1955

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Recommended Citation

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DIRECT PREPARATION OF SOME ORGANOLITHIUM COMPOUNDS FROM LITHIUM AND RX COMPOUNDS

by

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A Dissertation Submitted to the
Graduate Faculty in Partial Fulfillment of
The Requirements for the Degree of
DOCTOR OF PHILOSOPHY

Major Subject: Organic Chemistry

Approved:

Signature was redacted for privacy.

In Charge of Major Work

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Signature was redacted for privacy.

Dean of Graduate College

Iowa State College

1955

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INTRODUCTION

The importance of organolithium compounds has been so aptly demonstrated in the past two decades they have attained a status almost comparable to that of Grignard reagents. As a general rule, all reactions that can be carried out with Grignard reagents may also be accomplished with organolithium compounds, with yields being better in some cases and poorer in others. In addition, because of their greater reactivity, organolithium compounds can undergo reactions very rarely or never observed with Grignard reagents.

The general utility of organolithium compounds is obvious from the following types of reactions that they can undergo:

1. General reactions of Grignard reagents
2. Metalation reactions
3. Halogen-metal interconversion reactions
4. Addition to multiple bonds in many cyclic and open-chained molecules
5. Metal-metal interconversion reactions
6. Cleavage reactions other than the interconversion reactions
7. Coupling reactions with many organic halides.

The diverse types of reactions listed above are also the reason for the importance of utilizing proper experimental conditions and reagents because they may also be possible side reactions in experiments involving organolithium compounds.

Of all the methods for preparing organolithium compounds the three most important are direct reaction between lithium and the corresponding halides, halogen-metal interconversion and metalation. The last two methods have been adequately studied and reviewed but the first has not received as much attention.

In the Historical part, literature concerned with direct preparations of organolithium compounds from lithium and the corresponding halides has been reviewed thoroughly through 1953 and as well as possible through September 1954. Various factors influencing yields of organolithium compounds have been discussed and when possible correlations have been made.

In the investigations described in this dissertation many reagents of types and forms not readily available to earlier workers have been utilized for direct preparations of organolithium compounds. Many of the factors influencing yields have been reinvestigated. Organolithium intermediates have been involved either directly or indirectly in the syntheses of most of the organic and organometalloidal compounds prepared in the course of the work embodied in the Experimental part.

HISTORICAL

The isolation of naphthalene from the hydrolysis of the reaction mixture obtained from the interaction of lithium and 1-bromonaphthalene[1] was the first evidence for the existence of an organolithium compound. More extensive work on similar reactions was reported in 1910[2] but a direct evidence for the existence of an organolithium compound was not available until Schlenk and Holtz[3] prepared ethyllithium from the reaction between diethylmercury and lithium in benzene and in petroleum ether (b.p. 65°). The method was quite general but it had the disadvantage of being inconvenient for large scale preparations and required the use of toxic organomercury compounds.

The first practical method for the preparation of organolithium compounds for use as intermediates in organic syntheses was reported by Ziegler and Colonius[4], who prepared some simple alkyl- and aryllithium compounds from the direct

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[1] J. F. Spencer and M. L. Wallace, J. Chem. Soc., 93, 1827 (1908).

[2] J. F. Spencer and G. M. Price, ibid., 97, 385 (1910).

[3] W. Schlenk and J. Holtz, Ber., 50, 271 (1917).

[4] K. Ziegler and H. Colonius, Ann., 479, 135 (1930).

reaction of lithium and corresponding halides in a Schlenk tube.[5] However, the use of a Schlenk tube limited the method to relatively small scale preparations. When Gilman and co-workers[6] demonstrated that the conventional apparatus used for Grignard reactions could be used for the direct preparation of organolithium compounds, the last important barrier to their use in organic syntheses was removed.

In reviewing the literature on the preparation of organolithium compounds, the comparison, evaluation and correlation of factors influencing yields are complicated by the use of different experimental conditions and reagents of different purity and form. These compounds were generally prepared as intermediates; therefore, the experimental conditions used and the changes made in subsequent runs were those which seemed to promise maximum yields. The variables involved were generally not changed one at a time.

Analysis for Organolithium Compounds

In organic syntheses when working with an intermediate which is not isolated as such, it is generally convenient and frequently imperative to have both a qualitative test

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[5] W. Schlenk and A. Thal, <u>Ber.</u>, <u>46</u>, 2843 (1913).

[6] H. Gilman, E. A. Zoellner and W. M. Selby, <u>J. Am. Chem. Soc.</u>, <u>54</u>, 1957 (1932).

for determining the presence of the intermediate and a quantitative method to determine the amount present, so that an appropriate amount of it may be used for subsequent reactions.

Qualitative

Two necessary attributes for a good qualitative test are sensitivity and speed. These requirements are met by qualitative tests for organometallic compounds known as Color Test I,[7] Color Test II,[8] Color Test III[9] and Color Test IV.[10]

Color Test I. In this test a 1 ml. sample of a solution containing an organometallic compound is first added to an equal volume of a 1% solution of Michler's ketone (p,p'-tetramethyldiaminobenzophenone) in anhydrous benzene. The resulting lithium alkoxide is hydrolyzed with water and then oxidized with a 0.2% solution of iodine in glacial

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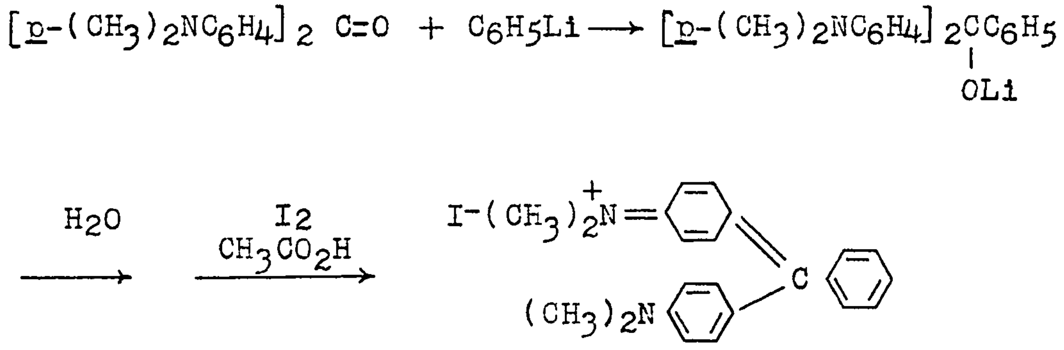
[7] H. Gilman and F. Schulze, ibid., 47, 2002 (1925).

[8] H. Gilman and J. Swiss, ibid., 62, 1847 (1940).

[9] H. Gilman and H. L. Yablunky, ibid., 63, 839 (1941).

[10] H. Gilman and L. A. Woods, ibid., 65, 33 (1943).

acetic acid. The appearance of a greenish-blue dye, malachite green, is the positive test.



$$[\underline{p}\text{-}(CH_3)_2NC_6H_4]_2\,C{=}O + C_6H_5Li \longrightarrow [\underline{p}\text{-}(CH_3)_2NC_6H_4]_2\underset{\displaystyle OLi}{\overset{}{C}}C_6H_5$$

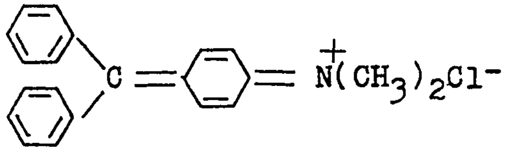
Since the key reaction is the addition of the organometallic compound to the carbonyl group, Grignard reagents, alkali metal and alkaline earth organometallic compounds also give positive test. This is the most sensitive of the 4 color tests.[7]

Color Test II. The most valuable qualitative test used in metalation and halogen-metal interconversion reactions with alkyllithium intermediates is Color Test II. By means of this test alkyllithium compounds may be differentiated from both Grignard reagents and aryllithium compounds since they do not give a positive test.

A 1 ml. sample of a solution containing an alkyllithium compound is added to an equal volume of a 15% solution of p-bromodimethylaniline in anhydrous benzene. Then 1 ml. of a 15% solution of benzophenone is added and after few seconds, the mixture is hydrolyzed with water and acidified with concentrated hydrochloric acid. The appearance of a red color in the aqueous layer indicates the presence of an alkyllithium compound. The differentiating reaction is the halogen-metal interconversion reaction involving the alkyllithium and p-bromodimethylaniline. The intermediate, p-dimethylaminophenyllithium, then adds to benzophenone. The carbinol which is formed upon hydrolysis is then converted to the observed red dye.

$$RLi + \underline{p}\text{-}(CH_3)_2NC_6H_4Br \longrightarrow \underline{p}\text{-}(CH_3)_2NC_6H_4Li + RBr$$

$$\xrightarrow{(C_6H_5)_2C=O} \quad \xrightarrow{HCl}$$



All alkyllithium compounds with the exception of methyllithium and ethynyllithium compounds (like phenylethynyllithium) gave a positive test.[8] Aryllithium compounds undergo halogen-metal interconversion reaction too slowly under the condition of the test to give a positive test.

When alkyllithium compounds are used for metalation of heterocyclic compounds or for halogen-metal interconversion reaction with aryl or heterocyclic bromides, the disappearance of a positive Color Test II indicates the completion of the reaction.

The sensitivity of the test is slightly less than Color Test I. With a 1 ml. sample of n-butyllithium solution the lowest concentration giving the test was between 0.02 and 0.03 molar.[8]

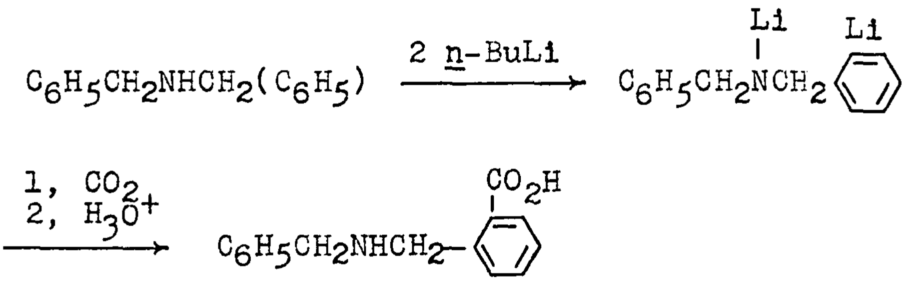
Color Test III. This test can be used to differentiate between reactive arylmetallic compounds (compounds more reactive than diphenylzinc or tri-(p-tolyl)-aluminum) from less reactive aryl- and alkylmetallic compounds.

Approximately 1 ml. of an organometallic solution is added to an equal volume of 1% solution of triphenylbismuth dichloride in anhydrous benzene. With aryllithium and arylmagnesium compounds a deep purple color forms immediately. To detect the presence of other reactive arylmetallic compounds the solution obtained as described is boiled, cooled and then hydrolyzed with 1 ml. of water. The presence of yellow, yellowish-brown or yellowish-orange color in the benzene layer signifies a positive test. When the test is negative no color is obtained before or after hydrolysis. Substantiated explanation for these colors and the reactions involved are not available. The sensitivity of the test is greater than Color Test II and is comparable to Color Test I.

Color Test IV. The test designated as Color Test IV was discovered incidental to the study of water-solubilizing groups in organometallic compounds[10] and can be used to distinguish organolithium compounds from less reactive organometallics such as Grignard reagents. Organometallics that are more reactive than organolithium derivatives also give a positive test.

The test is carried out by adding 1 ml. of an organometallic solution, without shaking, to 0.5 ml. of an approximately 1 molar solution of benzylamine or dibenzylamine in unsaturate-free, dry petroleum ether (b.p. 60-80°). The appearance of a cherry-red color is the positive test. The color may be transient if the organometallic solution is dilute, and the actual shade may depend upon the concentration of the solution.

The actual mechanism of the test is uncertain but the carbonation of the red solution obtained from the reaction of dibenzylamine with *n*-butyllithium gave N-benzyl-α-amino-*o*-toluic acid.[10] The postulated mechanism is as follows:



Color Test IV is particularly valuable because a prompt positive test is obtained with methyllithium. The sensitivity is slightly greater than Color Test II and slightly less than Color Test I.

Test B.[8] The ability of reactive organometallics such as those of lithium, sodium and potassium to metalate triphenylmethane has been utilized for a qualitative test to differentiate between these compounds and less active organometallics such as Grignard reagents. The positive test is an appearance of a yellow color within 2 minutes.

Quantitative

For rapid quantitative estimation of organolithium compounds prepared as intermediates for use in organic syntheses methods most commonly used are simple acid titration,[11] *n*-butyl bromide-dibenzylmercury titration[12] and benzyl chloride or double titration.[13,14]

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[11] H. Gilman, P. D. Wilkinson, W. P. Fishel and C. H. Meyers, *ibid.*, *45*, 150 (1923).

[12] K. Ziegler, F. Crössmann, H. Kleiner and O. Schäfer, *Ann.*, *473*, 1 (1929).

[13] H. Gilman and A. H. Haubein, *J. Am. Chem. Soc.*, *66*, 1515 (1944).

[14] A. H. Haubein, Doctoral Dissertation, Iowa State College, 1942.

Other methods used for a quantitative estimation of Grignard reagents such as gasometric, Volhard, gravimetric and iodometric methods[11] could be modified and used, but they will not be as simple and may not be any more accurate than the first three mentioned.

The yields of products obtained from the reaction of organolithium intermediates with other reagents have also been used for estimating the amount of organolithium compounds that were present. Yields as determined in this manner are minimum yields because some reactions of organolithium derivatives may not be quantitative, and even if they were, the products generally cannot be quantitatively isolated from the reaction mixture. Many different types of compounds have been allowed to react with organolithium compounds,[15] but the most common ones are carbon dioxide, oxygen, ketones and aldehydes. The amount of dehalogenated compounds obtained from the hydrolysis of the reaction mixture containing organolithium compounds does not necessarily represent the quantity of organolithium compounds that were present in the solution. They are often formed

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[15] F. Runge, "Organometallverbindungen", Wissenschaftliche Verlagsgesellschaft, m. b. h., Stuttgart 1944, pp. 137-176.

as by-products in decomposition of organolithium intermediates.[16,17]

Simple acid titration. Aryllithium compounds are generally determined by a simple acid titration because, under the condition of their preparation from lithium and the corresponding halides, practically all the alkalinity present in the solution is due to organolithium compounds. An aliquot sample is hydrolyzed with water and titrated directly with a standard acid using phenolphthalein as an indicator. Back-titration technique is unnecessary.

$$\mathrm{RLi} + \mathrm{HOH} \longrightarrow \mathrm{RH} + \mathrm{LiOH}$$

$$\mathrm{LiOH} + \mathrm{HCl} \longrightarrow \mathrm{HOH} + \mathrm{LiCl}$$

This procedure has the advantage of extreme speed and simplicity but is less accurate than either the double titration or dibenzylmercury-*n*-butyl bromide method because no differentiation is made between alkalinity due to organometallics and alkalinity from other sources. Although lithium hydride and lithium alkoxides may not be formed as by-products in the preparation of aryllithium compounds,

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[16] R. N. Meals, *J. Org. Chem.*, *9*, 211 (1944).

[17] K. Ziegler and H. G. Gellert, *Ann.*, *567*, 179 (1950).

there may be present colloidal lithium particles and lithium hydroxide from the initial lithium oxide coating on the lithium used. Unfortunately, the more accurate double titration and Ziegler's dibenzylmercury-n-butyl bromide methods do not work too well with aryllithium compounds.[12,14]

n-Butyl bromide-dibenzylmercury method. Ziegler's method for quantitative estimation of simple alkyllithium compounds is based upon a metal-metal interconversion reaction between an alkyllithium compound and dibenzylmercury. The benzyllithium which is formed immediately reacts with n-butyl bromide.

$$2\ RLi + (C_6H_5CH_2)_2Hg \longrightarrow R_2Hg + 2\ C_6H_5CH_2Li$$

$$C_6H_5CH_2Li + n\text{-}C_4H_9Br \longrightarrow C_6H_5CH_2\text{-}(\underline{n}\text{-}C_4H_9) + LiBr$$

In carrying out this determination a 1 ml. aliquot is hydrolyzed and titrated to obtain the total alkali. A second ml. aliquot is added to 10 ml. of ether containing about 2 ml. of n-butyl bromide. Dibenzylmercury is added bit by bit to this solution. As long as any alkyllithium compounds is present a yellow color of benzyllithium is noted with each addition. The failure of the yellow color to appear is the endpoint of the addition. The solution is then hydrolyzed and titrated to determine the amount of inorganic alkali that is present. The difference between the two titrations gives the concentration of the organolithium compound.

This method is accurate and can be used for titrating methyllithium which cannot be titrated by the double titration method. However, it is relatively time consuming (20-30 minutes for each titration) and requires the use of relatively expensive dibenzylmercury. Organomercury compounds are also toxic. The method failed with phenylethynyllithium[14] and the yield of 1-naphthyllithium as determined by the yield of 1-naphthoic acid obtained by carbonation was higher than that determined by the titration.[14] When organometallic compounds are colored, the method is unsuitable because the yellow color of benzyllithium may be masked.

Benzyl chloride or double titration. In this titration the reactivity of benzyllithium toward halogen-metal interconversion with alkyllithium compounds and the reactivity of the intermediate benzyllithium toward coupling reaction with alkylchloride and benzyl chloride are utilized.

$$RLi + C_6H_5CH_2Cl \longrightarrow RCl + C_6H_5CH_2Li$$

$$2\ C_6H_5CH_2Li + RCl + C_6H_5CH_2Cl \longrightarrow 2\ LiCl + C_6H_5CH_2CH_2C_6H_5 + C_6H_5CH_2R$$

The actual determination is carried out on two aliquot samples. The first is hydrolyzed with water and titrated for the total alkalinity. The second aliquot is added to 10 ml. of anhydrous ether containing 1 ml. of benzyl chloride. The mixture is allowed to stand at least 1 minute and then hydrolyzed and titrated with standard acid. When alkyllithium compounds were prepared in either petroleum ether or benzene, the addition of alcohol hastened the diffusion of lithium hydroxide from the organic to the aqueous layer and permitted the titration to be carried out rapidly.[18] The difference between the two titrations gives the concentration of the alkyllithium compound.

The main advantage of this procedure over that of Ziegler's is speed although the use of less expensive and non-toxic reagents is also important. The yields as determined by double titration were consistently 2% higher than that obtained by Ziegler's method for some accountable reasons.[14]

The double titration failed with methyllithium as well as with phenylethynyllithium.[14] With 1-naphthyllithium the yield was much lower than that determined by carbonation to

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[18] R. N. Meals, Doctoral Dissertation, Iowa State College, 1942.

1-naphthoic acid, and in this case it was even slightly lower than that obtained by Ziegler's method.

Factors Influencing Yields of Organolithium Compounds

Halides

The reactivity of halides toward lithium and the tendency of some halides toward coupling reaction with organolithium compounds place limitations on the type of organic halides that can be utilized for the preparation of the corresponding lithium compounds by a direct reaction with lithium. As a general rule, the fluorides are too inert toward lithium to be of practical value. The iodides are very reactive toward metallic lithium, but yields are reduced by the great reactivity of alkyl- or aryliodides toward coupling reactions with organolithium compounds present in the same reaction mixture.

The two halides that are almost always used are the chlorides and bromides. Methyl iodide is an exception since it is more convenient to use than either the chloride or the bromide and a comparable yield was obtained.[19,20]

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[19] H. Gilman, E. A. Zoellner and W. M. Selby, J. Am. Chem. Soc., 55, 1252 (1933).

[20] T. D. Perrine and H. Rapoport, Anal. Chem., 20, 635 (1948).

Gilman and co-workers[19] reported that in diethyl ether yields of RLi were in the order RBr > RCl > RI. Ziegler and Colonius[4] reported that the yields obtained were in the order RCl > RBr > RI. This difference is probably due to the fact that Ziegler added the halide all at once, thereby, employing a condition favorable for Wurtz-type coupling while Gilman added the halide over a period of 30-35 minutes. In ether solution the coupling reaction between *n*-butyllithium and *n*-butyl bromide was practically complete after 5 hours but with *n*-butyl chloride the half-life of *n*-butyllithium was about 40 hours.[4] In the case of long-chained alkyl halides in diethyl ether the chlorides gave better yields than the bromides.[16,18]

When petroleum ether or benzene was used as a solvent, the chlorides gave better yields than the bromides.[4,18,21]

Organic radicals

Since yields of organolithium compounds depend upon the stability of the organolithium derivatives themselves as well as on the reactivity of the organic halides toward lithium, proper experimental conditions must be used in their

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[21] H. Gilman, F. W. Moore and O. Baine, *J. Am. Chem. Soc.*, *63*, 2479 (1941).

preparation. This is generally a matter of using the right solvent.

For the preparation of low molecular weight normal alkyllithium compounds, the combination of _n_-alkyl bromide and diethyl ether was the best.[19] For low molecular weight secondary and tertiary alkyllithium compounds the corresponding chlorides in low boiling petroleum ether (b.p. 28-38°) or pentane[21,22] gave the best yields. The highest yields of long-chained normal alkyllithium compounds were obtained from the chlorides in diethyl ether or petroleum ether (b.p. 60-70°). Petroleum ether (b.p. 28-38° or 77-115°), benzene and toluene, respectively, gave poorer results.[16,18] Aryllithium compounds were obtained in highest yields from the reaction of the corresponding bromides in diethyl ether.[4,19,20]

Solvents

The ability of a solvent to facilitate the reaction between alkyl or aryl halide and lithium is a major factor in the choice of a solvent, but it is not the only one. The reactivity of the solvent toward reagents used and products formed in the reaction, the speed at which the reaction

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[22] L. J. Tyler, L. H. Sommer and F. C. Whitmore, _ibid._, _70_, 2877 (1948).

takes place and the subsequent use of the organolithium compound must also be considered.

Diethyl ether generally permits the preparation of organolithium compounds in good yields and may even be used as a catalyst when other solvents are used, but it is not a good solvent for storing alkyllithium compounds. Alkyllithium compounds cleaved diethyl ether and other aliphatic ethers fairly rapidly at room temperature.[13,14] The use of diethyl ether is also not recommended if the solvent is to be removed and replaced with a higher boiling one or baked at relatively high temperature without any solvent. Organolithium compounds form monoetherates which were stable at room temperature and required vacuum distillation or relatively high temperature (sometimes both) in order to remove the ether.[23]

Petroleum ether (b.p. 28-38°) was particularly suitable for the preparation of some organolithium compounds that were to be stored.[24] This solvent was generally better than diethyl ether for the preparation of lithium compounds from the corresponding chlorides and especially from

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[23] B. M. Mikhailov and N. G. Chernova, Doklady Akad. Nauk S. S. S. R., 78, 489 (1951). [C. A., 46, 449 (1952)].

[24] H. Gilman, W. Langham and F. W. Moore, J. Am. Chem. Soc., 62, 2327 (1940).

secondary and tertiary chlorides.[19,24] With long-chained alkyl chlorides the reaction took too long (several days);[16,18] however, the use of petroleum ether (b.p. 60-70°) reduced the time required to several hours and even improved yields.[16,18]

It has been reported[24] that three advantages of petroleum ether over diethyl ether are:

1. Secondary reactions like cleavage, present in diethyl ether, are obviated.
2. Indirect supplementary analysis is not necessary. Simple acid titration is sufficient.
3. By-products like lithium hydride are insoluble in petroleum ether and are removed on filtration.

However, subsequent work indicated that all three of the above statements should be modified. The considerable difference in yields of n-dodecyllithium from n-dodecyl chloride as determined by simple acid titration and double titration indicated that side reactions have occurred and emphasized the necessity of analysis by either Ziegler's or double titration method in order to get the true yield.[16,18] The filtration of the reaction mixture may also result in the loss of some organolithium compounds since they may not all be in solution. Methyllithium and ethyllithium had limited solubility in petroleum ether (b.p. 28-38°).[21]

Aryllithium compounds were also soluble only in moderate concentration.[21]

Benzene, toluene and cyclohexane have also been used when inert, relatively high boiling solvents were needed.[4,16,18] For determining yields of alkyllithium compounds prepared in these solvents double titration gave more accurate results.[18] Thermal stability studies carried out on alkyllithium compounds by Ziegler and Gellert[17] showed that at 100° the decomposition of alkyllithium derivatives into lithium hydride and the corresponding olefin was very extensive. Lithium hydride upon hydrolysis will contribute to the total alkalinity.

Some of the other solvents that have been used for the preparation of organolithium compounds are pentane, dibutyl ether, dioxane, ethylene glycol dimethyl ether and tetrahydrofuran. However, the only solvent which gave a better yield than either diethyl ether or petroleum ether was pentane in the preparation of <u>t</u>-butyllithium from <u>t</u>-butyl chloride.[22,25]

The great reactivity of lithium and organolithium compounds necessitates the use of pure solvents. Sodium is used to make all solvents anhydrous, and in the case of

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[25] L. J. Tyler, Doctoral Dissertation, The Pennsylvania State College, 1948.

ethers it also removes peroxides. With petroleum ether and pentane a thorough treatment with concentrated sulfuric acid has been used to remove any unsaturation.[22,26] Recent work by Talalaeva and Kocheshkov[27] showed that unsaturation may not be too important because pentane was a better solvent for preparing ethyllithium from ethyl bromide and lithium than pentane. Meals[16,18] found that the yield of _n_-dodecyllithium from _n_-dodecyl chloride in unsaturate-free petroleum ether (b.p. 30-35°) was not significantly better than that obtained in undried, unpurified petroleum ether (b.p. 28-38°). Since dodecene was a by-product in the preparation of _n_-dodecyllithium, even if the solvent were initially unsaturate-free it was not so at the end. Morton and co-workers[28] found that in the preparation of the more reactive organometallic compound, amylsodium, there was very little advantage in the use of unsaturate-free petroleum ether (b.p. 35-60°). However, Bartlett[29] showed that isopropyllithium and _t_-butyllithium added readily to ethylene even at -50°. Therefore,

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[26] F. D. Hager, and C. S. Marvel, _J. Am. Chem. Soc._, _48_, 2689 (1926).

[27] T. V. Talalaeva and K. A. Kocheshkov, _Doklady Akad. Nauk S. S. S. R._, _77_, 621 (1951) [_C. A._, _45_, 10191 (1951)].

[28] A. A. Morton, F. Fallwell and L. Palmer, _J. Am. Chem. Soc._, _60_, 1426 (1938).

[29] P. D. Bartlett, S. Friedman and M. Stiles, _ibid._, _75_, 1771 (1953).

for the preparation of secondary and tertiary alkyllithium compounds, unsaturate-free solvents should be used.

Organolithium compounds have been prepared from lithium and organic halides without the use of any solvent. However, yields were generally poor even if all dehalogenated compounds obtained were assumed to have been obtained from the hydrolysis of organolithium intermediates which were actually present.

Forms of lithium

The reaction between lithium and organic halides, being a heterogeneous reaction, the amount of lithium surface available at every instant is very important. The different forms of lithium in the order of decreasing surface area per weight of lithium are lithium dispersion > lithium sand > lithium foil > lithium ribbon > lithium wire > lithium block.

The difference between dispersion and sand is in particle sizes. The dispersion particles range up to 100 microns in diameter as compared to 0.3 to 3.0 mm. for sand or shot particles. For the preparation of either the dispersion or sand, helium has been recommended because lithium reacts with nitrogen at its melting point (185°);[20] however, nitrogen atmosphere has been used in the preparation of lithium sand.[25,30] In actual practice, the mixture of lithium and a high boiling inert solvent (boiling point greater than 250°) was heated until the lithium melted and then stirred in an appropriate manner. For the preparation of the dispersion, a high speed dispersion head was required; for sands a Hershberg stirrer or a vigorous shaking was sufficient.[20,25,28,31] Because of its adaptability toward large scale preparation, the sand is the form preferred by many workers.

Lithium foil has been prepared either by hammering out lithium block or wire[24] or by rolling them into thin sheets with an appropriately designed roller.[25] Mineral oil or toluene was used to coat the lithium during the milling process so as to prevent corrosion of the surface.

The other forms (block, ribbon and wire) are all commercially available. The most commonly used forms are ribbon and wire cut into pieces several millimeters in length.

For the preparation of organolithium compounds from halides as reactive as _n_-butyl bromide or bromobenzene with diethyl ether as the solvent, lithium with a surface greater than that of a wire was unnecessary although better yields

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[30] P. D. Bartlett, C. G. Swain and R. B. Woodward, _ibid._, _63_, 3229 (1941).

[31] R. West and E. G. Rochow, _J. Org. Chem._, _18_, 1739 (1953).

have been reported using lithium sand.[20] The use of relatively high-surface lithium, such as foil or sand, seemed to have been very important in the preparation of alkyldilithium compounds[31] and in the preparation of _t_-butyllithium from _t_-butyl chloride in pentane.[22,25] It can theoretically improve all yields of organolithium compounds prepared in petroleum ether or pentane because coatings, such as lithium halide, lithium oxide and lithium hydride, that form on the lithium surface will have less effect when greater surface area is present.

Concentration of reagents

Very few systematic studies have been made on the effect of the concentration of solvent and lithium on yields.[4,18,32] With aryl bromides the use of 10 or 12 equivalents of diethyl ether rather than 6 for each equivalent of aryl bromide improved the yields.[19] With long-chained alkylhalides in petroleum ether the results were erratic.[18] The use of a greater excess of lithium almost always increased yields of organolithium compounds.[18,32]

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[32] D. S. Tarbell and M. Weiss, _J. Am. Chem. Soc._, _61_, 1203 (1939).

Initiation of reaction

In most preparations of organolithium compounds from the corresponding halides, coupling reactions between organolithium derivatives and halides can be reduced if the halide concentration is at a minimum required to maintain the reaction with lithium. If possible the reaction should be started with a low concentration of the halide, and it should be added only at a rate sufficient to keep the reaction going. For the initiation of sluggish reactions, the use of a catalyst or initiator, relatively high initial temperature, vigorous stirring or high initial concentration of lithium and an organic halide may be employed.

The use of relatively high initial temperature was exemplified in the preparation of _n_-butyllithium from _n_-butyl bromide.[33] The reaction was initiated at room temperature with 30 drops of a solution of 68.5 g. (0.5 mole) of _n_-butyl bromide in 100 ml. of ether. After the reaction had started the dropwise addition of the rest of the solution was carried out at -10°.

Probably the most important factor in the initiation of the reaction is the condition of the lithium surface.

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[33] H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn and L. S. Miller, _ibid._, _71_, 1499 (1949).

The surface which may be coated with lithium oxide or lithium nitride can be cleansed with catalysts or initiators, or it may be cleaned mechanically by means of vigorous stirring. In the preparation of alkyllithium compounds in petroleum ether (b.p. 28-38°), the reaction mixture containing lithium pieces and the solvent was vigorously stirred at a gentle reflux before the addition of an alkyl halide solution.[21] This cleansed the surface, purified the solvent and furnished the necessary initial high temperature in one operation.

For initiation of some reactions a relatively high initial concentration of lithium and organic halides was required. This was accomplished with a very small amount of halide by adding several milliliters of a concentrated halide solution to the reaction flask containing the lithium in a small amount of solvent.[34] After the reaction had started the halide solution was diluted with more solvent and the addition was completed in the usual manner.

Catalysts or initiators are ordinarily used in the preparation of organolithium compounds when the reaction between the halide and lithium does not start readily. Initiators such as reactive organohalides (methyl iodide,[35]

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[34] H. L. Merten, unpublished studies.

[35] K. Ziegler and H. Colonius, German Patent 512,822 (Oct. 15, 1929) [C. A., 25, 2154 (1931)].

n-butyl bromide[18] and n-dodecyl iodide[18]) and iodine[18] react readily with lithium; thereby, exposing a very reactive surface for subsequent reactions with less reactive halides. The addition of a small amount of ether when petroleum ether is used may possibly catalyze the reaction by dissolving some of the lithium oxide coating on the surface. However, the reason for the initiating effect of tetrahydrofuran is not clear[36]. This is also true of the catalytic effect of a small amount of the organolithium compound to be prepared such as methyllithium,[37] phenyllithium[37] and n-dodecyllithium.[18]

Recently Thiec[38] added 0.2 mole of bromobenzene for each mole of 1-bromo-2,4,6-triisopropylbenzene employed and obtained a 58-76% yield of organolithium compound from the reaction with lithium. The carbonation of the reaction mixture gave no benzoic acid, only 2,4,6-triisopropylbenzoic acid (87% yield based upon the titration value and 43% based upon 1-bromo-2,4,6-triisopropylbenzene). The result indicated that the alkalinity was just due to 2,4,6-triisopropyllithium; therefore, the overall reaction probably proceeded

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[36] C. W. Gerow, unpublished studies.

[37] F. B. Kipping and F. Wild, J. Chem. Soc., 1239 (1940).

[38] J. Thiec, Ann. Chim., 9, 51 (1954).

in two steps. First the lithium reacted with bromobenzene to give phenyllithium. Phenyllithium then reacted with 1-bromo-2,4,6-triisopropylbenzene to regenerate bromobenzene and give 2,4,6-triisopropylphenyllithium.

$$C_6H_5Br + 2\ Li \longrightarrow C_6H_5Li + LiBr$$

$$C_6H_5Li + 2,4,6\text{-}(C_3H_9)_3C_6H_2Br \longrightarrow C_6H_5Br + 2,4,6\text{-}(C_3H_7)_3C_6H_2Li$$

For the preparation of bornyllithium from bornylchloride, n-butyl chloride was used in a similar manner.[38] The yield of bornyllithium ranged from 65-75%.

The rate of addition of the halide solution

The rate of addition of the halide solution has a great influence on yields of organometallic compounds. When the addition was too rapid, yields fell.[19] Coupling reactions may occur when an appreciable concentration of organolithium compounds and organic halides are present in the same solution. Generally the addition should be at a rate such that the organic halide reacts with lithium almost as fast as it is added; thereby, keeping the concentration of the halide in the reaction mixture low. The actual time required for the addition will vary according to the reactivity of the halide being added. The iodides are more reactive than the bromides which in turn are more reactive than the chlorides.[19,39]

In actual practice the rate of addition has been controlled by adding the halide solution at a rate sufficient to maintain a gentle reflux.[19,21] When the addition was made below the reflux temperature of the solvent, the temperature of the cooling bath was kept below that of the reaction mixture, and the addition was made at a rate such that the reaction between the lithium and the halide kept the temperature of the reaction mixture about 30° above that of the cooling bath.[33]

A rate of addition that is too slow may also decrease yields. In the preparation of phenyllithium from bromobenzene the regulation of the rate of addition so that it was sufficient to maintain a gentle reflux was emphasized.[40] When the addition rate is too slow the reaction between an organic halide and lithium may slow down or even stop. If the reaction stops, the concentration of the halide will rise and the condition would be favorable for the Wurtz- or

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[39] H. Gilman, E. A. Zoellner, J. B. Dickey and W. M. Selby, J. Am. Chem. Soc., 57, 1061 (1935).

[40] R. G. Jones and H. Gilman in R. Adams, "Organic Reactions", John Wiley and Sons, Inc., New York, N. Y. 1951, Vol. 6, p. 354.

Fittig-type coupling reaction. If the halide concentration becomes large, a vigorous uncontrollable reaction may occur when the reaction begins again.

The addition of the halide all at once at the beginning almost always resulted in lower yields.[19] When p-bromobiphenyl was added to lithium in diethyl ether an 86% yield of quaterphenyl was obtained.[41]

Some halides give organolithium compounds that are so unstable the halide and the reactant for the organolithium compound being prepared is added at the same time.[42] West and Rochow[31] recently prepared bis-(trimethylsilyl)-methane from a mixture of lithium, dibromomethane and trimethylchlorosilane.

Temperature

In studying the effect of temperature on yields the comparison should be made with one particular halide in one particular solvent in order to obviate the influence of

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[41] E. Müller and T. Töpel, Ber., 72, 273 (1939).

[42] This technique is known as the Barbier Technique after the procedure of P. Barbier, Compt. rend., 128, 110 (1899), who first used magnesium in synthetic organic chemistry by obtaining dimethylheptanol from the reaction of a mixture of methylheptanone, methyl iodide and magnesium in ether.

other factors that may be important. The yields of n-butyllithium from n-butyl bromide at 35, 0, -5 and -10° were 68.8, 77.3, 82.9 and 85.4%, respectively.[19,32]

If differences in yields of organolithium compounds prepared in petroleum ether of different boiling ranges can be attributed to temperature effect alone then the following relations between temperature and organolithium compounds can be made:

1. Temperature of 28-38° (Skelly A) is the best for preparing low molecular weight alkyllithium compounds (5 carbons or less).[21]
2. Temperature ranging from 60-70° (Skelly B) gives best yields of long-chained alkyllithium compounds (12 carbons or more). The reaction time is also considerably shortened.[16,18]
3. Temperature of 77-115° (Skelly D) is too high for the preparation of alkyllithium compounds.[18,21]

Side reactions

The two most common side reactions experienced in the preparation of organolithium derivatives are Wurtz-type coupling reactions and ether-cleavage reactions. Two other reactions that may occur in the preparation of some organolithium compounds are metalation and addition reactions.

Aliphatic iodides, except for methyl iodide, could not be used satisfactorily in the direct preparation of organolithium compounds because of their great tendency toward coupling reactions.[4] The addition of all the halide at the beginning of the reaction also ran into the same difficulty.[41] In some cases (2,2'-binaphthyl from 2-bromonaphthalene[43] and quaterphenyl from *p*-bromobiphenyl[41]) the only products obtained in significant amount were coupling products.

The ether-cleaving ability of organolithium compounds frequently limits the solvent that may be used in the preparation and storage of some organolithium derivatives. The half-lives of *n*-alkyllithium compounds (less than 5 carbons) in diethyl ether at 25° were in the order of 50-60 hours.[14,44] An 83.7% yield of *n*-butyllithium fell to 82.5% after storing 3.5 days at 10°.[33] The ether-cleavage rate of secondary and tertiary alkyllithium compounds was much more rapid.[14,44] The half-life of *sec*-butyllithium in diethyl ether at 25° was 30 minutes. Isopropyllithium and *tert*-butyllithium

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[43] V. Vesely and F. Storsa, *Collection trav. chim. tchecoslov.*, *4*, 139 (1932).

[44] H. Gilman, A. H. Haubein and H. Hartzfeld, *J. Org. Chem.*, *19*, 1034 (1954).

decomposed diethyl ether very readily at 0°.[29] The relative stability of aryllithium compounds in diethyl ether is much greater than that for alkyllithium compounds and is the main reason why a simple acid titration is sufficient in determining their yields. A typical example is phenyllithium which had a half-life of 11 days in diethyl ether at 35°.[14,44]

The rate of decomposition of organolithium compounds also varied with different ethers. The decomposition of n-butyllithium in dimethyl ether was 10-20 times faster than in diethyl ether[45]. The half-lives of n-butyllithium in ethyl, n-butyl, n-hexyl, n-dodecyl and isopropyl ether were approximately 60 hours, 1 month, 2 months, 36 hours and 18 days respectively.[14,44]

The decomposition of n-butyllithium also occurred rapidly in ethers such as dioxane, ethylene glycol dimethyl ether and N-methylmorpholine.[14,44]

Metalation has occurred as a side reaction in the preparation of lithium derivatives of aryl ethers.[46] In the reaction between p-bromoanisole and lithium followed by carbonation a 12% yield of p-methoxybenzoic acid and a 5.2% yield of 5-bromo-2-methoxybenzoic acid were obtained.

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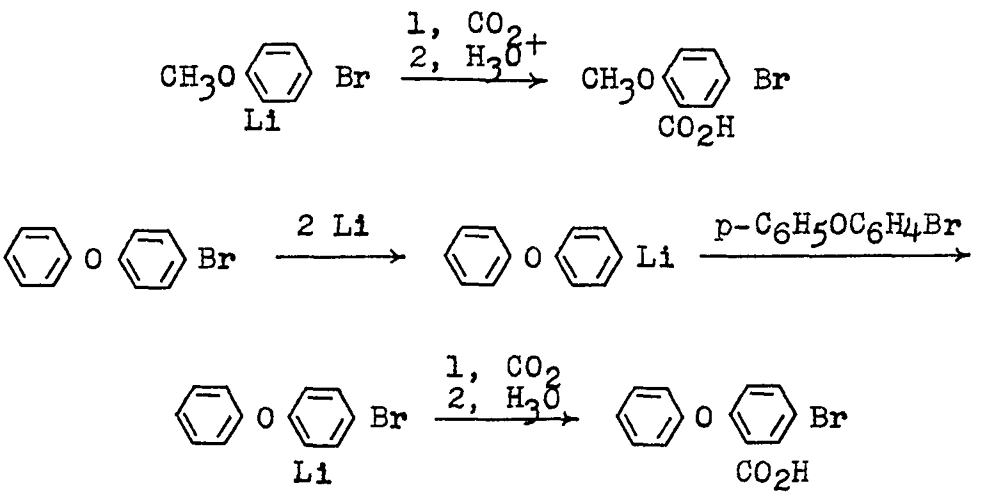
[45] K. Ziegler and H. G. Gellert, Ann., 567, 185 (1950).

[46] H. Gilman, W. Langham and A. L. Jacoby, J. Am. Chem. Soc., 61, 106 (1939).

From p-bromodiphenyl ether a 20% yield of 5-bromo-2-phenoxybenzoic acid and no p-phenoxybenzoic acid was isolated. The metalating agent undoubtedly was the expected organolithium compound which metalated the original aryl ether in the position ortho to the hetero atom in the following manner.

$$p\text{-}CH_3OC_6H_4Br \xrightarrow{2\ Li} p\text{-}CH_3OC_6H_4Li \xrightarrow{p\text{-}CH_3OC_6H_4Br}$$



The position ortho to the hetero atom has been shown to be highly activated toward metalation;[47] therefore, this type of auto-metalation must always be expected in the reaction of halogenated diaryl and alkylaryl ethers with lithium.

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[47] W. Langham, R. Q. Brewster and H. Gilman, ibid., 63, 545 (1941).

Yields of 9-anthryllithium and 9-phenanthryllithium from 9-bromoanthracene and 9-bromophenanthrene, respectively, were very poor because of their great tendency toward the formation of dilithium addition products.[41] In each case the intermediate, organolithium compound, cleaved ether very rapidly and was transformed into the parent hydrocarbon. The hydrocarbon then added 2 atoms of lithium to form the dilithium adduct.

Apparatus

Applications of organolithium compounds in organic syntheses were limited when reactions between organic halides and lithium were carried out in sealed tubes[1] or Schlenk tubes[5]. It was only after the work of Gilman and co-workers[6] demonstrated that organolithium compounds could be prepared in the type of apparatus used in Grignard reactions that the use of organolithium intermediates became practical.

A typical set-up for preparing organolithium compounds at reflux temperature of the solvent consists of a 3-necked, round-bottomed flask equipped with an addition funnel, reflux condenser and a mercury-sealed or Trubore stirrer. Both the reflux condenser and the addition funnel should be opened to an inert atmosphere. When the reaction is carried out at low temperature, a 4-necked flask is recommended, since in addition to the above equipment, a thermometer may be inserted into the reaction mixture. For a new reaction a reflux condenser is also recommended for better control of a possible vigorous reaction. Some of the types of stirring blades that have been employed are steel blades with knife edges,[19] Hershberg type and paddle blades.[48]

Various refinements have been made to overcome the necessity of preparing an organolithium compound in one set-up then transferring to another one for further reaction. Adams and co-workers[49] have devised an apparatus consisting of one flask above another and connected by means of a stopcock. An organolithium compound was prepared in the upper flask then transferred to the lower one where another reaction was carried out.

Perrine and Rapoport[20] used a very elegant assembly in which the preparation of the lithium sand and the subsequent reaction with an organic halide for the preparation of the corresponding organolithium derivative were carried out in the same flask. The essential part of the apparatus was a hollow-shaft stirrer with a sintered-glass filter at the

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[48] Workers in This Laboratory.

[49] R. Adams, H. Wolff, C. K. Cain and J. H. Clark, J. Am. Chem. Soc., 62, 1770 (1940).

bottom. The upper part of the stirrer shaft was adapted so that gas or liquid could be introduced or withdrawn through the sintered-glass filter. In an actual operation an inert gas was introduced through the stirrer shaft during the reaction. To remove the solvent used in the preparation of the lithium sand, an inert gas was introduced through one of the other necks of the 3-necked flask and the liquid was forced out through the shaft.

Inert atmosphere

The great reactivity of metallic lithium and organolithium compounds toward oxygen and water necessitates the use of an inert atmosphere in the preparation of organolithium compounds. Nitrogen is the most commonly used inert atmosphere, but helium[20] has been recommended for working with lithium sand and dispersion. The use of an atmosphere of solvent vapor has also been reported.[26]

Commercially available nitrogen is usually purified by passing it through an oxygen and a moixture removing train. Moisture may be removed by suitable dehydrating agents such as calcium chloride, phosphorus pentoxide, anhydrous silica gel and concentrated sulfuric acid. A suitable modification of many analytical procedures for determining oxygen in a gas may be used to remove oxygen. Most commonly used reagents are alkaline pyrogallol[50], vanadyl(IV) sulfate-amalgamated zinc[51] and alkaline sodium anthraquinone-β-sulfonate-amalgamated zinc.[52] The alkaline pyrogallol is the poorest of the three because it is effective for a relatively short period of time and its effectiveness cannot be determined by the appearance of the solution.

In the vanadyl(IV) sulfate method the amalgamated zinc reduces the vanadyl(IV) ions to vanadium(II) ions. Vanadium(II) ions are oxidized by oxygen in the nitrogen back to the vanadyl form. When the solution is effective, the color of the solution is purplish. When the color becomes brownish, the solution must be regenerated by the addition of sulfuric acid.

The amalgamated zinc in the sodium anthraquinone-β-sulfonate method serves a similar purpose. The sodium anthraquinone-β-sulfonate is reduced to a red form which can be oxidized by oxygen in the nitrogen to the colorless, oxidized form. As long as the solution is red, it can function as an oxygen "getter". Since there is a large

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[50] R. P. Anderson, J. Ind. Eng. Chem., 7, 587 (1915).

[51] L. Meites and T. Meites, Anal. Chem., 20, 984 (1948).

[52] L. J. Brady, ibid., 20, 1033 (1948).

excess of zinc present for reduction in both the vanadyl(IV) sulfate and in the sodium anthraquinone-β-sulfonate method, these solutions are effective for a long time.

Sodium dithionite has also been used in place of amalgamated zinc for reducing sodium anthraquinone-β-sulfonate[53].

Organic Halides Giving Corresponding Lithium Derivatives by Direct Reaction

In Table 1 are included all organic halides from which the corresponding organolithium compounds have been prepared by direct reaction with lithium. The references included are those of interest from a historical point of view, those in which experimental procedures are described in great detail, those in which the experimental procedures are different from that described in other references given and those in which reagents of different purity and form have been used.

The literature has been thoroughly surveyed through 1953. The *J. Am. Chem. Soc.* and *J. Org. Chem.* have been

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[53] L. F. Fieser, *J. Am. Chem. Soc.*, *46*, 2639 (1924).

Table 1

Organic halides giving corresponding lithium derivatives by direct reaction

Compound	Solvent	Yield, %	Ref.
allyl iodide	diethyl ether	trace[a]	37
m-amyl bromide	diethyl ether	81[b]	33
	diethyl ether	60	54
n-amyl chloride	petr. ether (b.p. 28-38°)	90[c]	20
	petr. ether (b.p. 28-38°)	85[c]	21
	petr. ether b.p. 60-70°)	86.8[a]	16
9-benzyl-9-bromomethylfluorene	diethyl ether	1.4[a]	55
bornyl chloride	petr. ether (b.p. 30-45°)	65-75[c]	38
p-bromoacetanilide	no solvent	12[d]	2

[a] Derivatized as an organic compound by a reaction with an organic reagent other than carbon dioxide.

[b] Double titration.

[c] Simple acid titration.

[d] Hydrolyzed to a dehalogenated compound.

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[54] G. Sumrell, J. Org. Chem., 19, 817 (1954).

[55] G. Wittig, P. Davis and G. Koenig, Ber., 84, 627 (1951).

Table 1 (Continued)

Compound	Solvent	Yield, %	Ref.
o-bromoanisole	diethyl ether	87.9[c]	19
	diethyl ether	66[e]	46
p-bromoanisole	diethyl ether	87.9[c]	19
	diethyl ether	12[e]	46
	diethyl ether	trace	56
	diethyl ether	36[f]	41
9-bromoanthracene	diethyl ether	48[d]	57
	diethyl ether	trace[e]	58
10-bromo-1,2-benzanthracene	diethyl ether-benzene	36.4[e]	59

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[e] Carbonated to an acid and/or a ketone.

[f] Oxidized to an alcohol or a phenol.

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[56] G. Wittig, U. Pockels and H. Dröge, *ibid.*, 1903 (1938).

[57] W. E. Bachman and M. C. Kloetzel, *J. Org. Chem.*, *3*, 55 (1938).

[58] M. Mikhailov, *Izvest. Akad. Nauk S. S. S. R. Otdel. Khim Nauk*, 420 (1938) [*C. A.*, *43*, 208 (1949)].

[59] B. M. Mikhailov and T. K. Kosminskaya, *Zhur. Obshei Khim.*, *21*, 1276 (1951) [*C. A.*, *46*, 2039 (1952)].

Table 1 (Continued)

Compound	Solvent	Yield, %	Ref.
bromobenzene	no solvent	--[d]	2
	diethyl ether	75[c]	4
	diethyl ether	97.5[c]	19
	diethyl ether	53[a]	37
	diethyl ether	90[a]	20
	diethyl ether	100[c]	60
_m_-bromobiphenyl	diethyl ether	72[c]	61
_o_-bromobiphenyl	diethyl ether	80[c]	61
	diethyl ether	98.5[c]	60
_p_-bromobiphenyl	diethyl ether	81.5[c]	19
	diethyl ether	87[c]	61
_p_-bromocumene	diethyl ether	57[a]	62
2-bromodibenzofuran	diethyl ether	trace[g]	60

[g] Positive Color Test I.

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[60] This Dissertation.

[61] H. Gilman and G. C. Gainer, _J. Am. Chem. Soc._, _69_, 877 (1947).

[62] R. A. Benkeser and R. G. Severson, _ibid._, _73_, 1424 (1951).

Table 1 (Continued)

Compound	Solvent	Yield, %	Ref.
4-bromodibenzofuran	diethyl ether	58^e	63
p-bromo-N,N-dibutylaniline	diethyl ether	25^a	64
p-bromo-N,N-dimethylaniline	diethyl ether	?	65
	diethyl ether	96.1^c	19
	diethyl ether	80^a	64
	diethyl ether	27^a	66
1-bromo-2,4-dimethylbenzene	diethyl ether	$--^a$	67
1-bromo-2,5-dimethylbenzene	diethyl ether	$--^a$	67
1-bromo-2,6-dimethylbenzene	diethyl ether	$--^a$	67
1-bromo-3,5-dimethylbenzene	diethyl ether	$--^a$	67
1-bromo-4-(2,5-dimethylpyrryl-1)-benzene	diethyl ether	80^e	68

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[63] H. B. Willis, Doctoral Dissertation, Iowa State College, 1943.

[64] L. Hellerman, C. C. Porter, H. J. Lowe and H. F. Koster, J. Am. Chem. Soc., 68, 1890 (1946).

[65] P. R. Austin, ibid., 54, 3726 (1932).

[66] A. C. Cope and A. A. D'Addieco, ibid., 73, 3424 (1951).

[67] A. C. Faber and W. T. Nauta, Rec. trav. chim., 61, 469 (1942).

[68] H. Gilman and G. J. O'Donnell, J. Am. Chem. Soc., 66, 840 (1944).

Table 1 (Continued)

Compound	Solvent	Yield, %	Ref.
bromodurene	diethyl ether	62[a]	69
1-bromo-2-ethoxybenzene	diethyl ether	82.6[c]	19
1-bromo-4-ethoxybenzene	diethyl ether	92.7[c]	19
_m_-bromoethylbenzene	diethyl ether	76[a]	70
_o_-bromoethylbenzene	diethyl ether	55[a]	70
_p_-bromoethylbenzene	diethyl ether	82[a]	70
2-bromo-4-isopropyltoluene	diethyl ether	90[c]	19
bromomesitylene	diethyl ether	82[c]	71
	diethyl ether	96[a]	69
	diethyl ether	90[c]	72
	diethyl ether	100[c]	60
1-bromo-4-methylnaphthalene	diethyl ether	50.2[a]	43
1-bromo-2-methyl-1-propene	diethyl ether	60[e]	73
	diethyl ether	33[a]	73

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[69] R. C. Fuson, G. P. Speranza and R. Gaertner, _J. Org. Chem._, _15_, 1155 (1950).

[70] R. G. Severson and R. J. Rosscup, _J. Am. Chem. Soc._, _76_, 4552 (1954).

[71] H. Gilman and R. D. Nelson, _ibid._, _70_, 3316 (1948).

[72] S. D. Rosenberg, _ibid._, _76_, 4389 (1954).

[73] E. A. Braude and C. J. Timmons, _J. Chem. Soc._, 2000 (1950).

Table 1 (Continued)

Compound	Solvent	Yield, %	Ref.
1-bromonaphthalene	no solvent	40[d]	1
	diethyl ether	96[c]	19
	diethyl ether	82[a]	43
	diethyl ether	28[f]	41
	diethyl ether	96[c]	74
2-bromonaphthalene	diethyl ether	83.1[c]	19
	diethyl ether	96[c]	74
	diethyl ether	100[c]	60
p-bromophenyldimethylarsine	diethyl ether	88[c]	75
p-bromophenyl-*sec*-octyl ether	diethyl ether	90	76
1-bromo-1-propene	diethyl ether	21[e]	77
-bromostyrene	diethyl ether	68[c]	78

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[74] H. Gilman and C. G. Brannen, *J. Am. Chem. Soc.*, *71*, 657 (1949).

[75] L. L. Tolman, Doctoral Dissertation, Iowa State College, 1945.

[76] P. R. Austin, *J. Am. Chem. Soc.*, *55*, 2948 (1933).

[77] E. A. Braude and J. A. Coles, *J. Chem. Soc.*, 2078 (1951).

[78] G. F. Wright, *J. Org. Chem.*, *1*, 457 (1936).

Table 1 (Continued)

Compound	Solvent	Yield, %	Ref.
5-bromo-1,2,3,4-tetrahydronaphthalene	diethyl ether	--[a]	79
	diethyl ether	47[f]	41
_m_-bromotoluene	diethyl ether	93.7[c]	19
	diethyl ether	--[f]	41
	diethyl ether	94.5[c]	60
_o_-bromotoluene	diethyl ether	97.0[c]	19
	diethyl ether	54[f]	41
_p_-bromotoluene	no solvent	24[d]	2
	diethyl ether	99.2[c]	19
	diethyl ether	37[f]	41
1-bromo-2,4,6-triisopropylbenzene	diethyl ether	50-73[c]	38
2-bromo-3,4,6-triphenylpyridine	diethyl ether	20-25[d]	80
_n_-butyl bromide	benzene	48[h]	4
	diethyl ether	68.8[c]	19

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[h] Dibenzylmercury and _n_-butyl bromide (Ziegler's method).

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[79] J. W. Cook and C. A. Lawrence, _J. Chem. Soc._, _138_, 1431 (1936).

[80] C. F. H. Allen and G. F. Frame, _J. Am. Chem. Soc._, _62_, 1301 (1940).

Table 1 (Continued)

Compound	Solvent	Yield, %	Ref.
	petr. ether (b.p. 28-38°)	70^{c}	21
	diethyl ether	90^{b}	33
	diethyl ether	85-93^{b}	60
sec-butyl bromide	diethyl ether	4^{c}	32
n-butyl chloride	diethyl ether	55.6^{c}	4
	benzene or cyclohexane	67^{c}	4
	diethyl ether	75.80^{c}	19
	benzene	70^{c}	19
	petr. ether (b.p. 28-38°)	85^{c}	21
sec-butyl chloride	diethyl ether	26.9^{c}	81
	petr. ether (b.p. 28-38°)	85^{c}	21
tert-butyl chloride	petr. ether (b.p. 28-38°)	50^{c}	21
	pentane	60-75^{-}	22
	pentane	46.8^{b}	60
n-butyl iodide	diethyl ether	poor	4
	benzene	negligible	4

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[81] H. Gilman, E. A. Zoellner, W. M. Selby and C. Boatner, *Rec. trav. chim.*, *54*, 584 (1935).

Table 1 (Continued)

Compound	Solvent	Yield, %	Ref.
m-chloroaniline	no solvent	80[d]	2
p-chloroaniline	no solvent	68[d]	2
chlorobenzene	diethyl ether	48.7[c]	19
	diethyl ether	92.5[c]	60
1-chlorocycloheptene	diethyl ether	48[a]	82
chlorocyclohexane	diethyl ether	24.3[c]	19
	petr. ether	70[i]	83
1-chlorocyclohexene	diethyl ether	60[e]	84
	diethyl ether	20[a]	85
1-chlorocyclopentene	diethyl ether	13.7[e]	86

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[i] Derivatized as an organometalloidal compound.

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[82] E. A. Braude, W. F. Forbes and E. A. Evans, *J. Chem. Soc.*, 2202 (1953).

[83] O. H. Johnson and W. H. Nebergall, *J. Am. Chem. Soc.*, *71*, 1720 (1949).

[84] E. A. Braude, J. A. Coles and C. J. Timmons, *Nature*, *166*, 58 (1950).

[85] E. A. Braude and C. J. Timmons, *J. Chem. Soc.*, 2014 (1950).

[86] E. A. Braude and F. W. Forbes, *ibid.*, 1755 (1951).

Table 1 (Continued)

Compounds	Solvent	Yield, %	Ref.
2-chlorodibenzofuran	ethylene glycol dimethyl ether	--^{g}	60
	dioxane	--^{g}	60
1-chloro-6,6-dimethylcyclohexene	diethyl ether	63^a	87
4-chlorohydrindene	diethyl ether	75^c	88
	diethyl ether	82^a	89
1-chloromethylheptamethyltrisilmethylene	pentane	85-90$^-$	90
3-chloro-1-methylnaphthalene	diethyl ether	26.2^a	43
1-chloromethylnonamethyltetrasilmethylene	pentane	85-90$^-$	90
1-chloromethylpentamethyldisilmethylene	pentane	94$^-$	90
chloromethyltrimethylsilane	pentane	86$^-$	90

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[87] E. A. Braude, T. Bruun, B. C. L. Weedon and R. J. Woods, *ibid.*, 1419 (1952).

[88] L. F. Fieser and E. B. Hershberg, *J. Am. Chem. Soc.*, *59*, 394 (1937).

[89] R. A. Barnes and L. Gordon, *ibid.*, *71*, 2644 (1949).

[90] L. H. Sommer, F. A. Mitch and G. M. Goldberg, *ibid.*, *71*, 2746 (1949).

Table 1 (Continued)

Compound	Solvent	Yield, %	Ref.
1-chloronaphthalene	no solvent	--[d]	2
	diethyl ether	76[a]	43
2-chloronaphthalene	diethyl ether	42.5[a]	43
2-chlorooctane	benzene	18[c]	32
	ethylene glycol dimethyl ether	10[c]	32
	diethyl ether	52	32
p-chlorophenol	no solvent	14[d]	2
p-chlorophenyltrimethylsilane	diethyl ether	39[e]	91
m-chlorotoluene	diethyl ether	71.3[c]	60
o-chlorotoluene	diethyl ether	64[c]	38
p-chlorotoluene	no solvent	7[d]	2
6-chloro-2,2,6-trimethyl-cyclohexanone	diethyl ether	65[d]	92
9,10-dibromoanthracene	diethyl ether	7.8[e]	58
1,4-dibromobutane	diethyl ether	63[i]	31
1,10-dibromodecane	diethyl ether	71[d]	31
	diethyl ether	70.6[b]	60

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[91] R. A. Benkeser and H. R. Krysiak, _ibid._, _76_, 599 (1954).

[92] A. Bell, T. H. Strickland and G. F. Wright, _J. Org. Chem._, _16_, 1742 (1951).

Table 1 (Continued)

Compound	Solvent	Yield, %	Ref.
1,6-dibromohexane	diethyl ether	42[i]	31
	diethyl ether	32[e]	31
dibromomethane	diethyl ether	6[i]	31
1,5-dibromopentane	diethyl ether	68[i]	31
1,3-dibromopropane	ethylene glycol dimethyl ether	--[g]	60
2,5-dimethyl-3-iodofuran	diethyl ether	69.2[c]	81
n-dodecyl bromide	diethyl ether	48-65[c]	16
	benzene	37[c]	16
n-dodecyl chloride	diethyl ether	76.6[b]	16
	petr. ether (b.p. 30-35°)	72[c]	16
	petr. ether (b.p. 60-70°)	80.3-86.2[c]	16
	benzene	83.4[c]	16
	petr. ether (b.p. 28-38°)	61.3[b]	60
	pentane	58.5[b]	60
ethyl bromide	petr. ether	40	93

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[93] N. N. Mel'nikov and G. P. Gracheva, *J. Gen. Chem.* (*U. S. S. R.*), *6*, 634 (1936) [*C. A.*, *30*, 5557 (1936)].

Table 1 (Continued)

Compound	Solvent	Yield, %	Ref.
	petr. ether (b.p. 28-38°)	50^{c}	21
	petr. ether (b.p. 28-38°)	92^{c}	20
	diethyl ether	$--^{a}$	94
	pentene	65^{j}	27
2-ethylhexylbromide	diethyl ether	35.6^{b}	60
fluorobenzene	diethyl ether	20.2^{c}	60
	ethylene glycol dimethyl ether	16.5^{i}	60
n-heptadecyl bromide	diethyl ether	75.2^{b}	34
n-hexadecyl chloride	diethyl ether	51^{e}	16
	petr. ether (b. p. 30-35°)	63^{c}	16
n-hexyl bromide	diethyl ether	77^{b}	33
iodobenzene	no solvent	70^{d}	2
	diethyl ether	82.8^{c}	19

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[j] Isolated as a crystalline organolithium compound.

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[94] R. M. Anker and A. H. Cook, *J. Chem. Soc.*, 323 (1941).

Table 1 (Continued)

Compound	Solvent	Yield, %	Ref.
1-iodonaphthalene	diethyl ether	54^{a}	43
	diethyl ether	8.4^{c}	81
isobutenyl chloride	diethyl ether	50^{a}	95
isobutyl chloride	petr. ether (b.p. 28-38°)	85^{c}	21
isopropyl bromide	petr. ether (b.p. 28-38°)	15^{c}	21
isopropyl chloride	petr. ether (b.p. 28-38°)	75^{c}	21
	diethyl ether	20^{c}	21
	petr. ether (b.p. 28-38°)	88^{c}	20
methyl chloride	diethyl ether	$70-80^{-}$	35
	diethyl ether	89^{c}	81
methyl iodide	no solvent	33^{d}	2
	diethyl ether	81.5^{c}	19
	diethyl ether	$56-73^{a}$	37
	diethyl ether	$--^{a}$	94
	diethyl ether	95^{c}	20
	diethyl ether	75^{c}	54

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[95] E. A. Braude and J. A. Coles, *ibid.*, 1425 (1952).

Table 1 (Continued)

Compound	Solvent	Yield, %	Ref.
n-octadecyl bromide	diethyl ether	56[c]	16
n-octadecyl chloride	diethyl ether	53[b]	60
	heptane	4.17[b]	60
sec-octyl iodide	no solvent	9[d]	2
n-propyl bromide	petr. ether (b.p. 28-38°)	60[c]	21
	diethyl ether	--[a]	94
	diethyl ether	78[b]	33
n-propyl chloride	diethyl ether	87.9[c]	81
	benzene	41.6[c]	81
	petr. ether (b.p. 28-38°)	85[c]	21
n-propyl iodide	no solvent	--[d]	2
n-tetradecyl bromide	diethyl ether	64[c]	16
triphenylmethyl chloride	diethyl ether	--[a]	96a
p-triphenylsilylbromobenzene	diethyl ether	70[c]	60
n-undecyl bromide	diethyl ether	38.5[c]	19

[96a] A. V. Grosse, Ber., 59, 2646 (1926).

covered through October, 1954. Current Chemical Papers have been checked through No. 10, 1954 for references to current foreign works.

The bibliography[96b] published by Metalloy Corporation has also been checked for references to syntheses of organolithium compounds by direct reaction.

The superscripts by percentage yields in the table denote the methods by which yields were determined.

[96b] Metalloy Corporation, "Annotated Bibliography on the Use of Organolithium Compounds in Organic Synthesis", Minneapolis, 1949. Supplement No. 1, 1950. Supplement No. 2, 1952.

EXPERIMENTAL[97,98]

General Procedure

Inert atmosphere

Nitrogen. Commercially available, prepurified (99.9% pure) nitrogen was used.

Nitrogen train. Nitrogen pressure from the cylinder was controlled by means of a two gauge regulator to about 2 lb./sq. in. This pressure was further reduced by having a needle valve control between the nitrogen cylinder and the nitrogen purification train. Starting from the inlet, the nitrogen train consisted of an excess pressure outlet, deoxygenating unit, dehydrating unit, outlets to reaction

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[97] All melting points reported are uncorrected values, unless otherwise stated, and were determined by the capillary tube method at a rate of heating of 1°/minute in the vicinity of the melting point. A silicone oil bath was used for melting points below 250° and a copper block for melting points above 250°.

[98] Infrared spectra of the compounds described were obtained by use of the Baird Double Beam Infrared Spectrophotometer of the Institute for Atomic Research, Iowa State College. The writer wishes to thank Dr. Marvin Margoshes, and Messrs. Richard M. Hedges, Robert D. Kross and Robert McCord for the determination of and assistance in the interpretation of the spectra.

For solid compounds, spectra were determined on Nujol mulls or carbon disulfide solutions. Capillary cells were used for liquids.

set-ups and a bubbler to act as an escape valve. The actual arrangement of the inlets and outlets to the various bottles should be according to Figure 1.

Deoxygenating agents

Alkaline pyrogallol. A solution containing 50 g. of pyrogallol in 150 ml. of water was mixed with another consisting of 75 g. of potassium hydroxide dissolved in 150 ml. of water. The resulting alkaline solution was poured into the deoxygenating bottles and immediately closed from air.[99]

Sodium anthraquinone-β-sulfonate. To a solution of 0.45 g. of sodium anthraquinone-β-sulfonate in 294 ml. of water were added 6 ml. of 30% sodium hydroxide solution.[100] This solution was poured over zinc amalgam in the trap bottles. The zinc amalgam was prepared by allowing 50 g. of mossy zinc to sit for 10 minutes in a solution of 3 g. of mercuric chloride in 50 ml. of water and then washing thoroughly with distilled water.[52]

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[99] Dr. T. C. Wu, private communication.

[100] Mr. L. A. Gist of This Laboratory has found that the addition of more base tended to decrease the formation of a whitish-precipitate which was frequently observed after continued use.

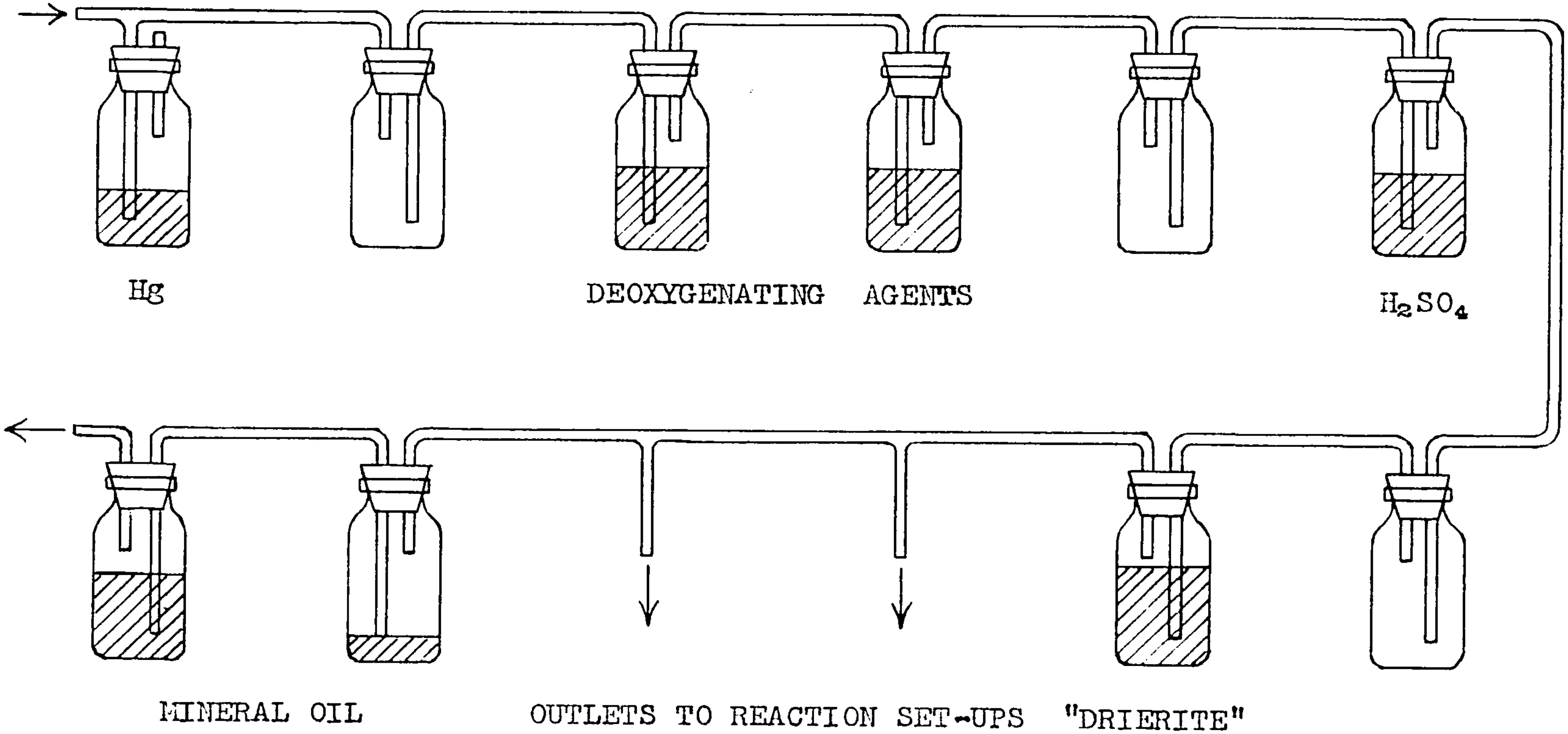

Figure 1

Nitrogen train

Dehydrating agents. The main dehydrating agent used was concentrated sulfuric acid. "Indicating" Drierite (anhydrous calcium sulfate) was also used to insure the removal of water and to check on the efficiency of the concentrated sulfuric acid trap.

Experimental set-up

The equipment used in the reaction was dried in an oven at 115° for at least 2 hours and then put together while hot and cooled under a nitrogen atmosphere. The ground-glass joints were lubricated with a silicone stopcock grease.

For a reaction at a reflux temperature a 3-necked, round-bottomed flask equipped with a Friedrich condenser, addition funnel and a Trubore stirrer with a glass paddle was used. When external heating was required, a heating mantle regulated by a variac was employed.

A low temperature reaction was carried out either with a 4-necked flask with a low temperature thermometer in the fourth neck or with a 3-necked flask equipped with a thermometer instead of a reflux condenser. The cooling bath for a temperature as low as -70° was Dry Ice-acetone. For maintaining a temperature of approximately -20°, a combination of Dry Ice and ice was the most convenient. Ice was used for reactions at 0°.

Reagents

Solvents

Diethyl ether. Commercially available, anhydrous ether was dried over sodium wire for at least 24 hours before using.

Petroleum ethers. Petroleum ethers of different boiling ranges were all dried with sodium wire.

Pentane[101] and heptane. Phillip's pure grade pentane and heptane were used as received. When these solvents were to be kept for a long time after the seals were broken, sodium was added to keep them dry.

Benzene, toluene and xylene. These solvents in "reagent grade" quality were dried over sodium before using.

Ethylene glycol dimethyl ether. Ethylene glycol dimethyl ether containing a small amount of benzophenone was heated to a reflux and stirred over sodium until the solution became blue (color of sodium ketyl). This generally took about 5 days. The ethylene glycol dimethyl ether fraction was distilled and stored over sodium.[36]

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[101] Technical grade pentane was purified by stirring with concentrated sulfuric acid for 24 hours and fractionally distilling the pentane fraction.

Dioxane. Two liters of dioxane were refluxed with 27 ml. of concentrated hydrochloric acid and 200 ml. of water for 12 hours. Nitrogen was bubbled through the solution during this period. To this solution potassium hydroxide pellets were added until no more dissolved. The dioxane was decanted and treated with more potassium hydroxide. The dioxane was carefully decanted into a clean flask and refluxed with sodium for 12 hours and then distilled and stored over sodium.[102]

Tetrahydrofuran. Tetrahydrofuran was heated to a gentle reflux and stirred with sodium for 24 hours and distilled. The distilled product was stored in a dark bottle and kept away from light in order to keep peroxide formation at a minimum.

Organic halides. Generally organic halides from which the corresponding organolithium compounds were prepared were of Eastman's "white label" or comparable grade in purity and were used without further purification. Refractive indices were determined for liquid reagents of doubtful purity, and purification by redistillation was carried out when required.

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[102] L. Fieser, "Experiments in Organic Chemistry", D. C. Heath, New York, 2nd Ed., 1941, p. 369.

Lithium. The lithium wire was one-eighth of an inch in diameter and weighed 3.6 to 4.1 g. per meter. The wire was stored under mineral oil. The ribbon was one-fourth by one-thirty second of an inch and weighed approximately 1.7 g. per meter and was stored in its original reel can in a dessicator. Lithium foil was prepared as required by hammering out the wire under mineral oil. The three forms mentioned were all cut into pieces, several millimeters in length, which were allowed to fall directly into a reaction flask under a stream of emerging nitrogen. The mineral oil or grease on the lithium was either wiped off before cutting or rinsed in the reaction flask with the solvent that was to be used in the subsequent reaction. Usually three 25-ml. portions of the solvent were used in rinsing, with each portion being removed with a pipet before adding the next.

The lithium dispersion used was a 25% dispersion in a special aromatic-free and unsaturate-free mineral spirits (b.p. 166-193°).[103] The dispersion contained 0.75% oleic acid as a dispersing and stabilizing aid. The particle sizes ranged from 5-85 microns with an average of 45 microns. The amount of lithium used in a reaction was calculated from the weight of the dispersion used.

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[103] The dispersion was kindly furnished by Dr. J. F. Nobis, National Distillers Chemical Co., Cincinnati, Ohio.

Determination of yield

When the form of lithium employed was wire, ribbon or foil, the reaction mixture was carefully poured through a narrow tube loosely plugged with glass wool (medium) into a graduated separatory funnel previously dried and then cooled under nitrogen. The reaction flask was rinsed with two 15-ml. portions of the solvent that was used in the reaction in order to complete the transfer. During the transfer the rate of flow of nitrogen was increased in order to prevent air from being sucked back into the reaction flask.

Yields of organolithium compounds prepared by the use of the lithium dispersion were determined from the acid obtained on carbonating the reaction mixture by pouring it jetwise to a mechanically stirred ether-Dry Ice slurry in a tall-form beaker.

Yields of alkyllithium compounds were determined by double titration;[13] for aryllithium compounds simple acid titration[11] was employed.

Alkyllithium Compounds

n-Butyllithium

The procedure used was essentially in accordance with that reported by Gilman and co-workers[33] modified by cooling the reaction mixture to a temperature between -20 to -30° during the addition of the n-butyl bromide-ether solution.

To a stirred suspension of 17.2 g. (2.5 g. atoms) of lithium wire in 400 ml. of ether were added 30 drops of a solution containing 137 g. (1 mole) of *n*-butyl bromide in 220 ml. of ether. As soon as the reaction started, as indicated by a cloudiness of the ether solution, the reaction mixture was cooled to -20° with a Dry Ice-acetone bath, and the dropwise addition of the rest of the *n*-butyl bromide-ether solution was started. The addition required 30 minutes with the temperature of the reaction mixture kept between -20 and -30°. The temperature was controlled by raising or lowering the cooling bath. The reaction mixture was stirred at this temperature for another 35 minutes and then raised to 0° and stirred for 3 more hours. The yield as determined by the double titration method was 88%.

In 15 preparations of *n*-butyllithium by the above method the yields ranged from 85-93%.

tert-Butyllithium

Large excess of lithium foil.[104] To a mixture of 6.2 g. (0.90 g. atom) of lithium foil in 120 ml. of pentane were added 20 ml. of a solution consisting of 18.5 g. (0.2 mole) of tert-butyl chloride in 60 ml. of pentane. In order to initiate the reaction, the mixture was heated to a gentle reflux and stirred for 10 minutes. The rest of the tert-butyl chloride solution was diluted with 100 ml. of pentane and added dropwise over a period of 3.5 hours. During the addition period and for 2 hours after the completion of the addition, the reaction mixture was heated to a gentle reflux and vigorously stirred. The yield by double titration was 46.8%.

High-speed, counter-rotating stirrer. Twenty drops of a solution of 18.5 g. (0.2 mole) of tert-butyl chloride in 60 ml. of pentane were added to a mixture of 3.1 g. (0.45 g. atom) of lithium foil and 60 ml. of pentane in a reaction flask equipped with a high-speed, counter-rotating stirrer. The reaction mixture was refluxed and stirred for 5 minutes;

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[104] This was the only run in which Phillip's "pure grade" pentane and Columbia Chemical's tert-butyl chloride were used. In the other runs redistilled tert-butyl chloride and redistilled technical grade pentane were used.

then the rest of the solution was added dropwise over a period of 30 minutes. Since this apparatus was not specially adapted for operation under an inert atmosphere, an excessive loss of the solvent resulted; therefore, the heating and stirring was stopped 30 minutes after the completion of the addition. In determining the yield by double titration, 3 ml. of benzyl chloride were required to react with the tert-butyllithium present in a 3 ml. aliquot of the suspension (total volume was 86 ml.). The yield was 19%.

Continuous addition of fresh lithium. In this run both the solution consisting of 18.5 g. (0.2 mole) of tert-butyl chloride in 40 ml. of pentane and the lithium (wire) were added portionwise throughout the course of the reaction. Unfortunately, the reaction had to be interrupted twice and the reaction mixture transferred to a new flask because of broken stirring paddles. The addition of lithium was continued until the surface of the newly added lithium remained lustrous. The yield by double titration was 8.1%.

Mild stirring. When a glass stirring paddle for a 250 ml. flask was used in a 500 ml. flask, the yield dropped to 3.75%.

Redistilled tert-butyl chloride. The reaction mixture consisting of 3.1 g. (0.4 g. atom) of lithium wire and 40 ml. of pentane (unsaturate-free) was heated and stirred vigorously. To this mixture were added 25 ml. of a solution of 18.5 g. (0.2 mole) of redistilled tert-butyl chloride in 60 ml. of pentane. After 10 minutes of stirring at the reflux temperature, the rest of the solution was added slowly over a period of 1 hour. The reaction mixture was heated just enough to maintain a gentle reflux. The yield was determined by double titration after 3 more hours of stirring and refluxing. It was 15.6%.

Rapid addition of tert-butyl chloride. In this run a solution of 18.5 g. (0.2 mole) of tert-butyl chloride in 60 ml. of pentane was introduced into a flask containing 3.1 g. (0.45 g. atom) of lithium in 40 ml. of pentane over a period of 20 minutes. The yield by double titration was 3.87%.

First attempt. The first run was made in accordance with the procedure reported by Tyler.[22] The poor result obtained in this case, and the good yield reported by Tyler may be due to a difference in the purity of the reagents employed.

To a mixture of 7.8 g. (1.1 g. atoms) of lithium wire in 188 ml. of pentane were added 20 ml. of a solution consisting of 46.3 g. (0.5 mole) of tert-butyl chloride in 150 ml. of pentane. After stirring at the reflux temperature (external heating) for 10 minutes, the solution became cloudy. About half of the tert-butyl chloride solution was added dropwise over a period of 1.5 hours. Since the reaction mixture did not reflux spontaneously, heat was applied and the remainder of the solution was added dropwise in 1.5 hours. After 6 more hours of stirring at the reflux temperature, the yield was determined by double titration. The yield was negligible because both aliquots required less than 0.5 ml. of 0.1049 N hydrochloric acid.

2-Ethylhexyllithium

A solution of 84.9 g. (0.25 mole) of 2-ethylhexyl bromide in 55 ml. of ether was introduced into a reaction flask containing 4.3 g. (0.62 g. atom) of lithium wire in 100 ml. of ether. The addition was carried out over a period of 45 minutes with the temperature of the reaction mixture maintained at around -20°. The stirring at -20° was continued for 4 hours, and then the temperature of the reaction mixture was allowed to rise to 20°. The yield as determined by double titration was 35.6%.

When the temperature of the reaction mixture was kept below -30° during the addition of the 2-ethylhexyl bromide-ether solution, the yield was 11.5%.

n-Dodecyllithium

Petroleum ether (b.p. 28-38°). A mixture of 1.67 g. (0.24 g. atom) of lithium ribbon and 20 ml. of petroleum ether (b.p. 28-38°) in a 250-ml., 4-necked, creased flask was heated to a gentle reflux and stirred for 5 minutes. This stirring at the reflux temperature was maintained during the entire reaction period. Several milliliters of a solution consisting of 8.19 g. (0.04 mole) of n-dodecyl chloride in 50 ml. of petroleum ether (b.p. 28-38°) were added. After 10 minutes the lithium surface became shiny, indicating the start of the reaction. The rest of the solution was added dropwise over a period of 2 hours. The reaction mixture was stirred at the reflux temperature for 54 hours. The yield by double titration was 61.3%. A simple acid titration gave a yield of 104%.

Pentane. The only modification employed in this run was the use of pentane instead of petroleum ether (b.p. 28-38°). The yield was 58.5% by double titration and 107% by a simple acid titration.

When the reaction period was reduced to less than an hour, no organolithium compound was obtained, as indicated by a negative Color Test I.

Heptane. In this run the n-dodecyl chloride-heptane solution was added in 15 minutes. After stirring at the reflux temperature for 1 hour, the reaction mixture was allowed to cool. Color Test I was strongly positive, but a relatively large amount of iodine-glacial acetic acid solution was required. The yield was 4.10% by double titration and 91% by single titration. Three days later the yield was determined on the clear supernatant liquid and on the suspension. On the supernatant liquid the yield by double titration was 2.45%; and by single titration, it was 82%. The suspension gave 2.68% by double titration and 91% by single titration. These values indicated that n-dodecyllithium decomposed upon standing and was not completely soluble in heptane. There were also some basic compounds other than an organolithium compound which were not completely soluble in heptane.

n-Octadecyllithium

Lithium ribbon at 0°. Into a flask containing 0.16 g. (0.088 g. atom) of lithium ribbon and 50 ml. of ether were added 30 drops of a solution consisting of 13.34 g. (0.04 mole) of n-octadecyl bromide in 20 ml. of ether. After stirring at room temperature for 25 minutes, no sign of any reaction was observed. The solution was heated to a gentle reflux for 5 minutes. Some cloudiness appeared, indicating the start of the reaction. The flask was cooled with an ice-salt bath and the rest of the n-octadecyl bromide solution, which was diluted with 100 ml. of ether, was added over a period of 3 hours. The reaction mixture was stirred for 2 more hours at 0°; then it was transferred to a graduated separatory funnel. The yield as determined by double titration was 53%.

When the addition of the n-octadecyl bromide-ether solution was carried out in 5 hours, the yield fell to 46%.

Preparation at -10°. Into a 500-ml., 3-necked, creased flask containing 1.67 g. (0.24 g. atom) of lithium ribbon and 25 ml. of ether were added 25 drops of a solution consisting of 20.0 g. (0.06 mole) of n-octadecyl bromide in 30 ml. of ether. After stirring at a room temperature for 5 minutes, the reaction started. The n-octadecyl bromide solution was diluted with 150 ml. of ether and the dropwise addition, which took a total of 2.5 hours, was started. The temperature of the reaction mixture during this addition period was -10°. After stirring at 0° for 2 hours, the yield was determined by double titration. The yield was 50.5%.

Preparation at 10°. Several milliliters of a solution consisting of 20.0 g. (0.06 mole) of *n*-octadecyl bromide in 30 ml. of ether were added into a flask containing 0.97 g. (0.14 g. atom) of lithium ribbon and 25 ml. of ether. The reaction started after stirring at room temperature for 5 minutes. The *n*-octadecyl bromide solution was diluted with 180 ml. of ether and added over a period of 5 hours at a temperature of 10°. The yield by double titration was 36.5%.

n-Octadecyl chloride and heptane. A 250-ml., 4-necked, creased flask containing 0.97 g. (0.14 g. atom) of lithium ribbon and 20 ml. of heptane was heated until the heptane refluxed gently. After stirring the mixture for 5 minutes, 4 ml. of a solution containing 11.2 g. (0.039 mole) of *n*-octadecyl chloride in 25 ml. of heptane were added. The solution became yellowish after stirring at the reflux temperature for several minutes. The *n*-octadecyl chloride solution was diluted with 25 ml. of heptane and added dropwise over a period of an hour. The stirring at the reflux temperature was continued for another 30 minutes. The yield by single titration was greater than 100%; by double titration it was 4.17%.

Alkyldilithium Compounds

Alkyldilithium compounds were first reported by West and Rochow[31] who prepared dilithium derivatives from 1,4-dibromobutane, 1,5-dibromopentane, 1,6-dibromohexane, 1,10-dibromodecane and dibromomethane, respectively.

1,10-Dilithiodecane

Lithium ribbon. Into a 250-ml., 4-necked flask equipped with a stirrer, reflux condenser and an addition funnel were placed 1.65 g. (0.238 g. atom) of lithium ribbon and 50 ml. of ether. To this stirred mixture were added 50 drops of a solution consisting of 15 g. (0.05 mole) of decamethylene bromide in 50 ml. of ether. After 5 minutes of stirring at room temperature, the solution became cloudy, indicating that the reaction had started. The reaction flask was cooled with an ice bath and the dropwise addition of the decamethylene bromide solution was started at a rate of about a drop per second. During the course of the addition, which took 1.5 hours, some difficulty was experienced with the clumping of the lithium pieces. When the clumping became too bad, the clumps were cut into smaller pieces with long nose scissors. After the addition was completed, the reaction mixture was stirred at an ice bath temperature for 2 more hours. The yield by double titration was 70.6%. When the equipment used in the titration was dried in air instead of nitrogen, the yield was 66%.

The reaction mixture was carbonated by pouring it onto a vigorously stirred ether-Dry Ice slurry. The carbonated mixture was stirred until the evolution of carbon dioxide stopped; then it was diluted with 400 ml. of water and filtered. The aqueous layer was separated from the ethereal layer and then heated on a steam plate to remove the residual ether. The acidification of the aqueous layer gave 4.88 g. (42.5%) of decamethylenedicarboxylic acid melting at 125-127°. The reported melting point is 127.8-128.[105]

Lithium wire. The only modification employed in this run was the use of lithium wire instead of ribbon. The yield by double titration was 54.5%. Carbonation gave 4.96 g. (42.8%) of decamethylenedicarboxylic acid melting at 124-125°.

Lithium dispersion. Thirty drops of a solution consisting of 15 g. (0.05 mole) of decamethylene bromide in 50 ml. of ether were added to a suspension of 6.60 g. of lithium dispersion (1.65 g., 0.238 g. atom of lithium) in

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[105] P. Chuit, Helv. Chem. Acta, 9, 264 (1926).

50 ml. of ether. A definite rise in the temperature of the reaction mixture was noted after 5 minutes of stirring at room temperature. The addition of the decamethylene bromide-ether solution was carried out over a period of 1 hour at a temperature of 20-25°. After stirring at 5° for 2 hours, the reaction mixture was carbonated by pouring it into a vigorously stirred ether-Dry Ice slurry. The decamethylene-dicarboxylic acid obtained weighed 5.97 g. (51.9%) and melted at 124-125.5°.

1,3-Dilithiopropane

Ethylene glycol dimethyl ether. To a suspension of 3.10 g. of lithium dispersion (0.78 g., 0.11 g. atom of lithium) in 50 ml. of ethylene glycol dimethyl ether and 3 drops of tetrahydrofuran were added 50 drops of a solution of 4.64 g. (0.023 mole) of trimethylene bromide and 25 ml. of ethylene glycol dimethyl ether. After stirring at room temperature for 10 minutes, the suspension was cooled to -5° and the rest of the solution was added in one portion. An hour later Color Test I[7] was positive. Fifteen minutes later, the reaction mixture was carbonated. The mixture was worked up in the usual manner, but only a minute trace of a material with a burnt-sugar odor was obtained.

When the trimethylene bromide-ethylene glycol dimethyl ether solution was added dropwise, Color Test I was negative after 30 minutes. Several drops of tetrahydrofuran were added, and the dropwise addition of the solution was continued. Color Test I became positive 30 minutes after the addition of tetrahydrofuran. In another 40 minutes the test became strongly positive. However, 30 minutes later, the test was very weak again. The reaction mixture was carbonated and worked up in the usual manner, but only a very small amount of product with a burnt odor was isolated.

Diethyl ether. To a suspension of 3.10 g. of lithium dispersion (0.78 g., 0.11 g. atom of lithium) in 50 ml. of diethyl ether was added, over a period of 1.5 hours, a solution consisting of 4.64 g. (0.023 mole) of trimethylene bromide in 25 ml. of diethyl ether. A positive Color Test I was obtained an hour after the start of the addition, but the test soon became negative. Carbonation did not give any pure product.

1,2-Dilithioethane

Ethylene bromide in diethyl ether. A solution of 9.39 g. (0.05 mole) of ethylene bromide in 50 ml. of ether was added to 6.71 g. of lithium dispersion (1.68 g., 0.24 g.

atom of lithium) in 50 ml. of diethyl ether at a temperature of -40 to -50°. The reaction mixture was stirred for another 30 minutes; then it was allowed to rise to 0°. At this temperature a vigorous evolution of gas, which decolorized bromine water and gave a positive Baeyer test for unsaturation, was noted. The reaction was stirred at 0° for 2 hours and then allowed to rise to room temperature. Finally the reaction mixture was refluxed for an hour. At 15-minute intervals throughout the reaction period, Color Test I was carried out, but a positive test was not obtained.

Ethylene bromide, tetrahydropyran and Dry Ice. To 3.95 g. of lithium dispersion (1.0 g., 0.14 g. atom of lithium) in 80 ml. of tetrahydropyran was added, over a period of an hour, a solution consisting of 4.70 g. (0.025 mole) of ethylene bromide in 20 ml. of tetrahydropyran. During this period, finely powdered Dry Ice was also added a little at a time. The reaction was carried out under carbon dioxide atmosphere. After stirring overnight, the reaction mixture was diluted with about 100 ml. of water and worked up in the usual manner. No acid was isolated.

Ethylene bromide in ethylene glycol dimethyl ether. In this run the proportion of reagents and solvent used was the same as in the reaction using diethyl ether. The addition of 10 ml. of ethylene bromide-ethylene glycol dimethyl ether solution was carried out at room temperature. The reaction mixture was cooled to about -10°, and the rest of the solution was added over a period of an hour. No positive Color Test I was obtained, but the gas evolved decolorized bromine water. Approximately 1 ml. of tetrahydrofuran was added, and the reaction was stirred at 0° for several hours and then allowed to warm up to room temperature over a period of 2 hours. At this time Color Test I was positive, but 30 minutes later the test was negative. The reaction mixture was immediately carbonated by pouring it jetwise into an ether-Dry Ice slurry. When the carbonated mixture was worked up in the usual manner, only a small amount of brown residue with a burnt-sugar odor was obtained.

In another run powdered Dry Ice was added simultaneously with the ethylene bromide-ethylene glycol dimethyl ether solution. The result was the same.

Ethylene chloride in pentane. To 6.30 g. of lithium dispersion (1.58 g., 0.23 g. atom of lithium) in 50 ml. of pentane was added, over a period of 1.5 hours, a solution of 4.95 g. (0.05 mole) of ethylene chloride in 50 ml. of pentane. The reaction mixture was initially at room temperature, but it was slowly cooled to -30° after several milliliters of the solution were added. A catalytic amount of tetrahydrofuran was added, but Color Test I remained negative.

The temperature of the reaction mixture was slowly increased until the solvent began to reflux. A positive Color Test I was never observed. Carbonation of the reaction mixture did not give any acid.

Aryllithium Compounds

Phenyllithium

Bromobenzene. Phenyllithium was prepared according to the procedure described by Jones and Gilman[40] modified by a slower addition of the bromobenzene-ether solution. The slower rate of addition obviated the necessity of using an ice-bath for controlling the reaction.

Lithium ribbon. Into a 250-ml., 3-necked flask containing 1.80 g. (0.12 g. atom) of lithium ribbon and 25 ml. of ether were added 25 ml. of a solution of 18.84 g. (0.12 mole) of bromobenzene in 60 ml. of ether. The ether solution became cloudy after stirring for 2 minutes at room temperature. The dropwise addition of the rest of the solution was carried out over a period of 2 hours. The rate was such that a gentle reflux was maintained without any external heating. After the addition was completed, the reaction mixture was heated to a gentle reflux and stirred for 20 minutes. The yield as determined by a simple acid titration was 99.4%.

Lithium wire. A similar preparation was carried out with lithium wire. Simple acid titration gave a yield of 101%. This abnormal yield is probably due to the precision of the quantitative estimation which certainly is no better than ±1%.

Chlorobenzene

Lithium ribbon and creased flask. Fifty drops of a solution of 18.0 g. (0.16 mole) of chlorobenzene in 100 ml. of ether were added to 2.78 g. (0.40 g. atom) of lithium ribbon and 100 ml. of ether in a 500-ml., 3-necked, creased flask. After 3 minutes of stirring at a reflux temperature, the reaction started, as indicated by a cloudy appearance of the ether solution and a shiny lithium surface. The dropwise addition of the chlorobenzene-ether solution was carried out over a period of 2 hours with just enough external heating to maintain a gentle reflux. The refluxing and stirring were continued for 2 hours after the completion of the addition. The yield, as determined by a simple acid titration, was 92.5%.

The reaction mixture was carbonated with an ether-Dry Ice slurry, diluted with water and filtered. The aqueous layer of the filtrate was separated from the ethereal layer and heated to remove the rest of the ether. The acidification of this solution gave a white product weighing 13.87 g. (m.p. 122-123.5°). A mixed melting point with an authentic specimen of benzoic acid melting at 123-123.5° was 123-123.5°. The yield was 71.5% based upon chlorobenzene and 78% based upon phenyllithium.

Lithium wire and creased flask. In this run 2.64 g. (0.38 g. atom) of lithium wire were suspended in 100 ml. of ether. Fifty drops of a solution consisting of 18.0 g. (0.16 mole) of chlorobenzene in 200 ml. of ether were added. The reaction mixture was stirred at the reflux temperature for 20 minutes in order to start the reaction. The rest of the solution was added over a period of 2 hours. The external heating was just enough to maintain a gentle reflux. After the addition was completed, the reaction mixture was stirred and refluxed for 2 more hours. The yield of phenyllithium, as determined by a single acid titration, was 87%. The yield of benzoic acid obtained by carbonation was 13.13 g. (m.p. 122-122.5°). This weight represented a 67.5% yield based upon chlorobenzene and 78.4% yield based upon the titration value.

The use of a creased flask was not necessary, because a yield of 88.5% by acid titration was obtained when an ordinary round-bottomed flask was used. The yield of benzoic acid obtained by the carbonation of the reaction mixture was 65% based upon chlorobenzene and 73% based upon the titration.

When the addition of the chlorobenzene-ether solution was completed in 20 minutes instead of 2 hours, the yield by titration was 56%. The yield of benzoic acid obtained from this run was 27.5% based upon chlorobenzene and 49.2% based upon the titration value.

Lithium dispersion. To a suspension of 5.26 g. of lithium dispersion (1.32 g., 0.19 g. atom of lithium) in 50 ml. of ether were added 30 drops of a solution of 9.0 g. (0.08 mole) of chlorobenzene in 25 ml. of ether. A few degrees rise in the temperature of the reaction mixture was noticed after stirring at room temperature for 15 minutes. The chlorobenzene-ether solution was diluted with 25 ml. of ether and added dropwise to the reaction mixture which was being vigorously stirred at the reflux temperature (external heating required). The addition took 2 hours. After 2 more hours of stirring, the reaction mixture was carbonated by adding it slowly to a vigorously stirred ether-Dry Ice slurry. When the carbonated mixture was worked up in the usual manner, 3.92 g. (40.3%) of benzoic acid were obtained.

Fluorobenzene

Lithium ribbon and initial addition of fluorobenzene. A reaction mixture of 1.11 g. (0.16 g. atom) of lithium ribbon and 7.69 g. (0.08 mole) of fluorobenzene in 50 ml. of ether was stirred at the reflux temperature for 24 hours. The total alkalinity, as determined by a simple acid titration, was 20.2%. The reaction mixture was carbonated and worked up in the usual manner to give 0.18 g. of an acidic material melting over the range 80-85°. This crude material was vacuum sublimed twice to yield 0.07 g. of a product which melted at 121.5-122.5°. A mixed melting point with an authentic specimen of benzoic acid (m.p. 122.5-123°) was 122-123°. The infrared spectrum of this product also indicated that the acid was benzoic acid. The yield of benzoic acid was 0.72% based upon fluorobenzene.

The non-acidic material from the ethereal layer of the carbonated mixture was also purified by sublimation. The products obtained weighed 0.26 g. (m.p. 69-70°) and 0.87 g. (m.p. 68-70°). Their identity as biphenyl was confirmed by the method of mixed melting point determination. The yield of biphenyl based upon fluorobenzene was 18%.

Lithium wire and slow addition. Into a flask containing 1.11 g. (0.16 g. atom) of lithium ribbon and 50 ml. of ether were added several ml. of fluorobenzene. After stirring at the reflux temperature for 30 minutes, the dropwise addition of the rest of the fluorobenzene (total amount of fluorobenzene was 7.69 g., 0.08 mole) in 50 ml. of ether was started. The addition required 1.5 hours. The reaction mixture was stirred for another hour and then allowed to cool. The yield of phenyllithium was negligible, because only 1.5 ml. of 0.1044 N hydrochloric acid were required to neutralize 3 ml. of the hydrolyzed aliquot.

Lithium ribbon and slow addition. When the reaction between lithium ribbon and fluorobenzene was carried out under the same experimental conditions as given above, the result was the same.

Lithium dispersion. Five milliliters of fluorobenzene were added to a suspension of 4.44 g. (1.11 g., 0.16 g. atom of lithium) in 50 ml. of ether. Fifteen minutes of stirring at room temperature did not initiate a reaction; therefore, several ml. of fluorobenzene were added, and the reaction mixture was heated to a gentle reflux. Color Test I was positive 55 minutes after the second addition of the fluorobenzene. The rest of the fluorobenzene (total amount of fluorobenzene was 7.69 g., 0.08 mole) was diluted with 25 ml. of ether and added over a period of 2 hours. The reaction mixture was stirred at the reflux temperature for 2 more hours and then carbonated by adding to an ether-Dry Ice slurry. The carbonated mixture was diluted with 200 ml. of water and filtered. The aqueous layer of the filtrate was separated from the ethereal layer and acidified. This suspension was extracted with ether which in turn was extracted with 10% sodium bicarbonate solution. The acidification of the bicarbonate solution gave a product, which on filtration and drying, weighed 0.14 g. and melted at 103-108°. This material was sublimed twice at 95° (0.05 mm.) to give 0.09 g., m.p. 111-116°. Recrystallization of this product from hot water gave 0.05 g., m.p. 118-119°. A mixed melting point with an authentic specimen of benzoic acid melting at 122.5° was 122-122.5°. The infrared spectrum of this compound was also that of benzoic acid. The yield was 0.51%.

Fluorobenzene, lithium ribbon and triphenylchlorosilane in ethylene glycol dimethyl ether. A mixture consisting of 7.69 g. (0.08 mole) of fluorobenzene, 1.11 g. (0.16 g. atom) of lithium ribbon and 23.6 g. (0.08 mole) of triphenylchlorosilane in 100 ml. of ethylene glycol dimethyl ether was gently refluxed and stirred for 18 hours. The unreacted lithium was carefully decomposed with water, and the reaction mixture was filtered. The crude product obtained by filtration was digested with ethanol and filtered to give a material melting over the range 218-240°.

Recrystallization from a mixture of toluene and ethanol yielded 8.3 g. of a product melting at 210-225°. Five recrystallizations from xylene gave 4.44 g. (16.5%) of tetraphenylsilane melting at 231-233°. A mixed melting point with an authentic sample of tetraphenylsilane melting at 231.5-232.5° was 231-233°.

A crude product melting over the range 146-147° was recovered from the filtrate of the first recrystallization. Recrystallization from xylene yielded 3.37 g. of a product melting at 151-153°. A mixed melting point with triphenylsilanol melting at 152-154° was 151-154°. This represented a 16.1% yield based upon triphenylchlorosilane.

The filtrate from the ethanol digestion was reduced in volume and cooled. The product obtained was stirred with a small amount of an ethanol-benzene mixture and filtered to give 4.61 g. of white powder melting at 222-223. This compound was identified as hexaphenyldisiloxane by the method of mixed melting point determination. Concentration of the mother liquor from the digestion with a mixture of benzene and ethanol gave 2.01 g. of crude material melting over the range 222-260°. When this product was digested with hot water, cooled and filtered, 1.47 g. of white powder melting at 224° were obtained. Its identity as hexaphenyldisiloxane was also confirmed by a mixed melting point determination. The total yield of hexaphenyldisiloxane was 6.08 g. (30.3%).

Lithium ribbon in tetrahydrofuran. A suspension of 1.67 g. (0.24 g. atom) of lithium ribbon in 20 ml. of tetrahydrofuran was heated to a reflux and stirred for 5 minutes. To this mixture were added 50 drops of a solution of 7.69 g. (0.08 mole) of fluorobenzene in 50 ml. of tetrahydrofuran. Within 5 minutes the solution became purplish, indicating the start of a reaction. The fluorobenzene solution was diluted with 25 ml. of tetrahydrofuran and the dropwise addition, which required 40 minutes, was started. The stirring at the reflux temperature was maintained throughout the addition period and for an hour after the completion of the addition. The yield by a simple acid titration was 152.5%. By double titration the yield was 26.6%. The latter value represents a minimum yield of aryllithium compounds, because the reaction between benzyl chloride and aryllithium derivatives is not complete under the condition of this titration.[14]

The reaction mixture was carbonated in the usual manner. The addition of water to the carbonation mixture, separation of aqueous layer from the ether-tetrahydrofuran layer and subsequent acidification of the aqueous layer gave a brown oil which could not be purified.

2-Biphenylyllithium

Lithium ribbon. Fifteen milliliters of a solution consisting of 93.2 g. (0.4 mole) of 2-bromobiphenyl were added to 5.82 g. (0.84 g. atom) of lithium ribbon and 200 of ether in a 1-liter, 3-necked, round-bottomed flask. Stirring at room temperature for 30 minutes did not initiate a reaction; therefore, the reaction mixture was heated to a reflux for 5 minutes. The external heat was removed, and the addition of the rest of the 2-bromobiphenyl solution at a rate sufficient to maintain a gentle reflux was started. The addition required 3 hours. After the addition was completed, the reaction mixture was heated to the reflux temperature and stirred for 2.5 hours. The yield as determined by a simple acid titration was 96.3%.

Lithium wire

Ordinary flask. To a suspension of 4.16 g. (0.60 g. atom) of lithium wire in 125 ml. of ether were added 10 ml. of a solution consisting of 58.2 g. (0.25 mole) of 2-bromobiphenyl in 125 ml. of ether. Spontaneous refluxing began after several minutes of stirring at room temperature. The dropwise addition of the rest of the 2-bromobiphenyl solution was carried out over a period of 2.5 hours at a rate such that a gentle reflux was maintained. After the addition was completed, the reaction mixture was heated to a reflux and stirred for 1.5 hours. The total alkalinity of the reddish-brown suspension was 93.5%.

Creased flask. When a similar reaction was carried out in a 500-ml., 3-necked, creased flask, the yield by a simple acid titration was 96%.

Large excess of lithium wire. In this run 17.8 g. (2.57 g. atoms) of lithium wire and 100 ml. of ether were added to a 1-liter, round-bottomed flask. A solution of 93.2 g. (0.4 mole) of 2-bromobiphenyl in 200 ml. of ether was added in the usual manner. The yield by an acid titration was 98.5%.

Very slow addition of 2-bromobiphenyl solution. Into a flask containing 2.91 g. (0.42 g. atom) of lithium wire in 50 ml. of ether were added 10 ml. of a solution consisting of 46.6 g. (0.2 mole) of 2-bromobiphenyl in 100 ml. of ether. After the reaction started, the rest of the solution was added over a period of about 7 hours. A constant gentle reflux was not maintained throughout the addition period. The yield was 54.3%.

m-Tolyllithium

m-Bromotoluene. To a stirred suspension of 2.08 g. (0.3 g. atom) of lithium ribbon in 15 ml. of ether were added 40 ml. of a solution of 22.2 g. (0.13 mole) of m-bromotoluene in 75 ml. of ether. The reaction started immediately. The rest of the m-bromotoluene solution was added over a period of 1.5 hours. The rate of the addition was sufficient to maintain a gentle reflux without any external heating. After stirring another hour without heating, the yield was determined by titrating for the total alkalinity. The yield was 94.5%.

m-Chlorotoluene. Unwiped lithium wire (9.85 g., 1.42 g. atoms) was cut into pieces several millimeters in length, and the pieces were allowed to fall directly into the flask under a stream of nitrogen. After the pieces were rinsed 3 times with 30-ml. portions of ether, 300 ml. of ether were added. The ether solution was heated to a reflux and to the vigorously stirred mixture were added 200 drops of a solution consisting of 75 g. (0.60 mole) of m-chlorotoluene in 400 ml. of ether. After stirring and refluxing for 10 minutes, the lithium pieces became shiny indicating that a reaction had started. The dropwise addition of the m-chlorotoluene solution required 3.5 hours. The mixture was stirred at the reflux temperature for another 2.5 hours. The yield as determined by a simple acid titration was 71.3%.

Mesityllithium

Bromomesitylene. Into a 300-ml., creased flask containing 2.08 g. (0.3 g. atom) of lithium wire and 15 ml. of ether were added 10 ml. of a solution of 24.9 g. (0.025 mole) of bromomesitylene in 90 ml. of ether. A reaction started almost immediately, as indicated by the refluxing of ether. The rest of the solution was added dropwise over a period of 1.5 hours at a rate sufficient to maintain a steady reflux. After the addition was completed, the white suspension was heated to the reflux temperature and stirred for 2 hours. The yield as determined by a simple acid titration was 101%.

When old bromomesitylene was used, the yield fell to 41.3%.

2-Naphthyllithium

2-Bromonaphthalene. When 40 drops of a solution of 2.72 g. (0.13 mole) of 2-bromonaphthalene in 75 ml. of ether were added to a 200-ml. flask containing 2.08 g.

(0.3 g. atom) of lithium ribbon and 15 ml. of ether, a reaction started immediately, as evidenced by an appearance of a purple color in the ether solution. The rest of the 2-bromonaphthalene solution was added to a rapidly stirred solution over a period of 1.5 hours. The rate was sufficient to maintain a steady reflux. The reaction mixture was stirred for another hour, and then the yield was determined by an acid titration. The yield was 104%, if all the alkalinity were due to 2-naphthyllithium. In addition to lithium oxide which may have been present on the lithium ribbon, the other possible product that may have added to the alkalinity is 1,4-dilithium addition derivative of naphthalene.[106]

p-Triphenylsilylphenyllithium

To a stirred mixture of 0.76 g. (0.11 g. atom) of lithium wire in 25 ml. of ether were added 5 ml. of a suspension of 20.7 g. (0.05 mole) of *p*-triphenylsilylbromobenzene.[60] No reaction resulted; therefore, 5 ml. more of the suspension were added, and the reaction mixture was heated to the reflux temperature. Addition of several

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[106] W. Schlenk and E. Bergmann, *Ann.*, *463*, 1 (1928).

milliliters of n-butyl bromide initiated a reaction. The dropwise addition of the rest of the suspension was started while maintaining a gentle reflux by heating. A copious amount of white product precipitated out when approximately one-half of the suspension was added. The content was transferred to another flask and diluted with 100 ml. of ether. The rest of the suspension was added, and the reaction mixture was stirred at the reflux temperature for 4 hours. The yield of p-triphenylsilylphenyllithium by a simple acid titration was 70%.

2-Dibenzofuryllithium

2-Bromodibenzofuran. A reaction mixture consisting of 0.87 g. (0.125 g. atom) of lithium wire, 10 ml. of ether and 5 ml. of a suspension of 6.18 g. (0.025 mole) of 2-bromodibenzofuran in 40 ml. of ether was vigorously stirred at the reflux temperature for 25 minutes, but Color Test I remained negative. Ten minutes after the addition of 1 ml. of tetrahydrofuran, the solution became reddish, and a very faint positive Color Test I was obtained. The 2-bromodibenzofuran suspension was diluted with 60 ml. of ether and added over a period of an hour. Color Test I at the end of the addition period was negative. Ten milliliters of tetrahydrofuran were added in one portion. Thirty minutes later the color of the solution became reddish again, and a positive Color Test I was observed. The reaction mixture was stirred at the temperature for another hour, and the yield was determined by an acid titration. The yield obtained was 190% based upon the amount of 2-bromodibenzofuran used.

When the reaction mixture was carbonated and worked up in the usual manner, a crude acid was obtained which could not be purified by digestion with ethanol, crystallization from ethanol-water mixture and sublimation.

2-Chlorodibenzofuran

Diethyl ether. Into a 250-ml., 3-necked, creased flask containing 1.74 g. (0.25 g. atom) of lithium ribbon and 10 ml. of ether were added 150 drops of a suspension of 10.1 g. (0.05 mole) of 2-chlorodibenzofuran in 40 ml. of ether. After stirring at the reflux temperature for 5 minutes the ether solution became cloudy, indicating that a reaction had started. The 2-chlorodibenzofuran suspension was diluted with 60 ml. of ether; and an addition which took an hour, was started. Vigorous stirring at the reflux temperature was maintained during this period. The yield as determined by titrating for the total alkalinity was 4.37%. The reaction mixture was carbonated and worked up in the usual manner. The aqueous layer from the carbonation upon acidification yielded only an insignificant amount of cloudy precipitate. The ethereal layer on removal of the ether gave 9.09 g. (90% recovery) of 2-chlorodibenzofuran melting at 97.5-99.5°.

Ethylene glycol dimethyl ether. Several milliliters of a solution of 10.1 g. (0.05 mole) of 2-chlorodibenzofuran in 40 ml. of ethylene glycol dimethyl ether were added to a vigorously stirred suspension of 1.74 g. (0.25 g. atom) of lithium ribbon in 10 ml. of ethylene glycol dimethyl ether. When the mixture was heated to 50°, a reaction started. The 2-chlorodibenzofuran solution was diluted with 50 ml. of ethylene glycol dimethyl ether and added to the reaction mixture over a period of 50 minutes. The temperature of the reaction mixture was maintained at approximately 77°. Color Test I was positive. After stirring for 10 more minutes, the reaction mixture was cooled with an ice bath, and the yield was determined by titrating for the total alkalinity. The yield of 157% indicated that a considerable amount of side reactions had occurred. The reaction mixture was carbonated by adding it to a vigorously stirred slurry of ether and Dry Ice and was worked up in the usual manner. The acidification of the aqueous layer did not give any precipitate. The crude product recovered from the ethereal layer was purified by chromatography on alumina, sublimation and crystallization from petroleum ether (b.p. 60-70°) to give 0.86 g. (8.5% recovery) of 2-chlorodibenzofuran melting at 97-98°. Its identity was confirmed by a mixed melting point determination with an authentic specimen.

Triphenylchlorosilane in ethylene glycol dimethyl ether. An attempt was made to derivatize 2-dibenzofuryllithium as 2-triphenylsilyldibenzofuran by a reaction involving lithium, 2-chlorodibenzofuran and triphenylchlorosilane in ethylene glycol dimethyl ether.

Seventy five milliliters of ethylene glycol dimethyl ether were added to a flask containing 0.87 g. (0.125 g. atom) of lithium wire, 8.36 g. (0.025 mole) of triphenylchlorosilane and 5.06 g. (0.025 mole) of 2-chlorodibenzofuran. An exothermic reaction which resulted was controlled by means of an ice bath. After the vigorous reaction had subsided, the reaction mixture was stirred at room temperature for 2 hours. At the end of this period, most of the lithium was consumed.

The reaction mixture was carefully hydrolyzed with 100 ml. of 0.5 N hydrochloric acid. The mixture was filtered, digested with ethanol and filtered again to give a product which melted over the range 200-245°. The filtrate from the digestion was reduced in volume and cooled. The product obtained was crystallized from a mixture of ethanol and water to give 4.03 g. (80% recovery) of 2-chlorodibenzofuran melting over the range 95-97°. A mixed melting point of this product with an authentic sample of 2-chlorodibenzofuran melting at 101-102° was 98-100°. Hexaphenyldisiloxane (1.12 g.) was also obtained from this run.

Dioxane. When the reaction between 20.3 g. (0.1 mole) of 2-chlorodibenzofuran and 2.1 g. (0.3 g. atom) of lithium was carried out in purified dioxane,[102] 0.5 g. (3%) of dibenzofuran, m.p. 78.5-80, and 3.0 g. (17.6%) of *o*-hydroxybiphenyl, m.p. 56.5-57.5, were obtained.[107]

Organosilicon Compounds

Tetra-2-biphenylylsilane (attempted)

A mixture containing 10.5 g. (0.02 mole) of tri-2-biphenylylchlorosilane[107] and 0.05 mole of 2-biphenylyllithium in 100 ml. of ether was stirred at the reflux temperature for 2 days. To this reaction mixture, which was now about one-half of the initial volume, were added

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[107] H. Gilman and K. Oita, *J. Org. Chem.*, *20*, 0000 (1955).

25 ml. of benzene. The stirring at the reflux temperature was continued. Color Test I was still slightly positive 48 hours later, but the reaction mixture was hydrolyzed with 60 ml. of water and filtered. The product was washed thoroughly with water and ethanol, respectively. The dried material weighed 8.53 g. and melted at 241-242°. A mixed melting point with tri-2-biphenylylchlorosilane, m.p. 241-242°, was 240-241°.

When the original filtrate was concentrated, a sticky product was obtained. This material was crystallized from ethanol to give 5.26 g. (68.4%) of biphenyl melting over the range 65-68.5°. A mixed melting point with an authentic specimen of biphenyl was 67-69°.

Tri-2-biphenylylchlorosilane

4 Equivalents of 2-biphenylyllithium. To a solution of 8.05 g. (0.047 mole) of silicon tetrachloride in 50 ml. of ether were added 241 ml. of an ethereal solution containing 0.19 mole of 2-biphenylyllithium. The reaction mixture gave a negative Color Test I after stirring at the reflux temperature for 16 days. The mixture was hydrolyzed with 2 N hydrochloric acid, and the ethereal layer was separated from the aqueous layer. The residue obtained on

removal of the ether was steam distilled. The steam distillate when filtered gave a white product melting over the range 64-68°. Recrystallization from 95% ethanol yielded 7.36 g. (26.2%) of biphenyl, m.p. 69.5-70.5°. The identity was confirmed by a mixed melting point determination.

The residue from the distillation was digested with benzene and filtered. The product obtained weighed 7.56 g., m.p. 242°. Recrystallization from benzene did not raise the melting point.

The benzene solution from the digestion was dried over anhydrous sodium sulfate and chromatographed on 80-200 mesh alumina with benzene and methanol, respectively, as eluants. The solid products obtained from the chromatography were crystallized from benzene to yield 4.82 g. of tri-2-biphenylylchlorosilane[107] melting at 241-242°. The total yield of tri-2-biphenylylchlorosilane was 13.4 g. (54.5%).

Hexa-2-biphenylyldisiloxane (attempted)

Tri-2-biphenylylsilanol and formic acid. This attempt was based upon the procedure reported for preparing hexaphenyldisiloxane from triphenylchlorosilane and formic acid in a quantitative yield.[108] Instead of the expected condensation to hexa-2-biphenylyldisiloxane the cleavage of biphenylyl groups occurred.[109]

Tri-2-biphenylylsilanol, sodium and tri-2-biphenylylchlorosilane. An attempt was made to synthesize hexa-2-biphenylyldisiloxane from the reaction of sodium tri-2-biphenylylsilanolate and tri-2-biphenylylchlorosilane according to the procedure used for preparing many symmetrical and unsymmetrical disiloxanes.[110,111]

Into a flask fitted with a stirrer and a reflux condenser were placed 4 g. (0.0074 mole) of tri-2-biphenylylsilanol,[107] 0.2 g. (0.0087 g. atom) of sodium and 75 ml. of ether. Since the tri-2-biphenylylsilanol did not dissolve even though the mixture was stirred at the reflux temperature, 65 ml. of benzene were added, and the ether was removed by distillation. When this mixture was stirred at the reflux temperature, tri-2-biphenylylsilanol dissolved. Most of the sodium was consumed after 3 hours.

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[108] H. W. Melvin, Doctoral Dissertation, Iowa State College, 1954.

[109] H. Gilman and K. Oita, J. Am. Chem. Soc., 77, 0000 (1955).

[110] H. Gilman, H. N. Benedict and H. Hartzfeld, J. Org. Chem., 19, 419 (1954).

[111] H. N. Benedict, Master's Thesis, Iowa State College, 1950.

After cooling the reaction mixture, the unreacted sodium was decomposed with absolute ethanol. Approximately 100 ml. of water were added and stirred thoroughly. The reaction mixture was filtered and air dried to give 0.87 g. of crude product, m.p. 229-231°. By the process of concentrating the mother liquor and cooling, the following crude fractions were obtained: 2.10 g., m.p. 226-230°; 4.31 g., m.p. 190-200° and 0.19 g., m.p. 166-171°. Although purification attempts were carried out by means of chromatography on alumina and recrystallizations from petroleum ether (b.p. 77-115) and from a mixture of ethanol and benzene, the only product isolated was tri-2-biphenylylchlorosilane.

Tri-2-biphenylyl-*n*-dodecylsilane

2-Biphenylyllithium and *n*-dodecyltrichlorosilane. To 12.2 g. (0.04 mole) of *n*-dodecyltrichlorosilane in a dry flask were added 171 ml. of an ethereal solution containing 0.16 mole of 2-biphenylyllithium. The flask was cooled with an ice-bath during the addition. Color Test I carried out after 10 hours of stirring at the reflux temperature was positive; therefore, the ether was removed by distillation over a period of 3 hours. The last trace of ether was removed under reduced pressure in order to avoid the use of a relatively high temperature which might result in loss of 2-biphenylyllithium through an ether-cleavage reaction.

The reaction mixture was baked at 100° for 2 hours and at 160° for 7 hours, but Color Test I was still positive. However, the mixture began to darken; therefore, after cooling, 100 ml. of benzene were added, and the mixture was hydrolyzed with 100 ml. of 2 N hydrochloric acid. The suspension was filtered and the benzene layer was separated from the aqueous layer. The residue obtained on removal of benzene by distillation was sublimed to give 4.08 g. of biphenyl melting at 67.5-69°. A mixed melting point with a sample of biphenyl melting at 69.5-70° was 68.5-70°.

The residue from the sublimation was dissolved in petroleum ether (b.p. 60-70°) and chromatographed on 80-200 mesh alumina using petroleum ether (b.p. 60-70°) and benzene, respectively, as eluants. The eluates which gave viscous liquids were combined and distilled in a molecular still. The first fraction was 0.18 g. of biphenyl melting at 69.5-70.5°. The second fraction weighed 10.75 g. and distilled over the range 195-265° (0.005 mm.). The second fraction was redistilled through a Vigreux column. The column and the still pot were heated in a distillation oven.[112] The following fractions were obtained:

1. 0.96 g., b.p. 230-250° (0.08-0.07 mm.)
2. 1.09 g., b.p. 250-257° (0.07 mm.)
3. 2.03 g., b.p. 257-295° (0.07 mm.)
4. 1.36 g., b.p. 295° (0.08 mm.)

The infrared spectrum of fraction 4 as a carbon disulfide solution showed an absorption band at 13.3 indicative of ortho disubstitution. However, an aliphatic band at 6.9 μ was absent.

Fraction 4 was analyzed for silicon in the usual manner.

Anal.[113] Calcd. for $C_{48}H_{52}Si$: Si, 4.27. Found: Si, 4.34, 4.33.

Tri-2-biphenylyl-n-dodecylsilane was an extremely viscous yellow liquid at room temperature. A small amount

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[112] The distillation oven was an electrically heated, insulated furnace large enough to accomodate both the still pot and the distillation column. Since the heating element was at the bottom, a difference of approximately 60° was maintained without any adjustment between the distillation temperature and that of the still pot.

[113] All silicon analyses reported in This Dissertation were carried out according to the procedure given by H. Gilman, B. Hofferth, H. W. Melvin and G. E. Dunn, J. Am. Chem. Soc., 72, 5767 (1950).

of brown condensate appeared above the block at 400°.[114] At its volatilization temperature of 410°, the compound separated into a brownish condensate and a colorless residue. Volatilization was complete at 460° leaving no residue.

Tri-2-biphenylylchlorosilane and *n*-dodecyllithium (attempted). To 10.5 g. (0.02 mole) of tri-2-biphenylylchlorosilane were added 59 ml. of petroleum ether (b.p. 28-38°) solution containing 0.22 mole of *n*-dodecyllithium. After stirring at the reflux temperature for 7 days, Color Test I became negative. The reaction mixture was hydrolyzed with 100 ml. of water. Filtration and air drying yielded 10.0 g. (96% recovery) of tri-2-biphenylylchlorosilane melting at 238-241°. A mixed melting point with an authentic sample melting at 242° was 239-241°.

A similar reaction was carried out using pentane as a solvent. The recovery of tri-2-biphenylylchlorosilane was 94% in this run.

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[114] Volatility was determined by inserting a melting point capillary tube containing a small amount of a sample into a copper block used for melting point determinations. The heating was done either electrically or with a Bunsen burner. The volatilization temperature was arbitrarily taken as the temperature at which about one-eighth of an inch of condensate appeared in the capillary tube above the copper block.

Tri-2-biphenylyl-*n*-octadecylsilane

2-Biphenylyllithium and n-octadecyltrichlorosilane

Run I. To a vigorously stirred solution of 20.0 g. (0.053 mole) of *n*-octadecyltrichlorosilane in 200 ml. of ether were added 209 ml. of an ethereal solution containing 0.18 mole of 2-biphenylyllithium. This reaction mixture was stirred at the reflux temperature for 15 days after which time Color Test I finally became negative. The reaction mixture was hydrolyzed with 100 ml. of 2 N hydrochloric acid. The ethereal layer was separated from the aqueous layer and then decolorized with Norit. The oily residue obtained on removal of the ether was dissolved in petroleum ether (b.p. 60-70°), dried over anhydrous sodium sulfate and chromatographed on 80-200 mesh alumina with petroleum ether (b.p. 60-70°), benzene, chloroform, and methanol, respectively, as eluants. A light yellow, sticky liquid, a semi-solid material and a dark brown resin were obtained from the eluates.

The main product, which was the semi-solid material, was chromatographed again on alumina using petroleum ether (b.p. 60-70°) as a solvent and eluant. The main product consisted of light yellow crystals in a sticky liquid. When this material was sublimed, 6.07 g. of biphenyl were obtained. The identity was confirmed by the method of mixed melting point determination.

The liquid residue from the sublimation was distilled in a Hickman molecular still. The fractions obtained were:

1. Crude biphenyl, m.p. 66-68.5°, b.p. 185° (0.015 mm.)
2. Yellow viscous liquid, b.p. 210° (0.005 mm.)
3. Yellow viscous liquid, b.p. 240° (0.005 mm.)

The infrared spectrum of fraction 2 showed only alkyl, phenyl and o-disubstituted benzene bands indicating that the product was tri-2-biphenylyl-n-octadecylsilane.

Anal. Calcd. for $C_{54}H_{64}Si$: Si, 3.79. Found: Si, 3.98.

The volatilization temperature of the compound analyzed was 400°, but at 470° some clear liquid residue was still left. The initial condensate was slightly more yellow than the later condensate.

Run II. In this run a mixture of 0.39 mole of 2-biphenylyllithium in 357 ml. of an ethereal solution and 30 g. (0.077 mole) of n-octadecyltrichlorosilane was stirred at the reflux temperature for 36 hours. The ether was removed by distillation and the mixture was stirred at a temperature of about 80° for 3 more days, but Color Test I was still positive. Subsequently a mixture of 200 ml. of wet ether and 200 ml. of water were added to the vigorously stirred mixture. The ethereal layer of the resulting solution was separated from the aqueous layer, decolorized with Norit and filtered. The residue remaining on removal of the ether was steam distilled. Biphenyl obtained from the distillate weighed 25.8 g. (43% based upon 2-biphenylyllithium) and melted at 69-70°. A mixed melting point determination confirmed its identity.

The residue was distilled in the distillation apparatus described previously.[112] The following fractions were obtained:

1. Yellow liquid, 6.21 g., b.p. 253-255° (0.03-0.02 mm.)
2. Yellow liquid, 9.34 g., b.p. 255-295° (0.02-0.03 mm.)

These fractions were combined and redistilled. The main product was a light yellow liquid weighing 4.04 g., b.p. 247-250° (0.003 mm.).

The analytical values obtained for the percentage of silicon present were 4.52% and 4.55%. The calculated value for tri-2-biphenylyl-n-octadecylsilane is 3.79%; for di-2-biphenylyl-n-octadecylchlorosilane it is 4.42%.

n-Octadecyllithium and tri-5-biphenylylchlorosilane (attempted)

Run I. To a suspension of 10.0 g. (0.019 mole) of tri-2-biphenylylchlorosilane in 50 ml. of ether were added 191 ml. of an ethereal solution containing 0.021 mole of *n*-octadecyllithium. Color Test I carried out after stirring for one hour at the reflux temperature was positive. Approximately 200 ml. of benzene were added, and the ether was slowly removed over a period of 4 hours. Color Test I was negative after stirring at the reflux temperature for 2 hours.

The mixture was hydrolyzed and then filtered to give a product which weighed 8.07 g. and melted over the range 234-240°. Recrystallization from benzene yielded 6.30 g. (63% recovery) of tri-2-biphenylylchlorosilane melting at 241-241.5°. A mixed melting point with an authentic sample was not depressed.

Run II. The reaction between 0.018 mole of *n*-octadecyllithium and 7.85 g. (0.015 mole) of tri-2-biphenylylchlorosilane gave a positive Color Test I after stirring at the reflux temperature for 3 days. Twenty five milliliters of benzene were added and the reaction mixture was stirred for 30 hours after which time Color Test I was negative.

The reaction mixture was carefully hydrolyzed with 2 N hydrochloric acid. The product obtained on filtration weighed 7.36 g. and melted at 240-241°. The recovery of tri-2-biphenylylchlorosilane was 93.7%.

Tri-2-biphenylylallylsilane (attempted)

Allylmagnesium bromide was prepared in 86% yield from 36.3 g. (0.03 mole) of allyl bromide and 43.6 g. (1.8 g. atoms) of magnesium turnings according to the procedure of Gilman and McGlumphy.[115]

To 17.25 g. (0.033 mole) of tri-2-biphenylylchlorosilane were added 265 ml. of an ethereal solution containing 0.25 mole of allylmagnesium bromide. The reaction mixture was stirred at the reflux temperature for 4 days and then hydrolyzed with 100 ml. of 1 N hydrochloric acid; although Color Test I was still slightly positive. The product obtained on filtration of the resulting mixture was extracted in a Soxhlet extraction apparatus with benzene. When the benzene extract was concentrated and cooled, 14.9 g. (86.5% recovery) of tri-2-biphenylylchlorosilane was

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[115] H. Gilman and J. H. McGlumphy, Bull. soc. chim. France, 43, 1322 (1928).

obtained. Identification was made by a mixed melting point determination with an authentic specimen and comparison of infrared spectra.

Tri-2-biphenylyl-2-naphthylsilane (attempted)

To a suspension of 10.2 g. (0.02 mole) of tri-2-biphenylylchlorosilane were added 105 ml. of an ether solution containing 0.13 mole of 2-naphthyllithium. Color Test I after 44 hours of stirring at the reflux temperature was positive. The ether was removed by distillation with the removal completed under a water-aspirator vacuum. The reaction was baked at 70° for 18 hours, diluted with 100 ml. of petroleum ether (b.p. 60-70°) and carefully hydrolyzed with 100 ml. of 1 N hydrochloric acid. The hydrolyzed mixture was carefully decanted, and the resulting sticky residue was dissolved in benzene. The addition of petroleum ether (b.p. 60-70°) to the benzene solution resulted in the formation of a precipitate weighing 1.00 g., m.p. 137-180°. Recrystallization from a mixture of benzene and petroleum ether (b.p. 60-70°) gave 0.31 g., m.p. 183-184°. A mixed melting point with 2,2'-binaphthyl melting at 186-187° was 186-187°.

The removal of the solvent from the mother liquor left a sticky black residue. This residue was dissolved in benzene and chromatographed on alumina with benzene as an eluant. The resins obtained from the chromatography were digested with petroleum ether (b.p. 60-70°) and filtered. The residue obtained on removing the solvent was dissolved in a mixture of ethanol and benzene and allowed to stand in a refrigerator for two weeks. A crystalline material weighing 1.77 g. and melting over the range 156-163° was obtained. Two recrystallizations from a mixture of benzene and petroleum ether (b.p. 77-115°) gave 0.82 g. of white crystalline compound melting at 165.5-166°. From the mother liquor 0.16 g. of white product, m.p. 164-165°, was recovered.

The compound melting at 165.5-166° has not been identified as yet. A silicon analysis of this compound gave values of 6.12 and 6.17%. The calculated value for tri-2-biphenylyl-2-naphthylsilane is 4.17%. This compound cannot be a tri-2-biphenylylsilyl derivative because the highest silicon percentage possible with this derivative is 5.76% (hexa-2-biphenylyldisilane). The infrared spectrum as a carbon disulfide solution differed in the region between 13-14 μ from those of other 2-biphenylylsilyl derivatives. A sharp absorption band was present at 13.8 μ.

Tri-2-biphenylyl-*m*-tolylsilane (attempted)

To 10.2 g. (0.02 mole) of tri-2-biphenylylchlorosilane was added 0.12 mole of *m*-tolyllithium in 100 ml. of an ethereal solution. Color Test I was positive after refluxing the reaction mixture for 24 hours. About two-thirds of the solvent was removed by distillation, and the remainder was removed *in vacuo*. Enough toluene was added to convert the solid reaction mixture into a slurry. Color Test I was positive after stirring this mixture at a reflux temperature for 60 hours.

The reaction mixture was hydrolyzed with 100 ml. of 1 N hydrochloric acid, stirred thoroughly and filtered. The toluene layer of the filtrate was separated from the aqueous layer. The solution remaining after removal of most of the toluene by distillation was diluted with 25 ml. of petroleum ether (b.p. 60-70°) and cooled in a refrigerator. The product which crystallized weighed 1.57 g. and melted over the range 169-174°. Repetition of this process gave 2.29 g. of product, melting over the range 154-172°. The two products were combined and recrystallized from a mixture of benzene and petroleum ether (b.p. 77-115°) to give 2.14 g. of a material, melting range 171-181°. From the filtrate a material weighing 0.20 g. and melting at 177-181° was recovered. Recrystallization of the main product from the same mixed solvent gave 1.29 g. of product melting over the range 174-184°. Recrystallization from a mixture of ethanol and benzene yielded 0.39 g. of an unidentified compound melting at 183.5-185°.

The infrared spectrum of the product melting at 183.5-185° as a carbon disulfide solution did not show any characteristic aliphatic bands, therefore, m-tolyl group was not present in the compound.

1,4-Bis-(triphenylsilyl)-benzene

Run I. To 252 ml. of an ethereal suspension containing 0.035 mole of p-triphenylsilyllithium prepared from the direct reaction of 20.7 g. (0.05 mole) of p-triphenylsilylbromobenzene[116] and 0.76 g. (0.11 g. atom) of lithium wire were slowly added 100 ml. of an ethereal solution containing 9.1 g. (0.035 mole) of triphenylchlorosilane. After stirring the reaction mixture overnight, without heating, Color Test I was negative. The mixture was hydrolyzed with 250 ml. of 2 N hydrochloric acid and filtered to give 18.7 g. of

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[116] H. Gilman and H. W. Melvin, J. Am. Chem. Soc., 72, 995 (1950).

product melting over the range 345-350°. Recrystallization from tri-n-butylphosphate yielded 13.9 g. (45.7% based upon p-triphenylsilylbromobenzene and 67% based upon p-triphenylsilylphenyllithium) of 1,4-bis(triphenylsilyl)-benzene melting at 362-362.5°.

Anal. Calcd. for $C_{42}H_{34}Si_2$: Si, 9.45. Found: Si, 9.43, 9.58.

Run II. In this run p-triphenylsilylphenyllithium was prepared by the halogen-metal interconversion reaction between p-triphenylsilylbromobenzene and n-butyllithium.

Eleven milliliters of an ethereal solution containing 0.014 mole of n-butyllithium were added to a stirred suspension of 5 g. (0.012 mole) of p-triphenylsilylbromobenzene in 100 ml. of ether. After 1.5 hours of stirring, without heating, Color Test II was negative.

The solution containing p-triphenylsilylphenyllithium was added slowly to a stirred solution of 4.8 g. (0.014 mole) of triphenylchlorosilane in 50 ml. of ether. One and one-half hours later, Color Test I was negative. The reaction mixture was hydrolyzed with 2 N hydrochloric acid and filtered. The product obtained weighed 5.1 g. and melted over the range 351-355°. One recrystallization from tri-n-butylphosphate gave 4.8 g. (67.5%) of pure 1,4-bis-(triphenylsilyl)-benzene melting sharply at 362.5°.

Tri-2-naphthyl-n-octadecylsilane (attempted)

To 10 g. (0.027 mole) of n-octadecyltrichlorosilane in a dry flask was slowly added 0.12 mole of 2-naphthyllithium in 151 ml. of an ethereal solution. After stirring at the reflux temperature for 24 hours, Color Test I was still positive. Approximately two-thirds of the solvent was removed by distillation, and the remainder was removed under vacuum. The reaction mixture was baked at 125° for 4 hours. Color Test I at the end of this period was negative. The reaction mixture was stirred with 100 ml. of benzene and then hydrolyzed with 100 ml. of 2 N hydrochloric acid. The resulting mixture was filtered, digested with hot water and filtered again to give a crude material melting over the range 200-260°. Purification was accomplished by means of recrystallizations from xylene, digestion with petroleum ether (b.p. 60-70°), sublimation, chromatography on alumina and molecular distillation. The two pure products isolated were 1.01 g. of 2,2'-binaphthyl and 0.23 g. of naphthalene. The light brown, viscous oil obtained from the molecular distillation was redistilled through a Vigreux column in a distillation oven. The main product distilled over the range 143-267° (0.002 mm.) without any distinct break, indicating the absence of any pure compound.

Triphenyl-*tert*-butylsilane (attempted)

To a suspension of 26.8 g. (0.091 mole) of triphenylchlorosilane in 200 ml. of *n*-pentane were added 364 ml. of a pentane suspension containing 0.091 mole of *tert*-butyllithium prepared in 46.8% yield from 18.5 g. (0.2 mole) of *tert*-butyl chloride and 6.2 g. (0.90 g. atom) of lithium foil. Color Test I remained positive until the nineteenth day of stirring at the reflux temperature. The reaction mixture was hydrolyzed with 100 ml. of 2 N hydrochloric acid and filtered. The sticky product obtained was dissolved in benzene, dried over anhydrous sodium sulfate and chromatographed on 80-200 mesh alumina using benzene, chloroform and methanol, respectively, as eluants. The most promising fraction was chromatographed again on alumina with benzene as the solvent and eluant. The product obtained was a white paste. A low temperature crystallization was attempted from acetone and petroleum ether (b.p. 60-70°), respectively. The product obtained did not have any distinct melting range. Recrystallization from a mixture of glacial acetic acid and ethyl acetate gave some material with a better melting range, but the work on this run was discontinued.

In a 14-hour run a 67.2% yield of triphenylsilanol was obtained.

Organoboron Compounds

2-Biphenylboronic acid

To a solution of 65 g. (0.28 mole) of tri-*n*-butylborate in 300 ml. of ether were added, over a period of 1.5 hours, 309 ml. of an ethereal solution containing 0.30 mole of 2-biphenylyllithium. The solution was vigorously stirred and maintained at -70° during the addition. Color Test I[7] carried out 1 hour after the completion of the addition was negative. The reaction mixture was stirred overnight, and the temperature was allowed to rise slowly. Ten hours later the temperature was -20°. Color Test I was not negative.

The reaction mixture was acidified with 3 N sulfuric acid, and the ethereal layer was separated from the aqueous layer and extracted with 10% potassium hydroxide. The acidification of this layer, after the removal of the residual ether by heating, gave a precipitate which weighed 33.2 g. and melted over the range 110-117°. Crystallization of this product from benzene gave a product, which when dried in a vacuum-desiccator over phosphorus pentoxide, weighed 17.50 g. and melted at 196-197°. The mother liquor on concentrating and cooling yielded 7.39 g. of product melting over the range 175-197°. This product was recrystallized from a mixture of acetone and water to give 5.01 g. of rhombic crystals which effervesced at 125° and then resolidified and melted at 190-194°.

Yabroff, Branch and Bettman[117] reported the melting point of 2-biphenylboronic acid as 126° and of 2-biphenylboronic acid anhydride as 196-197°. However, the infrared spectra of the two compounds prepared by this investigator were identical. Both had a hydroxyl band at 3.05 μ indicating that they were acids.

It was thought that the lower melting form was 2-biphenylboronic acid hydrate while the higher melting form was the anhydrous 2-biphenylboronic acid.

An attempt was made to convert the compound melting at 196-197° to the acid anhydride by heating at 260° for 4 hours under a slow stream of nitrogen. Recrystallization of the resultant product from benzene gave a white material which partially melted at 135° but primarily melted over the range 150-170°. This decrease in the melting point may be due to the presence of the anhydride or to decomposition products.

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[117] D. L. Yabroff, G. E. K. Branch and B. Bettman, ibid., 56, 1850 (1934).

The determination of the neutral equivalent of the product melting at 126° was attempted by titrating the compound complexed with mannitol with a standard base using phenolphthalein as an indicator.[118] The color change was so gradual the endpoint could not be determined.

Neutral equivalents for the two samples were determined potentiometrically by means of a Beckman Model G pH Meter with a Beckman glass electrode. The endpoints were determined graphically by plotting the change in pH per ml. of the base added against the total volume of the base added. The value obtained for the product melting at 196-197° was 190; for the compound melting at 126°, it was 198. The calculated values for the acid anhydride, anhydrous acid and hemihydrate are 180, 198 and 207, respectively. The results are not conclusive, but if the compound melting at 196-197° is the anhydrous acid; then the lower melting form is the hydrate.

The melting point of m-biphenylboronic acid (m.p. 207-208°)[120] and that of p-biphenylboronic acid (m.p. 232-234°)[120] also suggest that the form melting at 196-197° is the acid.

Potentiometric titrations of these two 2-biphenyl derivatives showed why the direct titration using phenolphthalein could not be carried out. In both titrations

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[118] G. E. K. Branch, D. L. Yabroff and B. Bettman, ibid., 56, 937 (1934).

the addition of 2 ml. of 0.1154 N sodium hydroxide raised the pH to above 8.0. The pH at the endpoint was 10.4 in one case and 10.6 in another, and the volumes of base required to reach these endpoints were 10.38 and 20.70 ml., respectively. The pH interval for phenylphthalein in water is 8.0-9.8.

4-Dibenzofuranboronic acid

An ethereal solution (174 ml.) containing 0.25 mole of *n*-butyllithium was added to a suspension of 42 g. (0.25 mole) of dibenzofuran in 100 ml. of ether in a 3-necked, 1-liter flask equipped with a reflux condenser and a stirrer. The reaction mixture was stirred at the reflux temperature for 18 hours. At the end of this period Color Test II[8] was negative.

A solution of 57.5 g. (0.25 mole) of tri-*n*-butylborate and 200 ml. of ether was cooled to -75° with a Dry Ice-acetone mixture. The ethereal solution of 4-lithiodibenzofuran prepared above was added dropwise over a period of 50 minutes. After stirring at this temperature for one hour, Color Test I was still faintly positive. Four hours later the test was negative. The stirring was stopped and the solution was allowed to stand at this temperature overnight.

The following morning the reaction mixture was carefully hydrolyzed with 2 N hydrochloric acid. The ethereal layer was separated from the aqueous layer and extracted with 5% potassium hydroxide until the alkaline extract remained clear when acidified. The alkaline extract was extracted with ether to remove residual butanol; then the ether was removed under reduced pressure. Acidification of the alkaline solution gave a copious amount of white precipitate. This material was filtered, partly dried under a heat lamp and then dried in a desiccator over phosphorus pentoxide. The white product obtained (44.5 g.) effervesced at 135° and resolidified and melted over the range 255-265.

When benzene was tested as a solvent for crystallization, it was observed that the product first dissolved but precipitated on further heating. When water was added, the precipitate dissolved again. This behavior suggested that the acid was more soluble in benzene than the anhydride.

From the crystallization of this product from a mixture of 900 ml. of benzene and 25 ml. of water (to prevent dehydration), 32.5 g. (61.5%) of 4-dibenzofuranboronic acid melting over the range 277-289° were obtained. A sharp melting point could not be obtained with the acid. When the melting point sample was inserted into the bath at 30° and heated, shrinkage was noticed from 275°, but the compound melted over the range 278-285°. However, the compound melted when it was inserted into the bath at 270°. From the mother liquor 3.31 g. of crude product melting over the range 235-245° was obtained. This material on crystallization from a mixture of acetone and water yielded a material weighing 2.89 g. and melting over the range 275-279°.

A sample of the acid was refluxed with benzene and recrystallized from a mixture of benzene and ethanol in order to convert it to the anhydride form. The compound obtained melted at 288-289°.

The neutral equivalent of 4-dibenzofuranboronic acid anhydride was determined by titrating with standard sodium hydroxide after complexing with mannitol.[118]

Anal. Calcd. for $C_{12}H_7O_2B$: Neut. equiv., 194. Found: Neut. equiv., 195, 198.

The neutral equivalent of 4-dibenzofuranboronic acid was determined potentiometrically with a Beckman Model G pH Meter using a Beckman glass electrode. The acid was complexed with mannitol in the usual manner.

Anal. Calcd. for $C_{12}H_9O_3B$: Neut. equiv., 212. Found: Neut. equiv., 212.

Mesityleneboronic acid (attempted)

To a solution of 28.5 g. (0.122 mole) of tri-*n*-butylborate and 100 ml. of ether were added 139 ml. of a white ethereal suspension containing 0.122 mole of mesityllithium. During the addition, which took 45 minutes, and for 4 hours after the completion of the addition, the mixture was vigorously stirred and maintained at a temperature of 0°. Color Test I carried out 30 minutes after the addition was positive, the test made 10 hours later was negative.

The reaction mixture was acidified with 10% sulfuric acid, and the ethereal layer was separated from the aqueous layer and extracted with 5% potassium hydroxide. The alkaline layer in turn was extracted with ether to remove butanol formed as a by-product. After heating on a steam plate to remove the ether, the solution was cooled and acidified with hydrochloric acid. No precipitate formed.

The ether layer was worked up by removing most of the ether and the butanol under a water-pump vacuum. Cooling the residue overnight in a refrigerator gave a product weighing 11.8 g., m.p. 130-140°.

Since the crude product obtained was possibly dimesityleneborinic acid, an attempt was made to derivatize it as aminoethyl dimesityleneborinate by a reaction with ethanolamine.[119]

A solution of 5 g. of the product melting at 130-140°, 30 ml. of ethanol and 10 ml. of ethanolamine was heated to a gentle reflux and then diluted with water until a faint turbidity was observed. Cooling and filtering gave 3.96 g. of white product melting over the range 132-137°. Recrystallization of this product from petroleum ether (b.p. 60-70°) yielded 3.22 g. of well-formed crystals melting sharply at 145-146°.

The rest of the product melting over the range 130-140° (6.79 g.) was recrystallized from petroleum ether (b.p. 60-70°) to give 4.79 g. of similar crystals melting at 145-145.5°.

The infrared spectrum measured as a carbon disulfide solution had sharp absorption bands at 2.8 μ and 3.5 μ, characteristic of a hydroxyl and an aliphatic group, respectively.

If the product obtained were dimesityleneborinic acid, the total yield was 53.8% (8.01 g.).

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[119] R. L. Letsinger, I. Skoog and N. Remes, <u>ibid.</u>, <u>76</u>, 4047 (1954).

Dibenzofuran Derivatives

2-Chloro-6-dibenzofurancarboxylic acid

Voegtli, Muhr and Lauger[120] reported the replacement of bromine of an aromatic bromide with chlorine by chlorinating with chlorine gas in the presence of an ultraviolet light; therefore, this reaction was carried out with 2-bromo-6-dibenzofurancarboxylic acid.

A solution of 2.89 g. (0.01 mole) of 2-bromo-6-dibenzofurancarboxylic acid and 25 g. of trichloroacetic acid in 200 ml. of carbon tetrachloride in a pyrex flask was heated to a gentle reflux. Chlorine gas was introduced for 4 hours. The flask was irriadiated with ultraviolet light from a mercury-vapor lamp during this period. When the solution was cooled, a precipitate melting at 272-272.5 was obtained. A mixed melting point with 2-bromo-6-dibenzofurancarboxylic acid melting at 267-269° was 266-269°, indicating that little or no reaction had occurred.

The entire reaction mixture was transferred to a quartz flask, heated to a reflux, irradiated with ultraviolet

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[120] W. Voegtli, H. Muhr and P. Lauger, <u>Helv. Chim. Acta</u>, **37**, 1627 (1954).

light and rechlorinated for 6 hours. On cooling and filtering, a product weighing 1.48 g. and melting at 279.5-280.5° was obtained. A mixed melting point with 2-chloro-6-dibenzofurancarboxylic acid[121] melting at 278-279° was 276-278°. A mixed melting point with 2-bromo-6-dibenzofurancarboxylic acid (m.p. 265-268°) was 265-268°.

The product was recrystallized from a mixture of carbon tetrachloride and glacial acetic acid to give 1.11 g. of white product melting at 279.5°. A mixed melting point with recrystallized 2-chloro-6-dibenzofurancarboxylic acid melting at 278° was 278-278.5°. A mixed melting point with recrystallized 2-bromo-6-dibenzofurancarboxylic acid melting at 271-272° was 271-272°.

The infrared spectrum of the product and that of 2-chloro-6-dibenzofurancarboxylic acid prepared by chlorinating 4-dibenzofurancarboxylic acid[121] were practically superimposable. The infrared spectrum of 2-bromo-6-dibenzofurancarboxylic acid differed in the regions near 14.3 μ and 10.6-11.0 μ. The spectrum of 2-bromo-6-dibenzofurancarboxylic acid showed an absorption band at 14.30 μ while that of 2-chloro-6-dibenzofurancarboxylic had a band at 14.05 μ. The bromo derivative also had a broad valley

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[121] K. Oita, R. G. Johnson and H. Gilman, J. Org. Chem., 20, 0000 (1955).

between 10.6-11.0 μ while the chloro compound had one band at 10.65 μ and another at 10.90 μ.

A small sample of the product was decomposed with sodium and a qualitative test for halogen was carried out. A flocculent white precipitate, typical of silver chloride, was obtained. A qualitative test for bromide ions was made by adding freshly prepared chlorine water and looking for a reddish-brown color in the carbon tetrachloride layer. The carbon tetrachloride solution remained colorless, indicating the absence of bromides.

From the comparison of melting points, infrared spectra and the qualitative tests for halogen and bromine, it can be stated that the compound prepared from the reaction of chlorine with 2-bromo-6-dibenzofurancarboxylic acid is the same as the one obtained by chlorinating 4-dibenzofurancarboxylic acid. However, because of the importance of this reaction in structure proof of chloro derivatives of dibenzofuran, neutral equivalent determination and quantitative analysis for chlorine should be carried out.

From the mother liquor 0.37 g. of 2-chloro-6-dibenzofurancarboxylic acid melting at 278-280° was obtained. A mixed melting point with 2-chloro-6-dibenzofurancarboxylic acid melting at 278-279° was 276-279°.

The total yield of 2-chloro-6-dibenzofurancarboxylic acid was 1.85 g. (75%).

4-Dibenzofurancarboxylic acid and lithium in dioxane

An attempt was made to cleave 4-dibenzofurancarboxylic acid with lithium in dioxane according to the method reported by Gilman and co-workers[122] for cleaving dibenzofuran. The reaction mixture consisting of 21.1 g. (0.1 mole) of 4-dibenzofurancarboxylic acid and 2.1 g. (0.3 g. atom) of lithium in 200 ml. of dioxane was refluxed and stirred for 10 hours. Color Test I was carried out every 2 hours, but it was negative each time. After the unreacted lithium had been removed by filtration, the solvent was removed *in vacuo*. The residue was acidified with 3 N hydrochloric acid and extracted with ether. There was recovered 18.4 g. (87%) of 4-dibenzofurancarboxylic acid, m.p. 211.5.

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[122] H. Gilman, D. L. Esmay and R. K. Ingham, *J. Am. Chem. Soc.*, *73*, 470 (1951).

2-Bromodibenzofuran

2-Bromodibenzofuran was prepared in the manner described by Ingham[123] modified by the use of iron powder as a carrier instead of irradiating with a mercury-vapor lamp.

To a solution of 84.0 g. (0.5 mole) of dibenzofuran in 500 ml. of glacial acetic acid were added 80.0 g. (0.5 mole) of bromine and 1 g. of iron powder. After stirring for 6 hours at a temperature in the neighborhood of 50°, the solution was allowed to cool overnight. The crude product obtained on diluting the solution with excess water was vacuum-distilled to give impure 2-bromodibenzofuran, melting range 93-104°. Two recrystallizations from petroleum ether (b.p. 60-70°) yielded 36.1 g. (30%) of 2-bromodibenzofuran melting at 109-110°.

2-Bromo-6-dibenzofurancarboxylic acid

To a stirred suspension of 21.2 g. (0.1 mole) of 4-dibenzofurancarboxylic acid and 1 g. of iron powder in 100 ml. of glacial acetic acid were added dropwise 140 ml. of glacial acetic acid solution which was 1 molar in bromine.

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[123] R. K. Ingham, Doctoral Dissertation, Iowa State College, 1952.

The suspension was stirred and heated for 5 hours; then it was poured into 2 liters of water. The product obtained on filtration weighed 38.9 g. and melted over the range 232-258°. Two recrystallizations from glacial acetic acid (decolorization with Norit-A) gave 18.5 g. (63.6%) of 2-bromo-6-dibenzofurancarboxylic acid melting at 271-271.5°.

Methyl 2-bromo-6-dibenzofurancarboxylate

Bromination of methyl-4-dibenzofurancarboxylate. Both of the methods employed were modifications of that reported by Hayes[124] for preparing methyl 2-bromo-6-dibenzofurancarboxylate in a 81.5% crude yield (m.p. 155-164°).

In the first run iron powder was used as a carrier. The crude product obtained weighed 32.6 g. and melted over the range 154-227°. Two recrystallizations from glacial acetic acid raised the melting range to 212-250°. Further work was discontinued.

In the second run benzoyl peroxide was used as a catalyst. Methyl 2-bromo-6-dibenzofurancarboxylate isolated weighed 2.7 g. (20%) and melted at 163-164.5°. Hayes[124]

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[124] D. M. Hayes, Master's Thesis, Iowa State College, 1934.

reported a melting point of 166-167° for pure methyl 2-bromo-6-dibenzofurancarboxylate.

Esterification of 2-bromo-6-dibenzofurancarboxylic acid. A solution of 8.7 g. (0.03 mole) of 2-bromo-6-dibenzofurancarboxylic acid in 200 ml. of methanol was saturated with hydrogen chloride and refluxed for an hour and allowed to cool. The precipitate which formed weighed 8.7 g. and melted over the range 162-166°. When this material was recrystallized twice from glacial acetic acid and once from a 1:1 mixture of absolute methanol and petroleum ether (b.p. 60-70°), 3.0 g. of white asbestos-like product melting at 168.5-169° were obtained. Crude products recovered from the filtrates were purified by repeated recrystallizations from a mixture of methanol and petroleum ether (b.p. 60-70°) to give 4.1 g. of the desired product melting at 167-168° and 1.2 g., m.p. 169-169.5°. The total yield of methyl 2-bromo-6-dibenzofurancarboxylate was 8.3 g. (91%).

2,7-Dinitrodibenzofuran

Dinitration of dibenzofuran. The reaction was carried out in a manner similar to the mononitration of dibenzofuran[125] except for the use of 150 ml. of glacial acetic acid instead of 300 milliliters. The crude product obtained from the reaction of 15 g. (0.089 mole) of dibenzofuran and 100 ml. of fuming nitric acid (sp. gr. 1.49) in 150 ml. of glacial acetic acid weighed 10 g. and melted over the range 235-241°. Recrystallization of this material from glacial acetic acid gave 8.0 g. (35%) of 2,7-dinitrodibenzofuran melting at 244-246°.

2,7-Diaminodibenzofuran

Cullinane[126] has reduced 2,7-dinitrodibenzofuran to 2,7-diaminodibenzofuran with tin or iron and hydrochloric acid in a yield of 80%. In this run Raney nickel and hydrogen were used because the reaction product is cleaner and easier to work up.

A hydrogenation flask containing 4.8 g. (0.019 mole) of 2,7-dinitrodibenzofuran and 1.5 g. of Raney nickel in 50 ml. of absolute ethanol was heated with steam and mechanically agitated during the hydrogenation. In 30 minutes the initial hydrogen pressure of 44 lb/sq. inch

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[125] W. H. Kirkpatrick, Doctoral Dissertation, Iowa State College, 1935.

[126] N. M. Cullinane, *J. Chem. Soc.*, 2366 (1932).

dropped to 36 lb./sq. inch where the pressure remained constant. The solution was filtered while warm, and the filtrate was diluted with water until a very slight turbidity was noticed at the boiling point of the solvent. The light brown precipitate obtained following cooling, filtration, washing with water and air drying weighed 2.4 g. (64%) and melted at 149-151.5°. Cullinane[126] reported a melting point of 152° for pure 2,7-diaminodibenzofuran.

2,7-Diacetamidodibenzofuran

This compound has been prepared by Cullinane[126] by acetylating with acetic anhydride. However, neither detailed experimental procedure nor the yield was given. The melting point of 2,7-diacetamidodibenzofuran was reported as about 290° with decomposition.[126] This run was modeled after that reported by Swislowsky[127] for acetylating 4-aminodibenzofuran.

To a solution of 3.8 g. (0.019 mole) of 2,7-diaminodibenzofuran in a mixture of 38 ml. of glacial acetic acid and 38 ml. of water were added dropwise 5 ml. of 90-95% acetic anhydride. The white precipitate was filtered,

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[127] J. Swislowsky, Doctoral Dissertation, Iowa State College, 1939.

washed with water and dried to give 5.7 g. of product melting over the range 277-280°. Recrystallization from glacial acetic acid, with Norit A treatment, yielded 4.3 g. (80%) of 2,7-diacetamidodibenzofuran which melted slightly at 265° and then resolidified and melted at 279-280°. When the melting point block was heated to 268° before inserting the melting point sample, the sample melted on insertion.

A sample of the 2,7-diacetamidodibenzofuran prepared was sent to Dr. N. M. Cullinane for a mixed melting point determination with the compound he had prepared. When melting points were determined with the author's sample, Dr. Cullinane's sample and a 50:50 mixture with an electrically heated melting point apparatus, the following results were reported:[128]

Author's compound: shrinkage at 258°, m.p. 274°

Dr. Cullinane's compound: shrinkage at 253°, m.p. 266°

Mixture: shrinkage at 255°, m.p. 267°

Dr. Cullinane also stated that his product did not appear to be as pure since it was less white in color.

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[128] Dr. N. M. Cullinane, private communication.

2-Aminodibenzofuran (attempted)

Attempts were made to convert 2-chlorodibenzofuran to 2-aminodibenzofuran with concentrated ammonium hydroxide with cupric sulfate as a catalyst in accordance with the procedure of Schimmelschmidt.[129]

An iron bomb containing a mixture of 5 g. of 2-chlorodibenzofuran, 17 ml. of concentrated ammonium hydroxide and 0.7 g. of cupric sulfate pentahydrate was heated electrically to a temperature of 200° and kept at that temperature for 10 hours. After allowing the bomb to cool, the mixture was digested with ether and filtered. The filtrate was acidified with hydrochloric acid and the aqueous layer was separated from the ethereal layer. The aqueous solution was made alkaline with sodium hydroxide and extracted with ether. No product was obtained upon removal of the ether from this ethereal extract. From the original ethereal layer 4.9 g. of impure 2-chlorodibenzofuran melting at 95-98° were recovered.

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[129] K. Schimmelschmidt, Ann., 566, 184 (1950).

4-Dibenzofuryloxyacetic acid

4-Dibenzofuryloxyacetic acid could not be prepared from the treatment of an alkaline solution of 4-hydroxydibenzofuran with chloroacetic acid; therefore, Haskelberg's method[130] was employed.

To a solution of 0.64 g. (0.0275 g. atom) of sodium in 21 ml. of absolute ethanol were added, in succession, 5.06 g. (0.0275 mole) of 4-hydroxydibenzofuran in 21 ml. of absolute ethanol and 4.62 g. (0.0275 mole) of ethyl bromoacetate. The solution was refluxed for 1.5 hours and allowed to cool. After the resulting precipitate was filtered and dried, it weighed 8.4 g. and melted at 134.5-137°. A very gummy material was obtained upon attempted recrystallization of this product from a mixture of glacial acetic acid and ethyl acetate. This crude ester was hydrolyzed with a 10% sodium hydroxide solution. The solution was acidified and filtered to give 3.8 g. of product which decomposed in the neighborhood of 225°. One recrystallization from glacial acetic acid and two from carbon tetrachloride containing a small amount of glacial acetic acid gave the following fractions of 4-dibenzofuryloxyacetic acid: 0.4 g., m.p.

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[130] L. Haskelberg, _J. Org. Chem._, _12_, 426 (1947).

155-157°; 0.9 g., m.p. 156-157° and 0.9 g., m.p. 157-157.5°. The total yield was 2.2 g. (33%).

DISCUSSION

Organolithium Compounds

Alkyllithium compounds

In most metalation and halogen-metal interconversion reactions carried out in This Laboratory, the organolithium compound used was n-butyllithium. The use of a reaction temperature of -10° gave 75-90% yields from n-butyl bromide with diethyl ether as the solvent.[33] A temperature in the neighborhood of -30° gave yields of 85-93%. Generally the yield was 88 _ 1% at this temperature.[131]

The great dependence of yields of organolithium compounds on slight changes in experimental conditions have been aptly demonstrated in the preparations of 2-ethyl hexyllithium from 2-ethylhexyl bromide. When the addition of the 2-ethylhexyl bromide-ether solution was carried out at -20°, the yield was 35.6%; at -30°, the yield was 11.5%. However, a yield of 67.8% was obtained by starting the

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[131] Mr. D. R. Swayampati of This Laboratory has found that the coating of grease and oil on the lithium wire did not affect the yield of n-butyllithium. Two hours of stirring at -30° after the completion of the addition of the n-butyl bromide was sufficient to complete the reaction.

reaction at room temperature, adding the 2-ethylhexyl bromide-ether solution at -30° over a period of one hour and then stirring at -10-0° for one hour.[132]

The use of <u>tert</u>-butyllithium as an intermediate for the introduction of the <u>tert</u>-butyl groups has been studied by many workers.[21,22,25,30,133] The most systematic work on the preparation of <u>tert</u>-butyllithium was carried out by Tyler[22,25] who obtained yields of 60-75% using a combination of lithium foil or sand and very pure <u>tert</u>-butyl chloride (b.p. 36.2-37.0) in equally pure pentane.

By employing a large excess of lithium foil, commercially available <u>tert</u>-butyl chloride (b.p. 51-52)[134] and commercially available "pure-grade" pentane,[135] a fair yield (57% by a simple acid titration and a 46.8% yield by double titration) of <u>tert</u>-butyllithium was obtained. This discrepancy in yields is significant and will be discussed in connection with the preparation of <u>n</u>-dodecyl- and <u>n</u>-octadecyllithium in petroleum ethers. The reaction of <u>tert</u>-butyl chloride and lithium in pentane resulted in

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[132] R. D. Gorsich, unpublished studies.

[133] L. H. Sommer, U. S. Patent 2,626,270 (Jan. 20, 1953).

[134] Columbia Organic Chemicals Co., Inc.

[135] Phillips Petroleum Co.

the formation of a dark coating on the metallic surface which undoubtedly reduced the reactivity of the lithium as the reaction proceeded. The effect of this coating was reduced by (1) using a large excess of lithium, (2) using lithium with a large surface and (3) employing a high speed stirrer with a steel blade capable of knocking the coating off the surface. In the preparations carried out, the yields as determined by double titration were: large excess of lithium foil, 46.8%; high-speed, counter-rotating stirrer, 19%; continuous addition of fresh lithium, 8.1% and stirring with a glass paddle, 3.75%.

n-dodecyl- and n-octadecyllithium were prepared as intermediates for the attempted syntheses of tri-2-biphenylyl-n-dodecylsilane and tri-2-biphenylyl-n-octadecylsilane, respectively, from the reaction with tri-2-biphenylylchlorosilane. When the preparations were carried out in pentane, heptane or petroleum ether, the experimental procedure used was in accordance with that reported by Meals.[16,18] The great difference in double and simple acid titration values obtained is significant in view of the following advantages that have been claimed[24] for petroleum ether (b.p. 28-38) as a solvent.

> First, the difficulty of secondary reactions like cleavage, present in diethyl ether is obviated. Second, indirect supplementary analyses are not necessary to determine the titer of solution, and

the simple acid titration analysis is adequate. Third, the by-products like lithium halide, are insoluble in petroleum ether and so are removed on filtration.

n-Dodecyllithium was prepared from n-dodecyl chloride and lithium ribbon in petroleum ether (b.p. 28-38°), pentane, and heptane, respectively. Yields as determined by double and simple acid titration were, in the same order, 61%, 104%; 58.5%, 107% and 4.10%, 91%, respectively. Yields of n-dodecyllithium prepared in heptane were redetermined after allowing the suspension to stand at room temperature for 3 days. The clear supernatant solution gave 2.45% by double titration and 82% by a simple acid titration. The values obtained on the suspension were 2.58% by double and 91% by single titration.

The results obtained by this investigator as well as those reported by Meals[18] indicate that these statements are not applicable to long-chained alkyllithium compounds. Side reactions occurred which resulted in formation of by-products which contributed to the total alkalinity; therefore, a double titration was essential. The decrease in yields after standing for 3 days showed that long-chained alkyllithium compounds did decompose on storing in heptane at room temperature. The greater yield (by single and double titration) of the suspension as compared to the supernatant liquid demonstrated that a considerable amount of inorganic base was soluble in heptane and some organolithium compound was insoluble. Limited solubility of methyllithium and ethyllithium in petroleum ether (b.p. 28-38°) has also been observed;[21] therefore, filtration of the reaction mixture is not advisable.

A possible explanation for the difference in yields by simple acid titration as compared to double titration may be the relatively slow rate of rate of reaction between long-chained alkyllithium compounds in petroleum ether and benzyl chloride. The reaction may be incomplete under the conditions of double titration. Results obtained by Meals[18] on yields of n-dodecyllithium and n-hexadecyllithium derivatives as determined by a simple acid titration, double titration and by carbonation showed that this is the case. n-Dodecyllithium prepared from n-dodecyl chloride in petroleum ether (b.p. 28-38°) gave yields of 71% and 35% by single and double titration, respectively. Carbonation gave 36.2% tridecanoic acid, 28% tetracosane and 9.1% dodecane plus dodecene; therefore, the yield of n-dodecyllithium actually present at the time of carbonation was at least 36.2%. Values obtained for n-hexadecyllithium were 63.1% by simple acid titration, 44.5% by double titration and 27.2% by carbonation to heptadecanoic acid. Other products isolated from the carbonation were hexadecane

(13.9%) and dotriacontane (20%). Results from the hexadecyllithium run were inconclusive. However, the great difference in yields of n-dodecyllithium and n-octadecyllithium by single and double titration when heptane was used as the solvent indicated that in this case at least the main reason was not the slowness of the reaction between benzyl chloride and long-chained alkyllithium compounds.

A clue on side reactions that could have occurred in the preparation of alkyllithium compounds in inert solvents and on the identity of the inorganic base was given in the work by Ziegler and Gellert[17] on thermal stability of alkyllithium compounds. The thermal decomposition was reported to have proceeded according to the following reactions:

$$(1)\quad CH_3CH_2CH_2CH_2Li \longrightarrow LiH + CH_3CH_2CH = CH_2\ (92\%)$$

$$(2)\quad CH_3CH_2CH = CH_2 + LiC_4H_9 \longrightarrow CH_3\text{-}CHLi\text{-}CH = CH_2 + C_4H_{10}\ (8\%)$$

$$(3)\quad CH_3\text{-}CHLi\text{-}CH = CH \longrightarrow LiH + CH_2 = CH\text{-}CH = CH_2 \longrightarrow \text{polymer}$$

When octane (b.p. 126°) was used as the solvent, 95% butene and 5% butane were obtained.

According to the above reactions, for every mole of butane and butene produced, 1 mole of lithium hydride is formed. This means that the single titration value for alkyllithium compounds prepared in an inert solvent should be close to the combined yields of alkanoic acid, alkane and alkene isolated from the carbonated reaction mixture. Data reported by Meals[18] are _n_-dodecyllithium; 71% by acid titration, 45.3% yield of tridecanoic acid plus dodecane and _n_-hexadecyllithium; 63.1% by acid titration, 41.1% yield of heptadecanoic acid plus hexadecane. The values are not close in both cases, but a considerable amount of products obtained from Wurtz-type coupling between alkyllithium and alkyl chloride were obtained. The similarity of physical properties of the coupling products to those of the alkane and alkene formed may make separation of these compounds very difficult.

The presence of unsaturation resulting from the preparation of _n_-dodecyllithium in heptane was also indicated from the large amount of iodine-glacial acetic acid solution that was required to get a positive Color Test I.

The thermal stability studies by Ziegler and Gellert showed the probable reason why forcing conditions (baking or use of high boiling solvent) were not effective in getting a reaction between tri-2-biphenylylchlorosilane and dodecyllithium and octadecyllithium, respectively, to yield tri-2-biphenylyldodecylsilane and tri-2-biphenylyloctadecylsilane.

Alkyldilithium compounds

The series of preparations and attempted preparations of alkyldilithium compounds were initiated by the receipt of lithium dispersion.[103] The publication by West and Rochow[31] on the preparation of dilithium derivatives of 1,4-dibromobutane, 1,5-dibromopentane, 1,6-dibromohexane, 1,10-dibromodecane and dibromoethane further stimulated the investigation. Since West and Rochow used lithium sand, it was hoped that the use of lithium with even greater surface, lithium dispersion, would permit the preparation of hitherto unreported 1,3-dilithiopropane and 1,2-dilithioethane.

When ethylene glycol dimethyl ether was used as the solvent with tetrahydrofuran as the catalyst, a positive Color Test I was obtained in the reaction of lithium dispersion with trimethylene bromide and ethylene bromide, respectively. However, neither of the two preparations gave an acid on carbonation. In both cases the reaction mixture gave a strong Color Test I, but after standing for about an hour the mixture gave a negative test. This indicated that decomposition of organolithium compounds was taking place. It was also observed that during the preparation, a gas was evolved which decolorized bromine water and gave a positive Baeyer test for unsaturation. These phenomena can be explained by postulating that the initially formed monolithium intermediate of trimethylene bromide and ethylene bromide decomposed into an olefin and lithium bromide. Organolithium compounds may have also been lost through ether-cleavage reactions.[14,44]

Reactions were also carried out in diethyl ether but carbonation again gave no acid although a positive Color Test I was observed. When a similar run was made with ethylene chloride and lithium dispersion in pentane, a positive Color Test I was never observed.

With decamethylene bromide the reaction with lithium dispersion, lithium ribbon and lithium wire, respectively, gave in the same order 51.9%, 42.5% and 42.8% yield of decamethylenedicarboxylic acid. These runs were in diethyl ether. The stability of the intermediate, 1-bromo-10-decyllithium, was undoubtedly due to the distance between the bromo and the lithium substituent.

Aryllithium compounds

One side reaction which can occur in the preparation of aryllithium compounds is a Wurtz-type coupling reaction. This reaction can be inhibited if the concentration of an aryl halide in the reaction mixture is maintained at a minimum concentration necessary for the reaction to proceed smoothly. This optimum concentration can be maintained by the use of experimental conditions that will permit the reaction between the halide and lithium to proceed as rapidly as the halide is added to the reaction mixture.

The usual preparation of phenyllithium from bromobenzene[40] was modified by dispensing with a cooling bath and adding the bromobenzene-ether solution at a rate just sufficient to maintain a gentle reflux. Quantitative yields of phenyllithium as determined by a single acid titration were obtained. The same technique was used with 2-bromobiphenyl, *m*-bromotoluene, bromomesitylene and 2-bromonaphthalene and in every case yields were improved over those previously reported (see Table 1).

The reactivity of chlorobenzene and *m*-chlorotoluene toward lithium was not sufficient to maintain a gentle reflux when their solutions in ether were added very slowly. Therefore, with these halides an external heat which was sufficient in maintaining a very gentle reflux was used. A 92.5% yield of phenyllithium and 71% yield of m-tolyllithium were obtained from the corresponding chlorides. These yields (especially that of phenyllithium) meant that these organolithium compounds were more cheaply obtained from the chlorides than the bromides because of the greater cost of the bromides.

Preparation of phenyllithium from fluorobenzene has hitherto not been reported. When the same experimental conditions as those used with chlorobenzene were used, no phenyllithium was obtained. The addition of fluorobenzene initially in one portion gave a 20% yield of phenyllithium by a simple acid titration but carbonation to benzoic acid gave a yield of 0.72%. The yield of biphenyl isolated from this reaction mixture was 18%. The isolation of only benzoic acid and biphenyl from the reaction mixture is significant, because Wittig[136] postulated o-biphenylyllithium as the primary intermediate in the formation of biphenyl from the reaction of fluorobenzene and phenyllithium followed by hydrolysis of the reaction mixture.

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[136] G. Wittig and W. Merkle, Ber., 76, 109 (1943).

$$C_6H_5F + C_6H_5Li \longrightarrow \underline{o}\text{-}FC_6H_4Li \xrightarrow{C_6H_5Li} \underline{o}\text{-}C_6H_5C_6H_4Li$$

$$\xrightarrow{H_2O} C_6H_5C_6H_5 + LiOH$$

If in the reaction reported in This Dissertation, o-biphenylyllithium were present in a concentration as high as 18%, some o-biphenylylcarboxylic acid would have been obtained. Wittig reported that the aqueous layer from the hydrolyzed mixture contained 17% lithium hydroxide, however, the yield of biphenyl isolated from the ether layer was 72%. If the reaction proceeded according to the above scheme, the concentration of lithium hydroxide should have been at least 72% since 1 mole of base is released for every mole of 2-biphenylyllithium hydrolyzed. The high yield of biphenyl and the low alkalinity titer was explained[137] by postulating a reaction between o-biphenylyllithium and fluorobenzene yielding o-fluorophenyllithium and biphenyl.

$$\underline{o}\text{-}C_6H_5C_6H_4Li + C_6H_5F \longrightarrow C_6H_5C_6H_5 + \underline{o}\text{-}FC_6H_4Li$$

The results obtained by this investigator indicate the absence of o-biphenylyllithium in an appreciable

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[137] G. Wittig, G. Pieper and G. Fuhrmann, Ber., 1193 (1940).

concentration; therefore, biphenyl must have been formed according to the second mechanism suggested by Wittig or by a coupling reaction between phenyllithium and fluorobenzene. However, studies being carried out by Mr. R. D. Gorsich of This Laboratory on _o_-fluorophenyllithium cast doubt on any mechanism which postulates the formation of _o_-fluorophenyllithium but omits its self-condensation to 2'-fluoro-2-lithiobiphenyl.

Lithium dispersion, high concentration of fluorobenzene and high boiling solvents, respectively, were used in order to overcome the inertness of fluorobenzene toward lithium wire and ribbon. The carbonation of the reaction mixture in which the dispersion was used gave a 0.51% yield of benzoic acid. An acid titration was not carried out because lithium dispersion cannot be filtered through a glass wool plug. When the run was carried out in the usual manner with lithium ribbon using tetrahydrofuran as the solvent, the single titration value was 152.5% but the yield by double titration was only 26.6%. Carbonation gave an acidic brown oil which could not be purified. A reaction involving tetrahydrofuran with lithium and phenyllithium must have occurred. In order to obviate the possibility of the loss of an organolithium intermediate through an ether-cleavage reaction a run was carried out using the Barbier technique[42] with fluorobenzene, lithium ribbon and triphenylchlorosilane in ethylene glycol dimethyl ether. The minimum yield of phenyllithium was 16.5%, since that was the yield of the tetraphenylsilane isolated. The possibility of tetraphenylsilane resulting from a diproportionation reaction is improbable because no tetraphenylsilane was isolated from a similar reaction with 2-chlorodibenzofuran and triphenylchlorosilane.

Attempts were made to prepare 2-dibenzofuryllithium directly from the reaction of lithium and the corresponding chloride and bromide. In the run with 2-bromodibenzofuran in tetrahydrofuran, single titration gave an alkalinity value of 190%. Carbonation, however, gave a crude acidic material which could not be purified. The preparation of 2-triphenylsilyldibenzofuran was attempted from the reaction of lithium, 2-chlorodibenzofuran and triphenylchlorosilane in ethylene glycol dimethyl ether by the Barbier method. An 80% recovery of 2-chlorodibenzofuran resulted. When the reaction of 2-chlorodibenzofuran and lithium was carried out in dioxane, a small amount of dibenzofuran and a 17.6% yield of _o_-hydroxybiphenyl were obtained.

Organosilicon Compounds

The reactions involving tri-2-biphenylylsilyl derivatives were carried out as a continuation in the study of 2-biphenylyl substituted silicon compounds.[107]

The failure to obtain the desired products from the reaction of tri-2-biphenylylchlorosilane and allylmagnesium bromide, n-dodecyllithium and n-octadecyllithium is attributed to the steric hindrance afforded by the 2-biphenylyl groups as well as to the instability of the alkyllithium compounds used. The low thermal stability of alkyllithium compounds[17] prevents the use of forcing conditions. Their relatively great tendency toward ether-cleavage reactions also prevents the use of a long reaction period.

Forcing conditions, however, were possible in the reaction between 2-biphenylyllithium and n-octadecyltrichlorosilane and n-dodecyltrichlorosilane, respectively. Purification of the products from these runs was extremely difficult because the desired products and most of the by-products were high-boiling, viscous liquids. The identity of tri-2-biphenylyloctadecylsilane and tri-2-biphenylyldodecylsilane has as yet not been rigorously confirmed. The infrared spectrum of tri-2-biphenylyloctadecylsilane checked very well for the compound but the silicon analysis was poor. The silicon analysis of tri-2-biphenylyldodecylsilane was good but its infrared spectrum as a carbon disulfide solution did not have an aliphatic C-H band at 6.9 μ.

Incidental to the preparation of sterically hindered 2-biphenylyl substituted silicon compounds, attempts were made to prepare tri-2-naphthyloctadecylsilane and triphenyl-*tert*-butylsilane.

Organoboron Compounds

Arylboronic acids were prepared by using a modification of the procedure reported by Bean and Johnson.[138] The two principal modifications were the use of organolithium compounds instead of Grignard reagents and the extraction of boronic acids from the ether-butanol layer with 10% potassium hydroxide instead of removing the ether and butanol by distillation.

Yabroff, Branch and Bettman[117] reported that 2-biphenylboronic acid melted at 126° with effervescence and 2-biphenylboronic acid anhydride melted at 196-197°. However, on the basis of their infrared spectra, neutral equivalent values and from the comparison of the melting points of

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[138] F. R. Bean and J. R. Johnson, *J. Am. Chem. Soc.*, *54*, 4415 (1932).

m-biphenylboronic acid and p-biphenylboronic acid, it seems as if the compound reported as the acid is actually a hydrated acid and the anhydride is actually the anhydrous acid.

It may also be significant that with 2-biphenylboronic acid and a compound believed to be mesityleneboronic acid[139] (both ortho substituted), direct titration with sodium hydroxide using phenolphthalein as an indicator was impossible although mannitol was added as a complexing agent.[118]

The melting point of 4-dibenzofuranboronic acid could not be determined accurately because of its great tendency to undergo dehydration to the anhydride form.

Mesityleneboronic acid could not be prepared by the method used for preparing 2-biphenylboronic acid and 4-dibenzofuranboronic acid. No acidic material was obtained but a 53.8% yield of a nonacidic compound which has been tentatively called dimesityleneborinic acid was isolated. A stable borinic acid is somewhat unusual,[119] but the two ortho substituents on the mesityl groups may possibly stabilize dimesityleneborinic acid through some steric effects.

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[139] E. A. Weipert, unpublished studies.

Dibenzofuran Derivatives

In the publication[121] on chloro derivatives of dibenzofuran from This Laboratory, the chlorination of 4-dibenzofurancarboxylic acid was assumed to have taken place in the unsubstituted ring, Para to the hetero atom. Decarboxylation of the chloro acid afforded 2-chlorodibenzofuran; therefore the chlorination was in the para position. The heteronuclear nature of the chlorination was suggested by analogy with the behaviour of the 4-acid on bromination which gave 2-bromo-6-dibenzofurancarboxylic acid. The deactivating influence of the carboxyl group and the similarity of the spectrum of the chloro acid with that of 2-bromo-6-dibenzofurancarboxylic acid also indicated that the chlorinated product was 2-chloro-6-dibenzofurancarboxylic acid.

For synthesizing 2-chloro-6-dibenzofurancarboxylic acid by an unambiguous method, the reaction reported by Voetgli, Muhr and Lauer[120] on the replacement of bromine of an aromatic bromide with chlorine by treating with chlorine gas in the presence of ultraviolet light was utilized.

2-Bromo-6-dibenzofurancarboxylic acid (identity established by ring closure synthesis[140]) was dissolved in carbon tetrachloride solution containing a small amount of trichloroacetic acid to increase its solvent power. The solution in a quartz flask was irradiated with ultraviolet light and treated with chlorine. The product obtained was established as 2-chloro-6-dibenzofurancarboxylic acid by comparison of melting points and infrared spectra of the corresponding chloro and bromo compounds. The compound prepared also gave a qualitative test for halogen but the test for bromine in the presence of chlorine was negative. A rearrangement occurring in this reaction is unlikely because the ring containing the carboxyl group is deactivated and the position occupied by the bromine displaced is the position in which halogenation occurs in dibenzofuran. The conversion of m-chlorobromobenzene to m-dichlorobenzene in an 85% yield without any side product[120] also indicates that rearrangement is unlikely.

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[140] H. Gilman, M. Van Ess and D. M. Hayes, J. Am. Chem. Soc., 61, 643 (1939).

Suggestions for Further Research

Further studies on the composition and reactions of lithium dispersion are required before its utility in organic syntheses can be properly evaluated. Lithium dispersion in different concentrations and in dispersing media of various viscosities should be tried. Direct preparation of organolithium compounds from the corresponding fluorides and chlorides should be attempted with this form of lithium. When petroleum ether is used as a solvent, the use of lithium dispersion may be profitable, since in this solvent the coating that forms on the lithium surface hinders the reaction.

The Barbier technique[42] should be employed in the preparation of compounds involving organolithium intermediates that are either unstable or difficult to prepare. Unstable organolithium compound may be derivatized as it is formed by having a reactant (benzophenone or triphenylchlorosilane) present in the reaction mixture with the lithium pieces. The instability of organolithium compounds may also be due to solvents such as ethylene glycol dimethyl ether, tetrahydrofuran and dioxane, which are readily cleaved by organolithium compounds. The Barbier technique should be used to take advantage of the great promoting effect these solvents have on reactions between lithium and organic halides and to reduce ether-cleavage reactions which result in the loss of organolithium compounds.

The estimation of yields of alkyllithium compounds prepared in petroleum ethers should be reinvestigated systematically. Yields should be determined on aliquot samples by a simple acid titration, double titration and by derivatizing with carbon dioxide, benzophenone or triphenylchlorosilane. Alkyllithium compounds prepared should be typical examples of normal, secondary and tertiary compounds prepared from the corresponding chlorides and bromides.

The recent work by Thiec[38] on the use of _n_-butyl bromide and bromobenzene in the "direct" preparation of organolithium compounds warrants further study. Attempts should be made to prepare organolithium compounds that have only been satisfactorily prepared by halogen-metal interconversion reactions in order to determine its scope and limitations.

Wittig's experiment[136] involving the reaction of fluorobenzene and phenyllithium in which 2-biphenylyllithium was postulated as an intermediate in the formation of biphenyl isolated should be reinvestigated. Aliquot samples of the reaction mixture should be titrated and carbonated every day for a week. Fluorobenzene should also be treated with 2-biphenylyllithium to determine whether biphenyl is formed.

For a systematic study of the relative steric hindrance afforded by various groups, reactions of tri-2-biphenylylchlorosilane with o-tolyl-, m-tolyl-, 1-naphthyl-, 2-naphthyl-, tert-butyl-, isopropyl, cyclohexyl- and cyclopentyllithium, respectively, under identical experimental conditions should be carried out. The steric effects of other trisubstituted chlorosilanes containing less than three 2-biphenylyl groups should also be examined. Tri-2-biphenylyltriphenyldisilane and tri-2-biphenylyltriphenyldisiloxane are also of interest from the standpoint of preparing sterically hindered organosilicon compounds. Possible syntheses for these compounds are as follows:

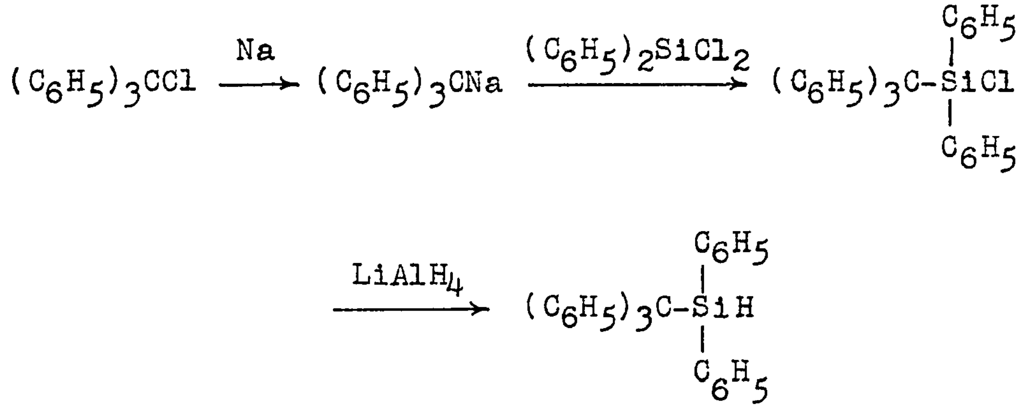
$$(1)\quad (C_6H_5)_3SiSi(C_6H_5)_3 \xrightarrow[\substack{\text{ethylene glycol}\\ \text{dimethyl ether}}]{\text{Li}} (C_6H_5)_3SiLi$$

$$\xrightarrow{(2\text{-}C_6H_5C_6H_4)_3SiCl} (2\text{-}C_6H_5C_6H_4)_3SiSi(C_6H_5)_3$$

$$(2)\quad (C_6H_5)_3SiOH \xrightarrow{\text{Na}} (C_6H_5)_3SiONa$$

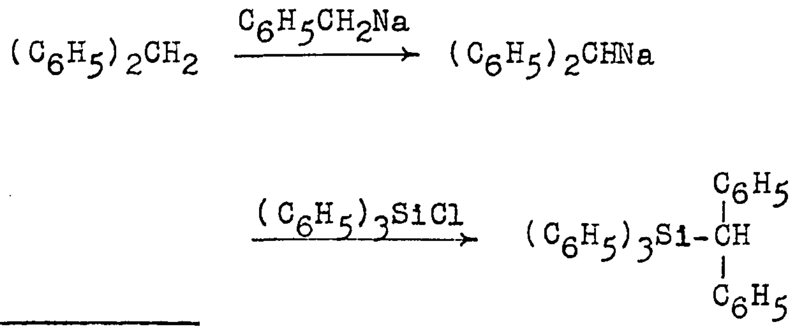
$$\xrightarrow{(2\text{-}C_6H_5C_6H_4)_3SiCl} (C_6H_5)_3SiOSi(2\text{-}C_6H_5C_6H_4)_3$$

In the polymerization of styrene it was found that triphenylsilane was a better chain transfer agent than triphenylmethane.[141] In view of the great reactivity shown by pentaphenylethane, triphenylmethyldiphenylsilane and triphenylsilyldiphenylmethane should be synthesized and their radical chain transfer abilities should be investigated. Triphenylmethyldiphenylsilane may dissociate very readily to form triphenylmethyldiphenylsilyl radical. These compounds may possibly be synthesized by the following reactions:

(1) 

$$(C_6H_5)_3CCl \xrightarrow{Na} (C_6H_5)_3CNa \xrightarrow{(C_6H_5)_2SiCl_2} (C_6H_5)_3C\text{-}\overset{C_6H_5}{\underset{C_6H_5}{SiCl}}$$

$$\xrightarrow{LiAlH_4} (C_6H_5)_3C\text{-}\overset{C_6H_5}{\underset{C_6H_5}{SiH}}$$

(2) 

$$(C_6H_5)_2CH_2 \xrightarrow{C_6H_5CH_2Na} (C_6H_5)_2CHNa$$

$$\xrightarrow{(C_6H_5)_3SiCl} (C_6H_5)_3Si\text{-}\overset{C_6H_5}{\underset{C_6H_5}{CH}}$$

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[141] J. S. Curtice, Doctoral Dissertation, Iowa State College, 1954.

The good yield of tri-2-biphenylylsilane obtained from the lithium aluminum hydride reduction of tri-2-biphenylylchlorosilane when ethylene glycol dimethyl ether was used as the solvent[107] suggests further investigation on its use as a solvent in lithium aluminum hydride reductions. It may prove to be much better than tetrahydrofuran which has a very explosive tendency when contaminated with peroxides.

More ortho substituted arylboronic acids should be prepared to determine whether complex formation with mannitol is hindered by the presence of ortho groups; thereby, preventing direct titration with sodium hydroxide solution using phenolphthalein as an indicator. Attempts should also be made to synthesize ortho substituted diarylborinic acids.

Further study should be made on the reactions of bromo derivatives of dibenzofuran with chlorine in the presence of ultraviolet light. One group of bromo compounds should contain a position susceptible to chlorination and a bromo substituent should be in a position activated for halogenation. 1-Bromo-4-hydroxydibenzofuran and 1-bromo-4-acetamidodibenzofuran are examples of these types of compounds. The other group of bromo compounds should also have a position susceptible to chlorination, but the bromine should be in a deactivated position as in 2-bromo-4-dibenzofurancarboxylic acid and 2-bromo-4-methoxydibenzofuran.

SUMMARY

A survey of the literature on the direct preparation of organolithium compounds from the direct reaction of lithium and the corresponding halides was made. The experimental conditions and other factors involved were correlated and re-evaluated.

The use of a temperature of -20 to -30° during the addition of *n*-butyl bromide consistently afforded 85-93% yields of *n*-butyllithium.

When long-chained alkyllithium compounds were prepared in petroleum ethers and similar solvents, considerable deviations in yields as determined by a simple acid titration and double titration were found.

1,10-Dilithiodecane was prepared, but attempts to prepare 1,3-dilithiopropane and 1,2-dilithioethane failed although lithium dispersion was used.

Yields of aryllithium compounds from aryl bromides were improved over those previously reported by adding the bromides at a rate just sufficient to maintain a gentle reflux of a solvent without any external heating or cooling.

Aryllithium compounds were prepared from the corresponding chlorides in good yields by maintaining a gentle reflux by external heating during the addition of the aryl chlorides.

Phenyllithium was prepared from the direct reaction of fluorobenzene with lithium.

Reactions involving tri-2-biphenylylchlorosilane and organolithium compounds were carried out.

Some boronic acids were prepared from the reaction of aryllithium compounds and tri-*n*-butylborate.

ACKNOWLEDGMENT

The author wishes to express his sincere appreciation to Dr. Henry Gilman for helpful advice, constructive criticism and encouragement given throughout the course of this investigation.