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ORGANOMETALLIC BIS(p-HYDROXYPHENYL) DERIVATIVES OF GROUP IV ELEMENTS AND RELATED COMPOUNDS

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SUMMARY

Dimethyl- and diphenylbis(p-hydroxyphenyl) Group IV metal compounds have been synthesized. Scope and limitations of the following methods were investigated: (a) reaction of the halogen–metal exchange product of p-bromophenol and n-butyllithium with organometallic dihalides; (b) protection of the phenolic group with trimethyl or benzyl groups and subsequent hydrolysis or hydrogenolysis.

Only the first method is generally applicable. The synthesis and properties of p-hydroxyphenyl and p-benzyloxyphenyl derivatives of silicon, germanium, tin and lead are described.

INTRODUCTION

Very few Group IVb organometallic bis(hydroxyphenyl) compounds have been reported in the literature (Table 1). In this paper three routes are described for the synthesis of this class of compounds. In each case, dialkyl- or diarylmetal dihalides are treated with a p-bromophenol derivative. In the first instance, the reactant is lithium lithiophenoxide and in cases two and three, the phenolic group is protected by prior substitution of the phenolic hydrogen with trimethylsilyl and benzyl groups respectively. Subsequent to the reaction with the organometallic halides, the free

TABLE 1

Compound	M.p. (°C)	Ref.
$Me_2Si(C_6H_4OH\text{-}p)_2$	171	3
$Me_2Si(2\text{-}Me\text{-}4OH\text{-}C_6H_3)_2$	208–210	3
$Et_2Si(C_6H_4OH\text{-}p)_2$	132	4
$Pr_2Si(C_6H_4OH\text{-}p)_2$	123	4
$Ph_2Si(C_6H_4OH\text{-}o)_2$	206–207	15
$Ph_2Sn(C_6H_4OH\text{-}o)_2$	136–138	1
$Ph_2Sn(C_6H_4OH\text{-}m)_2$	201–203	2
$[p\text{-}HOC_6H_4Si(CH_3)_2]_2O$	86–87	16

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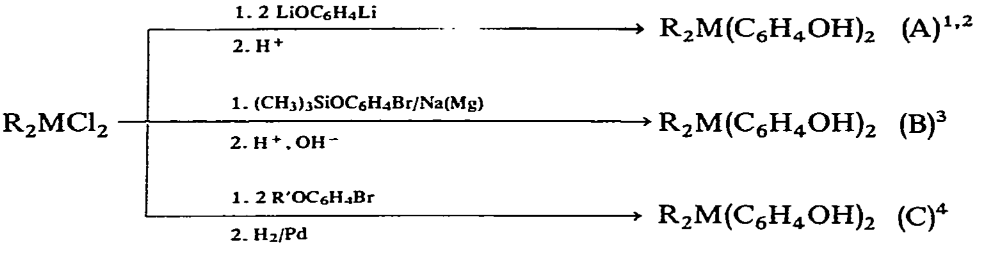
phenolic group is re-established by hydrolysis or hydrogenation as indicated below.



M = Group IVb metal, R = alkyl or aryl, R′ = benzyl

Of the three methods investigated, it would appear from our studies that only case (A), based on the halogen–lithium interchange, is of general applicability.

RESULTS AND DISCUSSION

The use of trimethylsilyl groups to protect the phenolic functionality in the synthesis of (organosilyl)hydroxyphenyl compounds has been documented in the literature[3,5–7]. These compounds have been reported to undergo Wurtz-type reactions, Grignard couplings and halogen–metal exchange reactions and the phenolic group is re-established by acid or base catalyzed hydrolysis reactions.

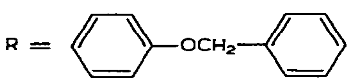
In the process of studying the use of these reactions to develop a general synthesis for Group IVb element analogs we found that simple refluxing of (*p*-bromophenoxy)trimethylsilane with sodium in toluene or with magnesium in THF, yielded considerable quantities of [(*p*-(trimethylsilyl)phenoxy]trimethylsilane even without the addition of trimethylchlorosilane. Only low yields of bis[*p*-(trimethylsilyl)-phenoxy]dimethylsilane (11%) were obtained upon addition of dimethyldichlorosilane. These experiments, along with Raubach's interpretations[4], suggested the method would have serious limitations as far as its utilization for a general synthetic method for Group IVb organometallic bis(*p*-hydroxyphenyl) compounds.

The synthesis of dimethyl- and diphenyl-bis(*p*-benzyloxyphenyl) Group IVb metal derivatives and their hydrogenolysis appeared to be much more promising since this method has already been successfully applied to the preparation of bis-(*p*-hydroxyphenyl)dialkylsilanes[4]. Accordingly, we synthesized a series of eight bis(*p*-benzyloxyphenyl) compounds of the Group IVb metals by reaction of (*p*-benzyloxyphenyl)magnesium bromide with the corresponding diorganometal dihalides. With the exception of the diphenylgermanium and dimethyllead derivatives, the yields were between 50 and 70%. The compounds prepared along with physical properties, melting point, and yields are presented in Table 2.

This method cannot be recommended as a general preparation of bis(*p*-hydroxyphenyl) Group IVb compounds, however, since there is an increasing tendency in going from silicon to tin for cleavage of the phenyl carbon–metal bond under hydrogenolysis conditions.

A third method, a halogen–lithium interchange reaction, proved to be the most general route by which the bis(*p*-hydroxyphenyl) derivatives of silicon, germa-

TABLE 2

R = 	M.p. (°C)	Yield (%)	Analysis found (calcd.) (%)		Mol.wt. found (calcd.)	Solvent
			C	H		
Me_2SiR_2[a]	109–110	68	79.55 (79.20)	6.63 (6.65)	392 (425)	($CHCl_3$)
Me_2GeR_2	104–105	70	71.70 (71.69)	5.98 (6.01)	451 (469)	($CHCl_3$)
Me_2SnR_2	95–96	62	65.25 (65.27)	5.56 (5.48)	532 (515)	(C_6H_6)
Me_2PbR_2	88–90	5	55.80 (55.70)	4.78 (4.68)	615 (604)	(C_6H_6)
Ph_2SiR_2	149–150	32–55[b]	83.35 (83.17)	5.89 (5.88)	531 (549)	(C_6H_6)
Ph_2GeR_2	143–144	17	76.45 (76.93)	5.14 (5.44)	583 (593)	($CHCl_3$)
Ph_2SnR_2	123–124	53	71.72 (71.39)	5.00 (5.04)	660 (639)	($CHCl_3$)
Ph_2PbR_2	123–125	52	62.30 (62.71)	4.28 (4.43)	701 (728)	($CHCl_3$)

[a] Literature m.p. 110^{c4}. [b] Yields depending on reaction conditions, see experimental part.

nium and tin could be prepared in satisfactory yields. It was not possible to isolate the corresponding lead compound even though the bis(*p*-lithiophenoxy) intermediate was formed. Table 3 tabulates the bis(*p*-hydroxyphenol) Group IVb compounds synthesized along with physical and analytical data.

Interchange reactions between halogen substituted phenols and n-butyllithium as used to synthesize organometallic hydroxyphenyl derivatives have been

TABLE 3

Compound	M.p. (°C)	Yield (%)	Analysis found (calcd.) (%)		Mol.wt. found (calcd.)	Solvent
			C	H		
$Me_2Si(C_6H_4OH\text{-}p)_2$[a]	173–174	75	68.57 (68.81)	6.75 (6.60)	250 (244)	($CHCl_3$)
$Me_2Ge(C_6H_4OH\text{-}p)_2$	163–164	75	58.30 (58.21)	5.59 (5.58)	283 (289)	($CHCl_3$)
$Me_2Sn(C_6H_4OH\text{-}p)_2$	96–98	20	50.08 (50.20)	4.77 (4.81)	343 (335)	($CHCl_3$)
$Ph_2Si(C_6H_4OH\text{-}p)_2$	221–222	65	78.41 (78.23)	5.52 (5.47)	368 (369)	(CH_3OH)
$Ph_2Ge(C_6H_4OH\text{-}p)_2$	218–219	55	69.50 (69.75)	4.98 (4.88)	432 (413)	($CHCl_3$)
$Ph_2Sn(C_6H_4OH\text{-}p)_2$	150–151	80	62.60 (62.79)	4.45 (4.39)	462 (459)	($CHCl_3$)
$Ph_2Pb(C_6H_4OSiMe_3\text{-}p)_2$	104–106	78	52.20 (52.10)	5.22 (5.24)	691 (692)	($CHCl_3$)

[a] Literature m.p. 171°C[3].

reported in the literature[1,2,8–11]. Diethyl ether was used in these reported reactions and it was found necessary to add magnesium bromide to the lithium lithiophenoxide before reaction with organotin halides[1,2]. In these studies it was suggested that lithium intermediate was converted into a Grignard type reagent as follows:

$$HOC_6H_4Br + n\text{-}C_4H_9Li \rightarrow LiOC_6H_4Li + C_4H_9Br + C_4H_{10} \qquad (1)$$

$$LiOC_6H_4Li + MgBr_2 \rightarrow LiOC_6H_4MgBr + LiBr \qquad (2)$$

We conducted halogen–lithium exchange reactions in n-butyllithium/hexane/*p*-bromophenol/tetrahydrofuran at low temperatures and after carbonation, obtained high yields of *p*-hydroxybenzoic acid (60–70%). It is advantageous to carry out the reaction in two steps. The first step conducted at −70° results in the formation of lithium *p*-bromophenoxide. No exchange between the bromine atom and n-butyllithium takes place at this temperature. This conclusion was reached by adding dimethyldichlorogermane to such a mixture. The only products isolated were dimethyldibutylgermane and *p*-bromophenol as illustrated below:

$$\begin{tikzcd}
2\,HOC_6H_4Br + 4\,n\text{-}C_4H_9Li \arrow[r, "-70^\circ"] & 2\,LiOC_6H_4Br + 2\,n\text{-}C_4H_9Li + C_4H_{10} \arrow[d, "-70^\circ"] \\
(CH_3)_2Ge(n\text{-}C_4H_9)_2 + 2\,LiOC_6H_4Br + LiCl & + (CH_3)_2GeCl_2 \arrow[l]
\end{tikzcd}$$

The second step in the exchange reaction occurs at −30°. A slight turbidity appears initially which changes quickly into a thick gel. The coupling product, *p*-butylphenol, was always formed in about 25% yield. It has not been ascertained whether the formation of this compound is a result of direct coupling,

$$LiOC_6H_4Br + LiC_4H_9 \rightarrow LiOC_6H_4C_4H_9 + LiBr$$

or occurs through the following sequence,

$$HOC_6H_4Br + 2\,LiC_4H_9 \rightarrow LiOC_6H_4Li + C_4H_{10} + C_4H_9Br$$

$$LiOC_6H_4Li + C_4H_9Br \rightarrow LiOC_6H_4C_4H_9 + LiBr$$

The low temperature at which the reaction occurs and the constant yield of *p*-butylphenol with time as long as the low temperature is maintained, would tend to lead to the conclusion that the direct coupling reaction is more likely. The final step of the reaction is the addition of the organometallic halide to the lithium *p*-lithiophenoxide suspension. The halides were dissolved in tetrahydrofuran with the exception of diphenyllead dichloride which was added as a solid. Generally, dichlorides gave satisfactory results; however, in one case, diphenyldifluorosilane gave better yields and less byproduct than the corresponding chlorosilane. Since the carbonation experiments had indicated about a 75% yield of *p*-hydroxybenzoic acid, approximately 70% of the theoretical amount of the organometallic dihalides was used to avoid excessive byproduct formation. In cases where the theoretical amounts of organometallic halides were used some difficulties were encountered in isolation and purification of the desired product. The details of the hydrolysis step of the reactions are given in the experimental portion of this paper and these vary with the stability of the hydroxyphenyl derivative being considered. The isolation of bis(*p*-hydroxyphenyl)diphenyllead, for example, could not be accomplished without extensive decomposition, even though the existence of the dilithio intermediate was indicated by separate reaction with trimethylchlorosilane to yield the bis(trimethylsilyl) derivative as follows:

$$(C_6H_5)_2Pb(C_6H_4OLi)_2 + 2\,(CH_3)_3SiCl \rightarrow (C_6H_5)_2Pb[C_6H_4OSi(CH_3)_3]_2 + 2\ LiCl$$

Finally, in an extension of earlier published work in which we reported on the reactions of organotin oxides and sulfides with organolithium compounds[12], we now report analogous reactions between diphenyltin oxide and diphenyllead oxide with lithium lithiophenoxide as follows:

$$2\,n\mathrm{LiOC_6H_4Li} + (\mathrm{Ph_2MO})_n \rightarrow n(\mathrm{C_6H_5})_2\mathrm{M}(\mathrm{C_6H_4OLi})_2 + \mathrm{Li_2O}$$
$$\mathrm{M = Sn,\ Pb}$$

Properties of bis(p-hydroxyphenyl) Group IVb compounds

The bis(*p*-hydroxyphenyl) organometallic derivatives reported in the paper are white crystalline substances which can be recrystallized from benzene or toluene. They are readily soluble in alcohol, acetone and other polar solvents. The dimethyl derivatives are less stable than the diphenyl derivatives. Bis(*p*-hydroxyphenyl)-dimethylsilane decomposes slowly on standing at room temperature. A strong phenolic odor develops within a few days from the odorless compound and eventually one can observe the formation of crystals of phenol in the vial. The dimethyl tin derivative decomposes at room temperature within minutes. The soluble white decomposition product sinters, turns reddish and becomes insoluble in organic solvents. The thermal rearrangement of silylphenols has been observed and discussed[3]. The rearrangement can be slowed down by keeping the compounds under refrigeration. The melting points of these bisphenols appear to be heat-rate dependent.

The IR spectra of the dimethyl derivatives are very similar to the IR spectrum of bisphenol[13] but show in addition, the characteristic absorption bands of Group IV metal–phenyl moieties (1050–1110 cm^{-1}) and some of the frequencies which can be assigned to Group IV metal–methyl vibrations[14]. The NMR spectra of the bis(*p*-hydroxyphenyl)dimethyl Group IV metal derivatives as well as bis(*p*-benzyloxphenyl) derivatives are in agreement with the assigned structures.

EXPERIMENTAL

All exchange reactions were carried out under argon and anhydrous conditions. Tetrahydrofuran was dried over lithium aluminum hydride and distilled under argon. All chemicals, with the exception of *p*-bromophenyl benzyl ether, are commercially available and were purified by established methods. The preparation of *p*-bromophenyl benzyl ether is described under Section C. IR spectra were obtained with a Perkin–Elmer 137 spectrophotometer and NMR data on a Varian A-60 Spectrometer. Molecular weights were determined with a Mechrolab vapor pressure Osmometer Model 301-A. Melting points (uncorrected) were obtained on a Thomas Hoover melting point apparatus.

A. General

1. *Preparation and reactions of lithium lithiophenoxide.* A solution of 500 ml of 1.5 *N* n-butyllithium in hexane (0.75 mole) was placed in 2 l, 3-neck flask, equipped with a gas-inlet (for argon), thermometer, mechanical stirrer and dropping funnel,

and cooled to −70°. A solution of 56.3 g *p*-bromophenol (0.375 mole) in 900 ml tetrahydrofuran was then added slowly at such a rate that the temperature of the reaction mixture did not rise above −50°. The temperature was allowed to rise to +5°. At about −30°, the originally clear solution became turbid and between −20° and −10° a thick white gel formed. Stirring was continued for 30 min at a somewhat higher rate to loosen the thick gel. The mixture was then cooled again to −50° and a solution of 0.1 mole of the respective organometallic dihalide dissolved in 100 ml tetrahydrofuran (approximately 65% of the theoretical amount of halide) was added within 5 min and the temperature was allowed to rise slowly to +10°. The occurrence of a deep lemon yellow color at about −10° was sometimes observed, which disappeared within a few minutes. The thick gel dissolved during the addition and a clear solution remained when dimethyldihalides of silicon, germanium and tin were added. During the addition of the diphenylmetal dihalides the occasional formation of a crystalline precipitate occurred. This precipitate was isolated during the preparation of bis(*p*-hydroxyphenyl)diphenyltin and identified as the dilithium intermediate. It represented in this case about 70% of the total yield of this bisphenol.

B. Isolation of bisphenol derivatives

As a general rule it can be stated that the tin and lead derivatives should be worked up without delay whereas the work up time of the silicon and germanium containing bisphenols is not critical.

1. *Bis(p-hydroxyphenyl)dimethylsilane.* The reaction mixture prepared as described above, can be either hydrolyzed with aqueous hydrochloric acid or treated with gaseous hydrogen chloride. An endpoint (salmon→yellow) is easily recognizable. The solvents (hexane and tetrahydrofuran) are then removed by distillation under vacuum and the residue dissolved in diethyl ether, washed with distilled water (three times), dried with anhydrous magnesium sulfate, and filtered. The clear solution, which should be only slightly colored, is again evaporated until a viscous clear residue remains in the flask. During this operation the temperature of the water or oil bath should not be allowed to rise above 40°. It is important to remove the solvent as completely as possible. The residue is then stirred for approximately 10 min with dry pentane or hexane and the solvent is decanted. The procedure is repeated. The remaining oil will frequently solidify at this point. The extractions serve to remove the coupling product (*p*-butylphenol) from the mixture. The solid is filtered, washed with hexane and air-dried for about 1 h before recrystallization from toluene or benzene. Crude yields are between 85–90% and 70–80% after one recrystallization.

2. *Bis(p-hydroxyphenyl)dimethylgermane.* The germanium derivative was isolated in the same manner as described under 1. above. The yields were similar.

3. *Bis(p-hydroxyphenyl)diphenylsilane and -germane.* Both compounds are prepared and isolated as under 1. above. Yields of 60–70% were obtained using diphenyldifluorosilane. The first reaction with diphenyldichlorosilane produced only 44% yield. The diphenylgermanium derivative was isolated in 55% yield from the dichloride. This latter experiment was carried out on a considerably smaller scale (0.050 mole *p*-bromophenol instead of 0.375 mole).

4. *Bis(p-hydroxyphenyl)dimethyltin and bis(p-hydroxyphenyl)diphenyltin.* Careful timekeeping is essential in the synthesis of the tin derivatives. The reaction can be carried out within 8 h. At this point the isolated crude solid can be stored, in a freezer

and recrystallized the next day. Very intense color changes were observed during the addition of the dihalides. In the case of diphenyltin dichloride the formation of a crystalline product was observed at about −10° (see general procedure A). The mixture is hydrolyzed immediately after reaching +10° with a saturated ammonium chloride solution and worked up in the same manner as described under B.1, with the exception of the evaporation temperature, which was never allowed to exceed +30°. The bis(*p*-hydroxyphenyl)diphenyltin was recrystallized from benzene. The yield was 80%.

The dimethyltin analog is very unstable. Recrystallization from warm benzene can be accomplished but with considerable losses in yield. This compound was analyzed immediately after preparation.

5. *Bis[p-(trimethylsiloxy)phenyl]diphenyllead.* Solid diphenyllead dichloride (21.4 g) was added to the lithium lithiophenoxide tetrahydrofuran mixture at −50° and allowed to come to 0° at which temperature 22 g trimethylchlorosilane (0.2 mole) was added while stirring. The solution became clear and after about 10 min a white precipitate formed. After stirring the mixture for 1 h the solvent was removed under vacuum and the residue treated with dry hexane. The lithium chloride was filtered and the hexane solution treated with carbon black, filtered and vacuum evaporated. A white solid remained in the flask which was extracted with cold, dry methanol, filtered and dried. Crude yield 27 g; 78%; m.p. 102–104°. A portion of the solid was dissolved in hexane, crystallized and filtered at −20°; m.p. 104–106°. The compound is soluble in chloroform, carbon tetrachloride, benzene and hexane but not in methanol or ethanol.

C. Bis(p-benzyloxyphenyl)derivatives

1. *Preparation of p-bromophenyl benzyl ether.* In a 2 l three neck flask fitted with stirrer and reflux condenser, one mole (23 g) sodium was dissolved in 500 ml absolute ethanol. One mole (173 g) *p*-bromophenol dissolved in 150 ml absolute ethanol was added followed by the addition of 144 g benzyl chloride over a period of half an hour. The reaction mixture was refluxed for 3 h, brought to room temperature and poured into ice-water. The resulting precipitate was filtered, washed with dilute ethanol and recrystallized from 600 ml hot ethanol. The yield of pure *p*-bromophenyl benzyl ether was 229 g (87%).

2. *Preparation of the Grignard reagent from p-bromophenyl benzyl ether.* Magnesium turnings (0.25 mole) were placed in a 250 ml round bottom three neck flask, equipped with reflux condensor, drying tube, magnetic stirrer and dropping funnel. The *p*-bromophenyl benzyl ether (0.20 mole) was dissolved in 150 ml anhydrous tetrahydrofuran. A small quantity of this solution was added to the magnesium turnings. The reaction was then initiated with 0.4 ml ethylene chloride and a short period of heating, after which the reflux was controlled by the addition of the bromide solution. Following the addition the Grignard solution was stirred at room temperature for 2 h. The solution was then filtered through glass wool into a 500 ml three neck flask equipped in the same fashion as described above.

3. *Addition of organometallic dihalides.* The dihalides (0.1 mole) were dissolved in 50 ml tetrahydrofuran and added to the Grignard solution. Dimethyl- and diphenyllead dichloride were added as solids. The reaction of the halides of germanium, tin and lead were exothermic. In the case of tin and lead the reflux was controlled through

the rate of addition, the germanium halides required external heating and the silicon halides were added to the refluxing Grignard solution. In order to obtain reasonable yields from diphenyldichloro- or difluorosilane it was necessary to use cuprous chloride as a catalyst. With the difluorosilane a yield of 43% bis(*p*-benzyloxyphenyl)-diphenylsilane was obtained after 4.5 h of reflux whereas the dichlorosilane yielded 52% of the compound after refluxing the mixture for 20 h.

The reaction mixtures were hydrolyzed with concentrated ammonium-chloride solution (about 100 ml). The aqueous layer was three times extracted with small portions of methylene chloride. The combined organic portions were dried with anhydrous magnesium sulfate, filtered and evaporated in vacuum. The bis(*p*-benzyloxyphenyl) derivatives were isolated from these residues as follows:

D. Workup and isolation of the individual bis(p-benzyloxyphenyl)derivatives

1. *Bis(p-benzyloxyphenyl)dimethylsilane.* The residue was redissolved in benzene, treated with carbon black, filtered, evaporated and then recrystallized once from ethanol and twice from ligroin.

2. *Bis(p-benzyloxyphenyl)diphenylsilane.* The purification procedure is the same as under 1. above. The material was crystallized from a methylene chloride/ligroin mixture followed by a crystallization from n-butanol.

3. *Bis(p-benzyloxyphenyl)dimethylgermane.* The reaction mixture was heated for 1 h to reflux after the addition of the halide to the Grignard solution. Purification and crystallization was conducted in a similar manner as described under 1. above.

4. *Bis(p-benzyloxyphenyl)diphenylgermane.* The reaction mixture was refluxed for 2 h after the addition of the halide. Purification and crystallization were difficult and caused the losses which account for the low yield (17%). The benzene solution of the viscous residue was filtered through a neutral alumina column. The material was finally crystallized from an ethanol/methylene chloride mixture. No attempt was made to obtain optimum yields.

5. *Bis(p-benzyloxyphenyl)dimethyltin.* The reaction mixture was stirred at room temperature for 2 h. The crude material was crystallized from boiling ethanol and recrystallized from ligroin.

6. *Bis(p-benzyloxyphenyl)diphenyltin.* The crude product was crystallized twice from n-butanol.

7. *Bis(p-benzyloxyphenyl)dimethyllead.* The crude material was crystallized first from n-butanol and then from an n-butanol/methanol mixture. The crystals were washed with cold methanol and dried. The difficult isolation and crystallization are the main reasons for the low yield (5%).

8. *Bis(p-benzyloxyphenyl)diphenyllead.* The crude product was crystallized twice from n-butanol and washed with methanol before drying.

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REFERENCES

1 H. Gilman and C. E. Arntzen, *J. Org. Chem.*, 15 (1950) 994.
2 H. Gilman and L. A. Gist, Jr., *J. Org. Chem.*, 22 (1957) 368.
3 J. L. Speier, *J. Amer. Chem. Soc.*, 74 (1952) 1003.
4 H. Raubach and A. Wende, *Germ. Pat.* 1,157,612, November 21, 1963.
5 K. C. Frisch and P. D. Shroff, *J. Amer. Chem. Soc.*, 75 (1953) 1249.
6 R. G. Neville, *J. Org. Chem.*, 25 (1960) 1063.
7 R. G. Neville, *J. Org. Chem.*, 26 (1961) 3031.
8 H. Gilman and C. E. Arntzen, *J. Amer. Chem. Soc.*, 69 (1947) 1537.
9 R. G. Jones and H. Gilman, *Organic Reactions*, Vol. VI, p. 339–366.
10 H. Gilman and R. W. Leeper, *J. Org. Chem.*, 16 (1951) 466.
11 H. Gilman, C. Arntzen and F. Webb, *J. Org. Chem.*, 10 (1945) 374.
12 H. F. Reiff, B. R. LaLiberte, W. E. Davidsohn and M. C. Henry, *J. Organometal. Chem.*, 15 (1968) 247.
13 M. Hacskaylo, *Anal. Chem.*, 26 (1954) 1410.
14 Minoru Tsutsui (Ed.), *Characterization of Organometallic Compounds*, Part I. Interscience, New York, 1969, p. 75.
15 K. Oita and H. Gilman, *J. Amer. Chem. Soc.*, 79 (1957) 339.
16 P. Moehs and W. Davidsohn, *J. Organometal. Chem.*, 20 (1969) 57.