that all four hydrogens of propyne can be replaced by lithium, while Eberly[265] has shown that butyne (**42**) is only dimetalated (**43**).



Addition of 3 equiv of butyllithium to butyne produces only a butynyldilithium–butyllithium adduct (**44**), and carbonation gives no evidence of a trimetalated compound.

In certain cyclic aliphatic systems, an acidic hydrogen can be created by the rigid steric requirements of the system. For example, tricyclo[4.1.0.0.^{2,7}]heptane (**45**) can be metalated.[266] Norbornadiene, after metalation and carbonation, gives *endo*-2-norcamphanecarboxylic acid.[267]



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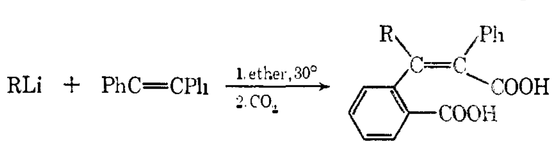
Internal acetylenes react with organolithium compounds to form products which arise either from addition or metalation depending upon the solvent, temperature, and type of metalating agent. For example, butyllithium (or ethyllithium) and diphenylacetylene do not react in pentane, whereas in ether, both addition and metalation occur to produce (**46**).[125,268] Under similar reaction conditions, *t*-butyllithium and diphenylacetylene in ligroin give a 30% yield of 1,2,3,4 tetraphenyl-1,3-butadiene.



46

Benzene is only slightly metalated by butyllithium in ether.[5,55] However, in the presence of potassium and an organolithium compound, benzene is metalated and produces, after carbonation, benzoic acid in yields up to 90%. The metalation probably proceeds through an organopotassium

$$\mathrm{RLi + K \longrightarrow RK + Li}$$

$$\mathrm{RK + PhH \longrightarrow PhK \longrightarrow PhCOOH}$$

intermediate, instead of through the lithium.[21]

Benzene can be readily metalated by butyllithium–TMEDA complexes (see data in Table III) in at least 60% yield.[41,42] Dilithiobenzene has also been prepared.[269]

Toluene is also very difficult to metalate by the usual organolithium reagents.[170] However, butyllithium–TMEDA metalates toluene to give benzyllithium–TMEDA quantitatively.[41,42] When the toluene molecule is further activated by a substituent, such as in duryl *o*-tolyl ketone, the side-chain hydrogens are sufficiently activated to be more readily metalated. In this case, metalation takes precedence over an addition to the carbonyl group. This unexpected route is probably attributable to steric hindrance by the bulky groups surrounding the carbonyl function.[270]

When toluene is α-substituted by phenyl groups, the hydrogens are sufficiently activated to give respectable yields of metalated products. Diphenylmethane gives 40–66% diphenylacetic acid,[171,271,272] and triphenylmethane, which is

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(258) T. L. Brown, *J. Organometal. Chem.*, **5**, 191 (1966).

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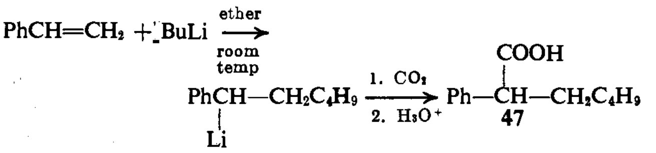
even more activated, gives higher yields, about 85-90%, of triphenylacetic acid.[170]

Styrene is not metalated by organolithium compounds to form styryllithium;[204, 273] instead the organolithium adds across the vinyl group. Usually this is followed immediately by addition of the adduct to more styrene in a polymerization reaction which leads to polystyrene. However, when this addition is carried out with a great excess of butyllithium, the product of the initial addition can be isolated. In the example illustrated above, the acid **47** has been identified as 2-phenylheptanoic acid,[273] thus establishing the direction of the addition across the double bond.

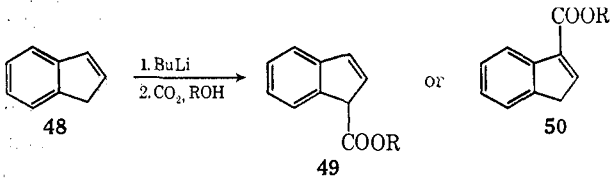


$$PhCH{=}CH_2 + BuLi \xrightarrow[\text{room temp}]{\text{ether}} \underset{\displaystyle Li}{PhCH}{-}CH_2C_4H_9 \xrightarrow[\text{2. } H_3O^+]{\text{1. } CO_2} Ph{-}\overset{\displaystyle COOH}{CH}{-}CH_2C_4H_9$$

47

An interesting series of competition reactions[204, 274] has shown the variable affinity of organolithium compounds for styrene *vs.* chlorotrimethylsilane. Primary organolithiums (butyl-, isobutyl-, vinyl-, and phenyllithium) react preferentially with chlorotrimethylsilane, whereas secondary and tertiary organolithiums (*sec*-butyl- and *t*-butyllithium) react preferentially with styrene. The benzylic intermediate, formed from styrene and a secondary or tertiary organolithium, also reacts exclusively with chlorotrimethylsilane instead of with more styrene. The results of these competitive reactions are in accord with those reported by Waack and Doran.[275]

Indene (**48**) is metalated by butyllithium at room temperature for several hours to produce a single product after carbonation. This is considered to be indene-1- (or -3-) carboxylic acid.[276, 277] Melera[278] studied the methyl ester of the product acid by nmr and showed unequivocally that the acid formed under these conditions is **50**, indene-3-carboxylic acid. He explained this product on the basis of isomerization of **49** to **50**, under the basic conditions of the metalation reaction. Further evidence for this assumption was provided by Meth-Cohn and Gronowitz,[279] who showed that indene, when metalated by butyllithium at −70° for 15–20 min followed by carbonation and rapid acidification, produced a high yield of indene-1-carboxylic acid (**49**). They showed further that tautomerism to **50** is rapid and is catalyzed by base.

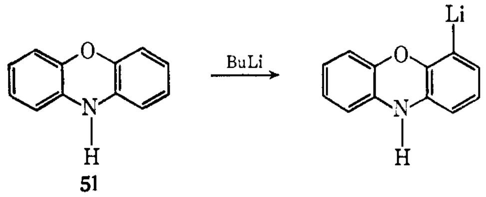


Fluorene, which contains two acidic hydrogens, is readily metalated by organolithium compounds in the 9 position. It has also been shown,[274] in a series of competition reactions, that butyllithium reacts more rapidly with 9-trimethylsilylfluorene than with unsubstituted fluorene, and that butyllithium reacts more rapidly with either of the above compounds than with trimethylchlorosilane. These reactions furnish indirect evidence that the 9 hydrogen in 9 trimethylsilylfluorene is more acidic than in unsubstituted fluorene. These reactions suggest also that experimenters should use great care in assigning structures of organolithium compounds based only on derivative formation, since the relative rates of the competitive reactions may not necessarily indicate the nature of the compounds present.

Metalation occurs as expected at the most acidic hydrogen in polynuclear hydrocarbons. For example, both pyrene[280−282] and perylene[283] have been metalated.

B. METALATION OF OXYGEN COMPOUNDS

Competitive metalation studies have established that the ethereal oxygen in dibenzofuran activates the molecule more strongly toward metalation than does the sulfur in dibenzothiophene or the nitrogen in 9-ethylcarbazole.[5] These metalation studies also established that the lithium atom enters at a position adjacent to the oxygen, in other words, *ortho* to oxygen in an aromatic system or α in a saturated system. Phenoxazine (**51**) is metalated in the 4 position, *ortho* to oxygen rather than nitrogen,[284] illustrating both the stronger effect of oxygen over nitrogen and the *ortho* position of metalation.



Furan is readily metalated in the α position and the product gives the typical reactions of an organolithium compound.[285] However, competitive reactions between thiophene and furan for an insufficient quantity of butyllithium show that thiophene is metalated almost exclusively.[286] These unexpected results seem to be in direct contrast to the above dibenzo systems. Shatenshtein[163] has studied the relative hydrogen–deuterium exchange in the α and β positions of both thiophene and furan and has shown that although the inductive effect of oxygen is greater than sulfur, thiophene metalates faster than furan because of the stabilization of sulfur in the transition state as a consequence of d-orbital participation. These results are in accord with those of Gol'dfarb,[286] who showed that in a similar competitive reaction, 96% of the metalated product was thienyllithium, and only 4% was furyllithium.

According to Shatenshtein,[162, 163] the β hydrogens in both

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(273) R. C. P. Cubbon and D. Margerison, *Proc. Chem. Soc.*, 146 (1960).

(274) A. E. Bey and D. R. Weyenberg, *J. Org. Chem.*, 31, 2036 (1966).

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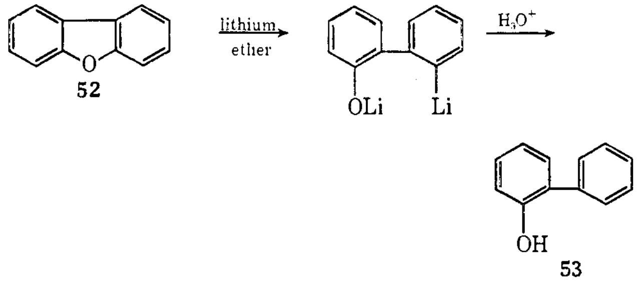
thiopene (**82**) and furan (**81**) are activated equally toward metalation. Similar results are not available for the dibenzo systems, but by extrapolation, it can be assumed that the *ortho* hydrogens are similar in activity to the β hydrogens of furan and thiophene, and the inductive effect of oxygen then becomes predominant.

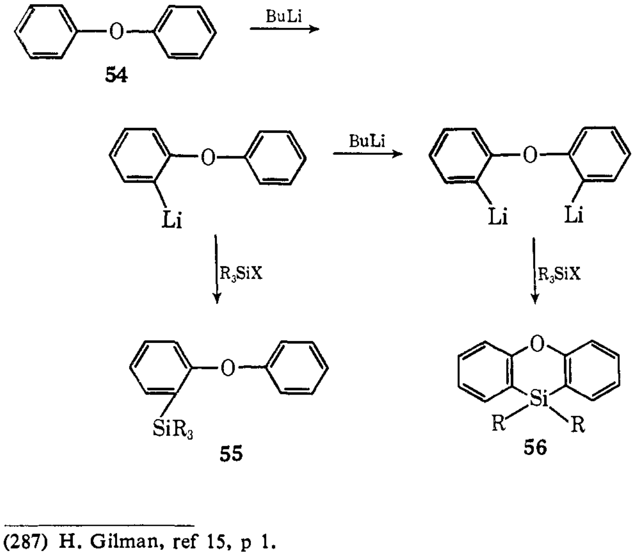
Dibenzofuran has been metalated by butyllithium in ether in relatively low yields. However, by the use of the mixed solvent system THF–ether, dibenzofuran is metalated in much higher yield (83–86% of acid after carbonation) even at low temperature (−60°).[156,157,287] The position of metalation is, as expected, *ortho* to the oxygen. Dibenzofuran (**52**) is cleaved by lithium metal in ether under more drastic conditions to give, after hydrolysis, *o*-hydroxybiphenyl (**53**).[288]



The metalation of aliphatic ethers, such as diethyl ether, has been discussed in the section covering solvents and ether cleavages. It must be remembered that when metalations are conducted in ethereal solvents, reaction of the cleavage products can lead to anomalous results.

Organolithium compounds react normally with small ring ethers to form alcohols. In this respect it is an interesting reflection on relative ring strain to note that while reactions with ethylene and propylene oxide[210] lead to the alcohols, butylene oxide (THF) is less reactive and can be used as a solvent for metalation reactions.

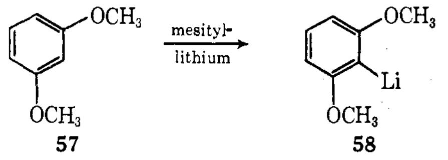
Metalation of diphenyl ether (**54**) can be controlled to give either mono- or disubstituted products.[158,289–292] The reactions illustrated above have been used to make a variety of interesting compounds such as **55** and **56** noted for their high thermal stability.



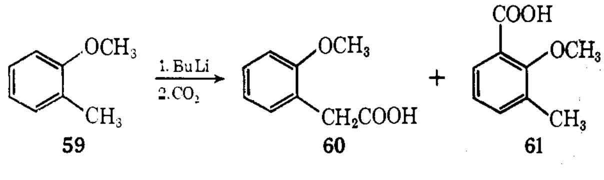
Conflicting results are reported regarding the metalation of methoxynaphthalenes. Gilman first stated that 1-methoxynaphthalene, after metalation and carbonation, gave the expected product, 2-methoxynaphthoic acid in 25% yield.[5] In a later study, Barnes[222] reported that 1-methoxynaphthalene metalates first at the 8 position, and, if the reaction proceeds long enough, the lithium rearranges to the 2 position. Using MO calculations, Barnes showed that the 8 hydrogen is the most acidic, a conclusion also confirmed by nmr. He suggested that there is sufficient steric hindrance between the 1 and 8 positions so that the 1 and 2 positions are the more thermodynamically stable. Thus, with longer reaction times, more of the 2 isomer is formed. Shirley[293] later reexamined the problem. By metalating 1-methoxynaphthalene-8-*d* and then analyzing for the deuterium content of the evolved butane, he was able to show that although a small amount of metalation does occur at the 8 position, the primary position of attack is at the 2 position, *ortho* to the methoxy group. He further demonstrated that the isomer distribution is affected by the amount and kind of salt present, *i.e.*, lithium bromide contained in the metalating reagent.

It would seem appropriate to repeat the above work, since all of the results were based on very low yields of acids.[5,222,293] Higher yields, being more representative of the reaction, would do much to clarify the issues. The metalation of triphenylamine is the only other example in the literature where the metal does not enter *ortho* to a heteroatom, and this has been ascribed to steric hindrance (see the Nitrogen section).

Mixed aliphatic–aromatic ethers are readily metalated by organolithium reagents, usually in the *ortho*, or α, position similar to the oxygen heterocycles.[5] Metalation of 4-methylanisole gives 5-methyl-2-methoxybenzoic acid after carbonation,[294] and resorcinol dimethyl ether (**57**) is metalated in the 2 position, *ortho* to both methoxy groups[172] to yield **58**.



When one of the positions *ortho* to the methoxy group is occupied, an intermolecular competition occurs in the molecule, and it is not always clear which position will be preferentially metalated. For example, *o*-methylanisole (**59**) after metalation and subsequent carbonation is reported to give equal amounts (albeit in very small yields) of both the sidechain (**60**) and ring (**61**) metalated products while *o*-ethylanisole gives only 2-methoxy-3-ethylbenzoic acid.[294] Kun and Cassidy studied the more complicated structure 1,4-dimeth-



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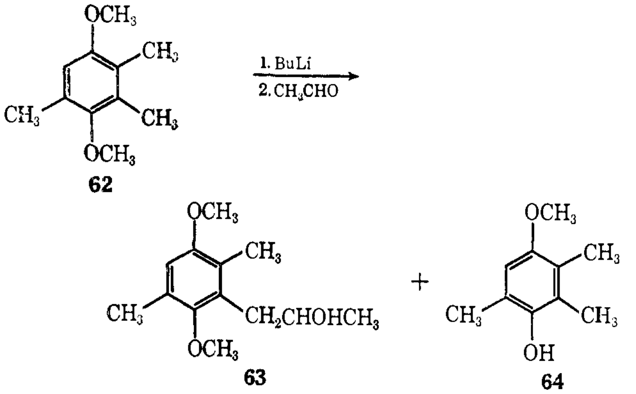
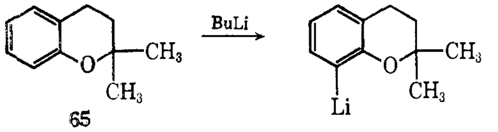
(287) H. Gilman, ref 15, p 1.
(288) H. Gilman and D. L. Esmay, *J. Am. Chem. Soc.*, **75**, 2947 (1953)
(289) H. Gilman and D. Miles, *J. Org. Chem.*, **23**, 1363 (1958).
(290) H. Gilman and W. J. Trepka, *ibid.*, **27**, 1418 (1962).
(291) K. Oita and H. Gilman, *ibid.*, **21**, 1009 (1956).
(292) K. Oita and H. Gilman, *J. Am. Chem. Soc.*, **79**, 339 (1957).
(293) B. M. Graybill and D. A. Shirley, *J. Org. Chem.*, **31**, 1221 (1966);
(294) R. L. Letsinger and A. W. Schnizer, *ibid.*, **16**, 869 (1951).

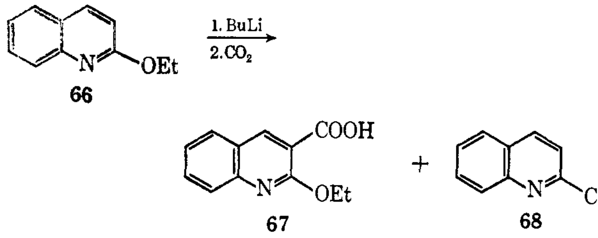
oxy-2, 3,5-trimethylbenzene (**62**) and found that after metalation and derivatization with acetaldehyde, the major product was the alcohol **63**; the only minor product isolated was 1-methoxy-4-hydroxy-2,3,5-trimethylbenzene (**64**). Clearly, in this case, attack occurred predominantly on the benzylic hydrogen.[295] However, when 2,2-dimethylchroman (**65**) is metalated by butyllithium, only the *ortho* ring position is involved.[296]



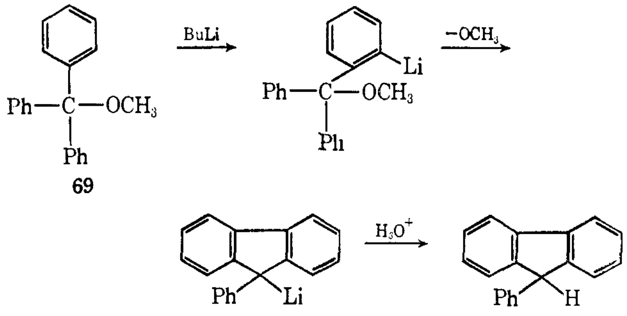


The above results indicate that for the anisoles, the order of preference for attack by butyllithium on hydrogen is benzylic > aromatic > aliphatic. In this respect, it is interesting to note that while aliphatic ethers are readily metalated (and cleaved) by organolithium compounds, anisole (methyl phenyl ether) is metalated only on the ring, and cleavage of the ether function does not seem to occur. However, in highly substituted compounds, such as **64**, some cleavage of the ether function does occur.

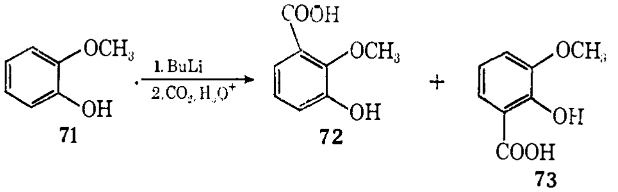
The strong *ortho*-directing effect of oxygen is further shown in the metalation of 2-ethoxyquinoline (**66**),[297] where only the position *ortho* to the oxygen is metalated, and the position *peri* to nitrogen is unaffected. The product **67** forms by way of *ortho* metalation, and **68** forms through the addition of butyllithium to the azomethine linkage with subsequent elimination of ethoxide.

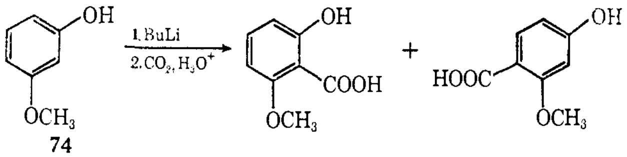


The metalation of triphenylmethyl ether **69** gives 9-phenylfluorene (**70**) after hydrolysis. Presumably this arises through the metalation of an *ortho* ring hydrogen, followed by attack at the central carbon, elimination of methoxide, and ring closure.[298] Even in dibenzhydryl ether, where both ring and doubly activated benzylic hydrogens are available, metalation is reported to occur only on the *ortho* ring position.[299]



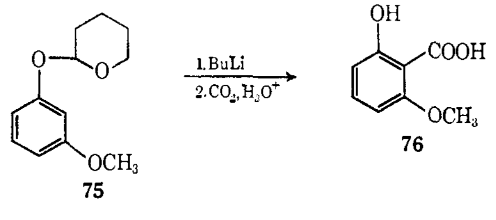
Gilman and Santucci[300] studied the metalation of substituted benzenes containing both hydroxy and alkoxy functions. Carbonation of metalated *o*-methoxyphenol (**71**) gave equal quantities of **72** and **73**. The same over-all yield of acidic products was obtained from *m*-methoxyphenol (**74**) but the major attack was *ortho* to the methoxy group. These results indicate that metalation is more strongly enhanced by methoxyl groups than hydroxyl groups.





Labile ethers are frequently used as temporary blocking agents to avoid the presence of free interfering groups during a reaction. The dihydropyranyl ether of hydroquinone can be metalated to give, after carbonation and hydrolysis, 2,5-dihydroxybenzoic acid.[301] Also, 1,3-dioxolanes can serve as effective blocking groups for carbonyl functions during metalations.[302]

When the pyranyl ether of *m*-methoxyphenol (**75**) is metalated and carbonated, the only acid isolated was **76**. The yield was about four times greater than for the free *m*-methoxyphenol (**74**), indicating the deactivating effect of the free hydroxyl group.[300] This latter effect may be a reflection of the



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(295) K. A. Kun and H. G. Cassidy, *J. Org. Chem.*, 27, 841 (1962).

(296) M. Hallet and R. Huls, *Bull. Soc. Chim. Belges*, 61, 33 (1952); *Chem. Abstr.*, 47, 9966 (1953).

(297) H. Gilman and J. A. Beel, *J. Am. Chem. Soc.*, 73, 32 (1951).

(298) H. Gilman, W. J. Meikle, and J. W. Morton, Jr., *ibid.*, 74, 6282 (1952).

(299) D. Y. Curtin and M. J. Fletcher, *J. Org. Chem.*, 19, 352 (1954).

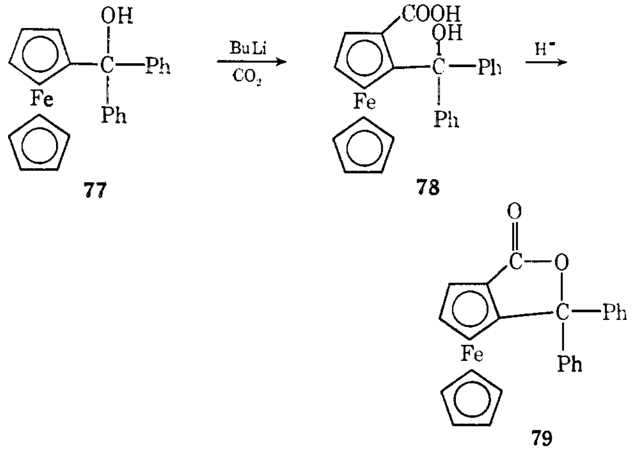
(300) L. Santucci and H. Gilman, *J. Am. Chem. Soc.*, 80, 4537 (1958).

(301) R. Stern, J. English, Jr., and H. G. Cassidy, *ibid.*, 79, 5797 (1957).

(302) S. F. Thames and J. E. McCleskey, *J. Heterocyclic Chem.*, 3, 104 (1966).

insolubility of the lithium alkoxide which would form first by reaction with the phenol.

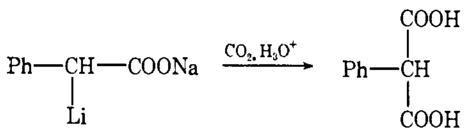
Compounds that contain free, nonphenolic, hydroxyl groups can also be metalated. Carbonation of metalated triphenylcarbinol yields the lactone of triphenylcarbinol-2,2′-dicarboxylic acid.[5,298] In an analogous reaction, metalation of diphenylferrocenylcarbinol (**77**) followed by carbonation leads to the acid **78** which can be readily converted to the lactone of 2-carboxydiphenylferrocenylcarbinol (**79**). It is interesting to note that in this internal competition reaction between ferrocenyl and phenyl rings, the ferrocenyl ring is preferentially metalated.[303]



77 **78** **79**

Ivanov and coworkers[173–182] studied the metalation reactions of carboxylic acid salts. They demonstrated that the α hydrogen in sodium phenylacetate (**80**) is sufficiently activated for metalation to proceed smoothly with a variety of organolithium compounds.

$PhCH_2COONa + RLi \longrightarrow$
80

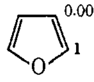


$$Ph-\underset{Li}{CH}-COONa \xrightarrow{CO_2,\ H_3O^+} Ph-\underset{COOH}{\overset{COOH}{CH}}$$

C. METALATION OF SULFUR COMPOUNDS

Competitive metalations have shown that sulfur heterocycles, except for thiophene, are intermediate between oxygen and nitrogen in their susceptibility toward metalation.[5] As is typical for the metalation of other heterocyclic systems, the lithium enters in the position *ortho* to the sulfur atom.

Thiophene is an exception to the relative order of reactivity of the heterocycles and has been discussed along with furan in the oxygen section. When a mixture of furan and thiophene is metalated competitively with an insufficient quantity of butyllithium, the predominant product is thienyllithum.[163,286] This is considered to be a result of d-orbital participation. These results are quite in line with the calculated relative activities for the two compounds, since the α position in thiophene (**82**) is 500 times more reactive than the equivalent position in furan (**81**).[163]



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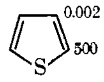
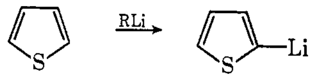


82

The hydrogen-isotope effect has been studied by several workers[227,228] for the thiophene series. Metalation of 2-deuteriothiophene shows the expected decrease in rate over nonsubstituted thiophene. These results are in accord with the accepted mechanism for ring metalation.

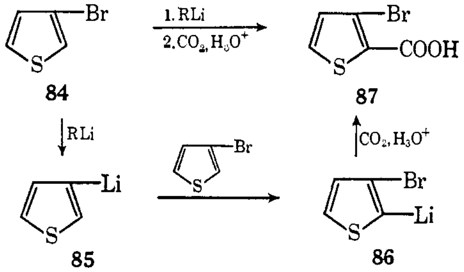
Gronowitz and his coworkers have studied extensively the metalation of thiophene and substituted thiophenes.[227,231,304–317] Thiophene (**82**) is metalated by organolithium reagents *ortho* to the sulfur. The resultant thienyllithium (**83**) reacts as a typical organometallic reagent in that it can be used as a metalating agent and undergoes the typical derivatization reactions.



82 83

When 2-methylthiophene is metalated, the lithium enters in the 5 position, *ortho* to the sulfur. However, metalation of 3-methylthiophene has been reported to go in the 5 position exclusively,[231,318] while other workers report a mixture of products.[319] Gronowitz has shown that the methyl group in the 3 position deactivates the ring toward metalation.[231] When a mixture of thiophene and 3-methylthiophene is metalated competitively, 95% thienyllithium and 5% 3-methyl-5-thienyllithium are produced.

Metalation of 3-bromothiophene (**84**) at low temperatures, followed by carbonation, leads to 3-bromo-2-thiophenecarboxylic acid (**87**).[231] Gronowitz suggests that the 3-bromothio-



84 87 85 86

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(303) R. A. Benkeser, W. P. Fitzgerald, and M. S. Melzer, *J. Org. Chem.*, **26**, 2569 (1961).

(304) S. Gronowitz, *Arkiv Kemi*, **12**, 239 (1958); *Chem. Abstr.*, **52**, 20115 (1958).

(305) S. Gronowitz, *Arkiv Kemi*, **13**, 269 (1958); *Chem. Abstr.*, **53**, 15056 (1959).

(306) S. Gronowitz, *Arkiv Kemi*, **13**, 295 (1958); *Chem. Abstr.*, **53**, 15056 (1959).

(307) S. Gronowitz, *Arkiv Kemi*, **16**, 363 (1960); *Chem. Abstr.*, **55**, 21092 (1961).

(308) S. Gronowitz and B. Eriksson, *Arkiv Kemi*, **21**, 335 (1963); *Chem. Abstr.*, **59**, 13918 (1963).

(309) S. Gronowitz and H. Frostling, *Tetrahedron Letters*, 604 (1961).

(310) S. Gronowitz and H. Frostling, *Acta Chem. Scand.*, **16**, 1127 (1962); *Chem. Abstr.*, **59**, 539 (1963).

(311) S. Gronowitz and B. Gestblom, *Arkiv Kemi*, **18**, 513 (1962).

(312) S. Gronowitz, B. Gestblom, and B. Mathiasson, *ibid.*, **20**, 407 (1963); *Chem. Abstr.*, **59**, 7459 (1963).

(313) S. Gronowitz and R. Hakansson, *Arkiv Kemi*, **17**, 73 (1961); *Chem. Abstr.*, **56**, 3497 (1962).

(314) S. Gronowitz and H. O. Karlsson, *Arkiv Kemi*, **17**, 89 (1960); *Chem. Abstr.*, **55**, 27261 (1961).

(315) S. Gronowitz, P. Moses, and A. Hornfeldt, *Arkiv Kemi*, **17**, 237 (1961).

(316) S. Gronowitz, P. Moses, A. Hornfeldt, and R. Hakansson, *ibid.*, **17**, 165 (1961); *Chem. Abstr.*, **57**, 8528 (1962).

(317) S. Gronowitz and G. Sorlin, *Arkiv Kemi*, **19**, 515 (1962); *Chem. Abstr.*, **58**, 5605 (1963).

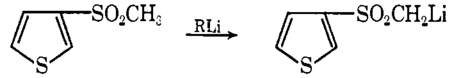
(318) J. Sicé, *J. Org. Chem.*, **19**, 70 (1954).

(319) V. Ramanathan and R. Levine, *ibid.*, **27**, 1667 (1962).

phene is first converted to 3-thienyllithium (**85**) *via* halogen-metal exchange and this then metalates the remaining 3-bromothiophene to yield 3-bromo-2-thienyllithium (**86**). This work has been substantiated by Ostman,[225] who found that excess butyllithium metalates 3-bromothiophene to yield 2,3-dicarboxythiophene.

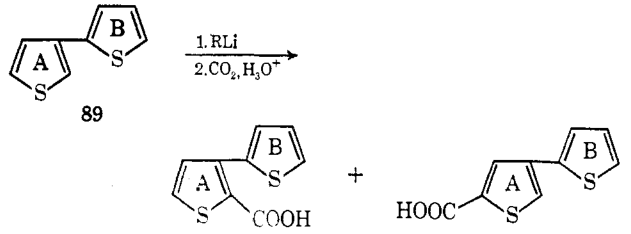
Methoxyl-substituted thiophenes undergo a normal metalation reaction. Thus 2-methoxythiophene is metalated in the 5 position,[320] strongly suggesting that the coordination of the metalating agent with the sulfur is much greater than with the ether oxygen. However, 3-methoxythiophene and 3-*t*-butoxythiophene[307] are metalated in the 2 position.

When the ether oxygen is replaced by a sulfur, as in methyl-3-thienyl sulfide, metalation occurs at the 2 position. However, when the sulfur is further activated, as in methyl 3-thienyl sulfone (**88**), the effect of the sulfone becomes predominant and the α-methyl hydrogen is attacked.



88

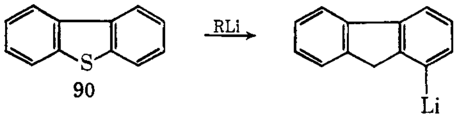
When the thiophene ring is substituted with another thiophene, as in 2,2-bithienyl, metalation occurs in the expected 5 positions.[321] However, 2,3-bithienyl (**89**) is metalated in both the 2 and 5 positions, but only in the A ring. There was no evidence of an acid formed in the B ring. The authors present several possible rationalizations for this.[321]



89

The general principle is that a 3-substituted thiophene, except for 3-methylthiophene, is metalated in the 2 position and apparently is unaffected by the nature of the 3 substituent. Thus 3-cyano-,[304] 3-bromo-,[231] and 3-methoxythiophene[304] are all metalated in the 2 position. The conclusion can be drawn that the coordination of the metalating agent with the heteroatom is the predominant influence in deciding the position of metalation. The reactions of the 3-substituted thiophenes have been reviewed.[306]

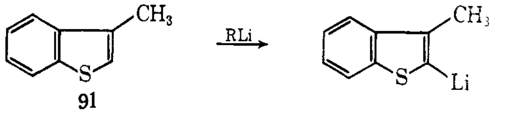
The position of metalation in the aromatic sulfur heterocycles, similar to the thiophenes, is adjacent to the heteroatom.[5] Dibenzothiophene (**90**) is readily metalated in the 4 position to yield 4-lithiodibenzothiophene.[322] The use of THF as the solvent greatly facilitates this metalation.[157] Dibenzofuran is more reactive toward metalation than is dibenzothiophene, and it is also cleaved much more readily by lithium in refluxing ether or dioxane.[288]



90

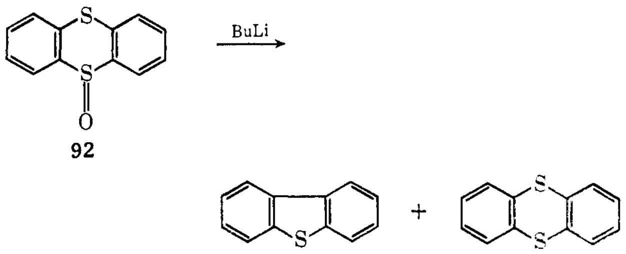
When the sulfur is in a higher oxidation state, as in dibenzothiophene 5-oxide and dibenzothiophene 5-dioxide, metalation can be readily accomplished without loss of the oxide portions;[323,324] however, low (−20 to −30°) temperatures are required to avoid cleavage reactions.

Metalation of thianaphthene is the most efficient procedure for the preparation of 2-substituted derivatives, illustrating again the activating influence of the sulfur through coordination. Other methods of substitution do not lead to the 2-substituted compounds. When thianaphthene is substituted in the 3 position with a methyl group (**91**), the site of metalation is still the 2 position.[325,326]



91

Thianthrene is readily metalated *ortho* to the sulfur. However, the higher oxidation states of sulfur, thianthrene 5-oxide and thianthrene 5,5,10-trioxide, are not stable under the conditions of metalation. For example, metalation of thianthrene 5-oxide (**92**) leads to dibenzothiophene (**93**) and thianthrene (**94**).[327] Thianthrene 5-dioxide (**95**) is not cleaved but produces 4-carboxythianthrene 5-dioxide (**96**).[328] However, thianthrene 5,5,10-trioxide (**97**) is cleaved, and the diphenyl sulfone derivative (**98**) is produced upon carbonation.[328]



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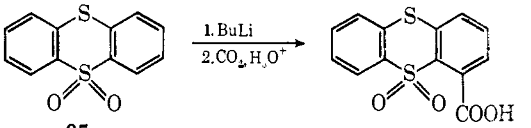

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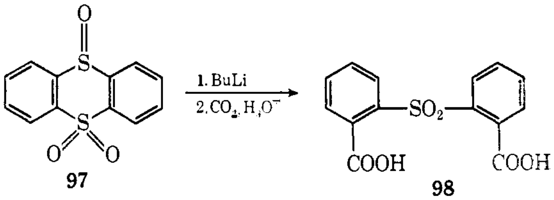

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98

The above examples illustrate that metalation increases in the order sulfide > sulfone > sulfoxide. The validity of this series is further confirmed in the nonheterocyclic sulfur compounds.

In the nonheterocyclic sulfur series, the entering metal goes *ortho*, or adjacent, to the sulfur; and when a choice is present,

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(320) J. Sicé, *J. Am. Chem. Soc.*, 75, 3697 (1953).

(321) H. Wynberg and A. Bantjes, *ibid.*, 82, 1447 (1960).

(322) H. Gilman and D. L. Esmay, *ibid.*, 75, 233 (1953).

(323) H. Gilman and D. L. Esmay, *ibid.*, 74, 266 (1952).

(324) H. Gilman and D. L. Esmay, *ibid.*, 75, 278 (1953).

(325) D. A. Shirley and M. D. Cameron, *ibid.*, 74, 664 (1952).

(326) D. A. Shirley, M. J. Danzig, and F. C. Canter, *ibid.*, 75, 3278 (1953).

(327) H. Gilman and D. R. Swayampati, *ibid.*, 77, 3387 (1955).

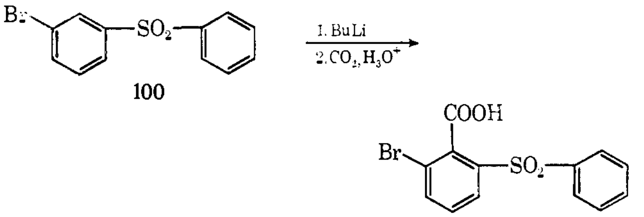
(328) H. Gilman and D. R. Swayampati, *ibid.*, 79, 208 (1957).

the preference is for an aliphatic, or benzylic hydrogen, over an aromatic hydrogen. For example, both benzyl phenyl sulfide and benzyl phenyl sulfone are metalated on the α carbon.[329] Thioanisole is only difficultly metalated on the side chain by butyllithium,[5] but a DABCO–butyllithium complex yields 97% side-chain metalated product in 45 min.[330]

The sulfone function readily activates the adjacent position and the sulfone is sufficiently stable to survive the metalation. For example, both dimethyl sulfone[331] and diphenyl sulfone[332] are readily metalated by butyllithium. The relatively low reactivity of fluorine in a trifluoromethyl group is illustrated by the metalation of the methyl group rather than a halogen-metal exchange in trifluoromethyl methyl sulfone (**99**).[333]

$$\underset{\mathbf{99}}{CF_3{-}SO_2{-}CH_3} \xrightarrow{\text{BuLi}} CF_3{-}SO_2{-}CH_2Li$$

Truce has studied the metalation of sulfones and substituted sulfones.[208,331,332,334] He demonstrated that, while a sulfone group is generally considered as one of the stronger *meta* directors in electrophilic aromatic substitution reactions, in metalation reactions the metal always enters a position *ortho* to the sulfone. If two aromatic ring systems are present, the metal enters the more activated ring, but still *ortho* to the sulfone group. For example, metalation of 3-bromophenyl phenyl sulfone (**100**), followed by carbonation, yields 54% of 3-bromo-2-carboxyphenyl phenyl sulfone (**101**). In this case the product is independent of any *ortho-para*-directing influences of the bromo group as well as the *meta*-directing influences of the sulfone. Clearly initial coordination between the sulfone and the metalating agent leading to an *ortho* substitution is the predominant factor in determining the position of metalation.[332] When the sulfone contains two different ring systems, as in phenyl 2-thienyl sulfone (**102**), the metal atom enters the more activated thiophene ring **103**.[332]



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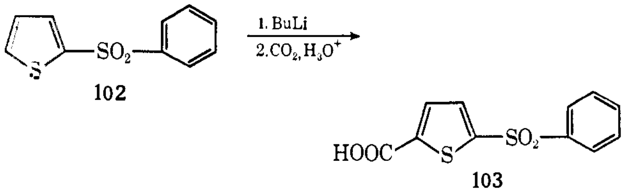

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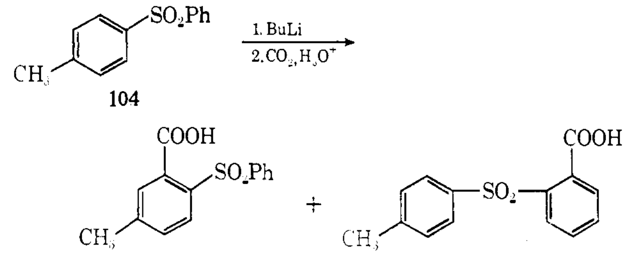
103

A *p*-methyl group does not have as strong an activating effect as does a bromo group in the metalation of sulfones. When *p*-tolyl phenyl sulfone (**104**) is metalated, the lithium enters both rings, with only a slight preference for the unsubstituted ring.[334] However, Shirley has shown in a competition reaction between diphenyl sulfone and di-*p*-tolyl sulfone for an insufficient quantity of butyllithium, that both compounds are metalated to approximately the same extent.[335] The deactivating effect of an aliphatic side chain is further substantiated in the case of *p*-tolyl *n*-butyl sulfone (**105**), where metalation occurs only on the α hydrogen of the butyl moiety (**106**).[336] A *p*-*t*-butyl group also has been shown to have a similar deactivating effect in this type of metalation.[230,334,337]



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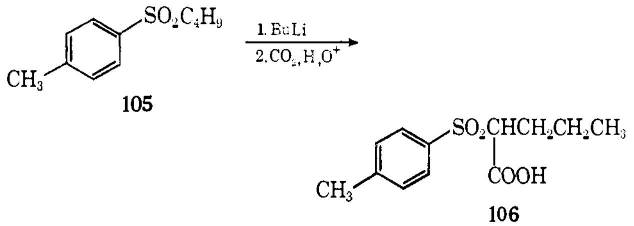

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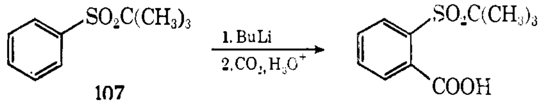
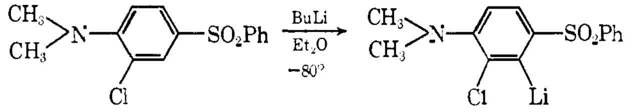
When the *t*-butyl group is directly linked to the sulfone, as in *t*-butyl phenyl sulfone (**107**), metalation leads to substitution on the phenyl ring.[338,339] This compound is sufficiently activated that it can be dimetalated.[340] Dimetalation is not restricted to the influences of a *t*-butyl group, since diphenyl sulfone can also be dimetalated.[341]



107

Wittig[342] has utilized the *ortho*-activating effect of the sulfone to prepare **108**, which is intermediate between *o*-chlorophenyllithium and benzyne in its reactivity. Below −60°, **108** is converted to a benzyne intermediate.



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(329) E. A. Lehto and D. A. Shirley, *J. Org. Chem.*, **22**, 989 (1957).

(330) E. J. Corey and D. Seebach, *ibid.*, **31**, 4097 (1966).

(331) W. E. Truce and K. R. Buser, *J. Am. Chem. Soc.*, **76**, 3577 (1954).

(332) W. E. Truce and M. F. Amos, *ibid.*, **73**, 3013 (1951).

(333) L. M. Yagupol'skii, A. G. Panteleimonov, and V. V. Orda *J. Gen. Chem. USSR*, **34**, 3498 (1964).

(334) W. E. Truce and O. L. Norman, *J. Am. Chem. Soc.*, **75**, 6023 (1953).

(335) D. A. Shirley, E. A. Lehto, C. W. Holley, and H. A. Smith, *J. Org. Chem.*, **22**, 1073 (1957).

(336) H. Fukuda, F. J. Frank, and W. E. Truce, *ibid.*, **28**, 1420 (1963).

(337) D. A. Shirley and E. A. Lehto, *J. Am. Chem. Soc.*, **79**, 3481 (1957).

(338) F. M. Stoyanovich and B. P. Fedorov, *Angew. Chem. Intern. Ed. Engl.*, **5**, 127 (1966).

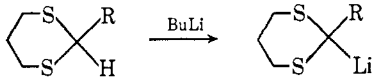
(339) F. M. Stoyanovich and B. P. Fedorov, USSR Patent 181,101; *Chem. Abstr.*, **65**, 10621 (1966).

(340) B. P. Fedorov and F. M. Stoyanovich, USSR Patent 162,154; *Chem. Abstr.*, **61**, 9525 (1964).

(341) K. Oita and H. Gilman, *J. Org. Chem.*, **22**, 336 (1957).

(342) H. E. Zieger and G. Wittig, *ibid.*, **27**, 3270 (1962).

The *ortho*-, or adjacent, directing influence of sulfur has been utilized to prepare an interesting series of carbonyl derivatives. The 1,3-dithianes (**109**) are readily metalated by organolithium reagents to give α-lithio derivatives, which can then be converted into a large number of compounds.[343,344]

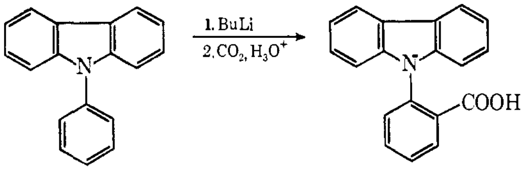


109

D. METALATION OF NITROGEN COMPOUNDS

Nitrogen heterocycles have been shown to be the least reactive in the series oxygen, sulfur, nitrogen. When a competition reaction is carried out between dibenzothiophene and N-ethylcarbazole for an insufficient quantity of butyllithium, only the dibenzothiophene is metalated.[5]

There are several exceptions to the general rule that metalations in systems containing a heteroatom are always metalated *ortho* to the heteroatom. Triphenylamine, triphenylarsine, and triphenylphosphine are all metalated in the *meta* position of the ring.[5] Gilman feels that, while steric hindrance is undoubtedly responsible for part of this effect, other factors must also participate. That the less sterically hindered diphenylmethylamine is metalated in the phenyl ring and, after carbonation, yields N-methyl-N-phenylanthranilic acid, indicates that the steric effect does not operate in this case.[345] If steric hindrance were the sole reason for the abnormal metalation, it could be expected that N-phenylcarbazole (**110**) would also be abnormally metalated, but this does not occur. Instead, N-phenylcarbazole undergoes normal metalation in the *ortho* position of the free phenyl ring. In fact, dimetalation of this molecule leads to 2,6 metalation in the free phenyl ring.[5]



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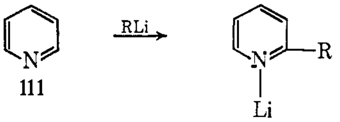
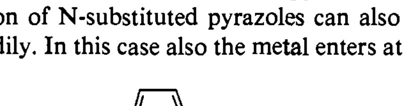
Metalation of nitrogen heterocycles proceeds in a normal fashion and the entering metal goes *ortho*, or adjacent, to the nitrogen. This is consistent with the proposed mechanism, which considers that the initial step in the metalation is coordination of the metalating agent with the free electrons on the nitrogen. However, some compounds which contain the azomethine linkage, such as pyridine (**111**) and quinoline, are not metalated. Instead, the organolithium adds to produce a 2-substituted lithium salt (**112**). However, 2-pyridyllithium, prepared through halogen–metal exchange, is stable and can be used as a metalating agent.[346,347]



111 112

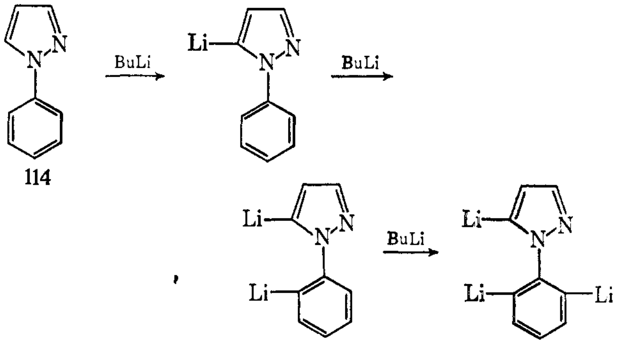
Picoline (2-methylpyridine) is smoothly metalated by organolithium reagents on the side-chain methyl group and reacts as a normal organometallic reagent.[348] In a series of experiments, it has been demonstrated that in polymethyl-substituted pyridines, the 2-methyl is preferentially metalated. For example, 2,4-dimethylpyridine and 2,4,6-trimethylpyridine are metalated at the 2-methyl group[349,350] and dimetalation is reported to occur on the same methyl group.[350] It has also been reported that 4-methylpyridine can be metalated on the methyl group by phenyllithium.[351–353]

Unsubstituted pyrrole, the nitrogen analog of furan and thiophene, is not metalated, even with excess metalating agent. Instead, only the lithium salt is formed.[354] However, N-substituted pyrroles (**113**) are smoothly metalated at the 2 position of the ring.[354] It is interesting to note that whereas N-phenylcarbazole is metalated on the free phenyl ring, N-phenylpyrrole is metalated in the pyrrole ring.[354,355] Dimetalation of N-methylpyrrole has also been accomplished, and carbonation produces N-methyl-2,5-dicarboxypyrrole.[354]



113

Metalation of N-substituted pyrazoles can also be accomplished readily. In this case also the metal enters at the 5 position, analogous to the thiophenes and furans. When N-phenylpyrazole (**114**) is polymetalated, however, the additional lithiums enter on the phenyl ring.[356] Metalation of 3-methyl-N-phenylpyrazoles also occurs at the 5 position of the pyrazole ring.[357]



114

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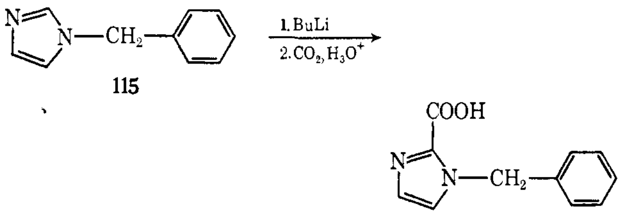
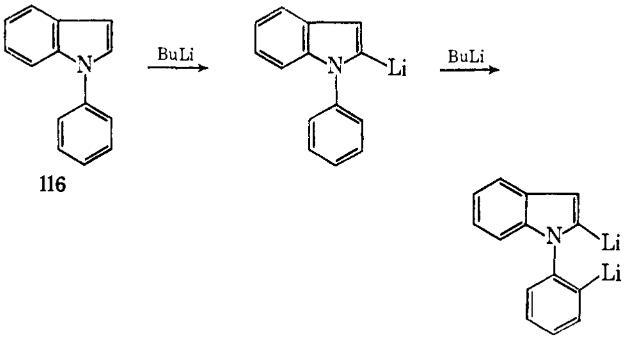


115

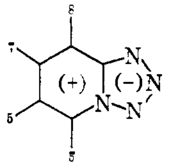
N-Substituted imidazoles (**115**) are metalated in the 2 position, adjacent to both nitrogens,[358] the 2 position of the ring taking precedence over the benzylic hydrogen. When N-phenylimidazole is dimetalated, the second lithium enters on the free phenyl ring.

The metalation of indole follows the same pattern as for pyrrole.[355] Unsubstituted indoles metalate only on the nitrogen. N-Phenylindoles (**116**) are metalated preferentially at the 2 position of the pyrrole ring; when dimetalated, the second lithium enters the free phenyl ring.[355] While N-substituted benzimidazoles are readily metalated in the 2 position, these reactions are much more successful at lower temperature. At room temperature dimers of the parent compound are frequently obtained.[359]



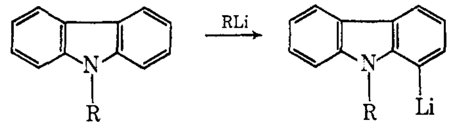
116

Metalation has also been reported for the pyridotetrazoles (**117**).[360] Unsubstituted pyridotetrazoles are metalated at both the 5 and 8 positions, 8-methylpyridotetrazole is metalated at the 5 position, but 5-methylpyridotetrazole is metalated on the methyl group. Pyrimidines[361] and 2,5-dimethylpyrazines[362] are not metalated by organolithium reagents; instead lithium salts are formed.



117

Relatively few metalations have been carried out on the N-substituted carbazoles compared to other nitrogen heterocycles.[157] In the few reported metalations using diethyl ether as the solvent, very low yields of acids were obtained after carbonation. However, it has recently been demonstrated that the use of THF–ether as the metalating solvent greatly increases the yield of metalated product. The N-substituted carbazoles (**118**) follow the general rules for normal metalation, and the lithium enters the 2 position, adjacent to the nitrogen.[157]

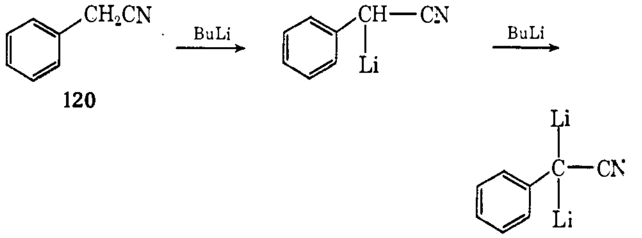


118

Many interesting nonheterocyclic nitrogen compounds have been metalated since the previous review.[5] Both diazomethane (**119**)[363,364] and diazoethane[365] have been metalated by methyllithium, and some of their reactions have been studied.[366–368]

119

Two groups working independently have discovered that phenylacetonitrile (**120**) can be smoothly metalated at the α carbon. Kaiser has shown that pure, α-substituted phenylacetonitriles can be prepared readily by this route,[155,369] and Ivanov[181,182] has explored the synthetic utility of the reaction. It has also been demonstrated that α-substituted phenylacetonitriles can be metalated.[370] In addition, phenylacetamide (**121**) undergoes trimetalation.[371]



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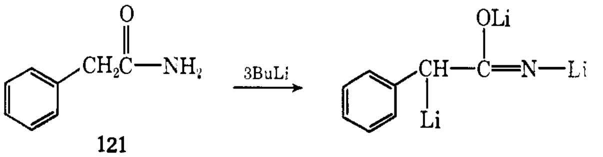

121

Primary, secondary, and tertiary amines can generally be metalated smoothly with the metal entering the α position adjacent to the nitrogen. The only exception to this, triphenylamine, has already been discussed. When unsubstituted primary and secondary amines are metalated, proportionally more of the metalating agent is required to replace that consumed by the active hydrogens on the nitrogen. In the case of tertiary amines, such as N,N-dimethylaniline, metalation proceeds smoothly to produce a ring-substituted derivative. There is no reported metalation of the methyl groups.[372]

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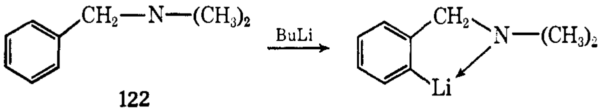
Hauser and his coworkers have studied extensively the metalation of N,N-dimethylbenzylamines (**122**). They demonstrated[373] that when this compound is treated with butyllithium, the lithium enters on the ring in the *ortho* position. When **122** is metalated by butylsodium, the initial site of metalation is the *ortho* position, but upon heating, it isomerizes to the α-sodio derivative. The α-sodio compound was converted to the lithium derivative *via* lithium bromide in ether–benzene–octane. When this α-lithio compound was heated to 48°, it reverted to the *ortho* ring derivative, indicating that the *ortho* position is more stable than the α position for lithium. This type of isomerization by sodium compounds has been observed and discussed by others.[223]

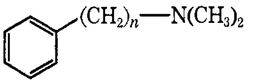


122

The initial step in the reaction between the benzyldimethylamines and butyllithium is assumed to be the coordination between the metal and the free pair of electrons on the nitrogen. The authors feel that the *ortho* position is more readily attacked by lithium because of the greater stabilization afforded by the formation of the five-membered ring.[373] Later work has shown that these *ortho* lithio derivatives react normally with a wide variety of derivatizing agents.[374, 375]

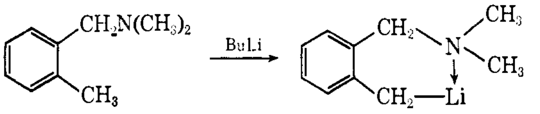
The *ortho* lithiation reaction has also been extended to other systems.[376–378] For example, N-methylbenzamide, after metalation, yields an *ortho* lithio derivative which undergoes normal organometallic reactions.[378] It is interesting to note that unsubstituted benzamide does not undergo this metalation reaction.

ortho lithiation can also be accomplished in systems that contain additional CH_2 groups between the phenyl ring and the nitrogen. Hauser has reported[379] that systems (**123**) with an odd number, *i.e.*, $n = 1$ or 3, of CH_2 groups in a chain can be *ortho* lithiated, whereas those where n is an even number cannot be metalated. These results are in conflict with the reported *ortho* lithiation of β-phenethyldimethylamine.[380] Hauser has demonstrated that α-phenylpropyldimethylamine, $n = 3$, is metalated on the benzylic carbon[379] and that (β,β-dimethyl-β-phenylethyl)dimethylamine is metalated at the *ortho* position.



123
$n = 1,2,3,$ or 4

When one of the *ortho* positions is substituted with a methyl group, as in *o*-methylbenzyldimethylamine (**124**), the methyl group is metalated in preference to the ring.[381] This type of methyl metalation has also been demonstrated in the case of 2-methyl-N-methylbenzamide.[382]



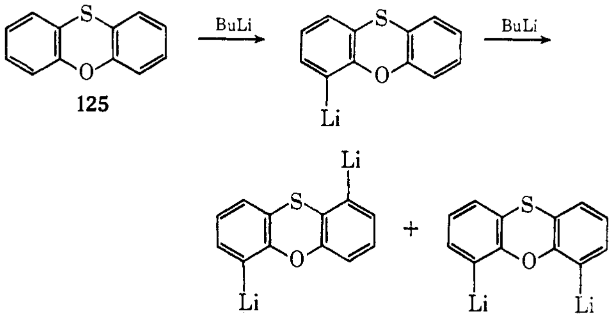
124

In view of the much greater metalating ability of butyllithium complexed with DABCO or TMEDA, both of which are tertiary amines, it is entirely possible that a similar type of situation prevails in the metalation of the benzyldimethylamines. In this case, the complexation occurs intramolecularly.

E. METALATION OF MIXED HETEROCYCLIC COMPOUNDS

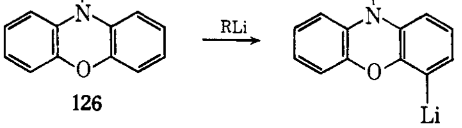
Metalation studies of mixed heterocyclic systems provide interesting insights into the relative reactivity of oxygen, sulfur, and nitrogen in intramolecular reactions. The same general rule of oxygen > sulfur > nitrogen in increasing order of reactivity prevails.

Phenoxathiin (**125**) is readily monometalated by butyllithium in the 4 position, *ortho* to the oxygen.[5, 383] However, dimetalation leads to a mixture of products. After carbonation, both the 4,6-diacids and the 1,6-diacids are obtained in a ratio of 4:1.[384, 385] Under more severe conditions, the sulfur moiety is cleaved and, after carbonation, the product is *o*-phenoxybenzoic acid.[386] When the sulfur is further activated, as in phenoxathiin 10-dioxide, the sulfone takes precedence over the oxygen, and metalation occurs in the 1 position, *ortho* to the sulfone.[385]



125

Monometalation of phenoxazine (**126**) has been reported,



126

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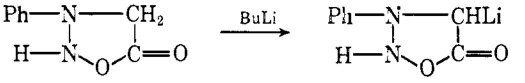
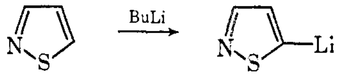
and the metal enters *ortho* to the oxygen.[284] Metalation of the sydnones (**127**) has also been accomplished, and in this case the metal enters the very activated 4 position.[387]



127

Considerably more work has been done on the mixed nitrogen–sulfur heterocycles. In all of the single ring compounds, the metal enters adjacent to the sulfur. Isothiazole (**128**), for example, is metalated in the 5 position, adjacent to the sulfur.[388] The *ortho* effect of both sulfur and nitrogen direct to the same position in the thiazole nucleus,[389] and metalation occurs only at this 2 position. Even 4-methylthiazole is metalated at the 2 position.[390] In fact, the preference for this position is so dominant that 2,5-dimethylthiazole (**129**) is metalated on the 2-methyl group.[391]



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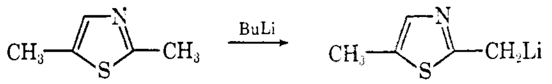
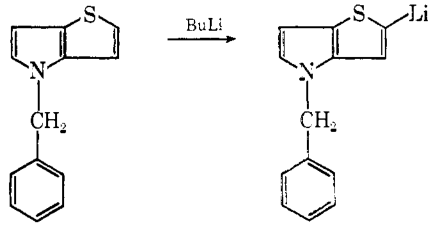


129

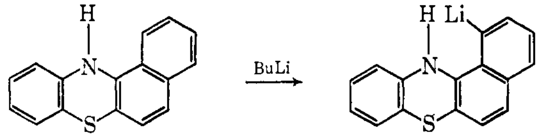
When the nitrogen and sulfur are in different rings, as in N-benzylthieno[3,2-*b*]pyrrole (**130**) and the nitrogen is substituted by a benzylic carbon, metalation still occurs *ortho* to the sulfur. Metalation of N-methylphenothiazine also produces an *ortho* sulfur derivative.[392]



130

The above reactions indicate the following order of decreasing reactivity: $SO_2 > O > S > N$. While this order is undoubtedly empirically correct for the compounds listed, it is unfortunate that in all of the nitrogen metalations, the nitrogen must be further substituted to prevent salt formation. This obviously does not allow for direct comparisons between groups to be made.

In an attempt to resolve this problem and to bring the nitrogen more clearly in line with the other relative metalation reactions, Shirley has studied the metalation of fused ring phenothiazines (**131**). These compounds are sufficiently sterically hindered that salt formation does not occur at the nitrogen.[393] He found that in every fused-ring phenothiazine examined, metalation always occurred adjacent to the nitrogen and preferably on the naphthalene ring.[393–396] These results indicate that the sulfur over nitrogen preference in the reactivity relationship may not be correct. However, more work is necessary before definite conclusions can be made.



131

F. METALATION OF GROUP IVA COMPOUNDS

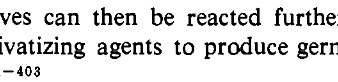
The preparations and reactions of many of the group IVA organometallic compounds have been reviewed.[16,17,44,397]

The organic derivatives of the group IVA elements are metalated very similarly to their more usual carbon analogs.[398] For example, triphenylbenzylsilane (**132**) is metalated adjacent to the silyl atom and undergoes the normal derivatization reactions.[399] Organogermyl compounds (**133**) are also smoothly

$$Ph_3GeH \xrightarrow{BuLi} Ph_3GeLi$$

133

metalated to produce organogermyllithium derivatives.[400,401] These derivatives can then be reacted further with a wide variety of derivatizing agents to produce germyl-substituted compounds.[401–403]



$$Ph_3SiCH_2Ph \xrightarrow{BuLi} Ph_3Si\underset{\displaystyle Li}{\underset{|}{C}}HPh$$

132

Many of these organometallic reagents have been used as metalating agents for other compounds and also to establish their relative metalating ability.[271,404–407]

It has been suggested that the group IVA organolithium compounds exist as an equilibrium mixture with the diphenyl-

$$Ph_3M{-}Li \rightleftharpoons Ph_2M + PhLi$$

$$M = Sn \text{ or } Pb$$

metallic compound and phenyllithium.[404] It was further suggested that the actual metalating agent in this case was phenyllithium and not the group IVA organometallic compound. Gilman[271,407] has shown that carbonation of the group IVA organometallic compound does not produce any benzoic acid, which surely would be formed if the above equilibrium existed to any extent.

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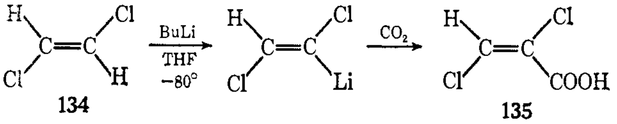
Most of the group IVA organometallic compounds prepared so far have contained phenyl groups. Gilman has recently reported the preparation of a branched aliphatic chain silyllithium compound.[408]

G. METALATION OF HALOORGANIC COMPOUNDS

One of the standard methods of preparing organolithium compounds is *via* halogen-metal exchange. Normally these compounds are prepared in ethereal or hydrocarbon solvents at room temperature.[409] Recently, Köbrich and his coworkers[187] demonstrated that, using different conditions, compounds containing halogens (chlorine and bromine) can be metalated to yield haloorganolithium compounds. For example, *trans*-1,2-dichloroethylene (**134**) has been metalated and, after carbonation, produced a 99% yield of *trans*-2,3-dichloroacrylic acid (**135**).[192,193] These haloorganolithium compounds are stable at low temperatures and undergo all of the normal organometallic reactions. Köbrich has applied the generic term "carbenoid" to these compounds.



134 **135**

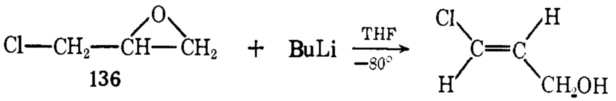
A wide variety of carbenoid compounds has been prepared,[187] for example, dichloromethyllithium[186,194,198,202] trichloromethyllithium,[186,194,195,240] and mono-, di-, and trichlorovinyllithium.[192,193,202] These syntheses have also been extended to the aromatic systems, where such compounds as α-chlorobenzyllithium[184,185] have been synthesized.

The successful synthesis of carbenoids is dependent upon reaction conditions which are both conducive to the synthesis and in which the carbenoids are relatively stable. THF accelerates their formation, and most of the carbenoids, except for trichlorovinyllithium, are stable in THF. The "Trapp" mixture (THF, ether, and hexane in a 4:1:1 ratio) has also been used. The advantages of THF have been demonstrated by other workers also.[184] Most of these preparations are successful only at low (-80 to $-100°$) temperatures.

The carbenoids have been employed in carbene-type syntheses[237–239,241,254,410–413] and various other syntheses.[414–416] Use has also been made of the tendency for carbenoids to eliminate lithium halide at higher temperatures.[197,417]

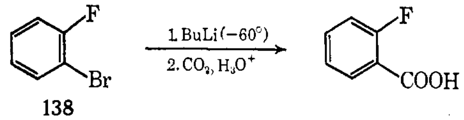
The following order of relative stability has been established for the carbenoids: $Ph_2C{=}C(Li)Cl = CH_3O < CH_3 < H < Cl$ and *ortho* < *para* for substituents on the phenyl ring;[201] *trans*-$CHCl{=}CClLi > CH_2{=}CClLi > CCl_2{=}CClLi >$ *cis*-$CHCl{=}CClLi$.[192] The reactivity decreases in the following order: $PhCCl_2Li \sim CCl_3Li \gg Ph_2CClLi \sim CCl_2HLi$.[186] Some bromolithium compounds have been prepared, but these are much less stable than the corresponding chloro compounds.[188]

An interesting practical application of a carbenoid reaction is illustrated by the reaction between butyllithium and α-chloropropylene oxide. (**136**). At low temperatures in THF only the *trans* isomer **137** is formed, but if the solvent is changed or the temperature raised, a mixture of *cis* and *trans* isomers is obtained.[153]



136 **137**

Both carbenoids and benzynes[44] can be considered as special cases of halohydrocarbon metalations. However, some aromatic halogen compounds can also be metalated in the normal sense of the term. Gilman[183] first demonstrated that *o*-bromofluorobenzene (**138**) could undergo metal–halogen exchange at very low temperatures without benzyne formation. Since then, many fluorinated compounds have been successfully metalated. For example, pentafluorobenzene (**139**) has been metalated and carbonated to produce pentafluorobenzoic acid in good yield.[418,419] Pentachlorobenzoic acid has been prepared similarly.[138,420]



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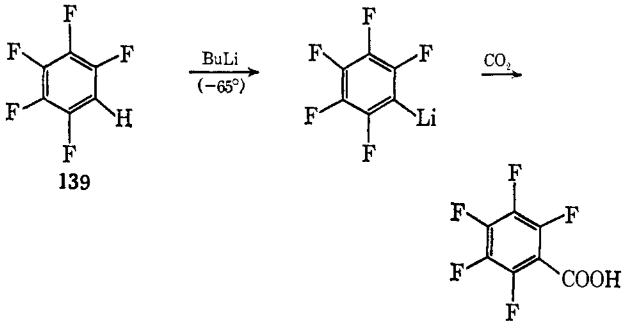
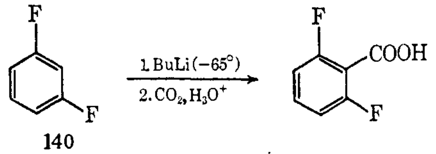


139

Tamborski has demonstrated that even 1,3-difluorobenzene (**140**) can be successfully metalated. This compound is relatively stable at low temperatures, but upon warming it quickly decomposes to benzyne.[421] Fluoroolefins are not normally metalated, but instead react with organometallic compounds.[422,423] The chemistry of organofluorine compounds, including the organometallic reactions, has been reviewed.[424]



140

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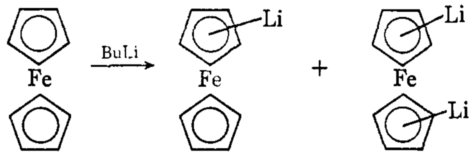
H. METALATION OF METALLOCENES

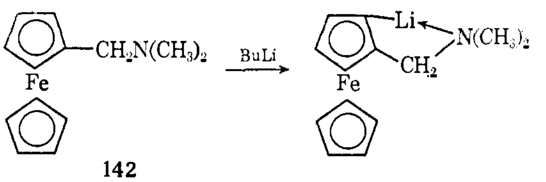
Since their initial discovery, the metallocenes, more specifically ferrocene, have provoked wide interest among chemists. There are numerous review articles covering the preparations, reactions, and metalations of these compounds.[44,425–428]

The first metalation of ferrocene was reported by two independent groups. Benkeser[429] found that butyllithium metalates ferrocene (**141**) to give a mixture of mono- and dilithiated ferrocenes. Similar results have also been reported by Nesmeyanov.[430] The hydrogens in ferrocene are evidently more acidic than in benzene, since the latter is not metalated appreciably by butyllithium.[429,431] Indeed, even in the metalation of phenyl-substituted ferrocenes, which can be considered to be an intramolecular competition reaction, there is no evidence of phenyl metalation.[303] The metalation procedures and yields have been improved by other workers.[432–437] The overall yield of metalated product can be increased by using the mixed solvent system THF–ether.[158]



141

One of the biggest difficulties in the metalation of ferrocene has been to control the reaction to obtain either mono- or dilithiated compounds. The *ortho* lithiation reaction, discovered by Hauser,[438,439] is presently the most efficient method to obtain a monolithiated ferrocene. Lithiation of these aminomethylated ferrocenes (**142**) is considerably faster than lithiation of unsubstituted ferrocenes.[438] This reaction has been extended by other workers to produce 2-substituted derivatives of aminomethylated ferrocenes.[376]



142

Metalation reactions have also been accomplished with substituted ferrocenes. Both isopropylferrocene[431] and diphenylferrocenylcarbinol[303] have been successfully metalated. Ferrocenylmethyllithium has been prepared *via* an ether cleavage reaction.[440]

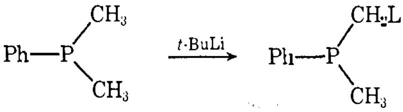
Treatment of lithiated ferrocenes with the appropriate reagents leads to substituted ferrocenes. For example, ferrocene derivatives containing silicon,[441] boron,[442–445] azo groups,[446] methyl groups,[447] and amino groups[448,449] have been prepared.

Lithiated cyclopentadienyl compounds react with ferrous chloride to produce ferrocenes.[447,450,451] This procedure has provided another route to ferrocenes of known structure.

Metallocenes other than ferrocene have been successfully metalated by organolithium compounds.[452,453] The general order of reactivity toward metalation decreases in the order ferrocene > ruthenocene > osmocene. Ditolylchromium has also been dimetalated by butyllithium, and carbonation yields a dicarboxylic acid.[454]

I. METALATION OF PHOSPHORUS COMPOUNDS

Metalation of the simple phosphines produces α-lithiophosphines. For example, diphenylphosphine is metalated to produce diphenylphosphinyllithium. If an aliphatic moiety is present, the first metalation usually occurs on the alkyl group,[455–458] but dimetalation is less discriminant.[456] Phenyldimethylphosphine (**143**) is monometalated in only the methyl group,[456] whereas the second lithium enters either the methyl or phenyl position.



$$Ph{-}P(CH_3)(CH_3) \xrightarrow{t\text{-BuLi}} Ph{-}P(CH_2Li)(CH_3)$$

143

Phosphorus shows a similar *ortho* effect to the oxygen, sulfur, nitrogen heteroatoms in that the metal usually enters adjacent to the phosphorus. This is true even in addition reacactions; the addition of butyllithium to disubstituted vinyl-

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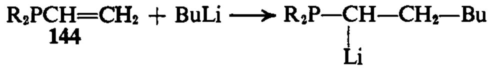


$$R_2PCH{=}CH_2 + BuLi \longrightarrow R_2P{-}\underset{\displaystyle Li}{\underset{|}{CH}}{-}CH_2{-}Bu$$

144

phosphine (**144**) results in the lithium adding adjacent to the phosphorus.[459]

It is interesting to contrast the behavior of diphenylmethylamine with diphenylmethylphosphine toward metalation. As discussed previously, the amine gives only *meta* ring metalation,[345] but the phosphine is metalated only on the methyl group.[457]

Seyferth has shown that triphenylphosphine oxide (**145**)

$$Ph_3PO + CH_3Li \longrightarrow Ph_2P(O)CH_3 + PhLi$$

145

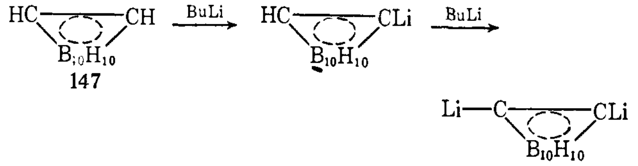
$$Ph_2P(O)CH_3 + PhLi \longrightarrow Ph_2P(O)CH_2Li + PhH$$

146

reacts with organolithium reagents through a combination of transmetalation and metalation reactions which over-all lead to a lithiated phosphine (**146**).[460,461] A similar reaction occurs with triphenylphosphine sulfide.[462] These same workers have also studied the reactions of phosphine-methylene compounds with organolithium reagents.[463–466]

J. METALATION OF ORGANOBORON COMPOUNDS

The metalation reactions of carboranes, which are known in the Russian literature as barenes, were described along with the first preparation of these new compounds.[467] For example, the parent carborane (**147**) compound has been metalated by butyllithium to yield a monolithium derivative which undergoes the normal organometallic derivatization reactions. The metalation reaction can be controlled to produce either mono- or dilithiated carboranes,[448,468–471] with a variety of organometallic compounds.[472–474] It is interesting to note that phenylcarborane (**148**) is similar to the ferrocenes in that metalation occurs only in the carboranyl moiety. There is no evidence of metalation in the phenyl ring.



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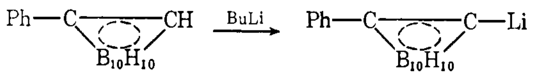


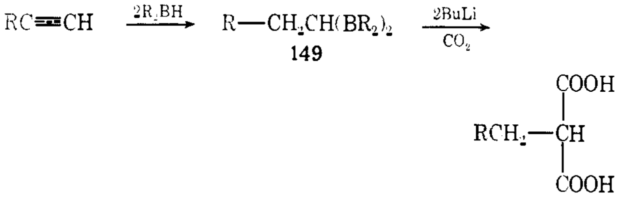
148

The metalation of carboranes has been used to prepare a wide variety of derivatives after treatment with the appropriate reagents. In this way carboxylic acids,[467,475–477] silane derivatives,[478,479] phosphine derivatives,[469] alcohols,[479–483] and mercury derivatives,[473] have all been prepared.

The preparation of carboranes and their derivatives has been the subject of several United States patents.[468,475,478,480,481]

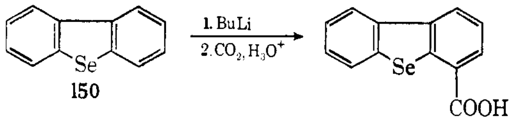
Metalation reactions have also been described for neocarboranes, which are isomers of the carboranes.[484]

Organoboron compounds other than the carboranes[485–487] can also be metalated. For example, metalation of dihydroborated terminal acetylenes (**149**) followed by carbonation is reported to yield substituted malonic acids.[485] However, this work has been questioned by others[487] who claim that there is no evidence for a 1,1-dilithiated compound.



149

In the years covered by this review, the first metalation of an aromatic selenium compound (**150**) has been reported. As expected, the metal enters the position *peri* to the heteroatom.[488]



150

VI. *Summary and General Trends in Organolithium Research*

Recent developments in the metalation reactions of organolithium compounds have been reviewed through 1966. Metal-

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ations have been demonstrated in almost every class of compounds which contain a replaceable, acidic hydrogen. The position of metalation has been generally established as occurring at the most acidic hydrogen in the compound, and *ortho*, or α, to a heteroatom, if one is present. Recent developments with the organolithium–amine complexes show that much interesting synthetic chemistry is still to be explored through the use of these relatively new compounds.

The present trend in organolithium research is concerned with mechanism, kinetic, and structural studies. These three previously neglected areas in organolithium chemistry are badly in need of much more intensive study. This work has been hampered in the past by the difficulties encountered in handling these very reactive materials. However, as more of these mechanical problems are solved, many interesting studies should be conducted in these areas.

VII. Glossary and Tables

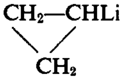
The following abbreviations are used.

BuLi	*n*-butyllithium
EGDE	ethylene glycol dimethyl ether
Ether	diethyl ether
GDME	glycol dimethyl ether
i-PrLi	isopropyllithium
MeLi	methyllithium
PhLi	phenyllithium
THF	tetrahydrofuran
THP	tetrahydropyran

Tables III–VI which follow give a summary of new organolithium compounds, relative activity of organolithium compounds, color of some organolithium compounds, and metalations by organolithium compounds, respectively.

Table III

Summary of Some New Organolithium Compounds

New compound	*Method of preparation*[a]	*Final state*	*% yield*	*Ref*
$CF_2{=}CFLi$	A	Ethyl ether	64[b]	*c*
	A	Pentane	51[b]	*c*
$CH_2{=}CHLi$	A	Ethyl ether	50–75[b]	*d, e*
	A	Solid		*e*
	C	Solid	55	*f*
	A	Ethyl ether		*f*
	C	Solid	90	*f*
	B	Ethyl ether	55	*g*
$CH_2{=}CHCH_2Li$	D	THF	65	*h*
	A	Ethyl ether	70[b]	*i, j*
	A	Solid	79	*i, j*
trans-$CH_3CH{=}CHLi$	A	Ethyl ether	61[b]	212
cis-$CH_3CH{=}CHLi$	A	Ethyl ether	49[b]	212
$CH_2{=}C(CH_3)Li$	A	Ethyl ether	14[b]	212
$CH_2{=}C(CH_3)CH_2Li$	A	Ethyl ether	53[b]	*i, j*
	A	Pentane	79[b]	*k*
	A	Solid	66[b]	*k*
trans-$PhCH{=}CHLi$	A	Ethyl ether	86[b]	*l*
CH_3Li	B	Solid		77, *m*
p-Tolyllithium	A	Solid	72–82	*n*
o-Tolyllithium	A	Solid	62	*n*
m-Tolyllithium	A	Solid	48	*n*
1-Naphthyllithium	A	Solid	56	*n*
$PhCH_2Li$	A	Solid		*o*
Fluorenyllithium	E	Solid	100	*p*
$PhCH{=}CHLi$	E	Solid		*p*
C_2H_5Li	B	Benzene	70–85	*q, r*
PhLi	E	Hydrocarbon	92[b]	41
	E	Hydrocarbon	93	41, 42
$PhCH_2Li$	E	Hydrocarbon	100	41, 42
p-Xylyllithium	E	Solid	75	

[a] A, transmetalation; B, lithium–metal exchange; C, transmetalation by lithium metal; D, ether cleavage; E, metalation.

[b] Yield based on derivative formation.

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Table IV

Relative Activity of Organolithium Compounds

	Ref
A. In competitive reactions toward the same substrate	
$Ph_3SiLi > Ph_3GeLi > Ph_3SnLi > Ph_3PbLi$	16
B. Order of reactivity based on the ability to initiate polymerization	
Bu > benzyl > allyl > vinyl > phenyl	275
C. Half-lives in diethyl ether at room temperature	
Butyllithium, 153 hr	140
Cyclopropyllithium, 138 hr	
Ethyllithium, 54 hr	
Propyllithium, 30 hr	
Cyclohexyllithium, 0.5 hr	
D. Decomposition of butyllithium in various solvents	135
THF, 2 hr	
Et_2O–THF, 24 hr	
Et_2O–THP, 1 week	
E. Relative stability of organolithiums *vs.* their metalating ability	

Stability,[a] *%/hr*	*RLi*	*Metalating ability,*[b] *%*	
−0.44	$PhCH_2Li$	27	*c*
−1.41	MeLi	29.2	
−2.14	$PhCH(CH_3)Li$	38.8	
−3.3	PhLi	55.3	

[a] Stability measured as the rate of disappearance per hour. [b] Metalating ability toward dibenzofuran. [c] H. Gilman and H. A. McNinch, *J. Org. Chem.*, **27**, 1889 (1962).

Table V

Color of Some Organolithium Compounds

Parent compound	*Metalating agent*	*Solvent*	*Metalated compound*	*Color*	*Ref*
Chloroform	BuLi	THF	Trichloromethyllithium	Purple-green	186
Carbon tetrachloride	BuLi	THF	Trichloromethyllithium	Pale pink	186
Tris(trifluorovinyl)phenyltin	PhLi	Ether	Perfluorovinyllithium	Brown	*a*
Tetravinyltin	BuLi	Hexane THF	Vinyllithium	Light yellow	216
Commercial preparation		Benzene THF	Ethyllithium	Pale straw	216
Propyne	4BuLi	Hexane	Tetralithiopropyne	Red-brown	264
Allyl phenyl ether	Li metal	THF	Allyllithium	Red	*b*
Tetraallyltin	BuLi	Hexane THF	Allyllithium	Yellow	216
Pyrimidine	BuLi		Pyrimidinyllithium	Orange	*c*
Butyne	BuLi	Hexane	Butynyllithium	Yellow	265
Butyne	2BuLi	Hexane	3-Methylpropynylenedilithium	Yellow	265
Butyne	3BuLi	Hexane	3-Methylpropynylenedilithium–BuLi adduct	Orange	265
Commercial preparation		Hexane THF	*n*-Butyllithium	Pale straw	216
Commercial preparation		Heptane THF	*sec*-Butyllithium	Yellow	216
Commercial preparation	3BuLi	Hexane THF	*t*-Butyllithium	Orange-yellow	216
Commercial preparation		Ether THF	Methallyllithium	Green-yellow	216
1-Methylpyrazole	BuLi	Ether	1-Methyl-5-lithiopyrazole	Yellow	356
2-Methoxythiophene	PhLi	Ether	2-Methoxy-5-lithiothiophene	Yellow	*d*
2-Methoxythiophene	PhLi	Ether	2-Methoxy-5-lithiothiophene	Green-yellow	320
2-Methylthiophene	BuLi	Ether	5-Methyl-2-thienyllithium	Green	*e*
Hexachlorobenzene	BuLi	THF	Pentachlorophenyllithium	Light orange-brown	138
Hexachlorobenzene	BuLi	Ether	Pentachlorophenyllithium	Light yellow	138
Bromobenzene	Li metal	THF	Phenyllithium	Deep red	133
Bromobenzene	Li metal	GDME	Phenyllithium	Deep green	407
Fluorobenzene	Li metal	THF	Phenyllithium	Red	*f*
Commercial preparation		Ether	Phenyllithium	Pink-yellow	216
o-Nitrobromobenzene	PhLi	THF	*o*-Nitrophenyllithium	Dark red	189
o-Phenylenemercury	Li metal	Ether	*o*-Dilithiobenzene	Deep red	*g*
5-Methylpyridotetrazole	BuLi	Ether	5-α-Lithiomethylpyridotetrazole	Deep purple	360
2-Methylpyridine	PhLi	Ether	2-Pyridylmethyllithium	Orange-brown	*h*
2-Methylpyridine	PhLi	Ether	2-Pyridylmethyllithium	Dark red	347

Table V (Continued)

Parent compound	*Metalating agent*	*Solvent*	*Metalated compound*	*Color*	*Ref*
2,4-Dichlorobenzyl chloride	BuLi	THF	2,4-Dichloro-α-chlorobenzyllithium	Deep red-purple	95
o-Chlorobenzyl chloride	BuLi	THF	*o*-Chloro-α-chlorobenzyllithium	Pale rose	95
Benzal chloride	BuLi	THF (−100°)	α,α-Dichlorobenzyllithium	Lavender	186
Benzal chloride	BuLi	THF (−60°)	α,α-Dichlorobenzyllithium	Deep red	186
2-(1-Propynyl)thiophene	BuLi	Ether	5-Lithio-2-(1-propynyl)thiophene	Red	*w*
Benzyl chloride	Li metal	Dioxane	Benzyllithium	Lemon yellow	38
Toluene	DABCO–BuLi	Hexane	Benzyllithium	Yellow	50
Tribenzyltin chloride	PhLi	Ether	Benzyllithium	Yellow	216
Triphenylbenzyltin	PhLi	Ether	Benzyllithium	Bright yellow	*i*
Tribenzyltin chloride	MeLi	Ether	Benzyllithium	Bright yellow	40
Methylphenyl sulfide	DABCO–BuLi	THF	Phenylthiomethyllithium	Pale yellow	330
Lutidine	PhLi	Ether	Lutidinyllithium	Orange-red	350
Bis(α-methylbenzyl) ether	Li metal	THF	α-Methylbenzyllithium	Cherry red	36
α-Methylbenzyltriphenyltin	PhLi	Ether	α-Methylbenzyllithium	Brown-yellow	216
o-Methylbenzyl chloride	BuLi	THF	*o*-Methyl-α-chlorobenzyllithium	Pale yellow-orange	185
p-Methylbenzyl chloride	BuLi	THF	*p*-Methyl-α-chlorobenzyllithium	Pale orange	185
N-Methylbenzamide	BuLi	THF	*o*-Lithio-N-methylbenzamide	Dark red	378
2-Methyl-2-(2-thienyl)-1,3-dioxolane	BuLi	Ether	2-Methyl-2-(2-thienyl-5-lithio)-1,3-dioxolane	Deep brown	302
trans-β-Styryltrimethyltin	MeLi		*trans*-β-Styryllithium	Red	498
Styrene	BuLi	Ether	Styryllithium	Deep red	273
1-Methylbenzimidazole	BuLi	Ether	1-Methyl-2-lithiobenzimidazole	Red liquid, green-yellow solid	359
Phenylacetonitrile	BuLi	THF	α-Lithiophenylacetonitrile	Yellow	369
Indene	BuLi	Ether	1-Indenyllithium	Rust	276
Indene	Ph$_3$SiLi	THF	1-Indenyllithium	Brown-yellow	271
1-Phenylpyrazole	BuLi	Ether	5-Lithio-1-phenylpyrazole	Dark red	356
1-Phenylpyrazole	2BuLi	Ether	1-(*o*-Lithiophenyl)-5-lithiopyrazole	Bright yellow	356
N-Methylindole	BuLi	Ether	1-Methyl-2-lithioindole	Green	355
Allylbenzene	BuLi	Ether	1-Phenylallyllithium	Green-red-orange	*j*
Allylbenzene	BuLi	THF	1-Phenylallyllithium	Red	216
N-Methyl-*o*-toluamide	BuLi	THF	*o*-Lithiomethyl-N-methylbenzamide	Dark red	382
Benzyldimethylamine	PhLi	Ether	*o*-Lithiobenzyldimethylamine	Brown	373
Benzyldimethylamine	BuNa	Octane	*o*-Sodiobenzyldimethylamine	Orange-red	373
Benzyldimethylamine	PhNa	Octane	*o*-Sodiobenzyldimethylamine	Red suspension	373
Benzyldimethylamine	PhK	Heptane	*o*-Potassiobenzyldimethylamine	Light red	373
1-Fluoronaphthalene	Li metal	THF	1-Naphthyllithium	Green	*f*
Ferrocene	BuLi	Ether	Ferrocenyllithium	Orange	*k*
Ferrocenylmethyl methyl ether	BuLi	THF	Ferrocenylmethyllithium	Dark red	440
1-Methoxynaphthalene-8-*d*	BuLi	Ether	Lithio-1-methoxynaphthalene-8-*d*	Red-orange	293
N,N-Dimethyl-α-phenylpropylamine	BuLi	Ether	*o*-Lithio-N,N-dimethyl-γ-phenylpropylamine	Red	379
Diazocyclopentadiene	PhLi	Ether	Phenylazocyclopentadienyllithium	Scarlet	448
Dibenzofuran	Li metal	Dioxane	Lithium 2-(2-lithiophenyl)phenoxide	Brick red	288
Dibenzofuran	Li metal	THF	Lithium 2-(2-lithiophenyl)phenoxide	Blue-green to brown	*l*
Dibenzothiophene 5-oxide	BuLi	Ether	4-Lithiodibenzothiophene 5-oxide	Dark orange	323
Thianthrene 5-oxide	BuLi	Ether	4,6-Dilithiothianthrene 5-oxide	Orange	328
Diphenyl sulfone	BuLi	Ether	*o*-Lithiodiphenyl sulfone	Yellow-orange Yellow	324 341
Diphenyl sulfone	2BuLi	Ether	*o,o'*-Dilithiodiphenyl sulfone	Orange-red	324
Phenoxathiin 10-dioxide	BuLi	Ether	1,9-Dilithiophenoxathiin 10-dioxide	Yellow-orange	384

Table V (Continued)

Parent compound	*Metalating agent*	*Solvent*	*Metalated compound*	*Color*	*Ref*
Dibenzothiophene 5-dioxide	BuLi	Ether	4,6-Dilithiodibenzothiophene 5-dioxide	Deep red	324
Diphenyl ether	BuLi	THF	2,2′-Dilithiodiphenyl ether	Dark green	158
Diphenyl phosphine	BuLi	THF	Diphenylphosphenyllithium	Orange-red	143
N,N-Dimethyl(β-phenylisobutyl)amine	BuLi	Ether	*o*-Lithio-N,N-dimethyl(β-phenylisobutyl)amine	Red	379
Fluorene	PhLi	Ether	9-Fluorenyllithium	Orange	*m*
Fluorene	EtLi	Benzene	9-Fluorenyllithium	Orange	*n*
Fluorene	BuLi	Benzene	9-Fluorenyllithium	Orange	253
Fluorene	BuLi	Hexane	9-Fluorenyllithium	Yellow	*o*
Fluorene	BuLi	Hexane–THF	9-Fluorenyllithium	Orange-brown	274
Fluorene	Triphenyllead-lithium	THF	9-Fluorenyllithium	Brown	271
Fluorene	Triphenyltin-lithium	THF	9-Fluorenyllithium	Red	271
N-Methylcarbazole	BuLi	Ether	1-Lithio-N-methylcarbazole	Dark red	345
Xanthene	Ph_3–SiLi	THF	9-Xanthyllithium	Dark red	271
Diphenylmethane	Ph_2–Li adduct	THF	Diphenylmethyllithium	Red	*p*
Diphenylmethane	Ph_3SiLi	THF	Diphenylmethyllithium	Red	271
Triphenylphosphine oxide	MeLi	Ether	α-Lithiomethyldiphenylphosphine oxide	Deep red	461
Triphenylphosphine oxide	MeLi	Ether	α-Lithiomethyldiphenylphosphine oxide	Orange-red	460
Triphenylphosphine sulfide	MeLi		α-Lithiomethyldiphenylphosphine sulfide	Red	462
Triphenylphosphine sulfide	EtLi		α-Lithioethyldiphenylphosphine sulfide	Red	462
2-Bromo-1,1-diphenylethylene	BuLi	Ether	1,1-Diphenyl-2-bromo-2-lithioethylene	Yellow	*q*
10-Methylacridan	BuLi	Ether	9-Lithio-10-methylacridan	Bright red	*r*
10-Ethylphenothiazine	Ph_3SiLi	THF	4-Lithio-10-ethylphenothiazine	Light green	271
Phenyl (3-chloro-4-N,N-dimethylaminophenyl) sulfone	BuLi	Ether	Phenyl (2-lithio-3-chloro-4-N,N-dimethylaminophenyl) sulfone	Yellow	342
α-Methyl-α′-(phenethyl)-pyridine	PhLi	Ether	2-Phenyl-1-(5-methyl-2-pyridyl)-ethyllithium	Orange-red	350
N-Phenylindole	BuLi	Ether	1-(*o*-Lithiophenyl)-2-lithioindole	Orange	355
2,2-Diphenyl-1-chloropropane	Li meta	Ether	2,2-Diphenyl-1-lithiopropane	Clear red	*s*
Pyrene	BuLi	Ether	Pyrenyllithium	Deep red	280
12H-Benzo[*a*]phenothiazine	BuLi	Ether	1-Lithio-12H-benzo[*a*]phenothiazine	Bright red	393
12H-Benzo[*b*]phenothiazine	BuLi	Ether	11-Lithio-12H-benzo[*b*]phenothiazine	Deep orange	395
Diphenylacetylene	EtLi	Ether	1-Phenyl-2-(*o*-lithiophenyl)-1-lithio-1-butene	Green to bright yellow	268
1,1-Diphenylethylene	Allyllithium	THF	1,1-Diphenyl-3-butenyllithium	Deep red	216
Diphenylacetylene	BuLi	Ether	1-Phenyl-2-(*o*-lithiophenyl)-1-lithio-1-hexene	Red	268
1,1-Diphenylethylene	BuLi	THF	1,1-Diphenyl-*n*-hexyllithium	Deep red	216
1,1-Diphenylethylene	BuLi		1,1-Diphenyl-*n*-hexyllithium	Deep red	61
1,1-Diphenylethylene	BuLi	Benzene	1,1-Diphenyl-*n*-hexyllithium	Cherry red	250, 251
Triphenylgermane	PhLi	Ether	Triphenylgermyllithium	Yellow	400
Triphenylgermane	BuLi	THF	Triphenylgermyllithium	Pale green	401
9-Phenylfluorene	BuLi	Ether	9-Phenyl-9-fluorenyllithium	Orange	298
Tritylmethyl ether	BuLi	Ether	9-Phenyl-9-fluorenyllithium	Scarlet	298
Triphenylmethane	*n*-PrLi	Ether	Triphenylmethyllithium	Red	205
Triphenylmethane	BuLi	Ether	Triphenylmethyllithium	Red	405
Triphenylmethane	BuLi	Hexane	Triphenylmethyllithium	Red	274
Triphenylmethane	Ph_2–Li adduct	THF	Triphenylmethyllithium	Deep red	*t*
Triphenylmethyl chloride	Li metal	THF	Triphenylmethyllithium	Brilliant red	216
14H-Dibenzo[*a*,*c*]phenothiazine	BuLi	Hexane	1-Lithio-14H-dibenzo[*a*,*c*]-phenothiazine	Red	394
14H-Dibenzo[*a*,*h*]phenothiazine	BuLi	Hexane	1-Lithio-14H-dibenzo[*a*,*h*]-phenothiazine	Dark red	394
7H-Dibenzo[*c*,*h*]phenothiazine	BuLi	Hexane	6-Lithio-7H-dibenzo[*c*,*h*]phenothiazine	Red	394

Table V (Continued)

Parent compound	*Metalating agent*	*Solvent*	*Metalated compound*	*Color*	*Ref*
3-(Triphenylsilyl)-2-chloropropene	Ph_3SiLi	THF	3-Lithio-3-(triphenylsilyl)-2-chloropropene	Purple to light orange	238
Cinnamylidenefluorene	PhLi	Ether	9-Cinnamylidene-9-fluorenyllithium	Dark red	*u*
Diphenylferrocenylcarbinol	BuLi	Ether	2-Lithioferrocenyldiphenylcarbinol	Dark yellow	303
Triphenylmethylcyclopentadiene	PhLi	Ether	Triphenylmethylcyclopentadienyllithium	Yellow	*v*
Tetraphenylphosphonium bromide	MeLi	THF ether	(*o*-Lithiophenyl)triphenylphosphonium bromide	Brown-deep red	466

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Table VI

Metalations by Organolithium Compounds

	Compound metalated	*RLi*	*Solvent*	*Reactant*	*Final product*	*% yield*	*Ref*
$CHCl_3$	Chloroform	BuLi	THF Ether Pet. ether	Benzophenone	Trichloromethyldiphenylcarbinol	84	195
		BuLi	THF Hexane	Carbon dioxide	Trichloroacetic acid	50	186
		BuLi	THF Ether Pet. ether	Mercuric chloride	Bis(trichloromethyl)mercury	91–96	195
CH_2Cl_2	Methylene chloride	MeLi	Ether	Benzene	Methyltropilidene	30	241
		BuLi	THF Ether Pet. ether	Benzophenone	Dichloromethyldiphenylcarbinol	80	202
		BuLi		*trans*-2-butene	1-Chloro-2,3-*trans*-dimethylcyclopropane	40	237
		MeLi	Ether	*t*-Butylbenzene	Methyl-*t*-butyltropilidene	25	241
		BuLi	THF Hexane	Carbon dioxide	Dichloroacetic acid	60	186
		MeLi	Ether	Cumene	Methylisopropyltropilidene	20	241
		BuLi		Cyclohexene	7-Chlorobicyclo[4.1.0]heptane	31	237
		BuLi	THF Ether Pet. ether	2,2′-Dichlorobenzophenone	Dichloromethylbis(2-chlorophenyl)carbinol		202
		BuLi		2,3-Dimethyl-2-butene	1-Chloro-2,2,3,3-tetramethylcyclopropane	67	237
		BuLi	Hexane THF	Mercuric chloride	Bis(dichloromethyl)mercury	82–97	194, 198 202
		MeLi	Ether	Toluene	Dimethyltropilidene	40	241
		MeLi	Ether	*p*-Xylene	Trimethyltropilidene	10	241
CH_2N_2	Diazomethane	MeLi	Ether	Benzonitrile	3- (or 5-) Phenyl-1,2,4-triazole	42	364
		MeLi	Ether	Benzoyl bromide	2-Phenyl-1,3,4-oxadiazole	35	364
		MeLi	Ether	Fluorenone	9-Fluoreneimine	41	364
		MeLi	Ether		Diazomethyllithium	50	363
C_2HCl_3	Trichloroethylene	BuLi	THF Ether Pet. ether	Bromine	Bromotrichloroethylene	36	193
		BuLi	THF Ether	Capraldehyde	3-Hydroxy-1-chloro-1-octyne		416
		BuLi	THF Ether Pet. ether	Carbon dioxide	Trichloroacrylic acid	81	192, 193

Table VI (Continued)

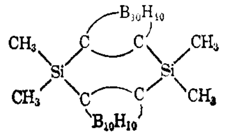
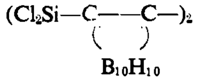
	Compound metalated	*RLi*	*Solvent*	*Reactant*	*Final product*	*% yield*	*Ref*
		PhLi	Ether	Cyclohexanone	1-Hydroxycyclohexylethynyl chloride	82	416
C_2H_2	Acetylene	PhLi	THF	Triphenylchlorosilane	Bis(triphenylsilyl)acetylene		254
$C_2H_2Cl_2$	*trans*-1,2-Dichloroethylene	BuLi	THF Ether Pet. ether	Bromine	*trans*-1,2-Dichlorobromoethylene	26	193
		BuLi	THF Ether Pet. ether	Carbon dioxide	*trans*-2,3-Dichloroacrylic acid	99	192, 193
C_2H_3Cl	Vinyl chloride	BuLi	THF Ether Pet. ether	Carbon dioxide	2-Chloroacrylic acid	99–100	192, 193
$C_2H_3F_3O_2S$	Methyl trifluoromethyl sulfone	BuLi	Ether	Carbon dioxide	Trifluoromethylsulfonylacetic acid	51	333
$C_2H_6O_2S$	Dimethyl sulfone	BuLi	Benzene	Benzaldehyde	(β-Phenyl-β-hydroxyethyl) methyl sulfone	85	331
		BuLi	Benzene	Benzophenone	(β,β-Diphenyl-β-hydroxyethyl) methyl sulfone	46	331
$C_2H_{12}B_{10}$	Carborane	BuLi	Ether	Acetaldehyde	1,2-Bis(α-hydroxyethyl)carborane	31	470
		BuLi	Ether	Acetic acid	1,2-Di(1-hydroxy-1-ethyl)-carborane		481
		BuLi	Ether	1,2-Bis(chlorodimethylsilyl)-carborane		23	479
		BuLi	Ether	1,2-Bis(chlorophenylphosphino)carborane	Dimeric phenylphospha(III)-carborane	20	469
		BuLi	Ether	1,2-Bis(trichlorosilyl)carborane	 $(Cl_2Si{-}\underbrace{C{-}{-}C}_{B_{10}H_{10}}{-})_2$	52	479
		PhLi	Ether	3-Bromopropene	1-Allylcarborane	70	470
		BuLi	Ether	*n*-Butyl bromide	*n*-Butylcarborane	69	470
		MeLi	Ether	Carbon dioxide	Carboranecarboxylic acid		468
		BuLi		Carbon dioxide	Carboranecarboxylic acid		471
		BuLi	THF Heptane	Carbon dioxide	1,2-Carboranedicarboxylic acid	24	472
		BuLi	Ether	Carbon dioxide	1,2-Carboranedicarboxylic acid	87	470
		2RLi	Benzene Ether	Dibutyltin dichloride	Dibutylcarboranylenetin	66	473
		BuLi	Ether	Dichlorodimethylsilane	1,2-Bis(chlorodimethylsilyl)-carborane	88	479
		MeLi	Ether	Dichlorodimethylsilane	Dimethylchlorosilylcarborane		478
		MeLi	Ether	Dichlorodimethylsilane	Dimethyldicarboranylsilane		478
		BuLi	Ether	Dichlorodimethylsilane	Dimethyldicarboran-1-ylsilane		470
		BuLi	Ether	Dimethyldichloromethylsilane	1,2-(2′,2′-Dimethyl-2′-silapropylene)carborane		470
		BuLi	Ether	Dichlorodiphenylsilane	1,2-Bis(chlorodiphenylsilyl)-carborane	23	479
		BuLi	Ether	Diphenylchlorophosphine	1,2-Bis(diphenylphosphino)-carborane	59	469
		BuLi	Benzene	Ethylene oxide	2-(Carboranyl)ethanol	48	474
		BuLi	Ether	Ethylene oxide	1,2-Bis(β-hydroxyethyl)carborane		470
		PhLi	Ether	Ethylene oxide	1,2-Bis(hydroxyethyl)carborane	35	472
		BuLi	Ether	Iodine	1-Iodocarborane	64	472
		BuLi	Ether	Mercuric chloride	Dicarboranylmercury	53	473

Table VI (Continued)

	Compound metalated	*RLi*	*Solvent*	*Reactant*	*Final product*	*% yield*	*Ref*
		RLi	Ether	Methylmercuric chloride	Methylcarboranylmercury	51	473
		BuLi	Ether	Methyltrichlorosilane	1,2-Bis(dichloromethylsilyl)carborane	70	479
		BuLi	Ether	Phenyldichlorophosphine	1,2-Bis(chlorophenylphosphino)carborane	58	469
		BuLi	Ether	Phosphorus trichloride	Dimeric chlorophospha(III)carborane	44	469
		BuLi	Benzene Ether	Propylene oxide	1-(Carboranyl)-2-propanol	50	474
		2BuLi	Benzene Ether	Propylene oxide	1,2-Bis(β-hydroxypropyl)carborane	80	474
		BuLi	Ether	Tetrachlorosilane	1,2-Bis(trichlorosilyl)carborane	60	479
		BuLi	Ether	Trimethylchloromethylsilane	Trimethyl(carboran-1-ylmethyl)silane		470, 478
		MeLi	Ether	Trimethylchlorosilane	Trimethylsilylcarborane		478
		BuLi	Ether	Trimethylchlorosilane	1-Trimethylsilylcarborane		470
		MeLi	Ether	Triphenylchlorosilane	Triphenylsilylcarborane		478
		BuLi	Ether	Triphenylchlorosilane	1-Triphenylsilylcarborane		470
		2RLi	Benzene Ether	Tri-*n*-propyltin chloride	Carboranylenebis(tri-*n*-propyltin)	30	473
		RLi	Ether	Tri-*n*-propyltin chloride	Tri-*n*-propylcarboranyltin	35	473
$C_2H_{12}B_{10}$	Neocarborane	BuLi	Ether	Carbon dioxide	C,C′-Neocarboranedicarboxylic acid	78	484
		BuLi	Ether	Methyl iodide	C-Methylneocarborane	39	484
		BuLi	Benzene	Paraformaldehyde	C,C′-Bis(hydroxymethyl)neocarborane	24	484
C_3H_2BrNS	4-Bromoisothiazole	BuLi	THF	Carbon dioxide	4-Bromo-5-isothiazolecarboxylic acid	70	388
		BuLi	THF	Dimethylformamide	4-Bromo-5-formylisothiazole	73	388
C_3H_2ClNS	4-Chloroisothiazole	BuLi	THF	Carbon dioxide	4-Chloro-5-isothiazolecarboxylic acid	68	388
		BuLi	THF	Dimethylformamide	4-Chloro-5-formylisothiazole	65	388
C_3H_2INS	4-Iodoisothiazole	BuLi	THF	Dimethylformamide	4-Iodo-5-formylisothiazole	33	388
C_3H_3NS	Isothiazole	BuLi	THF	Bromine	5-Bromoisothiazole	34	388
		BuLi	THF	Carbon dioxide	Isothiazole-5-carboxylic acid	48	388
		BuLi	THF	Dimethylformamide	5-Formylisothiazole	75	388
		BuLi	THF	Methyl iodide	5-Methylisothiazole	40	388
C_3H_3NS	Thiazole	BuLi	Ether	Acetaldehyde	2-(1-Hydroxyethyl)thiazole	30	391
		BuLi	Ether	Benzophenone	Diphenyl-2-thiazolylcarbinol	22	391
		BuLi	Ether	Butyraldehyde	2-(1-Hydroxybutyl)thiazole	90	391
		PhLi	Ether	Carbon dioxide	2-Thiazolecarboxylic acid	40	389
		BuLi	Ether	Ethylene oxide	2-(2-Hydroxyethyl)thiazole	30	391
		BuLi	Ether	Heptaldehyde	2-(1-Hydroxyheptyl)thiazole	90	391
		BuLi	Ether	Isobutyraldehyde	2-(1-Hydroxy-2-methylpropyl)thiazole	90	391
		BuLi	Ether	Propionaldehyde	2-(1-Hydroxypropyl)thiazole	50	391
C_3H_4	Propyne	BuLi	Hexane	Trimethylchlorosilane	1,3,3-Tris(trimethylsilyl)propyne + 1,1,3,3-tetra(trimethylsilyl)allene	50 25	264
		MeLi	Ether THF	Bromotrifluoroethylene	1-Bromo-1,2-difluoropent-1-en-3-yne	56	423
		MeLi	Ether THF	Chlorotrifluoroethylene	1-Chloro-1,2-difluoropent-1-en-3-yne	73	423
		MeLi	Ether THF	1,1-Dichlorodifluoroethylene	1,1-Dichloro-2-fluoropent-1-en-3-yne	51	423

Table VI (Continued)

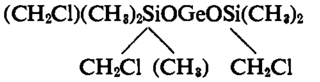
	Compound metalated	*RLi*	*Solvent*	*Reactant*	*Final product*	*% yield*	*Ref*
		MeLi	Ether THF	Hexafluoropropene	1,1,1,2,3-Pentafluorohex-2-en-4-yne	17	423
		MeLi	Ether THF	Tetrafluoroethylene	4,5-Difluoroocta-2,6-diyn-4-ene	35	423
		MeLi	Ether THF	1,1,2-Trifluoro-1,3-butadiene	3,4-Difluorohepta-1,3-dien-5-yne	64	423
$C_3H_4N_2$	Pyrazole	2BuLi	Ether	Carbon dioxide	3-Pyrazolecarboxylic acid	9	*a*
		2PhLi	Ether	Carbon dioxide	3-Pyrazolecarboxylic acid	7	*a*
C_3H_9ClOSi	Chloromethyldimethylsilanol	MeLi	Ether	Chloromethyldimethylgermyl chloride	$(CH_2Cl)(CH_3)_2SiOGe(CH_3)_2(CH_2Cl)$	74	*b*
		MeLi	Ether	Chloromethylgermyl dichloride	 $(CH_2Cl)(CH_3)_2SiOGe(CH_2Cl)(CH_3)OSi(CH_3)_2(CH_2Cl)$	68	*b*
		MeLi	Ether	Trimethylgermyl chloride	$(CH_2Cl)(CH_3)_2SiOGeMe_3$	80	*b*
$C_3H_{12}B_{10}O_2$	Carboranecarboxylic acid	BuLi		Carbon dioxide	Carboranedicarboxylic acid		471
$C_3H_{14}B_{10}$	1-Methylcarborane	BuLi		Benzaldehyde	1-(Methylcarboranyl)benzyl alcohol	70	*c*
		BuLi	Ether	Carbon dioxide	1-Methyl-2-carboranylcarboxylic acid	20	484, 471
		BuLi	Benzene Ether	Epichlorohydrin	1,3-Bis(methylcarboranyl)-2-propanol 1,2-Epoxy-3-methylcarboranylpropane	37 30	474
		RLi		Ethyl benzoate	Methylcarboranylphenylcarbinol	72	483
		BuLi	Benzene Ether	Ethylene oxide	1-(1-Methyl-2-carboranyl)ethanol	65–90	474
		RLi	Ether	Mercuric chloride	Bis(methylcarboranyl)mercury	72	473
		RLi		Methyl benzoate	1-Methyl-2-benzoylcarborane	61	483
		BuLi	Benzene Ether	Propylene oxide	1-(1-Methyl-2-carboranyl)-2-propanol	72	474
		BuLi	Benzene Ether	Styrene oxide	2-(1-Methyl-2-carboranyl)-1-phenylethanol	62	474
$C_3H_{14}B_{10}$	C-Methylneocarborane	BuLi	Ether	Carbon dioxide	C-Methyl-C′-neocarboranylcarboxylic acid	19	484
$C_4H_2Br_2S$	2,4-Dibromothiophene	BuLi	Ether	Carbon dioxide	3,5-Dibromo-2-carboxythiophene	36	*d*
$C_4H_2Br_2S$	3,4-Dibromothiophene	BuLi	Ether	Carbon dioxide	3,4-Dibromo-2-carboxythiophene	34	*d*
C_4H_3BrS	3-Bromothiophene	BuLi	Ether	Carbon dioxide	3-Thiophenecarboxylic acid + 2,3-dicarboxythiophene		225
		BuLi	Ether	Carbon dioxide	3-Bromo-2-thiophenecarboxylic acid	36	231, *d*
		PhLi	Ether	Carbon dioxide	3-Bromo-2-thiophenecarboxylic acid	72	231
		BuLi	Ether	Deuterium oxide	3-Deuteriothiophene + 2,3-dideuteriothiophene		225
		BuLi	Ether	Tritium oxide	Thiophene-2-*t* + thiophene-3-*t*		225
C_4H_3DS	Thiophene-2-*d*	BuLi	Ether Hexane	Carbon dioxide	2-Carboxythiophene		228
C_4H_3ST	Thiophene-2-*t*	BuLi 1:1	Ether	Carbon dioxide	2-Thiophenecarboxylic acid	87	227, 228
C_4H_3ST	Thiophene-3-*t*	BuLi 1:1	Ether	Carbon dioxide	2-Thiophenecarboxylic acid	95	227
C_4H_4BrNS	4-Bromo-3-methylisothiazole	BuLi	THF	Benzyl bromide	5-Benzyl-4-bromo-3-methylisothiazole + 4-bromo-3-methyl-5-(1,2-diphenylethyl)isothiazole	13 10	388
		BuLi	THF	Carbon dioxide	4-Bromo-3-methyl-5-isothiazolecarboxylic acid	56	388
		BuLi	THF	Dimethylformamide	4-Bromo-5-formyl-3-methylisothiazole	51	388

Table VI (*Continued*)

	Compound metalated	*RLi*	*Solvent*	*Reactant*	*Final product*	*% yield*	*Ref*
		BuLi	THF	Ethyl halide	4-Bromo-5-ethyl-3-methylisothiazole	34	388
		BuLi	THF	Methyl iodide	4-Bromo-3,5-dimethylisothiazole	40	388
		BuLi	THF	*n*-Propyl halide	4-Bromo-3-methyl-5-*n*-propylisothiazole	28	388
C_4H_4ClNS	4-Chloro-3-methylisothiazole	BuLi	THF	Carbon dioxide	4-Chloro-3-methyl-5-isothiazolecarboxylic acid	75	388
		BuLi	THF	Dimethylformamide	4-Chloro-5-formyl-3-methylisothiazole	47	388
C_4H_4INS	4-Iodo-3-methylisothiazole	BuLi	THF	Carbon dioxide	4-Iodo-3-methyl-5-isothiazolecarboxylic acid	58	388
		BuLi	THF	Dimethylformamide	4-Iodo-5-formyl-3-methylisothiazole	68	388
C_4H_4O	Furan	BuLi	Ether	Acetophenone	Methylphenyl-2-furylcarbinol	96	285
		BuLi	Ether	Benzaldehyde	Phenyl-2-furylcarbinol	98	285
		BuLi	Ether	Benzonitrile	2-Benzoylfuran	89	285
		BuLi	Ether	Benzophenone	Diphenyl-2-furylcarbinol	98	285
		BuLi	THF	*n*-Butyl bromide	2-*n*-Butylfuran	77	285
		BuLi	Ether	Carbon dioxide	2-Furoic acid	77	285
		BuLi	Ether	Cyclohexanone	1-(2-Furyl)cyclohexanol	95	285
		BuLi	Ether	Ethyl acetate	Di(2-furyl)methylcarbinol	94	285
		BuLi	Ether	Ethyl benzoate	Di(2-furyl)phenylcarbinol	44	285
		BuLi	Ether	Isobutyraldehyde	Isopropyl-2-furylcarbinol	93	285
		BuLi	Ether	Methyl ethyl ketone	Methylethyl-2-furylcarbinol	88	285
		BuLi	Ether	Sulfur dioxide	Lithium 2-furansulfinate	55	208
		BuLi	Ether	Sulfur, ethyl iodide	2-(Ethylthio)furan	53	*e*
		BuLi	Ether	Triphenyltin chloride	Triphenyl-2-furyltin	44	*f*
C_4H_4S	Thiophene	BuLi	Ether	Acetaldehyde	1-(2-Thienyl)ethanol	73	211
		BuLi	Ether	Benzaldehyde	2-Thienylphenylcarbinol	54	211
		BuLi	Ether	Benzyl bromide	2-Benzylthiophene	62	319
		BuLi	THF	Bromobenzene	2-Phenylthiophene + 2,5-diphenylthiophene	31 22	319
		BuLi	Ether	*n*-Butyl bromide	2-*n*-Butylthiophene	47	319
		BuLi	Ether	Butyraldehyde	1-(2-Thienyl)butanol	76	211
		N-Methyl-2-lithiopyrrole	Ether	Carbon dioxide	Thiophene-2-carboxylic acid		392
		2,4,6-Triphenylphenyllithium		Carbon dioxide	Thiophene-2-carboxylic acid	46	172
		Poly-*p*-styryllithium	Ether	Carbon dioxide	Thiophene-2-carboxylic acid	43	*g*
		BuLi	Ether	Cupric chloride	2,2′-Bithienyl	64	314
		BuLi	Ether	3-Cyclohexenylcarboxaldehyde	2-Thienyl-3-cyclohexenylcarbinol	64	211
		PhLi	Ether	*cis*-4-Dimethylaminocyclohexyl 2-thienyl ketone	*cis*-4-Dimethylaminodi(2-thienyl)cyclohexylcarbinol	66	*h*
		PhLi	Ether	*trans*-4-Dimethylaminocyclohexyl 2-thienyl ketone	*trans*-4-Dimethylaminodi(2-thienyl)cyclohexylcarbinol	88	*h*
		BuLi	Ether	N,N-Dimethylcarbamoyl chloride	Bis(α-thienyl) ketone		207
		BuLi	Ether	Dimethyl sulfate	2-Methylthiophene	65	319
		BuLi	Ether	Ethyl bromide	2-Ethylthiophene	61	319
		BuLi	Ether	2-Ethylbutyraldehyde	1-(2-Thienyl)-2-ethyl-1-butanol	72	211

Table VI (Continued)

	Compound metalated	*RLi*	*Solvent*	*Reactant*	*Final product*	*% yield*	*Ref*
		PhLi	Ether	*cis*-Ethyl 4-dimethylaminocyclohexylcarboxylate	*cis*-4-Dimethylaminodi(2-thienyl)cyclohexylcarbinol	86	*h*
		PhLi	Ether	*trans*-Ethyl 4-dimethylaminocyclohexylcarboxylate	*trans*-4-Dimethylaminodi(2-thienyl)cyclohexylcarbinol	68	*h*
		BuLi	Ether	2-Ethylhexaldehyde	1-(2-Thienyl)-2-ethyl-1-hexanol	75	211
		BuLi	Ether	*n*-Hexaldehyde	1-(2-Thienyl)hexanol	63	211
		PhLi	Ether	1-Methyl-4-piperidone	4-(2-Thienyl)-1-methyl-4-hydroxypiperidine	34	*i*
		BuLi	Ether	*n*-Octyl bromide	2-*n*-Octylthiophene	46	319
		BuLi	Ether	Perchloryl fluoride	2-Fluorothiophene	49	*j*
		BuLi	Ether	Phenyl thiocyanate	2-Thienyl phenyl sulfide	59	313
		BuLi	Ether	Propionaldehyde	1-(2-Thienyl)propanol	68	211
		BuLi	Ether	Sulfur dioxide	Lithium 2-thiophenesulfinate	57	208
		BuLi	Ether	Tritium oxide	2-T-Thiophene		228
C_4H_5N	Pyrrole	BuLi	Ether	Carbon dioxide	Pyrrole-1-carboxylic acid	34	354
C_4H_5NS	3-Methylisothiazole	BuLi	THF	Carbon dioxide	3-Methylisothiazole-5-carboxylic acid	50	388
		BuLi	THF	Dimethylformamide	5-Formyl-3-methylisothiazole	50	388
		BuLi	THF	Methyl iodide	3,5-Dimethylisothiazole	28	388
C_4H_5NS	4-Methylisothiazole	BuLi	THF	Carbon dioxide	4-Methylisothiazole-5-carboxylic acid	40	388
		BuLi	THF	Dimethylformamide	5-Formyl-4-methylisothiazole	55	388
C_4H_5NS	4-Methylthiazole	BuLi	Ether	Acetaldehyde	2-(α-Hydroxyethyl)-4-methylthiazole	48	390
		BuLi	Ether	Butyraldehyde	4-Methyl-2-thiazolylpropylcarbinol	93	391
		BuLi	Ether	Ethylene oxide	(Hydroxy-2-ethyl)-2-methyl-4-thiazole	42	391
		BuLi	Ether	Methyl iodide	2,4-Dimethylthiazole	26	391
		BuLi	Ether	Propylene oxide	2-(2-Hydroxypropyl)-4-methylthiazole	51	391
C_4H_6	1-Butyne	BuLi	Hexane	Carbon dioxide	2-Methylglutaric acid	39	265
		BuLi	Hexane	Trimethylchlorosilane	1,1,3-Tris(trimethylsilyl)-1,2-butadiene + 1,3,3-tris(trimethylsilyl)-1-butyne		264
$C_4H_6Br_2$	1,1-Dimethyl-2,2-dibromoethylene	BuLi	THF	Carbon dioxide	2-Bromo-3,3-dimethylacrylic acid	94	188
$C_4H_6Cl_2S$	1,2-Dichloroethylthioethylene	BuLi	Ether	Acetone	1-Thioethyl-3-methyl-3-hydroxybutyne	63	416
$C_4H_6N_2$	N-Methylimidazole	BuLi	Ether	Benzophenone	(2-Imidazolyl)diphenylcarbinol	86	358
		BuLi	Ether	Carbon dioxide	1-Methyl-2-imidazolecarboxylic acid + 1-methyl-5-imidazolecarboxylic acid	32 1.5	358
		BuLi	Ether	1-Naphthyl isocyanate	N-α-Naphthyl-1-methyl-2-imidazolecarboxamide	66	358
$C_4H_6N_2$	1-Methylpyrazole	BuLi	Ether	Benzophenone	Diphenyl(1-methyl-5-pyrazolyl)carbinol	87	*a*
		BuLi	Ether	Carbon dioxide	1-Methyl-5-pyrazolecarboxylic acid	54–66	*a*
		PhLi	Ether	Carbon dioxide	1-Methyl-5-pyrazolecarboxylic acid	39	*a*
		BuLi	Ether	Dimethyl sulfate	1,5-Dimethylpyrazole	75	*a*
C_4H_6O	Ethoxyacetylene	PhLi	Ether	Acetaldehyde	1-Ethoxybut-1-yn-3-ol	42	*k*
		PhLi	Ether	Benzaldehyde	1-Ethoxy-3-phenylprop-1-yn-3-ol	72	*k*
		PhLi	Ether	Heptaldehyde	1-Ethoxynon-1-yn-3-ol	50	*k*
		PhLi	Ether	Propionaldehyde	1-Ethoxypent-1-yn-3-ol	47	*k*

Table VI (*Continued*)

	Compound metalated	*RLi*	*Solvent*	*Reactant*	*Final product*	*% yield*	*Ref*
C_4H_6S	Ethylthioacetylene	PhLi	Ether	Carbon dioxide	Ethylthiopropynoic acid (isolated as S-benzylthiuronium salt)	63	*l*
		MeLi	Ether	Ethyl chlorocarbonate	Ethyl ethylthiopropynoate	56	*l*
$C_4H_8S_2$	1,3-Dithiane	BuLi	Hexane	Benzaldehyde	2-(Hydroxyphenylmethyl)-1,3-dithiane	91	343
		BuLi	Hexane	Benzophenone	2-(Dihydroxyphenylmethyl)-1,3-dithiane	80	343
		BuLi	Hexane	*β*-Bromoacetaldehyde diethyl acetal	2-(Acetaldehyde diethyl acetal)-1,3-dithiane	77	343
		BuLi	Hexane	Cyclohexanone	2-(1-Hydroxycyclohexyl)-1,3-dithiane	85	343
		BuLi	Hexane	Cyclopentanone	2-(1-Hydroxycyclopentyl)-1,3-dithiane	70	343
		BuLi	Hexane	1,3-Dibromopropane	1,3-Di(2-thianyl)propane	66	344
		BuLi	Hexane	1,4-Dibromobutane	1,4-Di(2-thianyl)butane	84	344
		BuLi	Hexane	Isopropyl iodide	2-Isopropyl-1,3-dithiane		343
		BuLi	Hexane	Propionaldehyde	2-(1-Hydroxypropyl)-1,3-dithiane	80	343
$C_4H_{10}O$	Ethyl ether	Cyclohexyllithium	Ether	Carbon dioxide	3-Cyclohexylpropionic acid		144
$C_4H_{12}BrN$	Tetramethylammonium bromide	PhLi	Ether	Benzaldehyde	Trimethyl(2-phenyl-2-hydroxyethyl)ammonium bromide	58	*m*
		PhLi	Ether	Benzophenone	Trimethyl-(2,2-diphenyl-2-hydroxyethyl)ammonium bromide	21	*m*
		PhLi	Ether	Fluorenone	Trimethyl(9-hydroxy-9-fluorenylmethyl)ammonium bromide	60	*m*
$C_4H_{14}B_{10}$	1-Vinylcarborane	BuLi		Carbon dioxide	1-Vinyl-2-carboxycarborane		471
		BuLi	Benzene Ether	Ethylene oxide	2-(1-Vinyl-2-carboranyl)ethanol	72	474
		RLi	Ether	Mercuric chloride	Bis(vinylcarboranyl)mercury	51	473
		RLi	Benzene Ether	Methylmercuric chloride	Methyl(vinylcarboranyl)mercury	51	473
		BuLi	Benzene Ether	Propylene oxide	1-(1-Vinyl-2-carboranyl)-2-propanol	72	474
C_5H_3NS	2-Cyanothiophene	BuLi	Ether	Carbon dioxide	5-Cyano-2-thiophenecarboxylic acid	4	308
C_5H_3NS	3-Cyanothiophene	3-Thienyllithium	Ether	Carbon dioxide	3-Cyano-2-thiophenecarboxylic acid	80	308
		BuLi	Ether	Carbon dioxide	3-Cyano-2-thiophenecarboxylic acid	68	308
$C_5H_4N_4$	Pyridotetrazole	PhLi	Ether	Carbon dioxide	5,8-Pyridotetrazoledicarboxylic acid	28	360
C_5H_5N	Pyridine	PhLi	Ether	1-Methyl-4-piperidone	4-(2-Pyridyl)-1-methyl-4-hydroxypiperidine	34	*i*
$C_5H_5NO_2S$	3-Methylisothiazole-4-carboxylic acid	BuLi	THF Hexane	Bromine	5-Bromo-3-methylisothiazole-4-carboxylic acid	52	388
C_5H_6	Cyclopentadiene	PhLi	Ether	Benzoyl chloride	1-Benzoyl-6-hydroxy-6-phenylfulvene	37	*n*
		BuLi	Ether	Carbon dioxide	Cyclopentadienecarboxylic acid	72	*o*
		PhLi	Ether	*o*-Chlorobenzoyl chloride	1-(*o*-Chlorobenzoyl)-6-hydroxy-6-(*o*-chlorophenyl)fulvene	26	*n*
		PhLi	Ether	*p*-Chlorobenzoyl chloride	1-(*p*-Chlorobenzoyl)-6-hydroxy-6-(*p*-chlorophenyl)fulvene	50	*n*
		BuLi	Ether	Chlorodiethylsilane	Diethylcyclopentadienylsilane	15	*p*
		BuLi	Ether	1,5-Dichlorohexamethyltrisiloxane	1-Cyclopentadienyl-5-chlorohexamethyltrisiloxane	40	441

Table VI (Continued)

	Compound metalated	*RLi*	*Solvent*	*Reactant*	*Final product*	*% yield*	*Ref*
		BuLi	Ether	1,3-Dichlorotetramethyldisiloxane	1-Cyclopentadienyl-3-chlorotetramethyldisiloxane	57	441
		BuLi	Ether	Dimethyldichlorosilane	Cyclopentadienyldimethylchlorosilane	69	441
		BuLi	Ether	2,3-Diphenylindone	2,3-Diphenyl-3-(2,4-cyclopentadienyl)-1-indanone	27	*q*
		PhLi	Ether	*p*-Methylbenzoyl chloride	1-(*p*-Toluoyl)-6-hydroxy-6-(*p*-toluoyl)fulvene	44	*n*
		BuLi	Ether	Methyltrichlorosilane	Cyclopentadienylmethyldichlorosilane	55	441
		PhLi	Ether	*p*-Nitrobenzoyl chloride	1-(*p*-Nitrobenzoyl)-6-hydroxy-6-(*p*-nitrophenyl)fulvene	39	*n*
		PhLi	Ether	Phenylazocyclopentadienyllithium, $FeCl_3$	Phenylazoferrocene	6	448
		BuLi	Xylene	Titanium tetrachloride	Dicyclopentadienyltitanium dichloride	74	451
		PhLi	Ether	*p*-Toluenesulfonyl azide	Diazocyclopentadiene	35	*r*
C_5H_6O	2-Methylfuran	BuLi	Ether	Sulfur, *n*-butyl bromide	5-(Butylthio)-2-methylfuran	66	*e*
		BuLi	Ether	Sulfur, ethyl iodide	5-(Ethylthio)-2-methylfuran	77	*e*
		BuLi	Ether	Sulfur, isobutyl bromide	5-(Isobutylthio)-2-methylfuran	59	*e*
C_5H_6OS	2-Methoxythiophene	PhLi	Ether	Acetophenone	5-(1-Phenyl-1-ethylidene)-2(5H)-thiophene	11	*s*
		PhLi	Ether	Allyl chloride	5-Methoxy-2-allylthiophene		320
		PhLi	Ether	Benzaldehyde	5-Benzylidene-2(5H)-thiophene	17	*s*
		BuLi	Hexane	Benzophenone	5-Diphenylmethylene-2(5H)-thiophenone	69	*s*
		PhLi	Ether	Benzophenone	5-Diphenylmethylene-2(5H)-thiophenone	72	*s*
		PhLi	Ether	Carbon dioxide	5-Methoxy-2-thenoic acid	61	320
		PhLi	Ether	N,N′-Dimethylformamide	2-Methoxy-2-thenaldehyde	67	320
		PhLi	Ether	Dimethyl sulfate	5-Methoxy-2-methylthiophene	40	320
		PhLi	Ether	Ethylene oxide	2-(5-Methoxy-2-thienyl)ethanol	50	*t*
		BuLi	Ether Hexane	9-Fluorenone	5-(9-Fluorenylidene)-2(5H)-thiophenone	58	*s*
C_5H_6OS	3-Methoxythiophene	BuLi	Ether	Carbon dioxide	3-Methoxy-2-thiophenecarboxylic acid	86	304
$C_5H_6O_2S_2$	Methyl 3-thienyl sulfone	BuLi	Ether	Carbon dioxide	2-(3-Thienylsulfonyl)acetic acid	60	305
		BuLi		Carbon dioxide	5-Methyl-2-thiophenecarboxylic acid	84	311
		BuLi	Ether	Perchloryl fluoride	2-Fluoro-5-methylthiophene	44	*j*
		BuLi	Ether	Sulfur, ethyl β-bromoacetate	(5-Methyl-2-thienylthio)acetic acid		*u*
C_5H_6S	3-Methylthiophene	BuLi	Ether	Carbon dioxide	3-Methyl-5-thiophenecarboxylic acid	68	231
		BuLi	Ether	Carbon dioxide	3-Methylthiophene-5-carboxylic acid + 3-methylthiophene-2-carboxylic acid	61 19	319
		PhLi	Ether	Carbon dioxide	3-Methylthiophene-5-carboxylic acid + 3-methylthiophene-2-carboxylic acid	68 19	319
		BuLi	Ether	N,N-Dimethylformamide	3-Methyl-5-thiophenaldehyde + 3-methyl-2-thiophenealdehyde	83 17	316
		BuLi	Ether	N,N-Dimethylformamide	3-Methyl-5-thenaldehyde	61	318

Table VI (Continued)

	Compound metalated	*RLi*	*Solvent*	*Reactant*	*Final product*	*% yield*	*Ref*
$C_5H_6S_2$	Methyl 2-thienyl sulfide	BuLi	Ether	Carbon dioxide	5-Methylthio-2-thiophenecarboxylic acid	87	*u*
		BuLi	Ether	Sulfur, methyl iodide	2,5-Bis(methylthio)thiophene	57	*u*
$C_5H_6S_2$	Methyl 3-thienyl sulfide	BuLi	Ether	Carbon dioxide	3-Methyl-2-thiophenecarboxylic acid	60–70	306
C_5H_7N	N-Methylpyrrole	BuLi	Ether	Carbon dioxide	N-Methylpyrrole-2-carboxylic acid	42	394
C_5H_7N	N-Methylpyrrole	3BuLi	Ether	Carbon dioxide	N-Methylpyrrole-2,5-dicarboxylic acid	58	354
C_5H_7NS	2,4-Dimethylthiazole	BuLi	Ether	Acetaldehyde	2,4-Dimethyl-5-(1-hydroxyethyl)-thiazole	57	391
		BuLi	Ether	Butyraldehyde	2,4-Dimethyl-5-(1-hydroxybutyl)-thiazole	72	391
$C_5H_8N_2$	1,5-Dimethylpyrazole	PhLi	Ether	Carbon dioxide	1,3-Dimethyl-5-pyrazolecarboxylic acid	34	*a*
$C_5H_{10}S_2$	2-Methyl-1,3-dithiane	BuLi	Hexane	Benzonitrile	2-Methyl-2-benzoyl-1,3-dithiane	80	344
		BuLi	Hexane	Benzophenone	2-Methyl-2-(diphenylhydroxymethyl)-1,3-dithiane	83	343
		BuLi	Hexane	Benzyl bromide	2-Benzyl-2-methyl-1,3-dithiane	90	343
		BuLi	Hexane	Benzylidene–aniline	2-Methyl-2(α-anilinobenzyl)-1,3-dithiane	70	343
		BuLi	Hexane	Cyclohexanone	2-Methyl-1-(1-hydroxycyclohexyl)-1,3-dithiane	80	343
		BuLi	Hexane	1,4-Dibromobutane	1,4-Di(2-methyl-2-thianyl)butane	89	344
		BuLi	Hexane	N,N-Diethyl-2-chloroacetamide	N,N-Diethyl-2-methyl-1,3-dithiane-2-acetamide	50	343
		BuLi	Hexane	Ethyl benzoate	2,2′-(α-Hydroxybenzylidene)bis-(2-methyl-1,3-dithiane)	95	344
		BuLi	Hexane	Ethyl chloroformate	2-Methyl-1,3-dithiane-2-carboxylic acid ethyl ester	60	344
		BuLi	Hexane	Ethyl cyclohexanecarboxylate	2-Methyl-2-cyclohexanoyl-1,3-dithiane	60	344
		BuLi	Hexane	Ethyl formate	α-Oxopropionaldehyde dithioketal	50	344
		BuLi	Hexane	Isopropyl iodide	2-Methyl-2-isopropyl-1,3-dithiane	84	343
		BuLi	Hexane	Styrene oxide	2-Methyl-2-(2-hydroxy-2-phenylethyl)-1,3-dithiane	70	343
$C_5H_{14}B_2$	1,1-Diboropentane	MeLi		Ethyl bromide ($NaOH$, H_2O_2)	3-Heptanol	90	487
		BuLi		Ethyl bromide ($NaOH$, H_2O_2)	3-Heptanol	55	487
$C_5H_{16}B_{10}$	1-Isopropenylcarborane	BuLi	Ether	Carbon dioxide	Isopropenylcarboranecarboxylic acid	79	470
		PhLi	Ether	Methyl iodide	Methylisopropenylcarborane		470
$C_5H_{18}B_{10}$	Isopropylcarborane	BuLi		Benzaldehyde	α-(Isopropylcarboranyl)benzyl alcohol	59	*c*
		BuLi		Carbon dioxide	1-Isopropyl-2-carboxycarborane		471
C_6HCl_5	Pentachlorobenzene	BuLi	THF	Carbon dioxide	Pentachlorobenzoic acid	91	420
C_6HF_5	Pentafluorobenzene	BuLi	Hexane THF	Carbon dioxide	Pentafluorobenzoic acid	82	418
$C_6H_2Cl_4$	1,2,4,5-Tetrachlorobenzene	BuLi	Ether	Carbon dioxide	2,3,5,6-Tetrachlorobenzoic acid + tetrachloroterephthalic acid	48 27	420
		2BuLi	THF	Carbon dioxide	2,3,5,6-Tetrachlorobenzoic acid + tetrachloroterephthalic acid	30 42	420
$C_6H_2F_4$	1,2,4,5-Tetrafluorobenzene	BuLi	Hexane THF	Carbon dioxide	2,3,5,6-Tetrafluorobenzoic acid + 2,3,5,6-tetrafluoroterephthalic acid	3 67	418, 419
		BuLi	Hexane Ether	Carbon dioxide	2,3,5,6-Tetrafluorobenzoic acid	85	419

Table VI (*Continued*)

	Compound metalated	*RLi*	*Solvent*	*Reactant*	*Final product*	*% yield*	*Ref*
$C_6H_2F_4$	1,2,3,4-Tetrafluorobenzene	BuLi	Hexane THF	Carbon dioxide	2,3,4,5-Tetrafluorobenzoic acid		418
$C_6H_2F_4O$	2,3,5,6-Tetrafluorophenol	BuLi	THF Hexane	Carbon dioxide	4-Hydroxy-2,3,5,6-tetrafluorobenzoic acid	83	421
$C_6H_2F_4S$	2,3,5,6-Tetrafluorothiophenol	BuLi	Ether Hexane	Carbon dioxide	4-Thiol-2,3,5,6-tetrafluorobenzoic acid	77	421
$C_6H_3F_4N$	2,3,5,6-Tetrafluoroaniline	BuLi	THF Hexane	Carbon dioxide	4-Amino-2,3,5,6-tetrafluorobenzoic acid	45	421
$C_6H_4F_2$	*m*-Difluorobenzene	BuLi	THF Hexane	Carbon dioxide	2,6-Difluorobenzoic acid	88	421
C_6H_5F	Fluorobenzene	BuLi	THF	Carbon dioxide	*o*-Fluorobenzoic acid	60	183
C_6H_5Li	Phenyllithium	BuLi	Pentane–benzene	Carbon dioxide	Terephthalic acid (2) Isophthalic acid (1)	5	21
C_6H_5OS	2-Methoxythiophene	BuLi	Ether	Methyl *p*-toluenesulfonate	5-Methoxy-2-methylthiophene	78	316
C_6H_5S	2-Methylthiophene	BuLi	Ether	Dimethyl sulfide	5-Methylthio-2-methylthiophene	75	316
$C_6H_6N_4$	5-Methylpyridotetrazole	PhLi	Ether	Carbon dioxide	5-Pyridotetrazoylacetic acid	42	360
$C_6H_8N_4$	6-Methylpyridotetrazole	PhLi	Ether	Carbon dioxide	6-Methylpyridotetrazole-5,8-dicarboxylic acid	11	360
$C_8H_6N_4$	8-Methylpyridotetrazole	PhLi	Ether	Carbon dioxide	5-Carboxy-8-methylpyridotetrazole	18	360
C_6H_7N	2-Methylpyridine	PhLi	Ether	2-Amino-4-methoxybenzophenone	(*o*-Aminophenyl)-(*p*-methoxyphenol)(2-pyridylmethyl)carbinol	78	347
		PhLi	Ether	Benzyl chloride	2-Phenethylpyridine + dibenzyl-2-pyridylmethane	38 52	*v*
		PhLi	Ether	3-Bromopropanal diethyl acetal	4-(2-Pyridyl)butanal diethyl acetal	37	*w*
		PhLi	Ether	2-Bromopyridine	Di(2-pyridyl)methane + tri(2-pyridyl)methane	30 25	*v*
		PhLi	Ether	*n*-Butyl bromide	2-Amylpyridine	79	*v*
		PhLi	Ether	3-Chloropropanal diethyl acetal	4-(2-Pyridyl)butanal diethyl acetal	60	*w*
		PhLi	Ether	$Cl(CH_2)_nC{\equiv}CH$	$C_5H_4NCH_2(CH_2)_nC{\equiv}CH$	40–65	*x*
		PhLi	Ether	2-Chloroethanal diethyl acetal	3-(2-Pyridyl)propanal diethyl acetal	38–49	*w*
		PhLi		Cinnamylideneacetophenone	1,5-Diphenyl-6-(2-pyridyl)-1,3-hexadien-5-ol		*y*
		PhLi	Ether	$\Delta^{5(10)}$-Dehydroquinolizidinium perchlorate	10-(*α*-Picolyl)quinolizidine	65	*z*
		PhLi	Ether	Ethyl benzoate	Phenyl 2-picolyl ketone	80	*aa*
		PhLi	Ether	Ethyl bromide	2-Propylpyridine	92	*v*
		PhLi		Isobutyl borate	Lithium triisobutoxy-2-picolylborate	97	348
		PhLi	Ether	Isopropyl bromide	2-Methyl-6-isobutylpyridine	93	*v*
		PhLi	Ether	Methyl acetate	Acetyl 2-picolyl ketone	36	*aa*
		PhLi	Ether	Methyl benzoate	Phenyl 2-picolyl ketone	82	*aa*
		PhLi	Ether	Methyl furoate	Furyl 2-picolyl ketone	58	*aa*
		PhLi	Ether	Methyl iodide	2-Ethylpyridine	73	*v*
		PhLi	Ether	Methyl isobutyrate	Isobutyryl 2-picolyl ketone	61	*aa*
		PhLi	Ether	Methyl isovalerate	Isovaleryl 2-picolyl ketone	67	*aa*
		PhLi	Ether	Methyl propionate	Propionyl 2-picolyl ketone	50	*aa*

Table VI (Continued)

	Compound metalated	*RLi*	*Solvent*	*Reactant*	*Final product*	*% yield*	*Ref*
		PhLi	Ether	Methyl 2-thiophenecarboxylate	2-Thienyl 2-picolyl ketone	74	*aa*
		PhLi	Ether	Phenyl di(isobutyl)borate	Lithium diisobutoxy-2-picolylphenylborate	37	348
		PhLi	Ether	5-Phenyl-2,4-pentadien-1-al	1-Phenyl-6-(2-pyridyl)-1,3,5-hexatriene	15	*bb*
		PhLi	Ether	Propionaldehyde	2-(β-Hydroxybutyl)pyridine		*cc*
		PhLi	Ether	*n*-Propyl bromide	2-Butylpyridine	74	*v*
C_6H_7N	4-Methylpyridine	PhLi	Ether	Acetyl bromide	1-(4-Pyridyl)-2-propanone	34	352
		MeLi	Ether	Benzyl chloride	4-Phenethylpyridine + dibenzyl-4-pyridylmethane	43 47	*v*
		PhLi	Ether	2-Bromoethanal diethyl acetal	3-(4-Pyridyl)propanal diethyl acetal	39	352
		MeLi	Ether	*n*-Butyl bromide	4-*n*-Amylpyridine	74	*v*
		PhLi	Ether	Carbon dioxide, ethanol	Ethyl β-(4-pyridyl)acetate	34	352
		MeLi	Ether	Ethyl bromide	4-*n*-Propylpyridine	74	*v*
		MeLi	Ether	Isopropyl bromide	4-Isobutylpyridine	82	*v*
		PhLi	Ether	*n*-Propyl bromide	4-*n*-Butylpyridine	60	353
		MeLi	Ether	*n*-Propyl bromide	4-*n*-Butylpyridine	69	*v*
C_6H_8	Methylcyclopentadiene	BuLi	Ether	Ferric chloride	1,1′-Dimethylferrocene		447
C_6H_8O	2-Ethylfuran	BuLi	Ether	Sulfur, ethyl iodide	5-(Ethylthio)-2-ethylfuran	76	*e*
C_6H_8OS	2-(Ethylthio)-furan	BuLi	Ether	Sulfur, ethyl iodide	2,5-Bis(ethylthio)furan	77	*e*
C_6H_8OS	2-Methoxy-5-methylthiophene	BuLi	Ether	Carbon dioxide	2-Methoxy-5-methyl-3-thenoic acid	50	320
C_6H_8S	2,3-Dimethylthiophene	BuLi	Ether	Carbon dioxide	4,5-Dimethyl-2-thenoic acid		318
C_6H_8S	3,4-Dimethylthiophene	BuLi	Ether	Carbon dioxide	3,4-Dimethyl-2-thenoic acid		318
C_6H_8S	3,5-Dimethylthiophene	BuLi	Ether	N,N-Dimethylformamide	3,5-Dimethyl-2-thenaldehyde	69	318
$C_6H_8S_2$	Ethyl 2-thienyl sulfide	BuLi	Ether	Carbon dioxide	5-Ethylthio-2-thiophenecarboxylic acid	77	*u*
$C_6H_8S_2$	Methyl 5-methyl-2-thienyl sulfide	BuLi	Ether	Carbon dioxide	2-Methylthio-5-methyl-3-thiophenecarboxylic acid	27	*u*
C_6H_9NS	5-Methyl-4-ethylthiazole	BuLi	Ether	Propylene oxide	5-Methyl-4-ethyl-2-(2-hydroxypropyl)thiazole	76	391
C_6H_{10}	1-Hexyne	RLi	Ether	Paraformaldehyde	Hept-2-yn-1-ol	80	209
$C_6H_{12}S_2$	1,2-Bis(ethylthio)ethylene	BuLi	Ether	Acetone	1-Ethylthio-3-hydroxy-3-methyl-1-butyne	70	147
		BuLi	Ether	Benzaldehyde	1-Ethylthio-3-hydroxy-3-phenyl-1-propyne	56	147
		BuLi	Ether	Cyclohexanone	1-(Ethylthioethynyl)-1-hydroxycyclohexane	55	147
$C_6H_{18}B_{10}O_2$	2-Carboranylethyl acetate	BuLi	Ether Heptane	Carbon dioxide	2-(2-Hydroxyethyl)carboranecarboxylic acid		475
$C_6H_{20}B_{10}$	1-Butylcarborane	BuLi		Carbon dioxide	1-Butyl-2-carboxycarborane		471
$C_6H_{26}B_{20}O$	Bis(1-carboranylmethyl) ether	BuLi	THF	Carbon dioxide	Bis(2-carboxy-1-carboranylmethyl) ether	50–91	*dd*
		BuLi	Ether	Ethylene oxide	Bis(2-β-hydroxyethyl-1-carboranylmethyl) ether	86	*dd*
		BuLi	Ether	Paraformaldehyde	Bis(2-hydroxymethyl-1-carboranylmethyl) ether	50	*dd*

Table VI (Continued)

	Compound metalated	*RLi*	*Solvent*	*Reactant*	*Final product*	*% yield*	*Ref*
C_7HF_7	2,3,5,6-Heptafluorotoluene	BuLi	Hexane THF	Carbon dioxide	4-Trifluoromethyl-2,3,5,6-tetrafluorobenzoic acid	77	421
$C_7H_2F_4O_2$	2,3,5,6-Tetrafluorobenzoic acid	BuLi	Hexane THF	Carbon dioxide	Tetrafluoroterephthalic acid	94	419
		BuLi	Hexane Ether	Chlorine	4-Chloro-2,3,5,6-tetrafluorobenzoic acid		419
		BuLi	Hexane THF	Sulfur	4-Thiol-2,3,5,6-tetrafluorobenzoic acid	69	419
$C_7H_4F_4$	2,3,5,6-Tetrafluorotoluene	BuLi	Hexane Ether	Carbon dioxide	4-Methyl-2,3,5,6-tetrafluorobenzoic	88	421
C_7H_5NS	Benzothiazole	BuLi	Ether	N,N-Dimethylcarbamoyl chloride	Bis(2-benzothiazolyl) ketone		207
		BuLi	Ether	Triphenylsilyl bromide	2-Triphenylsilylbenzothiazole	19	*ee*
$C_7H_6Cl_2$	Benzal chloride	BuLi	THF Hexane	Carbon dioxide	Phenylglyoxylic acid	42–61	186, 195
		BuLi	THF Hexane	Tetramethylethylene	1-Chloro-1-phenyltetramethylcyclopropane	48	186
C_7H_6S	2-(Propynyl)thiophene	BuLi	Ether	Carbon dioxide	5-(Propynyl)thiophene-5-carboxylic acid	37	*ttt*
		BuLi	Ether	N,N-Dimethylformamide	5-(1-Propynyl)-2-formylthiophene	21	*ttt*
C_7H_7BrO	*p*-Bromoanisole	Poly-*p*-styryllithium	Ether	Carbon dioxide	5-Bromo-2-methoxybenzoic acid	34	*g*
		2,4,6-Ph_3PhLi		Carbon dioxide	5-Bromo-2-methoxybenzoic acid	25	172
C_7H_7F	*o*-Fluorotoluene	BuLi	THF	Carbon dioxide	2-Fluoro-3-methylbenzoic acid	3	183
C_7H_7F	*p*-Fluorotoluene	BuLi	THF	Carbon dioxide	2-Fluoro-5-methylbenzoic acid	58	183
C_7H_7IO	*p*-Iodoanisole	Poly-*p*-styryllithium	Ether	Carbon dioxide	5-Iodo-2-methoxybenzoic acid	22	*g*
C_7H_8	Norbornadiene	BuLi	Ether	Carbon dioxide	*endo*-2-Norcamphanecarboxylic acid	15	267
C_7H_8	Toluene	BuLi–DABCO	Hexane	Benzophenone	Benzyldiphenylcarbinol	85	50
		BuLi	Ether THF	Carbon dioxide	Phenylacetic acid	24	170
C_7H_8O	Phenyl methyl ether	BuLi	Ether	Carbon dioxide	2-Methoxybenzoic acid	10	*ff*
$C_7H_8O_2$	*m*-Methoxyphenol	BuLi	Ether	Carbon dioxide	2-Methoxy-6-hydroxybenzoic acid + 2-methoxy-4-hydroxybenzoic acid	13 5	300
$C_7H_8O_2$	*o*-Methoxyphenol	BuLi	Ether	Carbon dioxide	2-Methoxy-3-hydroxybenzoic acid + 2-hydroxy-3-methoxybenzoic acid	2 2	300
$C_7H_8O_2S$	3-Thiophenecarboxaldehyde ethylene acetal	BuLi	Ether	Carbon dioxide	3-Formyl-2-thiophenecarboxylic acid	78	312
C_7H_8S	Phenyl methyl sulfide	BuLi	Ether	Tetraethoxysilane	Tetra(benzenethiomethyl)silane	42	*gg*
C_7H_8S	Thioanisole	BuLi–DABCO	Hexane	Acetone	1-Phenylmercapto-2-hydroxy-2-methylpropane	77	330
		BuLi–DABCO	THF	Benzophenone	Phenyl (2,2-diphenyl-2-hydroxy)ethyl sulfide	93	330
		BuLi–DABCO	Hexane	Deuterium oxide	Thioanisole-α-D	99	330
		BuLi–DABCO	Hexane	Isopropyl iodide	Phenyl isobutyryl sulfide	55	330

Table VI (Continued)

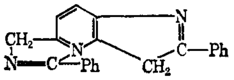
	Compound metalated	RLi	Solvent	Reactant	Final product	% yield	Ref
C_7H_9N	2-Ethylpyridine	PhLi	Ether	Ethyl bromide	2-*sec*-Butylpyridine	91	*v*
		PhLi	Ether	Methyl iodide	2-Isopropylpyridine	63	*v*
C_7H_9N	4-Ethylpyridine	PhLi	Ether	*n*-Butyl bromide	2-(4′-Pyridyl)hexane	30	353
C_7H_9N	2,4-Dimethylpyridine	PhLi	Ether	Benzaldehyde	4-Methyl-2-picolylphenylcarbinol	86	349
		PhLi	Ether	Benzonitrile		28	350
		2PhLi	Ether	Benzonitrile	α-Methyl-α′-phenacylpyridine	30	350
		PhLi	Ether	Benzyl chloride	2-Methyl-5-phenethylpyridine	20	350
		2PhLi	Ether	Benzyl chloride	2-Methyl-6-(dibenzylmethyl)pyridine	25	350
		PhLi	Ether	1-Chloro-1,2-diphenylethane	1,2-Diphenyl-3-(α-picolyl-α′)propane	15	350
		PhLi	Ether	Methyl benzoate, benzoyl chloride	2-Phenacyl-6-methylpyridine	67	*hh*
C_7H_{10}	Tricyclo[4.1.0.$0^{2,7}$]heptane	BuLi	Ether	Carbon dioxide	1-Carboxytricyclo[4.1.0.$0^{2,7}$]heptane		266
		BuLi	Ether	Deuterium oxide	1-Deuteriotricyclo[4.1.0.$0^{2,7}$]heptane		266
		BuLi	Ether	Methyl iodide	1-Methyltricyclo[4.1.0.$0^{2,7}$]octane		266
$C_7H_{11}NS$	2,5-Dimethyl-4-ethylthiazole	BuLi	Ether	Acetaldehyde	5-Methyl-4-ethyl-2(2-hydroxypropyl)thiazole	60	391
		BuLi	Ether	Butyraldehyde	5-Methyl-4-ethyl-2-(3-hydroxypentyl)thiazole	60	391
$C_7H_{14}S_2$	2-Isopropyl-1,3-dithiane	BuLi	Hexane	Benzophenone	2-Isopropyl-2-(diphenylhydroxymethyl)-1,3-dithiane	52	343
		BuLi	Hexane	Isopropyl iodide	2,2-Diisopropyl-1,3-dithiane	70	343
$C_7H_{20}B_{10}O_2$	3-Carboranylpropyl acetate	BuLi	Ether Heptane	Ethylene oxide	1,2-Bis-2,2′-hydroxyethylcarborane		480
C_8H_6	Phenylacetylene	Poly-*p*-styryllithium	Ether	Carbon dioxide	Phenylpropynoic acid	65	*g*
		Ph_3SiLi	THF	Carbon dioxide	Phenylpropynoic acid	40	271
		PhLi	Ether	N,N-Dimethylcarbamoyl chloride	N,N-Dimethylpropiolamide		207
		BuLi	Ether	Triphenylchlorosilane	Triphenylphenylethynylsilane	72	171
$C_8H_6N_2O_2$	3-Phenylsydnone	BuLi	Hexane Ether	Carbon dioxide	3-Phenylsydnone-4-carboxylic acid	60	387
C_8H_6O	Benzofuran	Poly-*p*-styryllithium	THF	Carbon dioxide	Benzofuran-2-carboxylic acid	15	*g*
		BuLi	Ether	N,N-Dimethylcarbamoyl chloride	Bis(2-benzofuranyl) ketone		207
$C_8H_6OCl_2$	Phenoxy-1,2-dichloroethylene	BuLi	Ether	Cyclohexanone	1-(Phenoxyethynyl)cyclohexanol	60	416
C_8H_6S	Thiaindene	BuLi	Ether	Diethyl sulfate	2-Ethylthiaindene	81–91	*ii–kk*
C_8H_6S	Thianaphthene	BuLi	Ether	Acetaldehyde	Methyl-2-thianaphthenylcarbinol	72	325
		BuLi	Ether	Benzaldehyde	Phenyl-2-thianaphthenylcarbinol	70	325
		BuLi	Ether	Bromine	2-Bromothianaphthene	39	325
		BuLi	Ether	Carbon dioxide	2-Thianaphthenecarboxylic acid	82	231
		BuLi	Ether	*p*-Chlorobenzaldehyde	*p*-Chlorophenyl-2-thianaphthenylcarbinol	68	325
		BuLi	Ether	*p*-Dimethylaminobenzaldehyde	*p*-Dimethylaminophenyl-2-naphthenylcarbinol	47	325
		BuLi	Ether	N,N-Dimethylcarbamoyl chloride	Bis(2-thianaphthenyl) ketone		207
		BuLi	Ether	Fluorobenzene	2-Phenylthianaphthene	55	*ll*
		BuLi	Ether	Formaldehyde	2-Thianaphthenylmethanol	48	*mm*

Table VI (Continued)

	Compound metalated	*RLi*	*Solvent*	*Reactant*	*Final product*	*% yield*	*Ref*
		BuLi	Ether	Methyl *o*-toluenesulfonate	2-Methylthianaphthene	43	325
		BuLi	Ether	Perchloryl fluoride	2-Fluorothianaphthene	70	*j*
		BuLi	Ether	Phenyl isocyanate	N-Phenylthianaphthene-2-carboxamide	81	325
		BuLi	Ether	*o*-Tolyl isocyanate	N-*o*-Tolylthianaphthene-2-carboxamide	41	325
		BuLi	Ether	Triphenylchlorosilane	2-Triphenylsilyldibenzothiophene	90	*ee*
$C_8H_6S_2$	2,2′-Bithienyl	PhLi	Ether	Carbon dioxide	5-(2′-Thienyl)-2-thenoic acid	74	321
$C_8H_6S_2$	2,3′-Bithienyl	PhLi	Ether	Carbon dioxide	2,3′-Bithienyl-5′-carboxylic acid (38) + 2,3′-bithienyl-2′-carboxylic acid (52)	75	321
C_8H_7N	Indole	BuLi	Ether	Carbon dioxide	1-Indolecarboxylic acid	61	355
C_8H_7N	Phenylacetonitrile	BuLi	Ether	Benzophenone	2,3,3-Triphenylacrylonitrile	30	180, 182
		BuLi	THF	*n*-Butyl bromide	Phenyl-*n*-butylacetonitrile	73	155
		BuLi	THF	*n*-Butyl bromide	α,α′-Di-*n*-butylphenylacetonitrile	69	155
		BuLi	THF	Carbon dioxide	Phenylcyanoacetic acid	38–47	180, 182, 369
		MeLi	Ether	Carbon dioxide	Phenylcyanoacetic acid	38–47	180, 182
		o-MePhLi	Ether	Carbon dioxide	Phenylcyanoacetic acid	38–47	180, 182
		α-Naphthyllithium	Ether	Carbon dioxide	Phenylcyanoacetic acid	38–40	182
		PhLi	Ether	Carbon dioxide	Phenylcyanoacetic acid	38–47	180, 182
		PrLi	Ether	Carbon dioxide	Phenylcyanoacetic acid	38–47	180, 182
		BuLi	THF Hexane	Deuterium oxide	α,α′-Dideuteriophenylnitrile	89	155
		BuLi	THF Hexane	Ethylene chloride	1-Phenyl-1-cyanocyclopropane	69	155
$C_8H_7O_2Na$	Sodium phenyl acetate	BuLi	Ether		2,4-Diphenyl-3-butyl-3-hydroxybutanoic acid	42–55	178
		BuLi	Ether	Benzalacetophenone	2,3-Diphenyl-4-benzoylbutyric acid	38	181
		BuLi	Dioxane	Benzophenone	2,3,3-Triphenyl-3-hydroxypropionic acid	28	179
		BuLi	Ether	Benzophenone	2,3,3-Triphenyl-3-hydroxypropionic acid	46–52	179, 182
		BuLi	Ether	Benzyl styryl ketone	4-Benzoyl-2,3-diphenylbutyric acid	38	182
		BuLi	Ether	Carbon dioxide	Phenylmalonic acid	30	179, 182
		BuLi	Ether	*p*-Chlorobenzalacetophenone	1-Phenyl-2-(*p*-chlorophenyl)-4-benzoylbutyric acid	51	181
		BuLi	Ether	*p*-Methoxybenzalacetophenone	1-Phenyl-2-(*p*-methoxyphenyl)-4-benzoylbutyric acid	29	181
		BuLi	Ether	*p*-Methoxystyryl benzyl ketone	4-Benzoyl-3-(*p*-methoxyphenyl)-2-phenylbutyric acid	29	182
		sec-BuLi	Ether	Benzophenone	2,3,3-Triphenyl-3-hydroxypropionic acid	18	179, 182
		t-BuLi	Ether	Benzophenone	2,3,3-Triphenyl-3-hydroxypropionic acid	12–14	179, 182
		Cyclohexyllithium	Ether	Benzophenone	2,3,3-Triphenyl-3-hydroxypropionic acid	20	179, 182
		3,5-Me_2PhLi	Ether	Benzophenone	2,3,3-Triphenyl-3-hydroxypropionic acid	72	182
		EtLi	Ether	Benzophenone	2,3,3-Triphenyl-3-hydroxypropionic acid	18–21	179, 182
		i-AmLi	Ether	Benzophenone	2,3,3-Triphenyl-3-hydroxypropionic acid	35	179, 182
		i-PrLi	Ether	Benzophenone	2,3,3-Triphenyl-3-hydroxypropionic acid	23–25	179, 182
		p-MeOPhLi	Ether	*p*-Methoxybenzyl ketone	2,4-Diphenyl-3-(*p*-methoxyphenyl)-3-hydroxybutyric acid	38	182
		MeLi	Ether	Benzophenone	2,3,3-Triphenyl-3-hydroxypropionic acid	3	179, 182

Table VI (Continued)

	Compound metalated	*RLi*	*Solvent*	*Reactant*	*Final product*	*% yield*	*Ref*
		m-MePhLi	Ether	*m*-Tolyl benzyl ketone	2,4-Diphenyl-3(*m*-tolyl)-3-hydroxybutyric acid	40–43	182
		o-MePhLi	Ether	Benzophenone	2,3,3-Triphenyl-3-hydroxypropionic acid	64–67	182
		o-MePhLi	Ether	Benzyl chloride	2,3-Diphenylpropionic acid	75–77	182, *nn*
		o-MePhLi	Ether	*o*-Chlorobenzyl chloride	3-Phenyl-2-(*o*-chlorophenyl)-propionic acid	71–74	182
		o-MePhLi	Ether	*p*-Chlorobenzyl chloride	3-Phenyl-2-(*p*-chlorophenyl)-propionic acid	70–72	182
		o-MePhLi	Ether	*p*-Chlorostyryl benzyl ketone	4-Benzoyl-3-(*p*-chlorophenyl)-2-phenylbutyric acid	51	182
		o-MePhLi	Ether	*p*-Cyanobenzyl chloride	3-Phenyl-2-(*p*-cyanophenyl)-propionic acid	80–85	182
		o-MePhLi	Ether	Styryl ketone	2,3,7-Triphenyl-5-oxo-6-heptenoic acid	45	181, 182
		p-MePhLi	Ether	*p*-Tolyl benzyl ketone	2,4-Diphenyl-3-(*p*-tolyl)-3-hydroxybutyric acid	45	182
		α-Naphthyl-($C_{10}H_7$)Li	Ether	Benzalaniline	2,3-Diphenyl-3-aminophenylpropionic acid	74	182
		α-$C_{10}H_7Li$	Ether	Benzal-*p*-methoxyaniline	2,3-Diphenyl-3-amino(*p*-methoxyphenyl)propionic acid	78	182
		α-$C_{10}H_7Li$	Ether	Benzal-*p*-methylaniline	2,3-Diphenyl-3-amino(*p*-tolyl)-propionic acid	60	182
		α-$C_{10}H_7Li$	Ether	Benzal-β-naphthylamine	2,3-Diphenyl-3-amino(β-naphthyl)propionic acid	70	182
		α-$C_{10}H_7Li$	Ether	Benzophenone	2,3,3-Triphenyl-3-hydroxypropionic acid	65–70	182
		α-$C_{10}H_7Li$	Ether	Carbon dioxide	Phenylmalonic acid	42	182
		α-$C_{10}H_7Li$	Ether	Iodine	2,3-Diphenylsuccinic acid	53	182
		α-$C_{10}H_7Li$	Ether	α-Naphthyl benzyl ketone	2,4-Diphenyl-3-(α-naphthyl)-3-hydroxybutyric acid	28	182
		PhLi	Ether	Benzophenone	2,3,3-Triphenyl-3-hydroxypropionic acid		177
		PhLi	Ether	Carbon dioxide	Phenylmalonic acid	42	177
		PhLi	Ether	Phenyl benzyl ketone	2,3,4-Triphenyl-3-hydroxybutyric acid	39–41	182
		PrLi	Ether	Benzophenone	2,3,3-Triphenyl-3-hydroxypropionic acid	42–48	179, 182
		PrLi	Ether	Carbon dioxide	Phenylmalonic acid	25	182
		RLi	Ether	*o*-Chlorobenzyl chloride	2-Phenyl-3-(*o*-chlorophenyl)-propionic acid	73	182
		RLi	Ether	*p*-Chlorobenzyl chloride	2-Phenyl-3-(*p*-chlorophenyl)-propionic acid	70	182
		RLi	Ether	*m*-Cyanobenzyl chloride	2-Phenyl-3-(*m*-cyanophenyl)-propionic acid	82	182
		o-CH_3-C_6H_4Li	Ether	Diethyl adipate	1,6-Diphenyl-2,5-hexadione + 7-phenyl-6-oxoheptanoic acid	16 33	173
		o-CH_3-C_6H_4Li	Ether	Diethyl malonate	1,5-Diphenyl-2,4-hexadione + ethyl 4-phenyl-3-oxobutyrate	6 12	173
		o-CH_3-C_6H_4Li	Ether	Ethyl acetate	Benzyl methyl ketone (66%) + 2,4-diphenyl-3-methyl-3-hydroxyglutaric acid (9%)		173
		o-CH_3-C_6H_4Li	Ethdr	Ethyl benzoate	2,3,4-Triphenyl-3-hydroxyglutaric acid + benzyl phenyl ketone	5 41	173
		o-CH_3-C_6H_4Li	Ether	Ethyl cinnamate	2,3,6-Triphenyl-5-oxo-hexanoic acid + benzyl styryl ketone	48 10	173
		o-CH_3-C_6H_4Li	Ether	Ethyl phenylacetate	2,4-Diphenyl-3-benzyl-3-hydroxyglutaric acid + benzyl ketone	2 40	173
		o-CH_3-C_6H_4Li	Ether	Ethyl sebacate	11-Phenyl-10-oxoundecanoic acid + 1,12-diphenyl-2,11-decadione	64 31	173
C_8H_8	Styrene	BuLi	Ether	Carbon dioxide	2-Phenylheptanoic acid	Trace	273
$C_8H_8N_2$	1-Methylbenzimidazole	BuLi	Ether	Carbon dioxide	1-Methyl-2-benzimidazolecarboxylic acid	45	359

Table VI (Continued)

	Compound metalated	*RLi*	*Solvent*	*Reactant*	*Final product*	*% yield*	*Ref*
C_8H_8S	5-Methyl-4H-cyclopenta-[*b*]thiophene	BuLi	Ether	Carbon dioxide	4-Carboxyindene		*oo*
C_8H_8S	5-Methyl-6H-cyclopenta-[*b*]thiophene	BuLi	Ether	Carbon dioxide	6-Carboxyindene		*oo*
C_8H_9NO	Phenylacetamide	BuLi	THF Hexane	*n*-Butyl bromide	Phenyl-*n*-butylacetamide	87	371
C_8H_9ON	N-Methylbenzamide	2.5BuLi	Hexane THF	Acetophenone	*o*-(1-Hydroxy-1-phenylethyl)-N-methylbenzamide	43	378
		2.5BuLi	Hexane THF	Benzaldehyde	3-Phenylphthalide	49	378
		2.5BuLi	Hexane THF	Benzonitrile	*o*-Benzimidoyl-N-methylbenzamide	53	378
		2.5BuLi	Hexane THF	Benzophenone	α,α'-Diphenyl-α-hydroxy-N-methyl-*o*-toluamide	81	378
		2.5BuLi	Hexane THF	*p*-Chlorobenzophenone	α-(4-Chlorophenyl)-α-hydroxy-α-phenyl-N-methyl-*o*-toluamide	51	378
		2.5BuLi	Hexane THF	Cyclohexanone	Spiro[cyclohexane-1,1′-phthalan]-3′-one	27	378
		2.5BuLi	Hexane THF	Cyclohexene oxide	1,2,3,4,4a,10b-Hexahydro-6H-dibenzo[*b*,*d*]pyran-6-one	11	378
		2.5BuLi	Hexane THF	Fluorenone	Spiro[fluorene-9,1′-phthalan]-3′-one	58	378
C_8H_{10}	Dimethylfulvene	MeLi	Ether	Ferric chloride	1,1′-Di-*t*-butylferrocene	94	434
		PhLi	Ether	Ferric chloride	1,1′-Bis(α,α'-dimethylbenzyl)-ferrocene	73–90	434
		PhLi	Ether	Tetrapyridine-nickel chloride	1,1′-Di(α,α'-dimethylbenzyl-cyclopentadienyl)nickel	63	452
C_8H_{10}	3,8-Octadiyne	RLi	Ether	Paraformaldehyde	Nona-2,4-diyn-1-ol	77	209
$C_8H_{10}O$	Benzyl methyl ether	2Li	THF	Triphenylchlorosilane	Triphenylbenzylsilane	75	39
$C_8H_{10}O$	*o*-Methylanisole	BuLi	Ether	Carbon dioxide	*o*-Methoxyphenylacetic acid + 2-methoxy-3-methylbenzoic acid	5	294
$C_8H_{10}O$	*p*-Methylanisole	BuLi	Ether	Carbon dioxide	2-Methoxy-5-methylbenzoic acid	16	294
$C_8H_{10}O_2$	Hydroquinone dimethyl ether	Poly-*p*-styryllithium	Ether	Carbon dioxide	2,5-Dimethoxybenzoic acid	6	*g*
$C_8H_{10}O_2$	Resorcinol dimethyl ether	Mesityllithium		Carbon dioxide	2,6-Dimethoxybenzoic acid	35	172
$C_8H_{10}O_2$	Resorcinol dimethyl ether	Poly-*p*-styryllithium	Ether	Carbon dioxide	2,6-Dimethoxybenzoic acid	48	*g*
$C_8H_{10}O_2S$	2-Methyl-2-(2-thienyl)-1,3-dioxolane	BuLi	Hexane Ether	Benzaldehyde	Phenyl-2-thienyl(5-acetylethylene-ketal)carbinol	60	302
		BuLi	Hexane Ether	Benzonitrile	2-Acetyl-5-benzoylthiophene	66	302
		BuLi	Hexane Ether	Carbon dioxide	2-Acetyl-5-thiophenecarboxylic acid	70	302
		BuLi	Hexane Ether	Chlorotrimethylsilane	2-Methyl-2-(2-thienyl-5-trimethylsilyl)-1,3-dioxolane	96	302
		BuLi	Hexane Ether	Phenyl isocyanate	Phenyl(2-acetylethylene ketal)-5-thiophenecarboxylic acid amide	65	302
$C_8H_{10}O_2S$	Methyl *p*-tolyl sulfone	BuLi	Ether	Triphenylchlorosilane	Triphenyl(*p*-toluenesulfonylmethyl)silane	31	*gg*

Table VI (*Continued*)

	Compound metalated	*RLi*	*Solvent*	*Reactant*	*Final product*	*% yield*	*Ref*
$C_8H_{10}S$	Methyl *p*-tolyl sulfide	BuLi	Ether	Tetraethoxysilane	Tetra(*p*-toluenethiomethyl)silane	53	*gg*
		BuLi	Ether	Trimethylchlorosilane	Trimethyl(*p*-toluenethiomethyl)silane	78	*gg*
		BuLi	Ether	Triphenylchlorosilane	Triphenyl(*p*-toluenethiomethyl)silane	67	*gg*
$C_8H_{11}N$	α-(Dimethylamino)fulvene	MeLi	Ether	Ferrous chloride	1,1′-Bis(1-dimethylaminoethyl)ferrocene	71	452
$C_8H_{11}N$	Dimethylaniline	BuLi	Hexane	Acetophenone	1-(*o*-Dimethylaminophenyl)-1-phenylethanol	25	372
		BuLi	Hexane	Benzophenone	*o*-(N,N-Dimethylamino)tritanol	56	372
		BuLi	Hexane	4,4-Bis(dimethylamino)benzophenone	*o*,*p*′,*p*′′-Tris(N,N-dimethylamino)tritanol	21	372
		BuLi	Hexane	2-Butanone	2-(*o*-Dimethylaminophenyl)-2-butanol	20	372
		BuLi	Hexane	Cyclohexanone	1-(*o*-Dimethylaminophenyl)cyclohexanol	31	372
		BuLi	Hexane	Cyclohexene oxide	2-(*o*-Dimethylaminophenyl)cyclohexanol + 1-(*o*-dimethylaminophenyl)cyclohexene	14 7	372
		BuLi	Hexane	Hexafluoroacetone	*o*-(Dimethylaminophenylbistrifluoromethyl)carbinol + *m*-(dimethylaminophenylbistrifluoromethyl)carbinol	71 19	372
$C_8H_{11}N$	2,4,6-Trimethylpyridine	PhLi	Ether	Benzaldehyde	2-(4,6-Dimethylpicolyl)phenylcarbinol	64	349
$C_8H_{11}P$	Dimethylphenylphosphine	*t*-BuLi	Pentane	Carbon dioxide, sulfur	Carboxymethylmethylphenylphosphine sulfide	36	457
		t-BuLi	Pentane	Chlorotrimethylsilane, sulfur	Methylphenyl(trimethylsilylmethyl)phosphine sulfide + bis(trimethylsilylmethyl)phenylphosphine sulfide		456
C_8H_{12}	1-Methyltricyclo[4.1.0.0.^{2,7}]heptane	BuLi	Ether	Methyl iodide	1,2-Dimethyltricyclo[4.1.0.0.^{2,7}]nonane		266
C_8H_{12}	Oct-1-yn-3-ene	RLi	Ether	Paraformaldehyde	Non-4-en-2-yn-1-ol	75	209
$C_8H_{12}OS$	3-*t*-Butoxythiophene	BuLi	Ether	Carbon dioxide	3-*t*-Butoxy-2-thiophenecarboxylic acid	62	307
$C_8H_{12}O_2S$	*t*-Butyl 2-thienyl sulfone	BuLi	Ether THF	N,N-Dimethylformamide	3-*t*-Butylsulfonyl-2,4-thiophenedicarboxaldehyde	38	340
$C_8H_{12}S$	2-*t*-Butylthiophene	BuLi	Ether	Carbon dioxide	2-*t*-Butyl-5-thiophenecarboxylic acid	68	316
$C_8H_{12}S_2$	Ethyl 5-ethyl-2-thienyl sulfide	BuLi	Ether	Carbon dioxide	2-Ethylthio-5-ethyl-3-thiophenecarboxylic acid	7	*u*
$C_8H_{12}Sn$	Tetravinyltin	PhLi	Ether	Acetone	Dimethylvinylcarbinol	75	*qq*
		PhLi	Ether	Arsenic trichloride	Trivinylarsine	51	*qq*
		PhLi	Ether	Carbon dioxide	Acrylic acid	18	*qq*
		PhLi	Ether	Tri-*n*-butyltin chloride	Tri-*n*-butylvinyltin	74	*qq*
		PhLi	Ether	Triphenylsilicon fluoride	Triphenylvinylsilane	60	*qq*
$C_8H_{13}Si$	Trimethylsilylcyclopentadiene	BuLi	Benzene–pet. ether	Ferric chloride	1,1-Bis(trimethylsilyl)ferrocene	50	433
$C_8H_{16}B_{10}$	Phenylcarborane	RLi	Benzene Ether	Antimony trichloride	Tris(phenylcarboranyl)antimony	57	473
		RLi	Benzene Ether	Arsenic trichloride	Tris(phenylcarboranyl)arsine	55	473

Table VI (*Continued*)

	Compound metalated	*RLi*	*Solvent*	*Reactant*	*Final product*	*% yield*	*Ref*
		BuLi		Benzaldehyde	α-(Phenylcarboranyl)benzyl alcohol	31	*c*
		BuLi	Benzene Ether	Carbon dioxide	Phenylcarboranecarboxylic acid	92	471, 476
		RLi	Ether	Cyanogen chloride	1-Phenyl-2-cyanocarborane + 1-phenyl-2-chlorocarborane		*rr*
		RLi		Diethyl phthalate	Phenylcarboranylphthalide	63	483
		RLi	Benzene Ether	Di-*n*-hexylchlorophosphine	Di-*n*-hexyl(phenylcarboranyl)phosphine	52	473
		BuLi	Benzene Ether	Epichlorohydrin	1-(1-Phenyl-2-carboranyl)-3-chloro-2-propanol		474
		RLi		Ethyl benzoate	Phenylcarboranylphenylcarbinol	74	483
		RLi		Ethyl *p*-chlorobenzoate	Phenylcarboranyl-*p*-chlorophenylcarbinol	72	483
		BuLi	Benzene Ether	Ethylene oxide	2-(1-Phenyl-2-carboranyl)ethanol	92	474
		RLi	Benzene Ether	Germanium tetrachloride	Bis(phenylcarboranyl)germanium dichloride	59	473
		RLi	Ether	Mercuric chloride	Bis(phenylcarborane)mercury	70	473
		RLi		Methyl benzoate	1-Phenyl-2-benzoylcarborane	62	483
		RLi		Methyl *p*-bromobenzoate	1-Phenyl-2-*p*-bromobenzoylcarborane	72	483
		2RLi	Benzene	Methyl cinnamate	2-(2-Phenyl-1-carboranyl)-2-phenyl ethyl ketone	86	482
		BuLi	Benzene	Methylmercuric bromide	Methyl(phenylcarboranyl)mercury	62	473
		RLi		Methyl *p*-toluate	1-Phenyl-2-*p*-toluoylcarborane	73	483
		RLi	Benzene	Phenyl styryl ketone	2-(2-Phenyl-1-carboranyl) 2-phenyl ketone	94	482
		RLi	Benzene Ether	Phosphorus trichloride	Bis(phenylcarboranyl)chlorophosphine	52	473
		BuLi	Benzene Ether	Propylene oxide	1-(1-Phenyl-2-carboranyl)-2-propanol	72	474
		RLi	Benzene Ether	Silicon tetrachloride	Bis(phenylcarboranyl)dichlorosilane	64	473
		RLi	Benzene	Stannic chloride	Tris(phenylcarboranyl)tin chloride + bis(phenylcarboranyl)tin dichloride	25 37	473
		RLi	Benzene	Styryl *t*-butyl ketone	2-(2-Phenyl-1-carboranyl) 2-*t*-butyl ketone	95	482
		RLi	Benzene Ether	Tin tetrabromide	Bis(phenylcarboranyl)tin dibromide	61	473
		RLi	Benzene	Trimethylchlorosilane	Trimethyl(phenylcarboranyl)silane	61	473
		RLi	Benzene	Triphenyltin chloride	Triphenyl(phenylcarboranyl)tin	84	473
$C_8H_{16}S_2$	2-*t*-Butyl-1,3-dithiane	BuLi	Hexane	Isopropyl iodide	2-*t*-Butyl-2-isopropyl-1,3-dithiane	45	343
C_9H_8	Indene	BuLi	Ether	β-Bromoethyl propionate	β-1- (or 3-) Indenyl propionate	14	276
		BuLi	Ether	Carbon dioxide	1-Indenecarboxylic acid	93	276, 278, 279, *oo*
		Ph_3SiLi	THF	Carbon dioxide	1-Indenecarboxylic acid	57	271
		BuLi	Pentane–xylene	Dimethyldichlorosilane	1-(Dimethylchlorosilyl)-1-indene	64	*ss*
		2BuLi	Pentane–xylene	Dimethyldichlorosilane	1-(1-Indenyl)dimethylsilyl-1-indene	24	*ss*
		BuLi	Ether	2,3-Diphenylindone	2,3-Diphenyl-3-(1-indenyl)indanone	57	*g*
		BuLi	Pentane–xylene	Methyltrichlorosilane	1-(Methyldichlorosilyl)-1-indene	74	*ss*
		PhLi	Ether	Nitrous oxide, carbon dioxide	Indene-1-carboxylic acid	62	277
		PhLi	Ether	Oxygen	Indene hydroperoxide		*tt*
		BuLi	Ether	Tetraphenylcyclopentadienone	2,3,4,5-Tetraphenyl-3-(1-indenyl)-4-cyclopenten-1-one	35	*g*

Table VI (Continued)

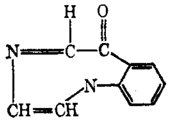
	Compound metalated	*RLi*	*Solvent*	*Reactant*	*Final product*	*% yield*	*Ref*
		BuLi	Pentane–xylene	Triethylchlorosilane	1-(Triethylsilyl)-1-indene	50	*ss*
		2BuLi	Pentane–xylene	Triethylchlorosilane	1,1-Bis(triethylsilyl)-1-indene	28	*ss*
		BuLi	Pentane–xylene	Trimethylchlorosilane	1-(Trimethylsilyl)-1-indene	59	*ss*
		2BuLi	Pentane–xylene	Trimethylchlorosilane	1,1-Bis(trimethylsilyl)-1-indene	15	*ss*
		n-PrLi	Ether	Triphenylchlorosilane	Triphenyl-1-indenylsilane + 1,1-bis(triphenylsilyl)indene	13 8	171, *uu*
$C_9H_8N_2$	N-Phenylimidazole	BuLi	Ether	Benzophenone	1,α,α-Triphenyl-1H-imidazole-2-methanol	76	358
		BuLi	Ether	Carbon dioxide	N-Phenyl-2-imidazolecarboxylic acid	60	358
		3BuLi	Ether	Carbon dioxide		5	358
		BuLi	Ether	Ethyl chloroformate	1-Phenyl-1H-imidazole-2-carboxylic acid ethyl ester	5	358
		BuLi	Ether	Ethyl chloroformate, hydrazine	1-Phenyl-1*H*-imidazole-2-carboxylic acid hydrazide	20	358
		BuLi	Ether	Phenyl isocyanate	1-Phenyl-1H-imidazole-2-carboxylic acid anilide	39	358
$C_9H_8N_2$	1-Phenylpyrazole	BuLi	Ether	Carbon dioxide	1-Phenyl-5-pyrazolecarboxylic acid + 1-(*o*-carboxyphenyl)-pyrazole	39 10	356
		2BuLi	Ether	Carbon dioxide	4-Oxopyrazolo[1,5-*a*]indolene + 8(?)-carboxy-4-oxopyrazole-[1,5-*a*]indolene	8 26	356
C_9H_8S	3-Methylthianaphthene	BuLi	Ether	Carbon dioxide	3-Methylthianaphthene-2-carboxylic acid	65	326
C_9H_9N	1-Methylindole	BuLi	Ether	Benzophenone	1-Methyl-2-indolyldiphenylcarbinol	53	355
		BuLi	Ether	Carbon dioxide	1-Methyl-2-indolecarboxylic acid	78	355
		BuLi	Ether	*p*-Chlorobenzaldehyde	1-Methyl-2-indolyl-(*p*-chlorophenyl)carbinol	50	355
		BuLi	Ether	N,N-Dimethylcarbamoyl chloride	1-Methyl-2-indolyl butyl ketone		207
		BuLi	Ether	Methyl *p*-toluenesulfonate	1,2-Dimethylindole	45	355
		BuLi	Ether	Naphthyl isocyanate	N-α-Naphthyl-1-methyl-2-indolecarboxamide	52	355
		BuLi	Ether	Phenyl isocyanate	N-Phenyl-1-methyl-2-indolecarboxamide	42	355
		BuLi	Ether	Quinoline	1-Methyl-2-(2′-quinolyl)indole	54	355
		BuLi	Ether	*o*-Tolyl isocyanate	N-(*o*-Tolyl)-1-methyl-2-indolecarboxamide	63	355
C_9H_{10}	Allylbenzene	BuLi	Ether	Benzophenone	1,1,4-Triphenyl-3-buten-1-ol	41	*vv*
		BuLi	Ether	Carbon dioxide	Cinnamic acid (68) 2-Phenyl-2-butenoic acid (32)	57	*vv*
		BuLi	Ether	(H^+)	Allylbenzene (54) Propenylbenzene (46)	84	*vv*
C_9H_{10}	Propenylbenzene	BuLi	Ether	Carbon dioxide	3,5-Dimethyl-2,4-diphenylnonanoic acid + 3-methyl-2-phenylheptanoic acid	10 5	*vv*
$C_9H_{10}O$	2-Methyldihydrobenzofuran	BuLi	Ether	Carbon dioxide	2-Methyl-7-carboxy-2,3-dihydrobenzofuran	66	*ww*
$C_9H_{11}NO$	N-Methyl-*o*-toluamide	BuLi	Hexane THF	Benzaldehyde	2-(β-Phenyl-β-hydroxy)ethyl-N-methylbenzamide	51	382
		BuLi	Hexane THF	Benzophenone	2-(β,β-Diphenyl-β-hydroxy)-ethyl-N-methylbenzamide	93	382

Table VI (Continued)

	Compound metalated	*RLi*	*Solvent*	*Reactant*	*Final product*	*% yield*	*Ref*
		BuLi	Hexane THF	Cyclohexanone	α-(1-Hydroxycyclohexyl)-N-methyl-*o*-toluamide	65	382
		BuLi	Hexane THF	Cyclopentanone	α-(1-Hydroxycyclopentyl)-N-methyl-*o*-toluamide	41	382
		BuLi	Hexane THF	Fluorenone	α-(9-Hydroxy-9-fluorenyl)-N-methyl-*o*-toluamide	50	382
$C_9H_{11}NO$	N-Acetylbenzylamine	BuLi		Benzaldehyde	$PhCHOHCH_2CONHCH_2Ph$		377
$C_9H_{12}O$	*o*-Ethylanisole	BuLi	Ether	Carbon dioxide	2-Methoxy-3-ethylbenzoic acid		294
$C_9H_{13}N$	Benzyldimethylamine	BuLi	Ether	Acetone	2-(Dimethylaminomethyl)phenyldimethylcarbinol	40–46	374
		BuLi	Ether Hexane	Benzaldehyde	2-(Dimethylaminomethyl)benzhydrol	78	374, *xx*
		BuLi	Ether Hexane	Benzonitrile	2-(Dimethylaminomethyl)benzophenone	63	374
		BuLi	Ether Hexane	Benzophenone	2-(Dimethylaminomethyl)triphenylcarbinol	84	374
		PhLi	Ether	Benzophenone	2-(Dimethylaminomethyl)triphenylcarbinol	21	373
		BuLi	Ether	2-Chlorobenzaldehyde	2-(Dimethylaminomethyl)-2′-chlorobenzhydrol	80	374
		BuLi	Ether Hexane	Cyclohexene oxide	2-(Hydroxycyclohexyl)benzyldimethylamine	36	374
		BuLi	Ether	Deuterium oxide	Benzyldimethylamine-2-*d*		375
		BuLi	Ether Hexane	2,3-Dibromo-2,3-dimethylbutane	*o*-Bromobenzyldimethylamine	69	376
		BuLi	Ether Hexane	2-(Dimethylaminomethyl)benzophenone	2,2′-Bisdimethylaminomethyltriphenylcarbinol	59	374
		BuLi	Ether Hexane	Hexachloroethane	*o*-Chlorobenzyldimethylamine	63	376
		BuLi	Ether	4-Methoxybenzaldehyde	2-(Dimethylaminomethyl)-4′-methoxybenzhydrol	78	374
		BuLi	Ether Hexane	Methyl benzoate	2,2′-Bisdimethylaminomethyltriphenylcarbinol	59	374
		BuLi	Ether Hexane	Methylene iodide	*o*-Iodobenzyldimethylamine	64	376
		BuLi	Ether Hexane	Phenyl isocyanate	2-(Dimethylaminomethyl)-N-phenylbenzamide	65	374
		BuLi	Ether	3,4,5-Trimethoxybenzaldehyde	2-(Dimethylaminomethyl)-3′,4′,5′-trimethoxybenzhydrol	56	374
		BuLi	Ether	*n*-Valerophenone	2-(Dimethylaminomethyl)diphenyl-*n*-butylcarbinol		374
$C_9H_{18}S_2$	2-*n*-Amyl-1,3-dithiane	BuLi	Hexane	*n*-Amyl bromide	2,2-Di-*n*-amyl-1,3-dithiane	82	343
		BuLi	Hexane	Benzophenone	2-*n*-Amyl-2-(diphenylhydroxymethyl)-1,3-dithiane	78	343
		BuLi	Hexane	Geranyl bromide	2-*n*-Amyl-2-geranyl-1,3-dithiane	80	343
		BuLi	Hexane	Isopropyl bromide	2-*n*-Amyl-2-isopropyl-1,3-dithiane	85	343
$C_{10}H_7F$	1-Fluoronaphthalene	BuLi	THF	Carbon dioxide	1-Fluoro-2-naphthalenecarboxylic acid	30	183
$C_{10}H_8$	Naphthalene	BuLi	THF Ether	Carbon dioxide	Naphthalene-1-carboxylic acid + naphthalene-2-carboxylic acid	9 9	157
$C_{10}H_9N$	1-Methylisoquinoline	BuLi	Ether	Allyl bromide	1-(3-Butenyl)isoquinoline	66	*yy*
		BuLi	Ether	Benzalacetophenone	β-Phenyl-γ-(1-isoquinolyl)butyrophenone hydrochloride	59	*yy*
		BuLi	Ether	Benzophenone	Diphenylisoquinaldylcarbinol	100	*yy*
		BuLi	Ether	Ethyl acetate	Methyl isoquinaldyl ketone	35	*yy*
		BuLi	Ether	Ethyl (bromomethyl)malonate	β-(1-Isoquinolyl)ethyl malonic ester	16	*yy*
		BuLi	Ether	Ethyl isobutyrate	Isopropyl isoquinaldyl ketone	33	*yy*
		BuLi	Ether	Ethyl methylenemalonate	β-(1-Isoquinolyl)ethyl malonic ester	14	*yy*

Table VI (Continued)

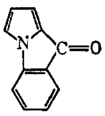
	Compound metalated	*RLi*	*Solvent*	*Reactant*	*Final product*	*% yield*	*Ref*
		BuLi	Ether	Isopropyl iodide	1-Isobutylisoquinoline	40	*yy*
		BuLi	Ether	Methallyl chloride	1-(3-Methyl-3-butenyl)isoquinoline	64	*yy*
$C_{10}H_9N$	N-Phenylpyrrole	BuLi	Ether	Carbon dioxide	N-Phenylpyrrole-2-carboxylic acid	20	354
						Trace	
$C_{10}H_9N$	Quinaldine	PhLi	Ether	5-Phenyl-2,4-pentadien-1-al	1-Phenyl-6-(2-quinolyl)-5-hydroxy-2,4-hexadiene	20	*bb*
$C_{10}H_{10}Fe$	Ferrocene	BuLi	Ether	Benzophenone	Bis(diphenylhydroxymethyl)-ferrocene		435
		BuLi		N-Benzylhydroxylamine	Ferrocenylamine	25	449
		BuLi	THF Ether	Butyl borate	Ferrocenylboronic acid + 1,1′-ferrocenylenediboronic acid	26–44 13–18	442, 443
		BuLi	Ether	Carbon dioxide	Ferrocenemonocarboxylic acid + ferrocenedicarboxylic acid	26–78	431, 432, 433, 159, 430, 453, 428
		BuLi	Ether	Carbon dioxide, diazomethane	Carboxymethylferrocene (59) + 1,1′-dicarbomethoxyferrocene (41)		431
		BuLi	THF	Chloroethylmethylsilane	(Ethylmethylsilyl)ferrocene + 1,1′-bis(ethylmethylsilyl)-ferrocene		*p*
		BuLi	Ether THF	Chlorodiethylsilane	Diethylsilylferrocene + 1,1′-bis(diethylsilyl)ferrocene		*p*
		BuLi	Ether	Cobalt chloride	Biferrocenyl		*zz*
		BuLi	Ether	Cobalt chloride, butyl bromide	Triferrocenyl + quaterferrocenyl		*zz*
		BuLi	Ether THF	Diferrocenyl ketone	Triferrocenylcarbinol	60–77	436, *aaa*
		BuLi	Ether	2-Dimethylaminoethyl chloride	N,N-Dimethyl-2-ferrocenyl-ethylamine	3	*bbb*
		BuLi	Ether	Epichlorohydrin	Ferrocenechlorohydrin	13	*zz*, *ccc*, *ddd*
		BuLi	Ether	Ferrocenecarbonitrile	Diferrocenyl ketone	80	436
		BuLi	Ether THF	Ferrocenecarboxaldehyde	Diferrocenylcarbinol	62	*aaa*
		BuLi	Ether THF	Nitrous oxide	Azoferrocene	25	446
		BuLi	Ether	Pyridine	α-Pyridylferrocene + 1,1′-bis-(α-pyridyl)ferrocene	24 3	444
		BuLi	Ether	Triethylsilane	Triethylsilylferrocene + 1,1′-bistriethylsilylferrocene		*p*
		BuLi	Ether THF	Tri-*n*-hexylbromosilane	Tri-*n*-hexylsilylferrocene + di(tri-*n*-hexylsilyl)ferrocene	32 35	433
		BuLi	Ether	Trimethylchlorosilane	Trimethylsilylferrocene + 1,1′-bis(trimethylsilyl)ferrocene	19–57 27–43	428, 431
		BuLi	Ether	Triphenylchlorosilane	Triphenylsilylferrocene	49	429
$C_{10}H_{10}N_2$	N-Benzylimidazole	BuLi	Ether	Carbon dioxide	1-Benzyl-2-imidazolecarboxylic acid	67	358
		BuLi	Ether	Quinoline	2-Quinolyl-1-benzylimidazole	29	358
$C_{10}H_{10}N_2$	1-Benzylpyrazole	PhLi	Ether	Carbon dioxide	1-Benzyl-5-pyrazolecarboxylic acid	57	*a*
$C_{10}H_{10}N_2$	3-Methyl-1-phenylpyrazole	BuLi	Ether	Carbon dioxide	3-Methyl-1-phenylpyrazole-5-carboxylic acid		357
$C_{10}H_{10}Os$	Osmocene	BuLi	Ether THF	Carbon dioxide	Osmocenemonocarboxylic acid (42) + osmocenedicarboxylic acid (58)		453

Table VI (*Continued*)

	Compound metalated	*RLi*	*Solvent*	*Reactant*	*Final product*	*% yield*	*Ref*
$C_{10}H_{10}Ru$	Ruthenocene	BuLi	Ether	Carbon dioxide	Ruthenocenemonocarboxylic acid + ruthenocenedicarboxylic acid	48–87	453
$C_{10}H_{10}S_2$	5-Methyl-2,2′-dithienylmethane	BuLi	Ether	Carbon dioxide	5′-Methyl-2,2′-dithienylmethane-5-carboxylic acid	55	*eee*
		BuLi	Ether	Ethylene oxide	5-(β-Hydroxyethyl)-5′-methyl-2,2′-dithienylmethane	75	*eee*
		BuLi	Ether	N-Formaldimethylamine	5′-Methyl-2,2′-dithienylmethane-5-carboxaldehyde		*eee*
$C_{10}H_{10}S_2$	5,5′-Dimethyl-3,3′-bithienyl	BuLi	Ether	Carbon dioxide	2,2′-Dicarboxy-5,5′-dimethyl-3,3′-bithienyl	45–60	309, 310
$C_{10}H_{11}ClO_2$	2-(*p*-Chlorophenoxy)-tetrahydropyran	BuLi	Ether	Carbon dioxide	2-Hydroxy-5-chlorobenzoic acid	25	*ff*
$C_{10}H_{12}N_2$	α-Dimethylaminophenylacetonitrile	BuLi	Ether	Ethyl bromide	Propiophenone	42	370
$C_{10}H_{12}O_2$	2-Phenoxytetrahydropyran	BuLi	Ether	Carbon dioxide	2-Hydroxybenzoic acid	60	*ff*
$C_{10}H_{12}S_2$	2-Phenyl-1,3-dithiane	BuLi	Hexane	Isopropyl bromide	2-Isopropyl-2-phenyl-1,3-dithiane	90	343
$C_{10}H_{13}N$	N,N-Dimethyl(β-phenylisobutyl)-amine	BuLi	Ether	Benzophenone	*o*-(α-Dimethylaminomethylisopropyl)triphenylcarbinol	17	379
$C_{10}H_{14}O_2S$	*t*-Butyl phenyl sulfone	BuLi	Ether THF	Carbon dioxide	2-(*t*-Butylsulfonyl)benzoic acid	40–45	338
		2BuLi	Ether THF	Carbon dioxide	2-Butylisophthalic acid	44	338
		2BuLi	Ether THF	Carbon dioxide	2-Ethylisophthalic acid	42	338
$C_{10}H_{15}N$	N,N-Dimethyl-β-phenylethylamine	BuLi	Ether	Benzaldehyde	*o*-(N,N-Dimethylamino-β-ethyl)-diphenylcarbinol		380
		BuLi	Ether	Benzophenone	*o*-(N,N-Dimethylamino-β-ethyl)-triphenylcarbinol		380
$C_{10}H_{15}N$	2-Methylbenzyldimethylamine	BuLi	Hexane Ether	Acetone	2-[α-(Dimethylamino)-*o*-tolyl]-1,1-dimethylethanol	46	381
		BuLi	Hexane Ether	Benzaldehyde	2-[α-(Dimethylamino)-*o*-tolyl]-1-phenylethanol	77	381
		BuLi	Hexane Ether	Benzophenone	2-[α-(Dimethylamino)-*o*-tolyl]-1,1-diphenylethanol	80	381
		BuLi	Ether	Deuterium oxide	2-Methyl-d_1-benzyldimethylamine		375
$C_{10}H_{15}P$	Phenylmethyl-*n*-propylphosphine	*t*-BuLi	Pentane	Carbon dioxide, sulfur	Phenyl *n*-propylcarboxymethylphosphine sulfide		*fff*
$C_{10}H_{15}PS$	Phenylmethyl-*n*-propylphosphine sulfide	*t*-BuLi		Carbon dioxide	Phenyl *n*-propylcarboxymethylphosphine sulfide		*fff*
$C_{10}H_{16}O$	Camphor	PhLi		Carbon dioxide	Camphocarbonic acid		415
$C_{11}H_8O_4S_2$	Phenyl 2-thienyl sulfone	BuLi	Ether	Carbon dioxide	2-Benzenesulfonyl-5-thiophenecarboxylic acid	60	332
$C_{11}H_9OD$	1-Methoxynaphthalene-8-*d*	BuLi	Ether	Carbon dioxide	1-Methoxy-2-naphthoic acid-8-*d*	32	293
$C_{11}H_{10}O$	1-Methoxynaphthalene	BuLi	Ether	Carbon dioxide	1-Methoxy-8-naphthoic acid		222
		BuLi	Ether Hexane	Carbon dioxide, diazomethane	Methyl 1-methoxy-2-naphthoate (83) + methyl 8-methoxy-1-naphthoate (17)	31	293

Table VI (Continued)

	Compound metalated	*RLi*	*Solvent*	*Reactant*	*Final product*	*% yield*	*Ref*
		BuLi LiBr	Ether Hexane	Carbon dioxide, diazomethane	Methyl 1-methoxy-2-naphthoate (86) + methyl 8-methoxy-1-naphthoate (14)	22	293
		BuLi LiOEt	Ether Hexane	Carbon dioxide, diazomethane	Methyl 1-methoxy-2-naphthoate (78) + methyl 8-methoxy-1-naphthoate (11)	25	293
$C_{11}H_{10}O$	2-Methoxynaphthalene	BuLi	Ether	Benzophenone	(2-Methoxy-3-naphthyl)diphenylcarbinol	50	*ggg*
		BuLi	Ether	Carbon dioxide	2-Methoxy-3-naphthalenecarboxylic acid	54	*ggg*
		BuLi	Ether	Methyl iodide	2-Methoxy-3-methylnaphthalene	45	*ggg*
		BuLi	Ether	Methyl 2-methoxy-3-naphthylcarboxylate	Tri(2-methoxy-3-naphthyl)carbinol	42	*ggg*
$C_{11}H_{11}NO$	2-Ethoxyquinoline	BuLi	Ether	Carbon dioxide	2-Ethoxy-3-quinolinecarboxylic acid	7	*hhh*
$C_{11}H_{12}S_2$	5,5′-Dimethyl-2,2′-dithienylmethane	BuLi	Ether	Carbon dioxide	5,5′-Dimethyl-2,2′-dithienylmethane-3- (or 4-) carboxylic acid	51	*eee*
$C_{11}H_{14}$	Pentamethylenefulvene	PhLi	Ether	Ferrous chloride	1,1′-Di(1-phenylcyclohexyl)ferrocene	96	434
$C_{11}H_{14}O$	Acetomesitylene	BuLi	THF Hexane	Deuterium oxide	Dideuterioacetomesitylene	60	155
$C_{11}H_{14}O$	2,2-Dimethylchroman	BuLi	Ether	Carbon dioxide	2,2-Dimethyl-8-chromancarboxylic acid	31	296
$C_{11}H_{14}O$	5-Methoxy-1,2,3,4-tetrahydronaphthalene	BuLi	Ether	Carbon dioxide	5-Methoxy-1,2,3,4-tetrahydronaphthalenecarboxylic acid	6	242
$C_{11}H_{14}O_2$	Phenol–2-tetrahydropyranyl ether	BuLi	Ether	Ethylene oxide	*o*-Phenoxy-*β*-phenylethanol	89	301
$C_{11}H_{14}S_2$	2-Benzyl-1,3-dithiane	BuLi	Hexane	Ethyl chloroformate	Ethyl 2-benzyl-2-(1,3-dithianyl)formate	78	344
$C_{11}H_{16}O$	1,4-Dimethoxy-2,3,5-trimethylbenzene	BuLi	Ether	Acetaldehyde	1,4-Dimethoxy-2,5-dimethyl-3-*β*-hydroxypropylbenzene		295
$C_{11}H_{16}O_2S$	*n*-Butyl *p*-tolyl sulfone	BuLi	Ether	Carbon dioxide	2-(*p*-Toluenesulfonyl)pentanoic acid	78	336
		BuLi	Ether	*p*-Toluenesulfonyl fluoride	1,1-Bis(*p*-toluenesulfonyl)butane	60	336
$C_{11}H_{17}N$	*α*,*α*-Dimethylbenzyldimethylamine	BuLi	Ether	Benzophenone	2-(N,N-*α*,*α*′-Tetramethylaminomethyl)benzhydrol	57	374
$C_{11}H_{17}N$	2,3-Dimethylbenzyldimethylamine	BuLi	Hexane Ether	Acetone	2-(2-Dimethylaminomethyl-6-methylphenyl)-1,1-dimethylethanol	61	381
		BuLi	Hexane Ether	Benzophenone	2-(2-Dimethylaminomethyl-6-methylphenyl)-1,1-diphenylethanol	80	381
		BuLi	Ether	Deuterium oxide	2-Methyl-d_1-3-methylbenzyldimethylamine		375
$C_{11}H_{17}N$	N,N-Dimethyl-3-phenylpropylamine	BuLi	Hexane Ether	Benzophenone	4-Dimethylamino-1,1,2-triphenyl-1-butanol	57	379
		BuLi	Ether	Deuterium oxide	N,N-Dimethyl-3-phenylpropylamine-*α*-d_1		375
$C_{12}H_2F_8$	2,2′,3,3′,5,5′,6,6′-Octafluorobiphenyl	BuLi	THF Hexane	Carbon dioxide	2,2′,3,3′,5,5′,6,6′-Octafluorobiphenyl-4,4′-dicarboxylic acid	97	421

Table VI (Continued)

	Compound metalated	*RLi*	*Solvent*	*Reactant*	*Final product*	*% yield*	*Ref*
$C_{12}H_8$	Biphenylene	BuLi	Ether	Carbon dioxide, diazomethane	1-Methoxycarbonylbiphenylene	49	*iii*
		BuLi	Ether	N,N-Dimethylformamide	Biphenylene-1-carboxaldehyde		*iii*
		BuLi	Ether	Oxygen	1-Hydroxybiphenylene	18	*iii*
$C_{12}H_9NS$	Phenothiazine	BuLi	Ether	Acetyl chloride	10-Acetylphenothiazine	40–88	*jjj*
		BuLi		Benzophenone	1-(Diphenylhydroxymethyl)-phenothiazine	70	*kkk*
		BuLi		Butyl acetate	1-Acetylphenothiazine		*lll*
		2BuLi	Ether	Carbon dioxide	Phenothiazine-1-carboxylic acid	53	*jjj*
		BuLi	Ether	Dimethyl sulfate	10-Methylphenothiazine	94–99	*jjj*
		1BuLi	Ether	Ethylene oxide	10-β-Hydroxyethylphenothiazine	83–92	*jjj*
		2BuLi	Ether	Lithium acetate	10-Acetylphenothiazine	40	*jjj*
		2BuLi	Ether	Lithium benzoate	10-Benzoylphenothiazine	42	*jjj*
		2BuLi	Ether	Lithium propionate	10-Propionylphenothiazine	33	*jjj*
$C_{12}H_8O$	Dibenzofuran	Li	Dioxane	Carbon dioxide	*o*-Hydroxybiphenyl	80	288
		Li	Ether	Carbon dioxide	3,4-Benzocoumarin	64	288
		$C_6H_5CH_2Li$	THF	Carbon dioxide	Dibenzofuran-4-carboxylic acid	35	*mmm*
		$C_6H_5CH_2Li$	THP	Carbon dioxide	Dibenzofuran-4-carboxylic acid	8	*mmm*
		BuLi	*n*-Butyl Ether	Carbon dioxide	Dibenzofuran-4-carboxylic acid	76	156
		BuLi	Ether	Carbon dioxide	Dibenzofuran-4-carboxylic acid	5–56	156, 157
		BuLi	THF Ether	Carbon dioxide	Dibenzofuran-4-carboxylic acid	69–86	156, 157
		BuLi	THF	Carbon dioxide	Dibenzofuran-4-carboxylic acid	75	157
		BuLi	Petroleum Ether	Carbon dioxide	Dibenzofuran-4-carboxylic acid	1	156
		MeLi	Ether	Carbon dioxide	Dibenzofuran-4-carboxylic acid	2	157
		MeLi	Ether THF	Carbon dioxide	Dibenzofuran-4-carboxylic acid	12	157
		MeLi	THF	Carbon dioxide	Dibenzofuran-4-carboxylic acid	29	157
		α-Me(CH_3-C_6H_4)Li	THF	Carbon dioxide	Dibenzofuran-4-carboxylic acid	39	*mmm*
		PhLi	Ether	Carbon dioxide	Dibenzofuran-4-carboxylic acid	8	157
		PhLi	THF Ether	Carbon dioxide	Dibenzofuran-4-carboxylic acid	44	157
		PhLi	THF	Carbon dioxide	Dibenzofuran-4-carboxylic acid	55	157
		Poly-*p*-styryllithium	Ether	Carbon dioxide	Dibenzofuran-4-carboxylic acid	21	*g*
		2,4,6-Ph_3-PhLi		Carbon dioxide	Dibenzofuran-4-carboxylic acid	4	172
		BuLi	Ether	N,N-Dimethylcarbamoyl chloride	Bis(4-dibenzofuranyl) ketone		207
		BuLi	Ether	Triphenylchlorosilane	1-Triphenylsilyldibenzofuran	69	*ee*
$C_{12}H_8OS$	Dibenzothiophene 5-oxide	BuLi	Ether	Carbon dioxide	Dibenzothiophene-4-carboxylic acid	36–55	323, 327
$C_{12}H_8OS$	Phenoxathiin	BuLi		Carbon dioxide	4-Phenoxathiincarboxylic acid + 1,6-phenoxathiindicarboxylic acid	37 1	383, 384
		2BuLi	Ether	Carbon dioxide	4,6-Dicarboxyphenoxathiin + 1,6-dicarboxyphenoxathiin	35 9	383, 384
		2MeLi	Ether	Carbon dioxide	4-Phenoxathiincarboxylic acid	12	384
$C_{12}H_8OS_2$	Thianthrene 5-oxide	BuLi	Ether	Carbon dioxide	Dibenzothiophene	46	*nnn*
		2BuLi	Ether	Carbon dioxide	Dibenzothiophene	10	
					Thianthrene	13	327
					Thianthrene-1-carboxylic acid	13	
		3BuLi	Ether	Carbon dioxide	Dibenzothiophene	55	
					Thianthrene	3	327
					o-Carboxyphenyl sulfide	3	
		3BuLi	Ether	Carbon dioxide	Dibenzothiophene	53	*nnn*
					Thianthrene	8	
		MeLi	Ether	Carbon dioxide	1-Thianthrenecarboxylic acid	1	*nnn*

Table VI (*Continued*)

	Compound metalated	*RLi*	*Solvent*	*Reactant*	*Final product*	*% yield*	*Ref*
		3MeLi	Ether	Carbon dioxide	Thianthrene	60	
					1-Thianthrenecarboxylic acid	1	*nnn*
$C_{12}H_8O_2S$	Dibenzothiophene 5,5-dioxide	1BuLi	Ether	Carbon dioxide	Dibenzothiophene-4-carboxylic acid 5,5-dioxide	22	324
		2BuLi	Ether	Carbon dioxide	Dibenzothiophene-4-carboxylic acid 5,5-dioxide	20	324
					Dibenzothiophene-4,6-dicarboxylic acid 5,5-dioxide	4	
		3BuLi	Ether	Carbon dioxide	Dibenzothiophene-4,6-dicarboxylic acid 5,5-dioxide	10	324
$C_{12}H_8O_2S$	Phenoxathiin 10-oxide	BuLi	Ether	Carbon dioxide	Thianthrene-1-carboxylic acid	20	385
		2BuLi	Ether	Carbon dioxide	Phenoxathiin	14	386
					Diphenyl ether	42	
					1-Carboxyphenoxathiin	16	
		3BuLi	Ether	Carbon dioxide	Diphenyl ether	14	
					Phenoxathiin	25	386
					Di(*o*-carboxyphenyl) ether	17	
					o-Carboxyphenyl phenyl ether	12	
					1-Carboxyphenoxathiin	6	
					Butyl mercaptan	7	
$C_{12}H_8O_2S_2$	Thianthrene 5-dioxide	BuLi	Ether	Carbon dioxide	4-Carboxythianthrene 5-dioxide	41	328
		BuLi	Ether	Carbon dioxide	4,6-Dicarboxythianthrene 5-dioxide	12	328
		PhLi	Ether	Carbon dioxide	4,6-Dicarboxythianthrene 5-dioxide	54	328
$C_{12}H_8O_3S$	Phenoxathiin 10,10-dioxide	BuLi	Ether	Carbon dioxide	1,6-Dicarboxyphenoxathiin 10,10-dioxide	8	384
		BuLi	Ether	Carbon dioxide	Phenoxathiin-1-carboxylic acid 10,10-dioxide	46	385
		BuLi	Ether	Carbon dioxide	1,9-Dicarboxyphenoxathiin 10,10-dioxide	48	383, 384
					1-Carboxyphenoxathiin 10,10-dioxide	15	
		2BuLi	Ether	Carbon dioxide	1,9-Dicarboxyphenoxathiin 10,10-dioxide	93	384
		MeLi	Ether	Carbon dioxide	1-Carboxyphenoxathiin 10,10-dioxide	18	
					1,9-Dicarboxyphenoxathiin 10,10-dioxide	3	384
$C_{12}H_8O_3S$	Thianthrene 5,5,10-trioxide	BuLi	Ether	Carbon dioxide	2,2-Dicarboxyphenyl phenyl sulfone	17	328
$C_{12}H_8S$	Dibenzothiophene	Li	Dioxane	Carbon dioxide	Biphenyl	21	288
					o-Thiobiphenyl	18	
		BuLi	Ether	Carbon dioxide	4-Dibenzothiophenecarboxylic acid	25–35	157, 384
		2BuLi	Ether	Carbon dioxide	Butyl 4-dibenzothienyl ketone	5	322
		BuLi	Ether THF	Carbon dioxide	Dibenzothiophene-4-carboxylic acid	60	157
		BuLi	THF	Carbon dioxide	Dibenzothiophene-4-carboxylic acid	41	157
		MeLi	Ether	Carbon dioxide	Dibenzothiophene-4-carboxylic acid	Trace	157
		MeLi	THF	Carbon dioxide	Dibenzothiophene-4-carboxylic acid	12	157
		MeLi	THF Ether	Carbon dioxide	Dibenzothiophene-4-carboxylic acid	5	157
		PhLi	THF	Carbon dioxide	Dibenzothiophene-4-carboxylic acid	47	157
		PhLi	Ether THF	Carbon dioxide	Dibenzothiophene-4-carboxylic acid	12	157
		PhLi	Ether	Carbon dioxide	Dibenzothiophene-4-carboxylic acid	Trace	157
		BuLi	Ether	N,N-Dimethylcarbamoyl chloride	Bis(4-dibenzothiophenyl) ketone		207

Table VI (Continued)

	Compound metalated	*RLi*	*Solvent*	*Reactant*	*Final product*	*% yield*	*Ref*
		BuLi	Ether	Triphenylchlorosilane	4-Triphenylsilyldibenzothiophene	42	*ee*
$C_{12}H_8S_2$	Thianthrene	BuLi	Ether	Carbon dioxide	1-Thianthrenecarboxylic acid	28	328
		BuLi	Ether	Methoxylamine	1-Aminothianthrene	55	328
		BuLi	Ether	Tri-*n*-butyl borate	1-Thianthreneboronic acid	23	328
		BuLi	Ether	Triphenylchlorosilane	1-Thianthrenyltriphenylsilane	10	328
$C_{12}H_8Se$	Dibenzoselenophene	BuLi	Ether	Carbon dioxide	Dibenzoselenophene-1-carboxylic acid	96	488
		BuLi	Ether	Dimethyl sulfate	1-Methyldibenzoselenophene	80	488
$C_{12}H_9BrO_2S$	*m*-Bromophenyl phenyl sulfone	BuLi	Ether	Carbon dioxide	3-Bromo-2-carboxyphenyl phenyl sulfone	54	332
$C_{12}H_9BrO_2S$	*p*-Bromophenyl phenyl sulfone	BuLi	Ether	Carbon dioxide	4-Bromo-2-carboxyphenyl phenyl sulfone	52	332
$C_{12}H_9ClO$	4-Chlorophenyl phenyl ether	BuLi	Ether	Diphenyldichlorosilane	Bis(2-phenoxy-5-chlorophenyl)-diphenylsilane	7	291
		BuLi	Ether	Triphenylchlorosilane	2-Phenoxy-5-chlorophenyltriphenylsilane	17	291
$C_{12}H_9N$	α-Naphthylacetonitrile	PhLi	Ether	Benzophenone	3,3-Diphenyl-3-hydroxy-2-(α-naphthyl)propionitrile	21	175, 182
		BuLi	Ether	Carbon dioxide	2-Naphthyl-2-carboxyacetonitrile	55	175, 182
		o-MePhLi	Ether	Carbon dioxide	2-Naphthyl-2-carboxyacetonitrile	24	175, 182
		α-$C_{10}H_7Li$	Ether	Carbon dioxide	2-Naphthyl-2-carboxyacetonitrile	41	175, 182
		PhLi	Ether	Carbon dioxide	2-Naphthyl-2-carboxyacetonitrile	50	175, 182
		PrLi	Ether	Carbon dioxide	2-Naphthyl-2-carboxyacetonitrile	38	175, 182
$C_{12}H_9NO$	Phenoxazine	BuLi	Ether	Carbon dioxide	Phenoxazine-4-carboxylic acid	69	284
$C_{12}H_9O_2Na$	Sodium α-naphthylacetate	BuLi	Pentane Dioxane	Benzophenone	3,3-Diphenyl-3-hydroxy-2-(α-naphthyl)propionic acid	41	182, *ooo*
		i-AmLi	Pentane Dioxane	Benzophenone	3,3-Diphenyl-3-hydroxy-2-(α-naphthyl)propionic acid	10	182, *ooo*
		i-PrLi	Pentane Dioxane	Benzophenone	3,3-Diphenyl-3-hydroxy-2-(α-naphthyl)propionic acid	16	182, *ooo*
		PhLi	Ether	Benzophenone	3,3-Diphenyl-3(hydroxy)-2-(α-naphthyl)propionic acid	57	182
		PrLi	Pentane Dioxane	Benzophenone	3,3-Diphenyl-3-hydroxy-2-(α-naphthyl)propionic acid	45	182, *ooo*
		BuLi	Ether Dioxane	Carbon dioxide	α-Naphthylmalonic acid	7	182, *ooo*
		p-$(Me)_2N$-PhLi	Ether	Carbon dioxide	α-Naphthylmalonic acid	29	174, 182
		m-MePhLi	Ether	Carbon dioxide	α-Naphthylmalonic acid	35	174, 182
		o-MePhLi	Ether	Carbon dioxide	α-Naphthylmalonic acid	42	174, 182
		p-MePhLi	Ether	Carbon dioxide	α-Naphthylmalonic acid	20	174, 182
		α-$C_{10}H_7Li$	Ether	Carbon dioxide	α-Naphthylmalonic acid	37	174, 182
		PhLi	Ether	Carbon dioxide	α-Naphthylmalonic acid	38	174, 182
		PhLi	Ether	Iodine	2,3-Di(α-naphthyl)succinic acid	30	182, *ppp*
$C_{12}H_9O_2Na$	Sodium β-naphthylacetate	BuLi	Pentane Dioxane	Benzophenone	3,3-Diphenyl-3-hydroxy-2-(β-naphthyl)propionic acid	32	182, *ooo*
		i-AmLi	Pentane Dioxane	Benzophenone	3,3-Diphenyl-3-hydroxy-2-(β-naphthyl)propionic acid	28	182, *ooo*
		i-PrLi	Pentane Dioxane	Benzophenone	3,3-Diphenyl-3-hydroxy-2-(β-naphthyl)propionic acid	8	182, *ooo*
		m-MePhLi	Ether	Benzophenone	3,3-Diphenyl-3-hydroxy-2-(β-naphthyl)propionic acid	17	176, 182
		o-MePhLi	Ether	Benzophenone	3,3-Diphenyl-3-hydroxy-2-(β-naphthyl)propionic acid	18	176, 182
		PhLi	Ether	Benzophenone	3,3-Diphenyl-3-hydroxy-2-(β-naphthyl)propionic acid	21	176, 182
		PrLi	Pentane Dioxane	Benzophenone	3,3-Diphenyl-3-hydroxy-2-(β-naphthyl)propionic acid	37	182, *ooo*
		p-$(Me)_2N$-PhLi	Ether	Carbon dioxide	β-Naphthylmalonic acid	19	176

Table VI (Continued)

	Compound metalated	*RLi*	*Solvent*	*Reactant*	*Final product*	*% yield*	*Ref*
		m-MePhLi	Ether	Carbon dioxide	β-Naphthylmalonic acid	20	176
		o-MePhLi	Ether	Carbon dioxide	β-Naphthylmalonic acid	48	176
		p-MePhLi	Ether	Carbon dioxide	β-Naphthylmalonic acid	22	176
		α-$C_{10}H_7Li$	Ether	Carbon dioxide	β-Naphthylmalonic acid	26	176
		PhLi	Ether	Carbon dioxide	β-Naphthylmalonic acid	18–20	176, 182
		PhLi	Ether	Iodine	2,3-Di(β-naphthyl)succinic acid	28	182
$C_{12}H_{10}$	Dihydro-*as*-indacene	BuLi	Hexane-dimethoxyethane	Ferrous chloride	Bis(*as*-indacenyliron)	10	*qqq*
$C_{12}H_{10}O$	Diphenyl ether	BuLi	Ether	Boron trifluoride etherate	10-Hydroxy-9-oxa-10-bora-anthracene	23	*rrr*
		BuLi	Ether	*n*-Butyl metaborate	10-Hydroxy-9-oxa-10-bora-anthracene	42	*rrr*
		BuLi	Ether	Carbon dioxide	Di(2-carboxyphenyl) ether	23–60	386, 292
		t-BuLi	Pet. ether	Carbon dioxide	2-Phenoxybenzoic acid	14	134
		Ph_3SiLi	THF	Carbon dioxide	Di(2-carboxyphenyl) ether	Trace	*sss*
		BuLi	Ether	Dibenzyldichlorosilane	10,10-Dibenzylphenoxasilin	52	289
		BuLi	Ether	Di-*n*-dodecyldichlorosilane	Di-*n*-dodecylbis(*o*-phenoxyphenyl)silane	17–29	289
		BuLi	Ether	Dimethyldichlorosilane	10,10-Dimethylphenoxasilin	25–51	158, 292
		BuLi	Ether THF	Diphenylsilane	10,10-Diphenylphenoxasilin	20	290
		BuLi	Ether	Diphenyldichlorosilane	Bis(2-phenoxyphenyl)diphenylsilane	34–40	291, 292
		BuLi	Ether THF	Phenylsilane	10-Phenylphenoxasilin	26	290
		BuLi	Ether	Phenyltrichlorosilane	Tris(2-phenoxyphenyl)phenyl silane	14	291
		2BuLi	Ether	Silicon tetrachloride	10,10′-Spirobiphenoxasilin	25	292
		BuLi	Ether	Silicon tetrachloride	Tetrakis(2-phenoxyphenyl)silane	12	291
		BuLi	Ether	Trimethylchlorosilane	(Oxy-di-*o*-phenylene)bis(trimethylsilane)	60	289
		BuLi	Ether	Triphenylchlorosilane	2-Phenoxyphenyltriphenylsilane	67	291
$C_{12}H_{10}O_2S$	Diphenyl sulfone	BuLi	Ether	Carbon dioxide	2-Carboxyphenyl phenyl sulfone	42–80	332, 335
		4BuLi	Ether	Carbon dioxide	Di(*o*-carboxyphenyl) sulfone	26	324
		BuLi	Ether	Dimethyldichlorosilane	10,10-Dimethylphenothiasilin 5,5-dioxide	24	341
		BuLi	Ether	Diphenyldichlorosilane	10,10-Diphenylphenothiasilin 5,5-dioxide	8	341
$C_{12}H_{11}N$	2-Benzylpyridine	PhLi	Ether	β-Dimethylaminoethyl chloride	1-(2-Pyridyl)-1-phenyl-3-dimethylaminopropane	79	*uuu*
$C_{12}H_{12}O_2$	1,7-Dimethoxynaphthalene	BuLi	Ether	Carbon dioxide	1,7-Dimethoxy-6-carboxynaphthalene	72	242
		BuLi	Ether	Dimethyl sulfate	1,7-Dimethoxy-6-methylnaphthalene	75	242
		BuLi	Ether	N-Methylformanilide	1,7-Dimethoxy-6-naphthaldehyde	84	242
$C_{12}H_{15}FeN$	2-(Ferrocenyl)ethylamine	BuLi	Ether	Ethyl formate	N-Formyl-2-(ferrocenyl)ethylamine	86	*vvv*
$C_{12}H_{16}O_3$	*m*-Methoxyphenyl 2-tetrahydropyranyl ether	BuLi	Ether	Carbon dioxide	2-Methoxy-6-hydroxybenzoic acid	26	300

Table VI (Continued)

	Compound metalated	*RLi*	*Solvent*	*Reactant*	*Final product*	*% yield*	*Ref*
$C_{12}H_{19}N$	2,4,6-Trimethylbenzyldimethylamine	BuLi	Hexane Ether	Benzaldehyde	2-[2-(Dimethylaminomethyl)-3,5-dimethylphenyl]-1-phenylethanol	81	381
$C_{12}H_{20}Sn$	Tetraallyltin	BuLi	Pentane	Carbon dioxide	Vinylacetic acid	36	*rrrr*
$C_{12}H_{28}Si_3$	1,3,3-Tris(trimethylsilyl)propyne	BuLi	Hexane	Trimethylchlorosilane	1,1,3,3-Tetra(trimethylsilyl)allene		264
$C_{13}H_{10}$	Fluorene	BuLi	Hexane Ether	Benzhydryl chloride	9-Benzhydrylfluorene	79	*www*
		BuLi	Hexane	Benzyl chloride	9-Benzylfluorene	58	*www*
		BuLi	Hexane	*n*-Butyl bromide	9-*n*-Butylfluorene	80	*www*
		BuLi	Ether	*p*-Chlorobenzyl chloride	9-(*p*-Chlorobenzyl)fluorene	68	*q*
		BuLi	Ether	*p*-Chlorophenyl styryl ketone	1-(*p*-Chlorophenyl)-3-phenyl-4-biphenylene-1-butanone	90	*q*
		BuLi	Ether	9-Diazofluorene	Fluorenone azine		*xxx*
		2PhLi	Ether	2-Benzyl chloride	9,9-Dibenzylfluorene	65	*yyy*
		PhLi	Ether	Benzyl chloride, formaldehyde	9-Benzyl-9-fluorene methanol	90	*yyy*
		PhLi	Ether	3-Bromo-1-propyne	3-(9-Fluorenyl)-1-propyne	40	*zzz*
		$Ph_2MeSiLi$	THF	Carbon dioxide	Fluorene-9-carboxylic acid	61	406
		Mesityllithium		Carbon dioxide	Fluorene-9-carboxylic acid	54	172
		Ph_5Si_2Li	THF	Carbon dioxide	Fluorene-9-carboxylic acid	42	406
		PhLi		Carbon dioxide	Fluorene-9-carboxylic acid	78	172
		PhLi	EGDE	Carbon dioxide	Fluorene-9-carboxylic acid	25	407
		$PhMe_2SiLi$	THF	Carbon dioxide	Fluorene-9-carboxylic acid	58	406
		Polystyryllithium	Ether	Carbon dioxide	Fluorene-9-carboxylic acid	76	*g*
		o-CH_3-C_6H_4Li		Carbon dioxide	Fluorene-9-carboxylic acid	85	172
		Ph_3GeLi	THF	Carbon dioxide	Fluorene-9-carboxylic acid	66	271
		Ph_3GeLi	THF	Carbon dioxide	Fluorene-9-carboxylic acid	50	406
		Ph_3GeLi	EGDE	Carbon dioxide	Fluorene-9-carboxylic acid	69	407
		Ph_3PbLi	THF	Carbon dioxide	Fluorene-9-carboxylic acid	0.5	271
		Ph_3PbLi		Carbon dioxide	Fluorene-9-carboxylic acid	22	404
		2,4,6-Ph_3PhLi		Carbon dioxide	Fluorene-9-carboxylic acid	65	172
		Ph_3SiLi	THF	Carbon dioxide	Fluorene-9-carboxylic acid	41–69	271, 406
		Ph_3SnLi	THF	Carbon dioxide	Fluorene-9-carboxylic acid	17–31	271, 404
		BuLi	Ether Benzene	4,4′-Dichlorobenzophenone	(*p*,*p*′-Dichlorobenzhydrylidene)-fluorene		*aaaa*, *bbbb*
		BuLi	Ether	N,N-Dimethylcarbamoyl chloride	Fluorene-9-(N,N-dimethylcarboxamide		207
		PhLi	Ether	3,3-Diphenyl-1-bromopropane	1-Biphenylene-4,4-diphenyl-1,3-butadiene		*cccc*
		PhLi	Ether	1,3-Diphenyl-1-chloropropane	1-Biphenylene-2,4-diphenylbutane		*cccc*
		PhLi	Ether	Diphenyldichlorosilane	Diphenylbis(9-fluorenyl)silane	11	*dddd*
		BuLi	Ether	2,3-Diphenylindone	2,3-Diphenyl-3-(9-fluorenyl)-indanone	83	*q*
		PhLi	Ether	6-Iodo-1-hexyne	6-(9-Fluorenyl)-1-hexyne	62	*zzz*
		PhLi	Ether	5-Iodo-1-pentyne	5-(9-Fluorenyl)-1-pentyne	68	*zzz*
		PhLi	Ether	11-Iodo-1-undecyne	11-(9-Fluorenyl)-1-undecyne	62	*zzz*
		BuLi	Ether	Nitrous oxide	Fluorenone azine	28	*xxx*
		PhLi	Ether	Nitrous oxide	Fluorenone azine		277
		PhLi	Ether	Phenyltrichlorsilane	Phenyltris(9-fluorenyl)silane	47	*dddd*
		BuLi	Ether	Tetraphenylcyclopentadienone	2,3,4,5-Tetraphenyl-3-(9-fluorenyl)-4-cyclopenten-1-one	72	*q*

Table VI (Continued)

	Compound metalated	*RLi*	*Solvent*	*Reactant*	*Final product*	*% yield*	*Ref*
		BuLi	THF Hexane	Trimethylchlorosilane	9-Trimethylsilylfluorene	74	274
		2BuLi	THF Hexane	2-Trimethylchlorosilane	9,9-Di(trimethylsilyl)fluorene	84	274
		BuLi	Ether	Trimethylene oxide	3-(9-Fluorenyl)-propanol-1	44	210
		n-PrLi	Ether	Triphenylchlorosilane	9-(Triphenylsilyl)fluorene	70	171
$C_{13}H_{10}N_2$	1-Phenylbenzimidazole	PhLi	Ether	Carbon dioxide	1-Phenylbenzimidazole-2-carboxylic acid	25	*eeee*
$C_{13}H_{10}O$	Xanthene	BuLi	Ether	Carbon dioxide	Xanthene-9-carboxylic acid	51	*fff*
		Ph_3SiLi	THF	Carbon dioxide	Xanthene-9-carboxylic acid	37	271
		Ph_3SiLi	THF	Chlorotriphenylsilane	9-Triphenylsilylxanthene	14	271
		BuLi	Ether	N,N-Dimethylcarbamoyl chloride	Xanthene-9-bis(N,N-dimethylcarboxamide)		207
$C_{13}H_{10}S$	Thioxanthene	BuLi	Ether	N,N-Dimethylcarbamoyl chloride	Thioxanthene-9-bis(N,N-dimethylcarboxamide		207
$C_{13}H_{11}N$	5-Methylcarbazole	BuLi	Ether	Carbon dioxide	N-Methylcarbazole-1-carboxylic acid	12	345
$C_{13}H_{11}NS$	N-Benzylthieno[3,2-*b*]pyrrole	BuLi	Ether Hexane	Carbon dioxide	2-Carboxy-4-benzylthieno[3,2-*b*]-pyrrole	87	*gggg*
		Excess BuLi	Ether	Carbon dioxide, diazomethane	4-(α-Carbomethoxybenzyl)-2,5-dicarbomethoxythieno[3,2-*b*]-pyrrole	68	*gggg*
$C_{13}H_{11}NS$	10-Methylphenothiazine	BuLi	Ether	Carbon dioxide	10-Methyl-1-phenothiazinecarboxylic acid + 10-methyl-4-phenothiazinecarboxylic acid		*jjj*
		BuLi	Ether	Carbon dioxide	4- (or 2-) 10-Methylphenothiazinecarboxylic acid	43	392
		BuLi	Ether	Dimethyl sulfate	4,10-Dimethylphenothiazine	25	*jjj*
		BuLi	Ether	Ethylene oxide	4-β-Hydroxyethyl-10-methylphenothiazine	10	*jjj*
		BuLi	Ether	Formaldehyde	4-Hydroxymethyl-10-methylphenothiazine	10	*jjj*
		BuLi	Ether	N-Formyl-N-methylaniline	4-Formyl-10-methylphenothiazine	10	*jjj*
		BuLi	Ether	Lithium acetate	4-Acetyl-10-methylphenothiazine	23	*jjj*
		BuLi	Ether	Lithium benzoate	4-Benzoyl-10-methylphenothiazine	21	*jjj*
		BuLi	Ether	Lithium propionate	4-Propionyl-10-methylphenothiazine	17	*jjj*
$C_{13}H_{12}$	Diphenylmethane	Li–naphthalene	THF	Carbon dioxide	Diphenylacetic acid	70	272
		Ph_3SiLi	THF	Carbon dioxide	Diphenylacetic acid	57	271
		n-PrLi	Ether	Triphenylchlorosilane	Benzhydryltriphenylsilane	66	171
$C_{13}H_{12}S$	Phenyl benzyl sulfide	BuLi	Ether	Carbon dioxide	2-Phenyl-2-(phenylthio)acetic acid	75	329
$C_{13}H_{12}O_2S$	Phenyl benzyl sulfone	BuLi	Ether	Carbon dioxide	2-Phenyl-2-(phenylsulfonyl)acetic acid	65	329
$C_{13}H_{12}O_2S$	*p*-Tolyl phenyl sulfone	BuLi	Ether	Carbon dioxide	2-Carboxy-4-methylphenyl phenyl sulfone (41) 2-Carboxy-4′-methylphenyl phenyl sulfone (59)		334
$C_{13}H_{12}S_2$	Bis(phenylthio)methane	BuLi	THF	Benzaldehyde	α-Phenyl-α-hydroxyacetaldehyde diphenyl thioacetal	87	330
		BuLi	THF	Benzophenone	α,α-Diphenyl-α-hydroxyacetaldehyde diphenyl thioacetal	80	330
		BuLi	THF	*n*-Butyl bromide	Pentanal diphenyl thioacetal	96	330
		BuLi	THF	Cyclohexanone	α-Hydroxycyclohexanecarboxaldehyde diphenyl thioacetal	92	330

Table VI (*Continued*)

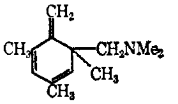
	Compound metalated	*RLi*	*Solvent*	*Reactant*	*Final product*	*% yield*	*Ref*
		BuLi	THF	Deuterium oxide	Bis(phenylthio)methane-α-*d*	78	330
		BuLi	THF	Methyl iodide	Acetaldehyde diphenyl thioacetal	67	330
$C_{13}H_{13}N$	N-Methyldiphenylamine	BuLi	Ether	Carbon dioxide	N-Methyl-N-phenylanthranilic acid	14	345
$C_{13}H_{13}N$	10-Methylacridan	BuLi	Ether	Chlorotriphenylsilane	10-Methyl-9-(triphenylsilyl)acridan	81	*tttt*
$C_{13}H_{13}OP$	Diphenylmethylphosphine oxide	BuLi	Hexane Ether	Benzaldehyde	(2-Hydroxy-2-phenylethyl)diphenyl phosphine oxide	31	458
		BuLi	Hexane Ether	Benzophenone	(2-Hydroxy-2,2-diphenylethyl)diphenylphosphine oxide	81	458
$C_{13}H_{13}P$	Methyldiphenylphosphine	BuLi	Ether	Carbon dioxide, sulfur	Carboxymethyldiphenylphosphine sulfide	21	457
		BuLi	Hexane Ether	Di-*n*-octylphosphinyl chloride	[(Di-*n*-octylphosphinyl)(diphenylphosphinyl)]methane	25	458
		BuLi	Hexane Ether	Diphenylphosphinyl chloride	Bis(diphenylphosphinyl)methane	25	458
		BuLi	Hexane Ether	3-Pentanone	(2-Ethyl-2-hydroxybutyl)diphenylphosphine oxide	61	458
$C_{13}H_{16}$	3-Butylindene	BuLi	Ether	Ferrous chloride	Di(3-butylindenyl)iron	20	450
$C_{13}H_{17}Fe$	Isopropylferrocene	BuLi	Ether	Trimethylchlorosilane	3-Isopropyl-1-trimethylsilylferrocene (30) 1′-Isopropyl-1-trimethylsilylferrocene (70)		431
$C_{13}H_{17}FeN$	Dimethylaminomethylferrocene	BuLi	Ether Hexane	Acetone	2-(α,α-Dimethylhydroxymethyl)dimethylaminomethylferrocene	14	439
		BuLi	Ether Hexane	Benzonitrile	2-(Dimethylaminomethyl)ferrocenylphenone	58	439
		BuLi	THF	Benzophenone	2,1′-Di(α,α-diphenylhydroxymethyl)dimethylaminomethylferrocene	45	439
		BuLi	Ether Hexane	Benzophenone	2-(α,α-Diphenylhydroxymethyl)dimethylaminomethylferrocene	71–75	438, 439
		BuLi	Ether Hexane	Deuterium oxide	Dimethylaminomethylferrocene-2-*d*	72	439
		BuLi	THF	Deuterium oxide	Dimethylaminomethylferrocene-2,1′-*d*	84	439
		BuLi	Ether Hexane	Hexachloroethane	2-Chlorodimethylaminomethylferrocene	60	376
		BuLi	Ether Hexane	Phenyl isocyanate	2-(Dimethylaminomethyl)-N-phenylferrocenecarboxamide	31	439
		BuLi	Hexane	Trioxymethylene	1-Hydroxymethyl-2-dimethylaminomethylferrocene		*hhhh*
$C_{13}H_{20}N$		BuLi	Ether		2-*n*-Amyl-1,3,5-trimethylbenzene	67	*bbb*
$C_{13}H_{29}OP$	Di-*n*-hexylmethylphosphine oxide	BuLi	Hexane Ether	Acetaldehyde	Di-*n*-hexyl-(2-hydroxy-*n*-propyl)phosphine oxide	44	458
		BuLi	Hexane Ether	Acetophenone	Di-*n*-hexyl-(2-hydroxy-2-phenylpropyl)phosphine oxide	51	458
		BuLi	Hexane Ether	Benzaldehyde	Di-*n*-hexyl(2-hydroxyphenylethyl)phosphine oxide	50	458
		BuLi	Hexane Ether	Benzophenone	Di-*n*-hexyl-(2-hydroxy-2,2-diphenylethyl)phosphine oxide	49	458
		BuLi	Hexane Ether	Butyraldehyde	Di-*n*-hexyl-(2-hydroxy-*n*-pentyl)phosphine oxide	33	458
		BuLi	Hexane Ether	Carbon dioxide	Carboxymethyl-di-*n*-hexylphosphine oxide	67	458
		BuLi	Hexane Ether	Di-*n*-hexylphosphinyl chloride	Bis(di-*n*-hexylphosphinyl)methane	35	458
		BuLi	Hexane Ether	Ethyl acetate	Acetonyldi-*n*-hexylphosphine oxide	30	458
		BuLi	Hexane Ether	Ethyl benzoate	Di-*n*-hexylphenacylphosphine oxide	33	458

Table VI (Continued)

	Compound metalated	RLi	Solvent	Reactant	Final product	% yield	Ref
		BuLi	Hexane Ether	3-Pentanone	(2-Ethyl-2-hydroxybutyl)-di-*n*-hexylphosphine oxide	46	458
$C_{13}H_{29}P$	Di-*n*-hexylmethylphosphine	*t*-BuLi	Pentane	Carbon dioxide, sulfur	Carboxymethyl di-*n*-hexylphosphine sulfide	46	457
$C_{14}H_{4}Cl$-NO_2S	3-Chloro-4-dimethylaminophenyl phenyl sulfone	BuLi	Ether	Carbon dioxide	3-Chloro-4-dimethylaminophenyl phenyl sulfone 2-carboxylic acid	83	342
$C_{14}H_9Cl_3$	1,1-Di(4-chlorophenyl)-chloroethylene	BuLi	THF Ether Hexane	Carbon dioxide	3,3-Di(4-chlorophenyl)-2-chloroacrylic acid	88	203
$C_{14}H_{10}$	Diphenylacetylene	EtLi	Ether	Carbon dioxide	2-Phenyl-3-(*o*-carboxyphenyl)-2-pentenoic acid + 2-phenyl-3-ethylindone	12–15 12–15	125, 268
		BuLi	Ether	Carbon dioxide	2-Phenyl-3-(*o*-carboxyphenyl)-2-heptenoic acid + 2-phenyl-3-butylindone	14–15 15–28	125, 268
$C_{14}H_{10}Cl_2$	1-Phenyl-1-*p*-chlorophenylchloroethylene	BuLi	THF Ether Hexane	Carbon dioxide	3-Phenyl-3-*p*-chlorophenyl-2-chloroacrylic acid	87	203
$C_{14}H_{10}Cl_3$	2,2-Bis(*o*-chlorophenyl)-chloroethylene	BuLi	THF Ether Pet. ether	Carbon dioxide	3,3-Bis(*o*-chlorophenyl)-2-chloroacrylic acid	76	201
$C_{14}H_{10}Cl_3$	2,2-Bis(*p*-chlorophenyl)-chloroethylene	BuLi	THF Ether Pet. ether	Carbon dioxide	3,3-Bis(*p*-chlorophenyl)-2-chloroacrylic acid	86	201
$C_{14}H_{11}Cl$	2,2-Diphenylchloroethylene	BuLi	THF Ether Hexane	Bromine	1,1-Diphenyl-2-chloro-2-bromoethylene	94	200
		BuLi	Ether THF	Carbon dioxide	3,3-Diphenyl-2-chloroacrylic acid	85–94	199–201, 203
		BuLi	THF Ether Hexane	Iodine	1,1-Diphenyl-2-chloro-2-iodoethylene	98	200
		BuLi	THF Hexane Ether	Mercuric chloride	(1-Chloro-2,2-diphenylvinyl)-mercuric chloride + bis(1-chloro-2,2-diphenylvinyl)-mercury	18 69	200
		BuLi	THF Ether Hexane	Methyl iodide	1,1-Diphenyl-2-chloro-1-propene	86	200
		BuLi	THF Ether Pet. ether	Silver chloride	1-Chloro-2,2-diphenylvinylsilver		196
		BuLi	THF Ether Pet. ether	Silver chloride, bromine	2,2-Diphenyl-1-chloro-1-bromoethylene	77	196
$C_{14}H_{11}N$	1-Phenylindole	BuLi	Ether	Carbon dioxide	1-(*o*-Carboxyphenyl)-2-indolecarboxylic acid	15	355
$C_{14}H_{12}$	9,10-Dihydroanthracene	Poly-*p*-styryllithium	Ether	Carbon dioxide	9,10-Dihydroanthracene-10-carboxylic acid	38	*g*
		Ph_3SiLi	THF	Carbon dioxide	9,10-Dihydroanthracene-10-carboxylic acid	72	271

Table VI (Continued)

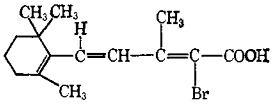
	Compound metalated	RLi	Solvent	Reactant	Final product	% yield	Ref
		BuLi	Ether	N,N-Dimethylcarbamoyl chloride	9,10-Dihydroxyanthracenebis-(N,N-dimethylcarboxamide)		207
$C_{14}H_{12}NS$	10-Ethylphenothiazine	BuLi		Benzophenone	4-(Diphenylhydroxymethyl)-10-ethylphenothiazine	55	*kkk*
		BuLi	Ether	Carbon dioxide	10-Ethylphenothiazine-1-carboxylic acid + 10-ethylphenothiazine-4-carboxylic acid	13 14	*jjj*, *iiii*
		Ph_3SiLi	THF	Carbon dioxide	10-Ethylphenothiazine-4-carboxylic acid	2	271
		BuLi	Ether	Lithium acetate	4-Acetyl-10-ethylphenothiazine	13	*jjj*
		BuLi	Ether	Lithium benzoate	4-Benzoyl-10-ethylphenothiazine	17	*jjj*
$C_{14}H_{13}N$	9-Ethylcarbazole	BuLi	Ether	Carbon dioxide	9-Ethylcarbazole-1-carboxylic acid	2	157
		BuLi	Ether THF	Carbon dioxide	9-Ethylcarbazole-1-carboxylic acid	21	157
		BuLi	THF	Carbon dioxide	9-Ethylcarbazole-1-carboxylic acid	1	157
		PhLi	THF	Carbon dioxide	9-Ethylcarbazole-1-carboxylic acid	10	157
		BuLi	Ether	Triphenylsilyl bromide	1-Triphenylsilyl-9-ethylcarbazole	12	*ee*
$C_{14}H_{12}N$	2-Methyl-6-styrylpyridine	PhLi	Ether	Propionaldehyde	2-Methyl-6-(α-benzhydryl-β-hydroxybutyl)pyridine		*cc*
$C_{14}H_{13}NO$	10-Ethylphenoxazine	BuLi	Ether	Carbon dioxide	10-Ethylphenoxazine-4-carboxylic acid	66	284
		MeLi	Ether	Carbon dioxide	10-Ethylphenoxazine-4-carboxylic acid	15	284
$C_{14}H_{13}NOS$	10-Ethylphenothiazine 5-oxide	BuLi	Ether	Carbon dioxide	4-Carbomethoxy-10-ethylphenothiazine		*jjjj*
		BuLi	Ether	Iodine	4-Iodo-10-ethylphenothiazine	23	*jjjj*
$C_{14}H_{13}P$	Diphenylvinylphosphine	BuLi	Ether Hexane	Carbon dioxide, sulfur	(α-Carboxy-*n*-hexyl)diphenylphosphine sulfide	45	459
$C_{14}H_{14}Cr$	Ditoluenechromium	BuLi		Carbon dioxide	Dilithium–chromium ditoluate		454
$C_{14}H_{14}O_2$	Ethylene glycol diphenyl ether	BuLi	Ether	Carbon dioxide	Ethylene glycol phenyl *o*-carboxyphenyl ether	14	291
		BuLi	Ether	Triphenylchlorosilane	Ethylene glycol phenyl *o*-triphenylsilylphenyl ether	7	291
$C_{14}H_{14}O_2S$	*p*-Tolyl sulfone	BuLi	Ether	Carbon dioxide	2-Carboxy-4,4′-dimethylphenyl phenyl sulfone	53	335
$C_{14}H_{14}S_2$	Acetaldehyde diphenyl thioacetal	BuLi DABCO	THF	Benzophenone	α,α-Diphenyl-α-hydroxyacetone diphenyl thioketal	74	330
$C_{14}H_{15}N$	2-Methyl-5-phenethylpyridine	PhLi	Ether	Benzyl chloride	2-Methyl-6-(dibenzylmethyl)-pyridine	25	350
$C_{14}H_{21}Br$	β-Ionylidenebromomethane	BuLi	THF	Carbon dioxide		24	188
$C_{15}H_{12}$	3-Phenylindene	BuLi	Ether	Ferrous chloride	Di(3-phenylindenyl)iron	18	450
$C_{15}H_{17}N$	Dibenzyl methylamine	BuLi	Ether	Benzaldehyde	2-(Benzylmethylaminomethyl)-benzhydrol	56	374
		BuLi	Ether	Deuterium oxide	Dibenzylmethylamine-2*d*		375
$C_{15}H_{18}OSi$	4-Trimethylsilylphenyl phenyl ether	BuLi	THF	Dichlorodiphenylsilane	2-Trimethylsilyl-10,10-diphenylphenoxasilin	17	290
$C_{15}H_{32}Sn$	Allyltri-*n*-butyltin	PhLi	Ether	4-Methyl-2-pentanone	4,6-Dimethyl-1-hepten-4-ol	70	*kkkk*
$C_{16}H_{10}$	Pyrene	BuLi	Ether	Carbon dioxide	Pyrene-1,2- and -3-carboxylic acid	85	280

Table VI (Continued)

	Compound metalated	RLi	Solvent	Reactant	Final product	% yield	Ref
$C_{16}H_{11}NS$	12H-Benzo-[*a*]phenothiazine	BuLi	Ether	Carbon dioxide	12H-benzo[*a*]phenothiazine-1-carboxylic acid	94	393
$C_{16}H_{11}NS$	12H-Benzo-[*b*]phenothiazine	BuLi	Ether Hexane	Carbon dioxide	12H-benzo[*b*]phenothiazine-11-carboxylic acid	82	395
$C_{16}H_{11}NS$	7H-Benzo-[*c*]phenothiazine	BuLi	Ether	Carbon dioxide	7H-benzo[*c*]phenothiazine-6-carboxylic acid	41	396
$C_{16}H_{14}$	3-Benzylindene	BuLi	Ether	Ferrous chloride	Di(3-benzylindenyl)iron	10	450
$C_{16}H_{14}Br_2O_2$	1,1-Bis-(*p*-methoxyphenyl)-2,2-dibromoethylene	BuLi	THF	Carbon dioxide	α-Bromo-β-bis(*p*-methoxyphenyl)acrylic acid	69	188
$C_{16}H_{15}Cl$	2,2-Dibenzyl-1-chloroethylene	BuLi	THF Ether Pet. ether	Carbon dioxide	3,3-Dibenzyl-2-chloroacrylic acid	92–93	190, **191**
$C_{16}H_{15}Cl$	2,2-Bis-(*p*-tolyl)-chloroethylene	BuLi	THF Ether Pet. ether	Carbon dioxide	3,3-Bis(*p*-tolyl)-2-chloroacrylic acid	78	199, **201**, **203**
$C_{16}H_{15}Cl$	2,2-Bis-(*o*-tolyl)-chloroethylene	BuLi	THF Ether Pet. ether	Carbon dioxide	3,3-Bis(*o*-tolyl)-2-chloroacrylic acid	45	201
$C_{16}H_{15}ClO_2$	2,2-Bis(*o*-methoxyphenyl)-chloroethylene	BuLi	THF Ether Pet. ether	Carbon dioxide	3,3-Bis(*o*-methoxyphenyl)-2-chloroacrylic acid	8	201, **203**
$C_{16}H_{15}ClO_2$	2,2-Bis(*p*-methoxyphenyl)-chloroethylene	BuLi	THF Ether Pet. ether	Carbon dioxide	3,3-Bis(*p*-methoxyphenyl)-2-chloroacrylic acid	67	199, **201**, 203
$C_{16}H_{15}Fe$	α-Ferrocenylfulvene	PhLi	Ether	Ferrous chloride	1,1′-Di(α-ferrocenylbenzyl)-ferrocene	21	452
$C_{16}H_{17}Si$	9-Trimethylsilylfluorene	BuLi	Ether	Methyl iodide	9-Methyl-9-(trimethylsilyl)-fluorene	31	*llll*
		BuLi	Ether	Trimethylchlorosilane	9,9-Di(trimethylsilyl)fluorene	17	*llll*
$C_{16}H_{18}$	2-Phenyl-2-*p*-tolylpropane	BuLi	Ether	Carbon dioxide	*p*-(α,α-Dimethylbenzyl)phenylacetic acid		*mmmm*
$C_{16}H_{18}O_2S$	4-*t*-Butylphenyl phenyl sulfone	BuLi	Ether	Carbon dioxide	2-Carboxy-4′-*t*-butylphenyl phenyl sulfone (69) + 2-carboxy-4-*t*-butylphenyl phenyl sulfone (31)		337
$C_{16}H_{19}N$	2-Methylbenzyldimethylaniline	BuLi	Hexane Ether	Benzonitrile	2-(Dimethylaminomethyl)benzyl phenyl ketone	68	381
		BuLi	Hexane Ether	Benzophenone	2-[α-(Dimethylamino)-*o*-tolyl]-1,1,2-triphenylethanol	88	381
$C_{16}H_{22}O_4$	Hydroquinonebis-(2-tetrahydropyranyl) ether	BuLi	Ether	Carbon dioxide	2,5-Dihydroxybenzoic acid	65	301
$C_{16}H_{34}Sn$	Methallyltriphenyltin	PhLi	Ether	Acetaldehyde	2-Methyl-1-penten-4-ol	59	495
$C_{18}H_{13}NO$	10-Phenylphenoxazine	BuLi	Ether	Carbon dioxide	10-Phenylphenoxazine-4-carboxylic acid	Trace	284
		MeLi	Ether	Carbon dioxide	10-Phenylphenoxazine-4-carboxylic acid	Trace	284

Table VI (*Continued*)

	Compound metalated	*RLi*	*Solvent*	*Reactant*	*Final product*	*% yield*	*Ref*
$C_{18}H_{15}OP$	Triphenylphosphine oxide	EtLi	Ether	Benzophenone	$(C_6H_5)_2P(O)CH(CH_3)C(OH)(C_6H_5)_2$	84	461
		MeLi	Ether	Benzophenone	$(C_6H_5)_2P(O)CH_2C(OH)(C_6H_5)_2$	74	461
		EtLi	Ether	Carbon dioxide	2-(Diphenylphosphinyl)propionic acid	50	460, 461
		MeLi	Ether	Carbon dioxide	Diphenylphosphinylacetic acid	47	460, 461
		MeLi	Ether	Diphenylchlorophosphine, sulfur	$(C_6H_5)_2P(O)CH_2P(S)(C_6H_5)_2$	25	461
		EtLi	Ether	Hydrobromic acid	Ethyl diphenylphosphine oxide	78	461
		MeLi	Ether	Hydrobromic acid	Methyl diphenylphosphine oxide	76	461
		MeLi	Ether	Triphenylchlorosilane	(Diphenylphosphinylmethyl)triphenylsilane	65	461
		BuLi	Ether	Triphenyltin chloride	$(C_6H_5)_2P(O)CH[Sn(C_6H_5)_3]CH_2CH_2CH_3$	69	461
		EtLi	Ether	Triphenyltin chloride	$(C_6H_5)_2P(O)CH(CH_3)Sn(C_6H_5)_3$	81	460, 461
		MeLi	Ether	Triphenyltin chloride	(Diphenylphosphinylmethyl)triphenyltin	76	460, 461
$C_{18}H_{15}PS$	Triphenylphosphine sulfide	MeLi	THF Ether	Carbon dioxide	Carboxymethyldiphenylphosphine sulfide	39	460, 462
		MeLi	Ether THF	Triphenyltin chloride	Triphenylstannylmethyldiphenylphosphine sulfide	74	460
$C_{18}H_{16}Ge$	Triphenylgermane	BuLi	Ether	Acetone	2-Triphenylgermyl-2-propanol	46	403
		BuLi	Ether	Acetophenone	1-Triphenylgermyl-1-phenyl-1-ethanol	68	403
		BuLi	THF	Acetyl chloride	1,1-Bis(triphenylgermyl)-1-ethanol	85	401
		BuLi	THF	Acetyl chloride	1,1-Bis(triphenylgermyl)-1-ethanol	67	401
		BuLi	Ether	Benzophenone	Triphenylgermyldiphenylcarbinol	81	403
		BuLi	THF	Benzoyl chloride	Bis(triphenylgermyl)phenylcarbinol	49	401
		BuLi	THF	Benzoyl chloride	Benzoyltriphenylgermane	80	401
		BuLi	THF	Benzoyltriphenylgermane	1,1-Bis(triphenylgermyl)phenylcarbinol	57	401
		BuLi	Ether	2-Butanone	2-Triphenylgermyl-2-butanol	37	403
		BuLi	Ether	Carbon dioxide	Triphenylgermanecarboxylic acid	97	400
		MeLi	Ether	Carbon dioxide	Triphenylgermanecarboxylic acid	77	400
		PhLi	Ether	Carbon dioxide	Triphenylgermanecarboxylic acid	83	400
		BuLi	Ether	Di-*n*-propyl ketone	4-Triphenylgermyl-4-heptanol	48	403
		BuLi	THF	*p*-Fluorobenzoyl chloride	Bis(triphenylgermyl)-*p*-fluorophenylcarbinol	60	401
		BuLi	Ether	Isobutyrophenone	1-Triphenylgermyl-1-phenyl-2-methyl-1-propanol	84	403
		BuLi	THF	*p*-Methoxybenzoyl chloride	*p*-Methoxybenzoyltriphenylgermane	84	401
		BuLi	Ether	3-Pentanone	3-Triphenylgermyl-3-pentanol	70	403
		BuLi	THF	Propionyl chloride	1,1-Bis(triphenylgermyl)-1-propanol	37	401
		BuLi	Ether	*p*-Trifluoromethylbenzoyl chloride	*p*-Trifluoromethylbenzoyltriphenylgermane	44	401
$C_{18}H_{16}Si$	Triphenylsilane	Ph_3SiLi	Ether Benzene	Carbon dioxide	Triphenylacetic acid, triphenylsilanol	22 46	405, *nnnn*
		Ph_3SiLi	EGDE Ether	Carbon dioxide	Hexaphenyldisilane, tetraphenylsilane	14 11	405, *nnnn*
$C_{18}H_{20}O$	Duryl *o*-tolyl ketone	BuLi	Ether	Carbon dioxide	*o*-Duroylphenylacetic acid	17	270
$C_{18}H_{22}O_2S$	Dimesityl sulfone	BuLi	Ether	Carbon dioxide	Monocarboxydimesityl sulfone	25	334
$C_{18}H_{23}PS$	Diphenyl-*n*-hexylphosphine sulfide	BuLi	Ether Hexane	Carbon dioxide	(α-Carboxy-*n*-hexyl)diphenylphosphine sulfide	12	459

Table VI (Continued)

	Compound metalated	*RLi*	*Solvent*	*Reactant*	*Final product*	*% yield*	*Ref*
$C_{19}H_{14}$	9-Phenylfluorene	BuLi	Ether	Carbon dioxide	9-Phenylfluorene-9-carboxylic acid	80	298
		PhLi		Carbon dioxide	9-Phenylfluorene-9-carboxylic acid	80	172
$C_{19}H_{16}$	2-Benzylbiphenyl	BuLi	Ether	Carbon dioxide	Phenyl-*o*-xenylacetic acid	25	*oooo*
$C_{19}H_{16}$	4-Benzylbiphenyl	BuLi	Ether	Carbon dioxide	Phenyl-*p*-xenylacetic acid	41	*oooo*
$C_{19}H_{16}$	Triphenylmethane	BuLi	Ether	Carbon dioxide	Triphenylacetic acid	71	405, *nnnn*, *oooo*
		BuLi	THF	Carbon dioxide	Triphenylacetic acid	87	170
		Excess PhLi	Ether	Carbon dioxide	Triphenylacetic acid	6	172
		o-CH_3-C_6H_4Li		Carbon dioxide	Triphenylacetic acid	8	172
		Ph_3SiLi	EGDE	Carbon dioxide	Triphenylacetic acid	37	405, *nnnn*
		BuLi	Ether	N,N-Dimethylcarbamoyl chloride	Triphenyl-N,N-dimethylacetamide		207
		n-PrLi	Ether	Triphenylchlorosilane	Triphenylmethyltriphenylsilane	34	205
		n-PrLi	Ether	Trimethylchlorosilane	Trimethyl(triphenylmethyl)silane	70	*gg*
$C_{19}H_{17}OP$	Diphenylbenzylphosphine oxide	PhLi	Ether	Benzaldehyde	Diphenyl(1,2-diphenyl-2-hydroxy-2-ethyl)phosphine oxide	90	*pppp*, *qqqq*
		PhLi	Ether	Carbon dioxide	Diphenyl(α-carboxybenzyl)phosphine oxide	65	*pppp*
$C_{20}H_{13}NS$	14H-Dibenzo[*a*,*c*]phenothiazine	BuLi	Hexane Ether	Carbon dioxide	Lactam of 1-carboxy-14H-dibenzo[*a*,*c*]phenothiazine	85	394
$C_{20}H_{13}NS$	14H-Dibenzo[*a*,*h*]phenothiazine	BuLi	Hexane Ether	Carbon dioxide	1-Carboxy-14H-dibenzo[*a*,*h*]-phenothiazine	80	394
$C_{20}H_{13}NS$	7H-Dibenzo[*a*,*h*]phenothiazine	BuLi	Hexane Ether	Carbon dioxide	6-Carboxy-7H-dibenzo[*c*,*h*]-phenothiazine	77	394
$C_{20}H_{16}$	9-Benzylfluorene	PhLi	Ether	Dibromomethane	9-Bromomethyl-9-benzylfluorene	61	*yyy*
$C_{20}H_{16}S$	Phenyl (2,2-diphenyl)vinyl sulfide	BuLi	THF	Deuterium oxide	Phenyl (2,2-diphenyl)vinyl-1-*d* sulfide	87	330
$C_{20}H_{18}O$	Triphenylmethyl methyl ether	BuLi	Ether	Carbon dioxide	3,3-Diphenylphthalide	18	172, 298
		PhLi	Ether	Carbon dioxide	9-Phenylfluorene-9-carboxylic acid	13–57	172, 298
		BuLi	Ether	Water	9-Phenylfluorene	20	298
		PhLi	Ether	Water	9-Phenylfluorene	71	298
$C_{21}H_{18}Si$	1-(Triphenylsilyl)propyne	PhLi	THF	Triphenylsilane	1,3-Bis(triphenylsilyl)propyne	32	411
		PhLi	THF	Chlorotriphenylsilane	Tris(triphenylsilyl)propadiene	23	411
					1,3-Bis(triphenylsilyl)propyne	13	
		Ph_3SiLi	Ether THF	Chlorotriphenylsilane	1,3-Bis(triphenylsilyl)propyne	5	411
		Ph_3SiLi	THF	Chlorotriphenylsilane	1,2-Bis(triphenylsilyl)propene	18	411
					Tris(triphenylsilyl)propadiene	32	
$C_{21}H_{20}Sn$	Allyltriphenyltin	PhLi	Ether	*n*-Amyl iodide	1-Octene	52	*rrrr*
		PhLi	Ether	Carbon dioxide	Vinylacetic acid	25	*kkkk*
		PhLi	Ether	4-Methyl-2-pentanone	4,6-Dimethyl-1-hepten-4-ol	65	*kkkk*, *rrrr*
		PhLi	Ether	Tri-*n*-butyltin chloride	Allyltri-*n*-butyltin	69	*rrrr*
		PhLi	Ether	Triphenyl germanium bromide	Allyltriphenylgermane	54	*rrrr*
		PhLi	Ether	Triphenylchlorosilane	Allyltriphenylsilane	74	*kkkk*, *rrrr*

Table VI (Continued)

	Compound metalated	*RLi*	*Solvent*	*Reactant*	*Final product*	*% yield*	*Ref*
		PhLi	Ether	Triphenylsilane	Allyltriphenylsilane	60	*rrrr*
$C_{22}H_{16}$	9-Cinnamylidenefluorene	PhLi	Ether	Water	1,1-Biphenylene-4,4-diphenyl-2-butene		*cccc*
$C_{22}H_{20}Si$	1-(Triphenylsilyl)-1-butyne	PhLi	THF	Triphenylsilane	1,3-Bis(triphenylsilyl)-1-butyne		411
$C_{22}H_{22}Sn$	Methallyltriphenyltin	PhLi	Ether	Acetaldehyde	2-Methylpent-1-en-4-ol	53	*rrrr*
		PhLi	Ether	Triethylbromosilane	Triethylmethallylsilane	68	*rrrr*
$C_{23}H_{20}FeO$	Diphenylferrocenylcarbinol	BuLi	Ether	Carbon dioxide	2-Carboxydiphenylferrocenylcarbinol	73	303
		BuLi	Ether	Methyl iodide	2-Methyldiphenylferrocenylcarbinol	69	303
$C_{24}H_{20}$	Triphenylmethylcyclopentadiene	PhLi	Ether THF	Ferric chloride	1,1′-Bis(triphenylmethyl)ferrocene	18	*pp*
$C_{25}H_{22}Si$	Triphenylbenzylsilane	BuLi	Ether	Carbon dioxide	Phenylacetic acid	43	399
$C_{25}H_{22}Sn$	Triphenylbenzyltin	PhLi	Ether	Carbon dioxide	Phenylacetic acid	39	*ssss*
$C_{26}H_{20}Si$	Triphenyl(phenethynyl)silane	BuLi	Ether	Carbon dioxide	Phenylpropiolic acid	19	399
$C_{26}H_{22}O$	Dibenzhydryl ether	BuLi	Benzene Ether	Carbon dioxide	Di(*o*-carboxy)benzhydryl ether	Low	299
$C_{26}H_{27}FeNO$	2-(α,α-Diphenylhydroxymethyl)dimethylaminomethylferrocene	BuLi	THF	Benzophenone	2,1′-Di(α,α-diphenylhydroxymethyl)dimethylaminomethylferrocene	71	439
$C_{28}H_{22}$	1,4-Diphenylenebutane	PhLi	Ether	Benzyl chloride	1,4-Dibenzyl-1,4-dibiphenylenebutane	65	*yyy*
$C_{30}H_{54}B_2$	1,1-Di(cyclohexylboronyl)hexane	BuLi	THF	Benzaldehyde	1-Phenylhept-1-ene	45–50	486
		BuLi	THF	Benzophenone	1,1-Diphenylhept-1-ene	45–50	486
		BuLi	THF Heptane	Carbon dioxide	2-Pentylmalonic acid	65–70	485
		BuLi	THF	Cholestanone	3-*n*-Hexylidene-5-α-cholestane	20–25	486
		BuLi	THF	Cyclohexanone	*n*-Hexylidenecyclohexane	20–25	486
		BuLi	THF	Di-*n*-amyl ketone	6-*n*-Amylundec-6-ene	30–35	486
$C_{31}H_{26}Sn$	Triphenyl(diphenylmethyl)silane	BuLi	Ether THF	Benzyl chloride	Triphenyl(1,1,2-triphenylethyl)silane	25	257
		BuLi	Ether THF	Dimethyl sulfate	Triphenyl(1,1-diphenylethyl)silane	58	257
$C_{39}H_{32}Si_2$	1,3-Bis(triphenylsilylpropyne	Ph_3SiLi	THF	Chlorotriphenylsilane	Tris(triphenylsilyl)propadiene	51	411
		PhLi	THF	Methyl iodide	1,3-Bis(triphenylsilyl)-1-butyne		411
$C_{57}H_{46}Si_3$	Tris(triphenylsilyl)propadiene	PhLi	THF	Chlorotriphenylsilane	Tetrakis(triphenylsilyl)propadiene	14	411
		PhLi	THF	Deuterium oxide	Tris(triphenylsilyl)propadiene-1-*d*	88	411
		PhLi	THF	Methyl iodide	1,1,3-Tris(triphenylsilyl)-1,2-butadiene	67	411

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