

1936

# Relative reactivities of organoalkali compounds

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RELATIVE REACTIVITIES OF  
ORGANOALKALI COMPOUNDS

by

Richard V. Young

124  
79-28

A Thesis Submitted to the Graduate Faculty  
for the Degree of

DOCTOR OF PHILOSOPHY

Major Subject      Organic Chemistry

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RELATIVE REACTIVITIES OF ORGANOALKALI COMPOUNDS

INTRODUCTION

Organometallic compounds are the most versatile types of organic compounds known at the present time. Their relative reactivities range from the superlatively active organoalkali compounds down through an almost imperceptible gradation of decreasing activity until we reach the types that are very inert and may be represented by the organoplatinum compounds. The utility of an organic compound for synthetic purposes depends upon its ability to react with certain functional groups of other molecules, and it may be said that the most active organometallic compounds react to some extent with all functional groups that may be found in organic compounds.

Organometallic compounds react at different rates with various groups, and by a judicious choice of the organometallic to be used for any synthetic purpose it may be possible to obtain selective reactions in which only certain groups of a polyfunctional molecule react to any marked extent. These selective types of reactions have not been applied to organoalkali compounds in general, but are found particularly in the chemistry of organomagnesium compounds (1) which have been studied much

- (1) Grignard, Compt. rend., 134, 849 (1902); (b) Mavrodin, Bull. soc. chim. Romania, 15, 99 (1933) [C.A., 28, 3396 (1934)]; (c) Fordyce and Johnson, J. Am. Chem. Soc., 55, 3398 (1933); (d) Entemann and Johnson, ibid., 55, 2900 (1933); (e) Hibbert, J. Chem. Soc., 101, 391 (1912).

more intensively. Of the greatest importance to the organic chemist, is the ability to predict, with reasonable accuracy, the course of reactions of this type, and this depends largely upon an accurate knowledge of the relative reactivities of these organometallic compounds.

Gilman and Nelson (2) have briefly summarized the work on the relative reactivities of organometallic compounds and have made several generalizations which make it possible to predict with reasonable accuracy, the relative reactivity of an organometallic compound. This study also clearly demonstrates the fact that an accurate knowledge of the relative reactivities of the organometallic compounds enables one to choose a type that has properties which will greatly increase yields of the reaction product.

An enormous amount of experimental data would be necessary to place all of the organoalkali compounds in an activity series, since the reactivity of an organometallic compound depends not only upon the metal, but upon the organic radical in the molecule. An organolithium compound may be prepared that is more reactive than an organosodium compound by the choice of appropriate and different organic radicals in each compound, but, in general, it may be said that the organic radicals that yield very reactive compounds with one metal, yield correspondingly active compounds with another and

(2) Gilman and Nelson, Rec. trav. chim., 55, 518 (1936).

Vice versa.

By the use of an appropriate organic radical combined with at least any two adjacent alkali metals it is possible to study the rates of the reaction of these organometallic compounds with various functional groups and by this method their relative reactivities may be determined. To make the series more valuable and reliable, however, it is necessary to study the relative reactivities of a variety of organic radicals in combination with the metal, as well as a miscellany of reactions of one organometallic compound.

### HISTORICAL PART

Until this time no systematic study of the relative reactivities of the organoalkali compounds has been made, and because of their extreme reactivity there has been a tendency of workers in that field to place them apart as a group of very reactive compounds in which very little distinction has been made between their relative reactivities.

Gilman and Kirby (3) and Kirby (4) have shown that organolithium compounds are more reactive than the corresponding organomagnesium and beryllium compounds but no other quantitative studies have been made involving the relative reactivity of an organoalkali compound. Some evidence may be gathered from the literature to indicate, in a general way, the relative reactivities of these organoalkali compounds, but much more experimental work is necessary to gain a true picture of their relative reaction velocities.

A series of generalizations, compiled from the available knowledge of the relative reactivities of organometallic compounds has been published by Gilman and Nelson (2); and the statement has been made that the organometallic compounds, derived from the metals in the A families of the first three groups of the periodic table, will increase in their

(3) Gilman and Kirby, *J. Am. Chem. Soc.*, **55**, 1265 (1933).

(4) Master's thesis of Mr. R. H. Kirby, Iowa State College, 1936.

reactivity with the increasing atomic weight of the metal. There is evidence in the literature that will support this prediction when it is applied to organoalkali compounds. Conant and Wheland (5), during their course of study of very weak acids (using hydrocarbons as the acids), state that  $\alpha$ -naphthyldiphenylmethylnsodium reacts erratically with triphenylmethane in periods of a few minutes to several months, while the potassium analog reacts smoothly and instantaneously. Benzyl-lithium does not decompose diethyl ether (6,7), and benzylnsodium decomposes this ether in a very short period of time (8). Ethyl-lithium may be prepared in a benzene solution (8) in which it is stable for a long period of time (9), while ethylnsodium metalates benzene to yield phenylnsodium (10) and a small amount of *o*- and *p*-phenylenedisodium (11). In the metalation reactions of dibenzofuran, Gilman and Young (12) observed that methyl-lithium metalates dibenzofuran slowly, while organosodium and -potassium compounds react much more rapidly. Dimetalation of dibenzofuran has never been accomplished with organolithium compounds, but proceeds smoothly with some organosodium and -potassium compounds (13).

- (5) Conant and Wheland, *J. Am. Chem. Soc.*, 54, 1212 (1932).  
(6) Ziegler, Crössmann, Kleiner, and Schafer, *Ann.*, 473, 1 (1929).  
(7) Ziegler and Dersch, *Ber.*, 64, 446 (1931).  
(8) Schlenk and Holtz, *Ber.*, 50, 269 (1917).  
(9) See page 64 of this thesis.  
(10) Schorigin, *Ber.*, 41, 2711 (1908).  
(11) Work by Mr. R. H. Kirby in this laboratory. See Morton and Hechenbleikner, *J. Am. Chem. Soc.*, 58, 1024 (1936).  
(12) Gilman and Young, *J. Am. Chem. Soc.*, 56, 1415 (1934).  
(13) *ibid.*, 57, 1121 (1935).

During a study of the reaction of organopotassium and -lithium compounds with phenylated ethylenic hydrocarbons, Ziegler and co-workers (6) made several observations concerning the relative reactivity of organoalkali compounds. Organopotassium compounds were found to add more rapidly to the ethylene bonds than the organolithium compounds. Certain types of organopotassium compounds that decompose diethyl ether have lithium analogs that are stable in the ether, and some simple organolithium compounds were found to decompose ether very slowly.

In view of the fact that the more reactive organometallic compounds are derived from the more active metals, a review of the studies of the action of the alkali metals with hydrocarbons yields some evidence of their relative reactivities (14). Hanriot and Saint Pierre (15) prepared triphenylmethylpotassium by the direct action of potassium on triphenylmethane at 200°. Fluorenylsodium and -potassium (16), fluorenyldipotassium (17), and indenylsodium (16, 18) have been prepared by fusion of the hydrocarbon with sodium or potassium. The lithium analogs of these compounds that are known have only

(14) For a summary of the chemistry of organoalkali compounds, see (a) Wooster, Chem. rev., 11, 1 (1932); (b) J. Schmidt, "Organometallverbindungen", Vol. II, Wissenschaftliche Verlagsgesellschaft m. b. H., Stuttgart, 1934, pp. 10-119.

(15) Hanriot and Saint Pierre, Bull. soc. chim., 37, 5, 774 (1889).

(16) Weissgerber, Ber., 41, 2913 (1908).

(17) Saint Pierre, Bull. soc. chim., 37, 5, 292 (1891).

(18) Weissgerber, Ber., 42, 569 (1909).

been prepared from the hydrocarbon by their reaction with organo-lithium compounds (19). With the exception of lithium which reacts too slowly, all of the alkali metals react with phenylacetylene in ether solution to form the corresponding phenylethynylalkali compound (20, 21). Sodium and potassium or the corresponding amides when dissolved in liquid ammonia will replace a hydrogen of diphenylmethane, triphenylmethane, or similar groups to yield a stable organometallic compound (22). The reaction of lithium and lithium amide with these hydrocarbons under similar conditions has not been reported.

Sodium-potassium alloy may be used to cleave certain ethers, and by this reaction a large number of organometallic compounds have been prepared (23). During this reaction the potassium analog is formed which shows the increased reactivity of potassium over sodium (24). Certain phenylated ethanes may also be cleaved by the alkali metals and by sodium-potassium alloy (23). This alloy is required to initiate reaction with tetraphenylethane, but only a one percent sodium amalgam is required to react with hexaphenylethane. With this in mind, Conant and Garvy (25) have developed a method for

(19) Schlenk and Bergmann, Ann., 463, 192 (1928).

(20) Nef. Ann., 308, 264 (1899)

(21) For other preparations, see page 74 of this thesis.

(22) Wooster and Ryan, J. Am. Chem. Soc., 54, 2419 (1932)

(23) (a) Ziegler and Thielman, Ber., 55, 1740 (1923); (b) Conant and Carlson, J. Am. Chem. Soc., 54, 4048 (1932).

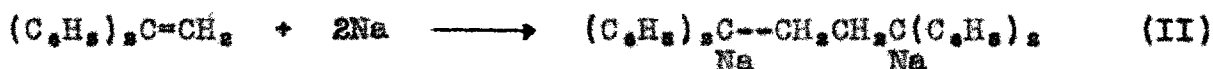
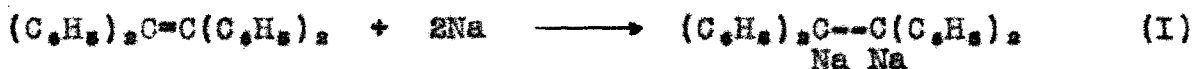
(24) See page 89 of this thesis.

(25) Conant and Garvy, J. Am. Chem. Soc., 49, 2599 (1927).



differentiating certain ethanes by their cleavage reactions with the alloy or with various concentrations of sodium in an amalgam. These tests have been applied further to aliphatic and aromatic ethanes by Marvel and co-workers (26), and while they were primarily designed to study the stability of certain carbon-carbon bonds, they indicate the greater reactivity of sodium-potassium alloy over sodium amalgams.

In 1914, Schlenk and co-workers observed a new type of reaction involving the addition of the alkali metals to various types of phenylated hydrocarbons (27, 28). The reaction proceeds by addition of the metal to the ethylenic bond, to form either a normal 1,2-addition product (I), or it may be accompanied with dimerization (II). Examples of both types of addition may be illustrated by the following reaction of tetraphenylethylene and 1,1-diphenylethylene:



Similar reactions have been observed with potassium, sodium, and lithium. Occasionally lithium reacts more rapidly than sodium, but in the large number of hydrocarbons investigated by Schlenk and co-workers (28), lithium generally acted more

(26) Ford, Thompson, and Marvel, *ibid.*, 57, 2619 (1935).

(27) Schlenk, Appenrodt, Michael, and Thal, *Ber.*, 47, 473 (1914)

(28) Schlenk and Bergmann, *Ann.*, 463, 1 (1928).

slowly than sodium. Preparations of the organopotassium compounds of this type were usually made in petroleum ether (gasoline) while the sodium and lithium compounds were generally prepared in diethyl ether. The use of petroleum ether for the organopotassium compounds is indicative of increased activity, and emphasizes the precaution that is necessary in choosing solvents for the more reactive types of organometallic compounds. No difference in the kind of chemical reactions of the alkali metals addition compounds has been reported.

That hydrocarbons react as very weak acids may be inferred from their reactions with basic materials. Certain hydrocarbons react smoothly with alkali metals to liberate hydrogen and form true organometallic compounds according to the following equation:

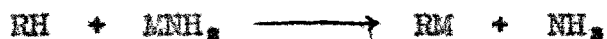


This reaction is limited, however, to hydrocarbons that contain, relatively speaking, a very acidic or active hydrogen. Further evidence for the acidic nature of the hydrogen in hydrocarbons is found in the fact that certain of these hydrocarbons react with potassium hydroxide to form the organopotassium compound. For example, fluorene reacts as follows (29):

(29) Weissgerber, Ber., 34, 1659 (1901).



and in a liquid ammonia solution of triphenylmethane, potassium hydroxide imparts the distinct characteristic color of triphenylmethylpotassium. Analogous reactions in liquid ammonia, with the alkali metals and their corresponding bases, the amides, yield a large variety of organoalkali compounds by the following type of reaction (22):



Considering the marked electropositive character of the alkali metals and the weakly acidic nature of the hydrocarbons, it might be predicted that the union of these two would produce substances that are polar in nature, resembling the inorganic salts of weak acids and strong bases, or the hydrides of these metals.

Confirmation of this view may be found in electrical conductivity measurements, as well as in certain reactions of the organoalkali compounds. Conductivity measurements are difficult for very few suitable solvents are available, and only certain of the organolithium compounds may be liquified without decomposition. Hein and co-workers (30) have

- (30) (a) Hein, Z. Elektrochem., 28, 269 (1922); (b) Hein, Petzchner, Wagler, and Segitz, Z. anorg. allgem. Chem., 141, 161 (1924); (c) Hein and Segitz, ibid., 158, 153 (1926).

determined the conductance of several of the simple organo-lithium, -sodium, and -potassium compounds dissolved in dimethyl-, diethyl-, and di-n-propylzinc; trimethyl- and triethylaluminum; and in diethylcadmium. These solvents, in themselves, are non-conductors of electricity. The triethylaluminum solvates of ethyl-lithium, -sodium, and -potassium are better conductors of electricity than those of diethylzinc, but the reverse is true for solutions of n-propylsodium and -potassium in di-n-propylzinc. Dilute solutions of alkylsodium compounds in dimethylzinc, and concentrated solutions of ethyl-lithium and -sodium in diethylcadmium are nonconductors. The general order of increasing molar conductances are parallel with the increasing atomic weight of the alkali metal. The organoalkali compounds form stable solvates with these substances, and the melting points increase with the increasing molecular weight of the metal, or increasing polarity of the compound. Table I will serve to illustrate the increasing molar conductivities and melting points of some diethylzinc solvates of the organo-alkali compounds (in the presence of diethylzinc).

TABLE I

MOLAR CONDUCTIVITIES AND MELTING POINTS OF SOME  
ALKYLALKALI SOLVATES OF DIETHYLZINC

	<u>Ethyl- lithium</u>	<u>Ethyl- sodium</u>	<u>Ethyl- potassium</u>
Concentration	3.97 N.	4.45 N.	5.43 N.
Molar conductance (at 50°)	0.19	4.01	6.47
Melting point of solvate.	--	26-27°	68-71°

These observations confirm the expectation that the salt-like character is more pronounced in the organic compounds of the more electropositive metals. A comparison of the conductance values of these alkylalkali compounds with inorganic salts of the alkali metals, serves to emphasize the similarity of these compounds. In Table II (31) are listed the molar conductivities of the alkali metal hydroxides, which may be considered salts of the weak acid, water.

TABLE II

MOLAR CONDUCTANCE VALUES OF A 0.1 NORMAL SOLUTION  
OF THE ALKALI METAL HYDROXIDES AT 18° C.

LiOH	74.5
NaOH	195.3
KOH	213.
RbOH	213.3
CsOH	-

(31) International Critical Tables, Vol VI, McGraw-Hill Book Co., New York, 1929, pp. 246-253.

It is interesting to note that in Tables I and II, the difference in the conductance values of lithium and sodium is much greater than in any other members of the series.

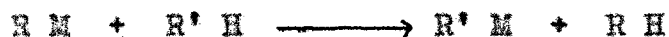
In the conductance experiments with solutions of ethylsodium in diethylzinc, the gases liberated at the anode consisted of about equal proportions of ethane and ethylene from disproportionation of the ethyl radical, and small amounts of butane, propane, and methane. The temperature coefficient of the conductance was found to be positive and the deposition of zinc (from the action of the elementary sodium on the diethylzinc) was found to be in quantitative agreement with Faraday's law. Several of the compounds show considerable variation in their polar character, and the fusible lithium alkyls resemble the organometallic compounds of the polyvalent metals in that they do not conduct an electric current. This is in agreement with the lower reactivity of the organolithium compounds.

Some of the colored organoalkali compounds have been found to conduct an electric current in ether solution (32, 33, 34, 8). Schlenk and Marcus (32) proposed a complex ion formation for the conductance of triphenylmethylsodium, because the equivalent conductance of these solutions decreased

- (32) Schlenk and Marcus, Ber., 47, 1664 (1914).  
(33) Schlenk and Holtz, ibid., 49, 603 (1916).  
(34) Schlenk and Bergmann, Ann., 463, 98 (1928).

with dilution, but Kraus and Rosen (35) have found that this behavior is characteristic of salts dissolved in solvents of low dielectric constant, and is not necessarily due to complex ion formation. When the conductance values were determined in solvents of higher dielectric constants, it was found that they behave in the manner characteristic of highly polar compounds (33). Ziegler and Wollschitt (36) found that triphenylmethylsodium and -potassium, and trinitrotriphenylmethylsodium behave in a normal manner in pyridine ( $D = 12.5$ ). Equivalent conductance measurements of these compounds showed triphenylmethylpotassium to be more polar in nature than the sodium analog, which is paralleled with the greater reactivity of the potassium compounds.

A characteristic reaction of salts is a metathetical reaction with acids. Similarly, organometallic compounds should yield similar reactions with hydrocarbons, if they act as salts and acids, respectively. This has been found to be the case, and the reaction of Schorigin (10) has been applied by Conant and Wheland (5) to a study of hydrocarbons with organometallics, as very weak acids and salts. The results demonstrated that the following reaction takes place when the salt of a weaker acid (RM) reacts with a stronger acid (R'H).



(35) Kraus and Rosen, J. Am. Chem. Soc., 47, 2739 (1925).

(36) Ziegler and Wollschitt, Ann., 479, 123 (1930).

By using this reaction, several phenylated hydrocarbons were placed in a series of decreasing relative acidity. During the course of this study they observed that  $\alpha$ -naphthyldiphenylmethylpotassium reacted instantaneously with triphenylmethane, while the sodium analog reacted erratically, requiring from a few minutes to several months.

Since the reactivity of the organometallic compound depends upon both the organic radical and the metal, a series of organometallic compounds using the same organic radical will have relative reactivities depending upon the character of the metal bond. As this linkage becomes more polar, the compounds become more salt-like in character, and also become more reactive. The relative reactivity of a compound may then be predicted by a study of the nature of the carbon-metal bond, and this in turn, may be correlated with the electropositive nature of the metal. The electromotive series of the metals will then serve to classify the organometallic compounds in a general way. The most electropositive element will give the most polar and most reactive organometallic compound. Lithium and calcium are exceptions to this, however, and the measured reactivities do not parallel this table, but it may serve as a valuable guide in predicting the approximate relative reactivity of an organometallic compound.

The electromotive series of the alkali metals with their oxidation potentials are found in Table III (37). It should

(37) International Critical Tables, Vol. VI, McGraw-Hill Book Co., New York, 1929, p. 332.



be noted that this series neither parallels the relative conductance values of the alkali metal hydroxides (Table II), nor does it follow the relative reactivity of the organoalkali compounds; but it places the organoalkali compounds as the most reactive group of organometallic compounds. Calcium is included in this series because of its relatively high oxidation potential, and reactivity, resembling that of the organoalkali compounds (38).

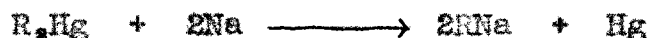
TABLE III  
ELECTROMOTIVE SERIES OF THE MOST  
ELECTROPOSITIVE METALS

Li	2.959
Cs	--
Rb	2.925
K	2.924
Ca	2.76
Na	2.714

Displacement reactions, so common in inorganic chemistry, may be applied to organometallic compounds, and are used extensively in the preparation of the more reactive organometallic types. Gilman and Straley (39) state that

- (38) Gilman, Kirby, Lichtenwalter and Young, Rec. trav. chim., 55, 79 (1936).  
(39) Gilman, and Straley, ibid., 55, (1936)

organometallic compounds of greater reactivity may be prepared from the lesser reactive types by the reaction of the more reactive metal on the lesser reactive compound. When applied to the displacement reactions of the electromotive series in inorganic chemistry, an analogy may be perceived readily.



The inorganic reaction proceeds to the right and essentially goes to completion. The organic reaction, however, rapidly reaches an equilibrium, and a large excess of sodium is required to obtain good yields of the organosodium compound (40). This demonstrates that there are factors other than the simple displacement that enter into this type of reaction, and only when all of the many factors that control a reaction, in both velocity and course, are elucidated, will we be able to accurately depict the exact nature of the reaction.

(40) Ziegler, Ber., 64, 445 (1931)

A. RELATIVE REACTIVITIES OF  
SOME DIBENZOFURYLALKALI COMPOUNDS

INTRODUCTION

During a course of study with dibenzofuran, Gilman and Young (12) discovered that dibenzofuran reacted smoothly with n-butyl-lithium, -sodium, or -potassium to yield the corresponding 4-dibenzofurylalkali compound by a metathetical reaction known as the Schorigin reaction (10), or more recently termed metalation (12) since it involves the direct replacement of a hydrogen atom by a metal to yield a true organo-metallic compound. This produced a new type of dibenzofuran derivative since no other direct substitution reaction of this molecule will introduce groups into the 4-position. Further study with organoalkali compounds showed that the use of the more reactive organosodium and -potassium compounds would introduce two atoms of the metal into the dibenzofuran molecule to form the corresponding 4, 6-dibenzofurylenedi-alkali compound (13), from which a number of new types of dibenzofuran derivatives were prepared; and from which it was hoped that compounds having analgesic and hypnotic action similar to that of morphine might be prepared (41, 42). These

- (41) Kirkpatrick and Parker, J. Am. Chem. Soc., 57, 1123 (1935).  
(42) Doctoral thesis of W.G. Bywater, Iowa State College, 1934.

dibenzofurylalkali compounds, accordingly, were very valuable for synthetic purposes, and to broaden our knowledge of their relative reactivities and to increase their utility, a study of their relative reactivities was begun.

Due to their inordinate activity with a wide variety of compounds and elements it is necessary to use extreme care in preparing and handling the organoalkali compounds. From the time of the preparation of the first organometallic compound by Frankland (43) until the present time, the more reactive organometallic compounds have been prepared under conditions that will rigidly exclude oxygen and moisture. Because the organoalkali compounds are the most reactive types of organometallic compounds known, great precaution has been used in preparing and handling them. To facilitate operations with these compounds numerous pieces of ingeniously shaped glassware have been devised. Probably, the most common apparatus that has the greatest utility for work in this field are the various types of tubes devised by Schlenk (44) and named after him. The purpose of this special glassware is to eliminate all joints, rubber stoppers, rubber connections, etc., so that no rubber may become involved in reactions with the organoalkali compounds, and also to prevent any influx of oxygen or water vapor from the atmosphere.

(43) Frankland, Ann., 71, 213 (1849).

(44) Schlenk and Thal, Ber., 46, 2843 (1913).

Ziegler and Colonius (45) were the first to prepare simple organolithium compounds by the reaction of the organic halide upon metallic lithium in an ether or benzene solution, although these compounds had been prepared previously by Schlenk and Holtz (8) and others (46) by the reaction of appropriate mercurials with metallic lithium. These procedures in general involved the use of this special glass apparatus that is difficult to prepare and very inconvenient to use. The Grignard reagent, however, is prepared with good yields in simple apparatus that is convenient to manipulate, and, although this organometallic compound is very sensitive to oxygen and moisture, this type of apparatus showed no deleterious effects. Gilman, Zoellner and Selby (47), accordingly prepared a series of simple organolithium compounds with the technique ordinarily used with the organomagnesium compounds, and were able to obtain yields of the desired lithium compound equivalent to or in excess of those reported by Ziegler and Colonius (45), showing that this much simpler and more versatile type of apparatus is equivalent or superior to the older and more complicated methods.

The 4-dibenzofurylalkali compounds were first prepared in Schlenk tubes, in petroleum ether solution, over a period

- (45) Ziegler and Colonius, Ann., 479, 135 (1930).  
(46) Hager and Marvel, J. Am. Chem. Soc., 48, 2689 (1926).  
(47) (a) Gilman, Zoellner and Selby, J. Am. Chem. Soc., 54, 1957 (1932). (b) ibid., 55, 1252 (1933).

of one to two weeks. By using this method the work was slow, the reaction products were difficult to handle, and this general technique did not lend itself readily to reactions that required frequent examination of the products, such as those required in the study of relative reaction velocities.

Experimentation immediately revealed that the simpler technique could easily be applied to the dibenzofurylsodium and -potassium compounds, and that yields of product, using this technique, were equal or superior to those yields obtained by using the older and less flexible methods. Further work has revealed that a similar technique may be employed in the preparation of practically all of the organosodium and -potassium compounds without perceptible deleterious effects.

In the study of relative reaction rates it is obviously necessary to choose reagents that react in a reasonable and measurable period of time. Many reactions such as carbonation, oxidation, and hydrolysis proceed almost instantaneously while others may require weeks or months for an initial reaction. Because of the wide range of reactivities of the organoalkali compounds, it is almost impossible to use one reactant for all of these types. The reactions may be carried out in a step-wise manner in which only two or three of the organometallics may be compared with one reactant. The most active organometallic of one particular group may then be used as the least reactive member of a more active group or vice versa, and by this method a complete series of relative reactivities

of the organometallic compounds may be obtained.

The most convenient type of reaction that may be employed in these measurements is one that progresses slowly and goes to completion in a few hours or days. Either an indicator must be available to follow the course of the reaction, or the products must be isolated and a comparison must be made of their relative quantities. The more reactive compound will yield the greater quantity of product in a period of time that is insufficient for complete reaction. The various types of reactions will be discussed more completely under individual headings.

The errors involved in the study of these relative reaction velocities will vary considerably with the type of reaction employed. Color reactions, when they are applicable, are desirable because they are sensitive, may be conveniently and accurately applied, and do not involve the isolation and identification of any reaction product. They may be misleading, however, because they give no indication of the course of the reaction or its state of progression. Their sensitivity undoubtedly will differ with various reactants, but in this event, the quantities required for the color reaction are so small when compared to the total amount of the reactant that this factor may generally be neglected. Color reactions for these purposes may be two types. One involves the color due to the organometallic compound, and the other involves the color test generally used for the more reactive organometallic

compounds (48). The colored types of organoalkali compounds are those for which we may write a quinoidal structure, such as benzyl-, diphenylmethyl-, triphenylmethyl-, and others. This type of structure has never been proved, but it may serve as a valuable method to classify the compounds. A few colored organoalkali compounds have been prepared in both the aromatic and aliphatic series for which it is impossible to write a quinoidal structure (28). An illustration of this type is tri-tert.-butylethynylpotassium prepared by Salzberg and Marvel (49). Only very small quantities of these compounds are required to give a deeply colored, generally red or blue, solution, and the disappearance of this characteristic color may be used as the end-point of the reaction, provided that colorless or only slightly colored products are formed in the reaction mixture. This type of reaction, however, is very limited in its scope, and would confine the study to a small class of organoalkali compounds that may or may not give us a true picture of the relative reactivity of the organoalkali compounds in general.

The color reactions involving the use of Michler's ketone and an active organometallic compound was developed by Gilman and Schulze (48) and has a much wider application in following the course of this type of reaction. All of the

(48) Gilman and Schulze, J. Am. Chem. Soc., 47, 2002 (1925).

(49) Salzberg and Marvel, J. Am. Chem. Soc., 50, 1737 (1928).



organoalkali compounds that have been tested, with the exception of triphenylmethylsodium and -potassium (50), yield the color reaction by this procedure. This then serves as a valuable tool in any reaction in which the end point is marked by the depletion of organometallic compound. It has been successfully employed by Gilman and Kirby (3), Kirby (4), Gilman and Marple (51), and Gilman and Nelson (2), and others (52), to determine the relative reactivity of the moderately active organometallic compounds, and needs no further introduction.

Rates of reaction may also involve the measurement of some product in the reaction mixture. This may introduce an error since it is quite difficult to quantitatively isolate and separate many of the products of reaction, especially those that contain no active functional group. In reactions of this type it may be feasible or possible to measure only the principal product or products of reaction, and these may be dependent upon the velocity and extent of the side reactions, as well as the speed of the principal reaction. This may be illustrated by the reaction of an organolithium and -sodium compound with an aliphatic nitrile, when the yield of ketone is taken as a criterion of reaction velocity. The yield of

(50) For a discussion of this reaction, see page 48 of this thesis.

(51) Gilman and Marple, Rec. trav. chim., 55, 133 (1936).

(52) (a) Gilman and Pickens, J. Am. Chem. Soc., 47, 2406 (1928);

(b) Gilman, Heck and St. John, Rec. trav. chim., 49, 212 (1930); (c) Gilman and St. John, ibid., 49, 222 (1930).

ketone with both of the reactions may be reduced by side reaction with the enolized hydrogen; the yield of the ketone, however, may be much better with the organolithium compound than with the -sodium compound, because this side reaction is much less evident. By using ketone formation as a criterion of relative reactivity in this case, we might conclude that organolithium compounds are more reactive than organosodium compounds, when actually the organosodium compound was influenced to a greater extent by the side reaction.

From this example, it is evident that the course of a reaction is an important factor in measuring relative reaction velocities. In the event that the course of reaction is different in two otherwise comparable reactions, the results or velocities of these reactions are not applicable to relative rate measurements. In general, the comparative reactions of the organoalkali compounds will proceed along the same lines, and any deviation from this course will be evidenced by an abnormally long or short reaction time. Slight variations in the reaction mechanism may occur, but if reactants are chosen so that there is a large difference in the time element for each reaction, small variations in the course of the reaction become negligible (33).

There are other factors that may enter into the

(33) A more complete discussion of the factors that enter into the measurement of relative reaction velocities will be found in Adkins, *J. Chem. Ed.*, **2**, 1865 (1932).

comparative reactions, and produce errors of various magnitude. The reaction may be exothermic and the heat may abnormally accelerate the reaction. An insoluble product may be formed during the course of the reaction, in which the reactants may be occluded, or if they are insoluble, they may be coated. If the reaction involves a heterogeneous system, the size of the particles in the various comparative reactions may differ, and by these variations of reaction surface, the velocity may be increased or decreased proportionately. Solubility effects may play an important rôle. Organolithium compounds are notably more soluble than the corresponding members of this series, and it is generally true that the solubility of an organoalkali compound decreases as the atomic weight of the metal increases. Some of the organosodium and -potassium compounds are unstable, and decompose slowly at room temperature (54). After initial decomposition, evidenced by gas evolution during preparation, they appear to be much more stable and may be used in the reaction without introducing any serious error (55).

These errors influence the reaction velocities, but should not be considered as any determining factor in the measure of relative reaction rates. The rates are comparative, and errors introduced in the reaction of one organoalkali compound

(54) (a) Carothers and Coffman, J. Am. Chem. Soc., 51, 588 (1929); (b) ibid., 52, 1254 (1930).

(55) See page 63 of this thesis.

are undoubtedly carried over to a certain extent in the analogous reactions, and either cancel or remain negligible. As much as possible conditions are controlled to minimize these errors. Reaction products are isolated where it is feasible to establish the course of the reaction. Rapid stirring and dilute solutions may be used to prevent or minimize the coating of the reactants. Reaction media are chosen so that the organometallic compounds would be either completely soluble or, as nearly as possible, insoluble, so that comparable conditions would exist for the various reactions. By employing a large variety of organoalkali compounds in a variety of different reactions, many of the errors present in one reaction are absent in another, and by correlating the data from the various types of reactions, we are able to prepare a reasonably accurate series of the relative reactivities of organoalkali compounds.

EXPERIMENTAL PART

The reaction velocities of 4-dibenzofurylpotassium and -sodium with fluorobenzene, chlorobenzene, and *o*-tolunitrile were studied. The procedure, generally used during the course of these experiments, involved the addition of the reactant to a standardized diethyl ether solution of the 4-dibenzofuryl-alkali compound, and subsequently measuring the time required for the reaction to reach completion. The end-point of the reaction was determined by the color test method (48), commonly employed with organomagnesium and -lithium compounds, and is evidenced by a negative reaction when all of the organo-alkali compound has disappeared.

The compounds used in these experiments were purified by the following procedures. The dibenzofuran was distilled under reduced pressure (b.p. 135°/4mm.), and was recrystallized from ethanol. The product melted at 85°. The phenyl halides were the c.p. variety, obtained from Eastman Kodak Co., and they were dried over anhydrous calcium chloride, and distilled at atmospheric pressure. The *o*-tolunitrile was the same variety, and was dried with anhydrous sodium sulfate, and distilled at atmospheric pressure. The ether was dried over sodium wire. The nitrogen was purified by bubbling through two Milligen gas wash bottles containing strongly alkaline pyrogallol solutions, and then through two gas towers containing concentrated sulfuric acid, and finally by passing it over

phosphorous pentoxide. The purification of the nitrogen is quite important, and it was found that bubbling the nitrogen through ordinary gas towers, containing an alkaline solution of pyrogallol, did not remove the last traces of oxygen, and that the organoalkali compounds, consequently, were slowly oxidized in this atmosphere.

Preparation of 4-Dibenzofurylsodium and -potassium.

These compounds are conveniently prepared in a 3-necked balloon flask, equipped with a Liebig condenser, mercury-sealed stirrer, and with facilities for working in an atmosphere of purified nitrogen. To a solution of 12.6 g. (0.075 mole) of purified dibenzofuran, dissolved in 400 c.c. of anhydrous diethyl ether, is added 7.85 g. (0.025 mole) of di-n-butyl-mercury and 0.1 atom of the alkali metal. Heat may be applied to start the reaction, but, following this, it should be allowed to proceed of its own accord until reaction subsides. It is then refluxed for three or four hours and allowed to stir for twelve hours with the sodium compound, or twenty hours with the potassium analog. A large portion of the 4-dibenzofurylalkali compound remains insoluble and mixed with the alkali metal amalgam. This should not be discarded when derivatives of the compound are desired.

Preparation of 4-Dibenzofuryl-lithium. This compound is more readily prepared from an ether solution of n-butyl- or phenyl-lithium and dibenzofuran. The organolithium

compound is prepared according to the method described by Gilman, Zoellner, and Selby (47), and the excessive amount of lithium is removed from the solution. To this solution is added a 10% excess of dibenzofuran, and allowed to stir with refluxing over a period of 12 hours or more. The 4-dibenzofuryl-lithium is soluble and stable in the diethyl ether solution.

Standardization of the 4-Dibenzofurylalkali solutions.

At first, the ether solutions of the organoalkali compounds were standardized by the acid titration method developed by Gilman and co-workers (56), and later applied to organolithium compounds by Gilman and Zoellner and Selby (47). These values were checked by the "n-butyl bromide method", developed by Ziegler and co-workers (6), for the organoalkali compounds, and it was found that the solutions were considerably more dilute than had been indicated by the first method. A clear, saturated diethyl ether solution of dibenzofurylpotassium was found to be 0.010 normal by the acid titration method, but it was only 0.001 normal by the n-butyl bromide method. Ziegler and co-workers have shown that values obtained from this latter method are reliable for ether solutions of active organoalkali compounds. Similarly, ether solutions of 4-dibenzofurylsodium were found to be 0.041 normal by the former method, and 0.001 normal by the latter method. The

(56) Gilman, Wilkinson, Fishel and Meyers, J. Am. Chem. Soc., 45, 150 (1923).

ether solutions of this concentration (0.001N.) were used in the following experiments.

Reactions of 4-Dibenzofurylalkali Compounds with Phenyl Halides and o-Tolunitrile. A 250 c.c. 3-necked balloon flask equipped with reflux condenser, mercury-sealed stirrer, and facilities for working in an atmosphere of purified nitrogen, was conveniently used in these experiments. A clear solution of the organoalkali compound was obtained by allowing the reaction mixture to settle for a period of six to eight hours. The ether solution was transferred to the reaction flask by using a pipette of appropriate size. During this pipetting procedure, precaution must be taken to prevent air from coming in contact with the solution. To avoid this, and to prevent the inhalation of ether vapor, a rubber tube of about four or five feet in length was joined to the pipette, and a rapid stream of nitrogen was passed through this to expel the air. The pipette was immediately filled with the ether solution by applying suction at the end of the rubber tube, and the transfer of the solution was made as rapidly as possible. This method provided an accurate and simple way for transferring ether solutions of organoalkali compounds without the use of any intricate apparatus. This procedure has been applied conveniently to graduated pipettes.

To a clear solution of the 4-dibenzofurylalkali compound was added the appropriate reagent, and the mixture was allowed to stir at the reflux temperature. At convenient intervals



of time, usually every five or ten minutes, the refluxing was stopped and a small portion of the solution was removed and color-tested by the ordinary procedure. Samples, that were to be used for color testing, were removed by the use of small dropping tubes made from ordinary 6 mm. glass tubing. They were filled to a height of about 10-12 mm. by inserting them this depth into the solution and closing the top of the tube with the forefinger. The reaction was discontinued when two dropping tubes filled with the solution failed to give a color test with the Michler's ketone. Each reaction was checked at least one time, and several of them were repeated three and four times.

The following procedure and proportion of reactants was used in each experiment. To 50 c.c. of a 0.001 normal solution of the 4-dibenzofurylalkali compound was added 0.001 mole of the phenyl halide or o-tolunitrile. Color tests were made at intervals of five or ten minutes, and the solution was allowed to reflux during the course of the reaction. Constant and rapid stirring was used. The results of the experiments with 4-dibenzofurylsodium and -potassium reacting with fluorobenzene, chlorobenzene, and o-tolunitrile are given in Table IV. The numbers, with the exception of zero, indicate time in minutes. Zero indicates an almost instantaneous reaction.

4-Dibenzofuryl- sodium	4-Dibenzofuryl- potassium
Fluorobenzene 20, 25.	Fluorobenzene 15, 20, 20.
Chlorobenzene 25, 30, 30.	Chlorobenzene 35, 40, 30.
o-Tolunitrile 3, 0.	o-Tolunitrile 0, 0.

TABLE IV  
 REACTIONS OF 4-DIBENZOFURYLAALKALI COMPOUNDS WITH  
 PHENYL HALIDES AND o-TOLUNITRILE

### DISCUSSION OF RESULTS

It was hoped that these reactions would, in a general way, elucidate the relative reactivities of the sodium and potassium compounds of dibenzofuran. As may be observed, the results are not gratifying, and very little difference can be noted in the periods of time required for the reactions of the 4-dibenzofurylalkali compounds that were studied. To produce results that are more significant it would be necessary to employ reactants that require greater intervals of time for reaction, and solutions of the alkali compounds that are more concentrated. Unfortunately, neither of these are available at present.

Experimentation with the 4-dibenzofurylalkali compounds was begun before their concentration was accurately determined by the butyl bromide titration method. Work with these very dilute solutions is unreliable because of the errors that are introduced in standardizing them, and because a very small amount of oxygen or moisture, entering into the solution, would greatly diminish the concentration of the organoalkali compound.

Fluorobenzene reacted more rapidly than chlorobenzene under conditions that were comparable. Two different samples of fluorobenzene were employed in these experiments, and they were purified in a manner similar to that of chlorobenzene. These results were unexpected, and an analogy may be drawn

with the work of Entemann and Johnson (1d) which indicated that some acid fluorides react more rapidly with phenylmagnesium bromide than do the corresponding acid chlorides. Entemann and Johnson attributed this apparent anomaly to a more rapid addition of the Grignard reagent to the carbonyl group in the acid fluorides. This bit of evidence, the more rapid reaction of phenyl fluoride, may indicate that the halide actually is the reactive atom in the action of organometallic compounds with acid halides.

This work demonstrated that acid titration methods are not reliable for standardizing ether solutions of the very reactive organometallic compounds.

B. RELATIVE REACTIVITIES OF SOME  
TRIPHENYLMETHYLALKALI COMPOUNDS

INTRODUCTION

The preparation of the first triphenylmethylalkali compound may be accredited to Hanriot and Saint Pierre (14) who heated triphenylmethane with potassium in an inert atmosphere to 220°, and observed the formation of a red body which they rightly supposed to be triphenylmethylpotassium. The next analog of this series, triphenylmethylsodium, was prepared by Schlenk and Marcus (32) by the reaction of triphenylchloromethane with sodium amalgam. A similar method was used by von Grosse (57) to prepare the three remaining members of the series, triphenylmethyl-lithium, -rubidium, and -cesium. These compounds form the only representative series of the organoalkalis reported in the literature that comprise all five of the metals. The carbides of this series were prepared by Moissan and others (58), but they are not typical examples of organoalkali compounds; and ethylrubidium and -cesium, which would complete the series of the ethylalkali compounds, are known only in the form of a diethylzinc complex or solution (57).

The preparation of the triphenylmethylalkali compounds has been confined to a limited number of reactions. The

(57) von Grosse, Ber., 59, 2646 (1926).

(58) Moissan, Compt. rend., 136, 1217 (1903).

procedure most generally employed was developed by Schlenk and co-workers (32, 59) and involved the reaction of triphenylchloromethane with the alkali-metal amalgam in an anhydrous ether solution. Kraus and Kawamura (60) prepared triphenylmethylsodium by the action of sodium on triphenylmethane, and triphenylchloromethane in liquid ammonia. Sodium is without action on these compounds in organic solvents. Norton and Stevens (61) have prepared the organosodium compound by the action of sodium on triphenylchloromethane in diethyl ether solution, by using the "metal halys", or in other words, by using either bromobenzene, chlorobenzene, *n*-butyl chloride, benzophenone, or tetraphenylethylene as a metal carrier or activator. More recently they have been prepared in this laboratory by a reaction similar to this latter one, but by using triphenylmethane instead of the trityl halide (62); and by the action of some alkylalkali compounds on triphenylmethane.

The triphenylmethylsodium and -potassium compounds have been extensively studied, and they show the characteristic reactions of the organoalkali, and organomagnesium compounds, with only a few exceptions (32). They are stable in liquid ammonia, but are ammonolyzed at room temperature by gaseous ammonia. They react with enolizable aldehydes and ketones to form triphenylmethane and the metal enolates. Non-enolizable

- (59) Schlenk and Ochs, Ber., 49, 808 (1916).  
(60) Kraus and Kawamura, J. Am. Chem. Soc., 45, 2736 (1923).  
(61) Norton and Stevens, Ibid., 54, 1918 (1932).  
(62) See page 87 of this thesis.

aldehydes react normally, but diaryl ketones are converted to the corresponding metal ketyl and the triarylmethyl is formed. One molecule of triphenylmethylsodium reacts with only one molecule of methyl benzoate yielding the corresponding ketone, or with one molecule of ethyl chloroformate to give ethyl triphenylmethylacetate (59). Oxidation yields triarylmethyl peroxide (32). They react with some oxides of nitrogen to give well defined compounds of questionable structure (28), and with many aliphatic halides (32) to yield by a coupling reaction the hydrocarbon which is formed by the elimination of the alkali halide.

The reactions of triphenylmethyl-lithium, -rubidium, and -cesium have not been extensively studied. von Grosse (57) reports only hydrolysis reactions, and no others are recorded in the literature. In contrast to triphenylmethylsodium and -potassium which yields no color test with Michler's ketone, triphenylmethyl-lithium produces a very good test, indicating the addition of the alkali metal compound to the diaryl ketone (63).

Because the triphenylmethylalkali compounds have been prepared with all of the alkali metals, and have been reported as ether soluble, some of these compounds were used in a study of their relative reaction velocities. To make the method of preparation of these compounds more convenient, and comparable

(63) See page 48 of this thesis.

to the method employed with the 4-dibenzofurylalkali compounds, these tritylalkalis were prepared by a metalation reaction similar to that used with dibenzofuran.



This method of preparation of these compounds, using aliphatic mercurials and the alkali metals (which form alkylalkali compounds), has not been reported in the literature, and gives very good results.

The study involved the reactions of triphenylmethyl-lithium and -sodium with bromobenzene, chlorobenzene, and o-tolunitrile. The reaction velocity was measured by the time required for the organoalkali compound to react with a definite excessive amount of one of the reagents. The end of the reaction was determined by the disappearance of the characteristic color of the organoalkali compound.



EXPERIMENTAL PART

The general technique employed in these experiments was the same as that used in the study of the reaction velocities of the 4-dibenzofurylalkali compounds. The di-n-butylmercury, used in these experiments, was prepared from n-butylmagnesium bromide or chloride and mercuric chloride, by the improved method of Gilman and Brown (64). Very little difference in yields could be noted when n-butylmagnesium chloride was substituted for the bromide, but the reaction is definitely less cumbersome to work up when the bromide is employed, because there is less caking of the magnesium halide. Excellent yields were obtained, when runs of twice the reported size were made. The triphenylmethane was the c.p. variety obtained from Eastman Kodak Co., and melted at 93°. Crystallization from petroleum ether did not raise the melting point or improve the reaction.

Preparation of Triphenylmethyllsodium. A 1 liter 3-necked balloon flask was equipped with a reflux condenser, mercury-sealed stirrer, and facilities for working in an atmosphere of purified nitrogen. The air in the flask was dispelled by nitrogen and 550 c.c. of anhydrous ether was added, together with 17 g. (0.07 mole) of triphenylmethane, and 2.3 g. (0.1

- (64) (a) Gilman and Brown, J. Am. Chem. Soc., 51, 928 (1929).  
(b) Gilman, Zoellner, Selby and Boatner, Rec. trav. chim., 54, 584 (1935).

atom) of sodium cut into small pieces. When the triphenylmethane dissolved, 9.42 g. (0.03 mole) of di-n-butylmercury was added and the reaction was allowed to stir for 30 hours. At the end of this time the solution was colored red, and was allowed to settle for 6 hours. From this there may be obtained a clear solution of triphenylmethylsodium. Carbonation of an aliquot quantity of this solution yielded triphenylacetic acid.

Preparation of Triphenylmethylpotassium. The preparation was made in a similar manner to that described for triphenylmethylsodium. The same molecular proportions of materials were used, but the reaction was allowed to stir for 45 hours. The solution was less intensely colored than that of the sodium analog, and a large amount of red precipitate was formed. Carbonation of a portion of clear red solution yielded only traces of triphenylacetic acid; but carbonation of an ether suspension of the red solid, yielded comparatively large quantities of the corresponding acid.

Preparation of Triphenylmethyl-lithium. This compound was prepared by two methods.

1. From n-Butyl-lithium. n-Butyl-lithium was prepared by the method described by Gilman and co-workers (47) from an adequate amount of n-butyl bromide and lithium in an ether solution. When the reaction was complete, the excess of lithium was removed, and the solution was diluted to the desired volume. A 10% excess of triphenylmethane was added

and the solution was allowed to reflux over a water bath for 20 hours. After this the mixture was allowed to settle for six hours, and carbonation of a portion of the clear, red solution yielded triphenylacetic acid.

2. From Di-n-butylmercury and Lithium. This run was made in accordance with the directions given for the preparation of triphenylmethylsodium. The reaction was allowed to proceed for a period of five days instead of the 30 hours that was required for the preparation of triphenylmethylsodium. Carbonation of a portion of the clear, red solution with solid carbon dioxide yielded triphenylacetic acid.

Standardization of the Triphenylmethylsodium and -lithium Solutions. The clear ether solutions were standardized by the acid titration method (47,56), and checked by carbonation and subsequent isolation of the triphenylacetic acid. Twenty five c.c. of the solutions were used for the standardizations by titration, and 150 c.c. were used for the carbonation experiments. Carbonation, with solid carbon dioxide, of the solutions standardized by the titration method, yielded 90% of the theoretical amount of triphenylacetic acid, for the organosodium compound, and 82% of the theory for the organolithium compound. Solutions of these organometallic compounds were diluted to a concentration of 0.04 normal for use in the study of their relative reaction velocities. Triphenylmethylpotassium yielded a solution of such low concentration that it could not be used in these experiments.

Reaction of Triphenylmethylsodium and -lithium with Phenyl Halides and o-Tolunitrile. The reactions were carried out in a 250 c.c. 3-necked balloon flask, equipped with a reflux condenser, mercury-sealed stirrer, and facilities for working in an atmosphere of purified nitrogen. To 100 c.c. of a 0.04 normal ether solution of the organoalkali compounds was added 0.008 mole of the halide or nitrile. The reactions were allowed to proceed at the refluxing temperature, and were terminated when the characteristic red color of the organoalkali compound disappeared. The ether solutions of the organo alkali compounds were transferred by means of pipettes, as described for the 4-dibenzofurylalkali compounds. The phenyl halides or nitrile were conveniently measured by using one or two c.c. calibrated pipettes.

The results of the experiments are given in Table V. The numbers indicate the reaction time in hours of the run and the check. A plus sign after the number indicates that the reaction was not complete in the given length of time.

TABLE V

REACTIONS OF TRIPHENYLMETHYLALKALI COMPOUNDS WITH  
PHENYL HALIDES AND o-TOLUNITRILE

	<u>Triphenylmethyl- lithium.</u>	<u>Triphenylmethyl- sodium.</u>
Chlorobenzene	14, 16, 17	40+, 40+.
Bromobenzene	10, 8, 12	40+, 40+.
<u>o</u> -Tolunitrile	0.04, 0.04	0.02, 0.03.

Color Tests with Triphenylmethyl-lithium and -sodium.

The color tests were made in the usual manner with these two compounds. Triphenylmethyl-lithium reacted in the normal way and yielded a strong positive color. The sodium analog, however, would yield no color reaction after standing with the solution of Michler's ketone for fifteen minutes, with subsequent hydrolysis, and acidification with an iodine-acetic acid solution.

## DISCUSSION OF RESULTS

The results of the experiments indicate that triphenylmethyl-lithium was more reactive toward phenyl halides than the triphenylmethylsodium. The results with *o*-tolunitrile were just reversed.

Reactions of triphenylmethyl-lithium with various reagents have not been studied, so that it is difficult to compare it with the sodium analog. However, we do know that triphenylmethylsodium exhibits many anomalies (65), and its uncommonly slow reaction with phenyl halides may be one more of these. One difference between these two compounds is evidenced in the reaction with Michler's ketone (63). Kraus and Kawamura (60) have studied the reaction of triphenylmethylsodium with phenyl halides in liquid ammonia solution, and they have found this to be an excellent method to prepare tetraphenylmethane. The course of the reaction in ether solution, however, may be different, and we have no evidence concerning the nature of the reaction.

The reactions of the triphenylmethylalkali compounds were not studied further, because the insolubility of triphenylmethylpotassium in ether precluded its incorporation in this series, and because the anomalies in the chemical reactions of the triphenylmethylalkali compounds might easily lead to error if generalizations were made from these results.

(65) See page 48 of this thesis.

C. RELATIVE REACTIVITIES OF SOME

ALKYLALKALI COMPOUNDS

INTRODUCTION

The preparation of the first alkylalkali compound may be attributed to Wanklyn (66) who treated diethylzinc with sodium and obtained ethylsodium. This method of preparation of alkylalkali compounds has been extended so that a general method, almost exclusively employed for their preparation, involves the reaction of a lesser reactive organometallic compound with the alkali metal. The reaction of alkylmercurials with alkali metals is generally used (8,14), but alkyllead (67), -aluminum (30), -cadmium (30), and -magnesium (68) compounds have also been employed. Alkyl-lithium compounds, with the exception of ethyl-lithium, are now more commonly prepared by the action of lithium on the alkyl halide (47). Alkylsodium compounds are probably formed as intermediate products in the Wurtz, and related reactions, when sodium reacts with organic halides (69). Ethylrubidium and -cesium have been prepared, only, by the reaction of the metal with diethylzinc (57), and were never isolated in pure form. The general reactions for preparation given above, however, are in all probability, applicable to

(66) (a) Wanklyn, Ann., 107, 125 (1858); (b) ibid., 108, 68 (1858); (c) ibid., 111, 234 (1859).

(67) Buckton, Ann., 112, 222 (1859).

(68) See Franz Runge, "Organometallverbindungen", Vol. I, Wissenschaftliche Verlagsgesellschaft, m.b.H., Stuttgart, 1932, p. 279.

(69) Gilman and Wright, J. Am. Chem. Soc., 55, 2893 (1933).

these most active organoalkali compounds. The general physical properties of these alkylalkali compounds are recorded by Schlenk and Holtz (8), and, with the exception of ethyl-lithium which is a solid melting at 70° and n-propyl-lithium which is reported as a distillable liquid, they are thermolabile (54), infusible solids, that are very reactive chemically. They are insoluble in all common organic solvents, but dissolve in some of the liquid organometallic compounds of the second and third group in the periodic table; dialkylzinc, -cadmium, and trialkylaluminum compounds are exceptionally good solvents (30).

The chemical properties of these alkylalkali compounds resemble those of the Grignard reagent, although, because of their enhanced reactivity, they show a greater variety, as well as certain variations of the same kinds of reactions. The apparent differences between the reactions of the alkylalkali compounds and the lesser reactive types may be only one of degree, but certain reactions, discussed later, have never been observed with organomagnesium and lesser reactive types. Organo-calcium compounds are more reactive than organo-magnesium compounds, and show reactions similar to those of the organoalkalis (38), however, they have not been extensively studied.

The alkylalkali compounds react with enolizable aldehydes and ketones to form the metal enolate, but react similar to the organomagnesium compounds with non-enolizable carbonyl



groups (70,10); they cleave ethers with the resulting formation of alkoxides and hydrocarbons (71); reactions with organic halides are rapid, producing coupling and disproportionation products (10), and they react with hydrocarbons, and heterocycles, yielding either addition, polymerization, or metalation products, depending upon the hydrocarbon and the organoalkali compound employed (72).

The reactions of the organoalkali compounds with hydrocarbons have been extensively investigated (6,14), and are of particular interest because they were employed in this study of relative reaction velocities of the alkylalkali compounds.

The course of the reaction of hydrocarbons with organoalkali compounds depends upon the nature of the hydrocarbon, and the organoalkali compound. Schorigin (10) first observed that alkylsodium compounds reacted with benzene, homologs of benzene, and thiophene. The reaction followed the general scheme.



As an example of this, benzene (R'H) reacts with ethylsodium (RNa) to yield phenylsodium (R'Na) and ethane (RH). These reactions have wide application in the preparation of organoalkali compounds (14). Conant and Wheland (5) have demonstrated that organoalkali compounds derived from a

(70) Schluback, Ber., 52, 1910 (1919).

(71) Schorigin, Ber., 43, 1931 (1910).

(72) Ziegler and Bahr, Ber., 61, 253 (1928).

hydrocarbon, containing a lesser acidic hydrogen, will react with a hydrocarbon containing a more acidic hydrogen to form a new organoalkali compound, and liberate the hydrocarbon containing the lesser acidic hydrogen. This type of reaction has been named "metalation" (12) and "solvent exchange" (11).

The term "metalation" is general, and includes any substance that will react with a hydrocarbon to yield an organometallic compound. Metalating agents, other than organometallic compounds, are common; but a comparison of the degree of reactivity, as evidenced by the rate and type of reaction, of the various metalating agents, will show that organoalkali compounds are the most reactive types.

The alkali metals react directly with hydrocarbons containing "highly acidic" hydrogens to form the organometallic compound and liberate hydrogen. With the exception of lithium, phenylacetylene will react with the alkali metals at room temperature with the formation of the phenylacetylenylalkali compounds (73). Triphenylmethane, fluorene, and indene react similarly at elevated temperature (73). By substituting organoalkali compounds for the alkali metal, it is possible to carry out these reactions at room temperature, and in addition, many hydrocarbons may be metalated that are, otherwise, unaffected by the alkali metal. Liquid ammonia solutions of the alkali metals are more vigorous metalating agents than

(73) See page 10 of this thesis.

suspensions of the metals in organic solvents, as evidenced by the metalations of di- and triphenylmethane, which are unaffected in organic solvents. Liquid ammonia solutions of the alkali metal amides are stronger metalating agents than the alkali metals, and react more rapidly with these hydrocarbons (74). Many organoalkali compounds are ammonolyzed by liquid ammonia, and only those that contain the diphenylmethyl and more highly phenylated groups joined to the alkali metal, are stable in liquid ammonia (74).

Sodium-potassium alloy reacts more vigorously than either of its constituents. It reacts rapidly with dibenzofuran to form 4-dibenzofurylpotassium and other products (12), but either of the metals is without rapid action. Lithium, instead of metalation, cleaves the ether linkage of dibenzofuran, with the formation of o-hydroxybiphenyl (75).

No report of metalation reactions by use of alkali metal amalgams has been found in the literature. By drawing an analogy between the cleavage reactions of ethanes, that were extensively studied by Conant and Garvey (25), and Marvel and co-workers (26), amalgams may be predicted to be less reactive than the alloys of the alkali metals.

Metalation by means of salts of the alkali metals is unknown. Mercury salts are extensively used to prepare the

(74) Wooster and Mitchell, J. Am. Chem. Soc., 52, 688 (1930).  
(75) Studies in this laboratory by Mr. C. W. Bradley.

arylmercury compounds, and in many instances react much more readily than the corresponding organoalkali compound in metalation (76).

A series that, in general, indicates the relative decreasing effectiveness of metalating agents in the alkali metal group will be found in Table VI. M. and M' indicate different alkali metals.

TABLE VI  
DECREASING ORDER OF REACTIVITY OF METALATING AGENTS  
IN THE ALKALI METAL GROUP

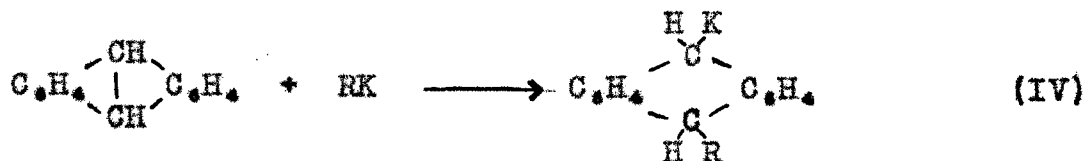
RM	
MNH <sub>2</sub>	( in liquid NH <sub>3</sub> )
M	( in liquid NH <sub>3</sub> )
M	( at elevated temperatures )
M-M'	( in organic solvents )
M	( in organic solvents )
HgM	
MX	

It should be noted that many organoalkali compounds are ammonolyzed in liquid ammonia, and therefore can not be prepared in this medium (74).

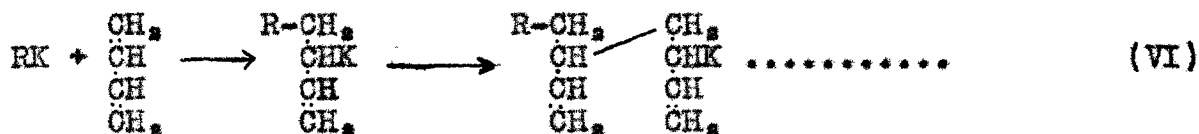
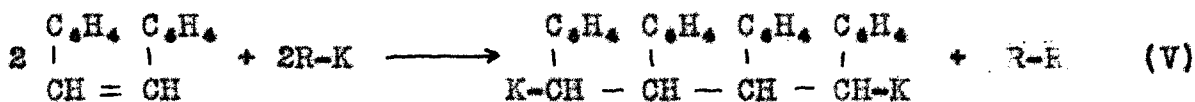
In addition to the metalation reactions of hydrocarbons with organoalkali compounds, Ziegler and Bahr (72) observed that anthracene will react with phenyl-iso-propylpotassium to yield an addition product (IV).



(76) Gilman and Kirby, J. Org. Chem., 1, July (1936).



and with phenanthrene and butadienes to yield a dimerized and polymerized product, respectively (V), (VI).



These reactions illustrate the variety of courses that may follow from the action of an organometallic compound with a hydrocarbon. Many times, the course of the reaction can not be predicted. Metalation may occur when only simple aromatic nuclei are involved, such as benzene and its homologs, and heterocycles such as thiophene (10), furan (77) dibenzofuran (12,13), and others (14), but condensed benzene nuclei may react with either polymerization, addition, or metalation.

Phenanthrene will polymerize, anthracene will allow addition (72) and naphthalene will metalate (78).

(77) Gilman and Breuer, *J. Am. Chem. Soc.*, **56**, 1123 (1934).

(78) Work in progress in this laboratory by Mr. R. L. Ebb.

Polymerization reactions of the hydrocarbons are not unique. Before the reactions of the hydrocarbons with organoalkali compounds were known, Harries (79) and later Schlenk and co-workers (27) demonstrated that unsaturated hydrocarbons such as butadienes, phenylbutadienes, styrene and others were polymerized by the action of the alkali metals.

The addition reactions of the organoalkali compounds depend upon the nature of the hydrocarbon, and the metallic compound (6). Addition has been observed only to unsaturated carbon atoms directly linked or conjugated with a benzene ring or other unsaturated system. The presence of three or more aromatic rings in an ethylene may hinder the reaction, or substitution (metalation) may take place with some types. Phenyl-iso-propylpotassium  $\overline{[C_6H_5(CH_2)_2CK]}$  will add to 1,1-diphenylethylene  $\overline{[(C_6H_5)_2C = CH_2]}$ , but it will not react with triphenylethylene  $\overline{[(C_6H_5)_3C = CH(C_6H_5)]}$ , however, diphenylmethylene  $\overline{[(C_6H_5)_2C = CCH_2(C_6H_5)]}$ , will metalate in the methyl group under similar conditions. Ziegler and co-workers (6) have observed that addition occurs more rapidly with organopotassium than with organolithium compounds, but no comparative reaction with organosodium compounds has been reported.

To compare the reactivities of the ethylalkali compounds, the rate of metalation of dibenzofuran with ethyl-lithium, -sodium, and -potassium was studied. Dibenzofuran metalates readily, with measurable velocity, to form the  
(79) Harries, Ann., 383, 213 (1911).

4-dibenzofuryl and 4, 6-dibenzofurylenedi-alkali compound which upon carbonation, give good yields of the corresponding acids (12,13). In these reactions, comparable conditions were employed with each of the ethylalkali compounds, and the results were gratifying.

EXPERIMENTAL PART

In the following experiments, equal molar quantities of the ethylalkali compounds were allowed to react with a standard excessive amount of dibenzofuran in a petroleum ether solution. The reactions were terminated after a definite interval of time, usually two and one-half hours, by carbonating the reaction mixture with solid carbon dioxide. The extent of the reaction was determined by isolating the resulting products, which were 4-dibenzofurancarboxylic acid and 4,6-dibenzofurandicarboxylic acid. All of the ethylalkali compounds were prepared from diethylmercury and the alkali metal in petroleum ether (b.p. 77-115°).

Standard quantities of the ethylalkali compounds are difficult to obtain if the procedure involves the preliminary isolation of the compound. However, if the compounds are prepared by using a standard quantity of diethylmercury, and a definite excess of the alkali metal, the standard may be based upon the quantity of mercurial employed. This latter procedure involves two assumptions. First, the reaction between mercurials and alkali metals either goes to completion, or, if equilibrium is established, it is the same for each alkali metal employed. Second, any decomposition of the organometallic compounds is essentially the same for each one. Ziegler (40) has demonstrated that the reaction of mercurials with alkali metals is reversible, but by using an excessive



amount of the metal, the reaction essentially goes to completion. With this in mind, a large and definite excessive amount of the alkali metal was used in each reaction.

Carothers and Coffman (54) have shown that ethylsodium, and methylsodium and -potassium are thermally labile, and that some decomposition takes place at room temperature. Observations under conditions of these experiments indicate that decomposition of ethylsodium and -potassium (evidenced by gas evolution) does take place to some extent during preparation of the compounds, but that they are stable after this initial decomposition. To minimize this effect, the ethylalkali compounds were prepared without the application of heat, and any rise in temperature of the reaction mixture was checked by rapid cooling with a water bath.

In these experiments, the weight of diethylmercury was used as the basis for calculating the quantities of the ethylalkali compounds present. To check these values, ethyl-lithium, -sodium, and -potassium, prepared from a definite quantity of diethylmercury and alkali metals, were allowed to react with dibenzofuran until the reactions had reached completion (15 days). Carbonation and acidification of the dibenzofurylalkali compounds prepared in this period of time, yielded almost identical quantities of solid acidic materials as evidenced by similar titration values with 0.1 normal sodium hydroxide.

During the course of these reactions of the ethylalkali

compounds with dibenzofuran, it was observed that ethyl-lithium exclusively monometalated dibenzofuran; ethylsodium produced small amounts of dimetalated product mixed with the monometalated compound; and ethylpotassium produced relatively large quantities of the dimetalated product mixed with the monometalated compound. To accurately determine the amount of metalation that had taken place, since a mixture of 4-dibenzofurancarboxylic acid and 4,6-dibenzofurandicarboxylic acid was formed, the solid dibenzofuran acid mixtures were thoroughly washed, and titrated. The amounts of metalation, evidenced as dibenzofuran acids, were compared as titration values of 0.1 normal sodium hydroxide.

The diethylmercury used in these experiments was prepared by the method of Gilman and Brown (64). The petroleum ether was dried with sodium wire, and the other reagents were purified by methods previously described (80).

Preparation of Ethyl-lithium, -sodium, and -potassium.

The reactions were carried out in a 250 c.c. 3-necked balloon flask, equipped with a reflux condenser, mercury-sealed stirrer, and facilities for working in an atmosphere of purified nitrogen. To a solution of 2.59 g. (0.01 mole) of diethylmercury in 25 c.c. of petroleum ether (b.p. 68-77°) was added 0.04 atom of the alkali metal, cut into small pieces. If the reaction mixture became warm after the addition of the alkali metal, it was cooled with a water bath. The mixture

(80) See page 32 of this thesis.

was allowed to stir rapidly for 4 days with lithium, 1 1/2 days with sodium, or 2 days with potassium. At the end of this time, the reaction mixture was used to measure the relative reaction velocities of the ethylalkali compound. The time employed in the preparation of the ethylalkali compounds, is the approximate time of completion of the reaction, as evidenced by a cessation of gas evolution during the preparation of ethylsodium and -potassium. No effort was made to determine the amount or rate of evolution of gas from the preparation of ethyl-lithium. Four days was arbitrarily chosen as sufficient amount of time for the reaction to reach completion.

Standardization of the Ethylalkali Compounds.

To a petroleum ether suspension of the ethylalkali compound prepared in the manner described above, was added 4.20 g. (0.025 mole) of dibenzofuran dissolved in 25 c.c. of petroleum ether. The reaction was allowed to proceed for 15 days at room temperature, with constant stirring. At the end of this time, the reaction was poured upon 20 to 30 g. of solid carbon dioxide. When this mixture had warmed to room temperature, it was filtered with suction, and the solid residue was slowly added to 75 c.c. of cold water and subsequently heated to boiling. The hot solution was filtered, and the residue was extracted with 50 c.c. of hot water, filtered, and this filtered extract was added to the original solution. The combined filtrates were then cooled to room temperature, and

acidified with 10% hydrochloric acid. The insoluble dibenzofuran acids were immediately precipitated, filtered with suction, and washed thoroughly with cold water. The acids that were obtained from this procedure by the reaction of ethyl-lithium, -sodium and -potassium with dibenzofuran were then compared by titrating them with 0.1360 N sodium hydroxide. The titrations were carried out by dissolving the acids in 50 o.o. of a 50% water-acetone solution that had been previously neutralized with the base. Phenolphthalein was used as an indicator. The results of the experiment will be found in Table VII. The values given, are in cubic centimeters of standard sodium hydroxide. No attempt was made to check these values.

TABLE VII

TITRATION OF THE DIBENZOFURAN ACIDS WITH

STANDARD SODIUM HYDROXIDE

Ethyl-lithium	85.6
Ethylsodium	29.7
Ethylpotassium	30.9

These values represent about 20% of the theoretical amount of acid that should be obtained from the diethylmercury.

Reactions of Ethylalkali Compounds with Dibenzofuran.

The ethylalkali compounds were prepared as previously described and the reactions were carried out in a manner identical to those for the standardization of the ethylalkali compounds,

with the exception that each reaction was allowed to proceed for 2 1/2 hours, and then it was carbonated by pouring onto solid carbon dioxide. The dibenzofuran acids were titrated with 0.1580 N. sodium hydroxide. The results of these experiments will be found in Table VIII. The quantities of organic acids are given in cubic centimeters of standard sodium hydroxide. The several values indicate check runs.

TABLE VIII  
TITRATION OF DIBENZOFURAN ACIDS WITH  
STANDARD SODIUM HYDROXIDE

Ethyl-lithium	0.1,	0.05	--
Ethylsodium	4.5,	4.7,	4.5,
Ethylpotassium	14.1,	12.5,	15.0

During the course of these experiments it was noted that metalation with ethyl-lithium yielded only 4-dibenzofuran-carboxylic acid. Metalation with ethylsodium gave, largely, 4-dibenzofuran-carboxylic acid, with some 4,6-dibenzofurandi-carboxylic acid, and metalation with ethylpotassium yielded relatively large quantities of the dibasic acid, as well as, the monobasic acid. No attempt was made to determine the quantities of mono- and dibasic acid present.

Decomposition of Ethylsodium and -potassium. During the preparation of ethylsodium or -potassium, by the method described above, gas is liberated. The evolution of gas starts almost immediately after the addition of the alkali metal to

the petroleum ether solution of diethylmercury, and proceeds for a period of 30 to 36 hours for ethylsodium, and from 36 to 48 hours for ethylpotassium. In two experiments in the preparation of ethylsodium, 65 c.c. and 90 c.c. of gas were evolved. Similar experiments with ethylpotassium yielded 84 c.c. and 200 c.c. of gas. These volumes of gas were obtained from 0.01 mole of diethylmercury reacting with 0.04 atom of the alkali metal, and the volumes are given at standard temperature and pressure. No correction was made for the vapor pressure of the petroleum ether, and the gas was collected over mercury. After the initial period of gas evolution, the ethylalkali compounds appeared to be stable and no gas was evolved. They reacted with the further liberation of gas when a compound, such as benzene, was added to the mixture. The rates of gas evolution of ethylsodium or potassium during reaction were not constant, and could not be duplicated.

#### Attempted Metalation of Benzene with Ethyl-lithium.

The experiment was carried out in a Schlenk tube, in which the air was displaced by purified nitrogen. To 50 c.c. of benzene, contained in this tube, was added 3.45 g. (0.5 atom) of lithium and 10 g. (0.038 mole) of diethylmercury. The tube was sealed, and the mixture was allowed to react, with constant shaking, over a period of eight weeks. At the end of this time, the tube was cooled in a freezing mixture, opened, and poured upon solid carbon dioxide. Examination of the reaction

products revealed large quantities of propionic acid, but no trace of benzoic acid could be found.

DISCUSSION OF RESULTS

The results of these experiments, with ethyl-lithium, -sodium, and -potassium and dibenzofuran, indicate that ethylpotassium reacts more rapidly than ethylsodium, which reacts more rapidly than ethyl-lithium. This order of decreasing relative reactivities is in agreement with the predictions of Gilman and Nelson (2), and follows the most reasonable order of decreasing relative rates. It is of interest to note that ethylpotassium yields relatively large quantities of dimetalated dibenzofuran, and it may be that polymetalation is a criterion of reactivity. Polymetalation of benzene, with good yields, has also been accomplished with ethylpotassium, while ethylsodium yields very small quantities of dimetalated product (81), and ethyl-lithium will not metalate benzene.

If polymetalation of a compound is a stepwise procedure, in which dimetalation is preceded by monometalation, then polymetalation of an organopotassium compound may be due to an enhanced labilizing effect of the potassium atom, that facilitates further metalation in the monometalated nucleus; and it may not be due to greater reactivity of the organopotassium compound.

Morton and Hechenbleikner (11) have recently shown that some alkylsodium compounds exist as the dimetallo compound;

(81) Work by Mr. R. H. Kirby in this laboratory.



for example, amylsodium, prepared from amylmercury and sodium, actually contains some amylienedisodium, and produces butylmalonic acid upon carbonation and acidification with mineral acids. Dimetalation of hydrocarbons and heterocycles may be the result of the action of a dimetallo compound, and not upon the greater reactivity of the organopotassium compound. Further experimentation will be necessary to elucidate and evaluate the dimetalation reactions, but at present it is reasonable to suppose that dimetalation is a criterion of increased reactivity.

D. RELATIVE REACTIVITIES OF PHENYLETHINYLSODIUM

COMPOUNDS

INTRODUCTION

Phenylethynylsodium is the only member of this series of organoalkali compounds that is reported in the literature. It was prepared by Glaser (82), by the reaction of sodium and phenylacetylene in diethyl ether, and by Conant and Wheland (5) by metalation of phenylacetylene with indenylsodium. These methods of preparation illustrate the strongly acidic nature of the acetylenic hydrogen in this compound, resembling acetylene, and emphasize the acidic nature of hydrocarbons. The compound is a white crystalline powder that is spontaneously inflammable in air. In its method of preparation, it resembles acetylenes, but in synthesis it exhibits reactions characteristic of organomagnesium compounds.

The chemical reactions of phenylethynylsodium have been studied by Nef (20), Meyer and Schuster (83), Moureu and Desmots (84), and others (14). It reacts readily with ketones to yield tertiary alcohols; with aldehydes to yield secondary alcohols; with carbon dioxide it forms phenylpropionic acid. With acid halides, preferably the bromides, it yields ketones (85), and it reacts with isothiocyanates to form thio-amides (86).

(82) Glaser, Ann., 154, 161 (1870).

(83) Meyer and Schuster, Ber., 55, 819 (1922).

(84) Moureu and Desmots, Bull. soc. chim., 3, 27, 360, 366 (1902).

(85) Andre, Compt. rend., 151, 75 (1910).

(86) Worrall, J. Am. Chem. Soc., 39, 697 (1917).

In its reactions, it many times behaves more like the Grignard reagent than like the organoalkali compounds. It reacts with enolizable aldehydes and ketones to form the carbonyl addition product, and the reaction with acid halides may be stopped at the ketone stage. Reaction with ethyl chloroformate yields the corresponding ethyl phenylpropiolate (20). Conant and Wheland (5) found that phenylacetylene contains a very acidic hydrogen, and may be metalated by organometallic compounds such as indenylsodium.

During the course of this investigation with phenylethynylalkali compounds, it was found that all of the alkali metals, with the exception of lithium react with phenylacetylene to yield the same types of organoalkali compounds, as evidenced by their carbonation to phenylpropolic acid. Phenylethynyllithium may be prepared by metalating phenylacetylene with phenyl-lithium, n-butyl-lithium, and in all probability, by using any organolithium compound derived from a hydrocarbon containing a lesser acidic hydrogen than phenylacetylene.

The phenylethynylalkali compounds are ideally suited to the study of relative reaction velocities because they exhibit a lesser reactivity than most of the organoalkali compounds, and they may be prepared in good and consistent yields.

The lesser reactivity allows a direct comparison of each of the organoalkali compounds with one reactant, and one method of preparation is applicable to four of the five

members of the series, only lithium is excepted.

Benzonitrile was employed as the reactant with these compounds because nitriles were known to react with moderately reactive organometallic compounds at a measurable velocity (3), and the non-enolizable types, such as benzonitrile may be depended upon to follow the same general course of reaction. In addition to this, benzonitrile was found to react with the phenylethynylalkali compounds in a period of time that was suitable for this type of study.

EXPERIMENTAL PART

The relative reaction rates of the phenylethynylalkali compounds were determined by measuring the time required for the organoalkali compound to react with a definite excessive amount of benzonitrile. The reactions were carried out using equal molar quantities of the organoalkali compound, suspended in a definite volume of anhydrous diethyl ether. The reactions were terminated when approximately 0.2 c.c. of the ether suspension failed to give a color test with Michler's ketone, which indicated that the organoalkali compound had completely reacted with the benzonitrile.

Phenylethynylmagnesium bromide was included in these experiments so that a direct comparison of organomagnesium and organoalkali compounds could be made.

In these experiments, the relative reactivities of phenylethynylcesium, -rubidium, -potassium, -sodium, -lithium, and -magnesium were determined. The relative reactivities of these compounds were made by direct comparison of their reaction velocities with benzonitrile. The experiments that included phenylethynylpotassium, -sodium, -lithium, and -magnesium, were run on a comparatively larger scale and with slightly higher concentrations than those that involved phenylethynylcesium and -rubidium. To make the relative rates of reaction of these last two members of the series comparable to those of the first four, phenylethynylpotassium was run under conditions,

and with concentrations comparable to those of phenylethynylcesium and -rubidium.

The reactions of phenylethynylcesium, -rubidium, and potassium were carried out in a special 150 c.c. 3-necked balloon flask, that contained a mercury-sealed stirrer, reflux condenser and stopper joined to it by ground glass joints. By use of this flask, the ether vapors could not come in contact with rubber stoppers, and by greasing only the upper portion of the ground glass joints, the lubricant (vaseline) was not contacted by the ether vapor. Reactions carried out in this flask might be comparable to those carried out in sealed tubes. Check runs were made in the standard 3-necked flasks, and the results will be discussed later. The phenylacetylene was obtained from the Eastman Kodak Co., and was dried over anhydrous calcium chloride, and distilled at atmospheric pressure. The benzonitrile was obtained from the same company, and was dried over anhydrous sodium sulfate and distilled at atmospheric pressure. The ether used in these experiments, was dried over sodium wire, and then further purified by distilling it under nitrogen from a mixture of sodium-potassium alloy and benzophenone. This procedure has been employed by Ziegler and co-workers (6), and yields very pure ether.

The solid alkali metals used in these experiments were cut into small pieces under anhydrous petroleum ether and transferred rapidly to the reaction flask. The liquid metals were transferred by means of graduated pipettes, which served as a

convenient and rapid method to measure them. Care must be exercised in handling rubidium and cesium. They are spontaneously inflammable in air, and when they are handled in pipettes, it is advisable to have a small layer of high boiling petroleum ether covering the top of the metal, as well as a thin layer under the bottom of the metal contained in the pipette. The petroleum ether (b.p. 115-150°) used to protect the metal from the atmosphere was dried over sodium-potassium alloy for several days.

Preparation of Phenylethynyl-lithium and -magnesium.

The phenyl-lithium and phenylmagnesium bromide, used in these experiments, was prepared in the usual manner, and the excess metal was removed. The reactions were carried out in a 250 c.c. 3-necked balloon flask, equipped with a mercury-sealed stirrer, reflux condenser, and facilities for working in an atmosphere of purified nitrogen. To 30 c.c. of a clear diethyl ether solution containing 0.02 mole of phenyl-lithium or -magnesium bromide was added 3.06 g. (0.03 mole) of phenylacetylene. The reaction was allowed to proceed for about eight hours at room temperature with constant stirring and no shorter time was employed. At the end of this time the reaction had reached completion, as evidenced by carbonation of the reaction mixture, with the subsequent isolation of phenylpropionic acid, m.p. 133°, and no benzoic acid. Preliminary tests showed that very small amounts of benzoic acid appreciably lowered the

melting point of phenylpropionic acid, when they were admixed with it.

Preparation of Phenylethynylsodium and -potassium.

The reactions were carried out in a 250 c.c. 3-necked balloon flask, equipped with a reflux condenser, mercury-sealed stirrer, and facilities for working in an atmosphere of purified nitrogen. To a solution of 3.06 g. (0.03 mole) of phenylacetylene in 30 c.c. of absolute ether was added 0.02 atom of the alkali metal, cut into small pieces. The reaction was allowed to proceed at room temperature with constant stirring until all of the alkali metal had reacted with the phenylacetylene, as evidenced by the absence of gas formation (hydrogen), from a few drops of the suspension in about an equal volume of water. The reaction with sodium is complete in about 8 hours, but potassium requires about 48 hours. The reactions were checked four to five times. Under similar conditions, lithium and magnesium do not react with phenylacetylene in a period of three days, to form the organometallic compound, although the metal became slightly coated. The color test of the solution with Michler's ketone was negative. Phenylethynylpotassium is light tan in color, but the -sodium, -lithium and -magnesium analogs are colorless.

Preparation of Phenylethynylpotassium, -rubidium, and



-cesium. The reactions were carried out in a 150 c.c. 3-necked balloon flask, equipped with a reflux condenser and stirrer attached to it by means of ground glass joints, and with facilities for working under an atmosphere of purified nitrogen. To a solution of 25 c.c. of absolute diethyl ether containing 2.04 g. (0.02 mole) of phenylacetylene was added 0.01 atom of the alkali metal. The reaction was allowed to proceed at room temperature, with constant stirring until the alkali metal had completely reacted. Potassium required about 40 hours, rubidium about 12 hours, and cesium about 25 hours. At the end of this time the phenylethynylalkali compound was present as a suspended solid, and yielded a color test with Michler's ketone; upon carbonation at room temperature and subsequent acidification with 10% hydrochloric acid, it yielded phenylpropionic acid. The colors of these phenylethynylalkali compounds varied progressively from a dark tan for -cesium and -rubidium, light tan for potassium to colorless for the -sodium and -lithium compound.

Standardization of the Diethyl Ether Suspensions of the Phenylethynylalkali Compounds. Standardization of the ether suspensions of these organoalkali compounds was accomplished by carbonating the compounds. In each preparation that was carried out, an equivalent amount of the alkali metal was employed, and this should, in each case, yield an equivalent amount of the organoalkali compound. The quantities of

phenylpropionic acid, obtained by carbonating and acidifying the ether suspensions of the phenylethynylalkali compounds, were used to check the amount of organoalkali compound present. The values recorded are percentages of the total amount of organoalkali compound present, based upon the quantity of alkali metal employed in the preparation. The results are given in Table IX. The values were not checked.

TABLE IX  
PERCENT YIELD OF PHENYLPROPIOLIC ACID FROM  
THE PHENYLETHINYLLALKALI COMPOUNDS

<u>Alkali compound</u>	<u>% yield</u>
Phenylethynyl-lithium	68
Phenylethynylsodium	74
Phenylethynylpotassium	71
Phenylethynylrubidium	74
Phenylethynylcesium	78
Phenylethynylmagnesium	--

The carbonation of the organoalkali compounds was carried out at room temperature, with the exception of the lithium compound. This was carbonated by use of solid carbon dioxide  
(87)

Reactions of the Phenylethynylalkali Compounds with

(87) See page 91 of this thesis.

Benzonitrile. The reactions were carried out directly in the flasks employed in the preparation of the phenylethynylalkali compounds, and the amounts represented by their method of preparation were used in these experiments. The reactions of phenylethynylmagnesium bromide, phenylethynyl-lithium, -sodium, -potassium were carried out with 4.12 g. (0.04 mole) of benzonitrile that was dissolved in 10 c.c. of absolute ether. The ether solution of the nitrile was added to the ether suspension of 0.02 mole of the organometallic compound, and the reaction was allowed to proceed at room temperature with rapid stirring until a small portion of the ether suspension failed to give a color test with Michler's ketone.

A similar procedure was employed for comparing the relative reaction velocities of phenylethynylcesium, -rubidium, and -potassium. To the 25 c.c. ether suspension of 0.01 mole the organoalkali compound was added 2.06 g. (0.02 mole) of benzonitrile from a graduated pipette. The reaction was then allowed to proceed at room temperature, until the color testing procedure indicated the absence of organoalkali compound.

Table X summarizes the time required for the reaction of phenylethynylalkali compounds with benzonitrile to reach completion. The various values for one reaction indicate check runs. Two different sets of values for phenylethynylpotassium are given. The first values given are those that were obtained under conditions comparable to the organometallic compounds above them. The second values are those that were obtained

under conditions similar to those of the compounds given below them. The values indicate time in hours required for the reaction to reach completion.

TABLE X

REACTION OF PHENYLETHINYLLALKALI COMPOUNDS  
WITH BENZONITRILE

Phenylethynylmagnesium bromide	87,	85
Phenylethynyl-lithium	57,	63
Phenylethynylsodium	6.5,	7.0
Phenylethynylpotassium	4.3,	4.5
Phenylethynylpotassium	5.3,	<u>5.1</u>
Phenylethynylrubidium	4.8	<u>5.2</u>
Phenylethynylcesium	3.7	<u>3.6</u>

The underscored values indicate check runs made in standard 3-necked balloon flasks with rubber stopper connections.

## DISCUSSION OF RESULTS

The results indicate that the order of decreasing relative reactivity of the phenylethynylalkali compounds is -cesium, -rubidium, -potassium, -sodium, and -lithium. -Magnesium was included in the series, and was found to be less reactive than the organolithium compound. The results substantiate the prediction made by Gilman and Nelson (2), that the organometallic compounds derived from the metals in the A families of the first three groups of the periodic table, will increase in relative reactivity with increasing atomic weight of the metal.

The results with the organopotassium, -rubidium, and -cesium compounds, found in Table X, indicate that these very reactive organoalkali compounds can be prepared under conditions similar to those used for the Grignard reagent and organolithium compounds; and that many of the special precautions and technique previously employed are not necessary. Extreme caution, however, must be employed in handling these compounds, and the use of more convenient apparatus, should not be confused with carelessness.

The phenylethynylalkali compounds, with the exception of -lithium, are insoluble in diethyl ether; and the ether, without suspended compounds, will fail to give a color test with Michler's ketone. Phenylethynyl-lithium is moderately soluble in ether, and a clear ether solution of this compound will yield a color test with Michler's ketone.

E. MISCELLANEOUS EXPERIMENTS

I. REACTIONS OF SODIUM-POTASSIUM ALLOY

INTRODUCTION AND EXPERIMENTAL PART

Sodium-potassium alloy is applicable in the synthesis of many organopotassium compounds. First reports of the use of liquid sodium-potassium alloy were made by Lecher (88), although he states that it had previously been used by Schlenk in unpublished work. Lecher employed this alloy to cleave disulfides. Although, this does not lead to the formation of organoalkali compounds, the greater reactivity of the alloy was evidenced by its ability to cleave diphenyl disulfide under conditions that were uneffective by either of the metals.

Ziegler and Thielman (23) were the first to employ sodiumpotassium alloy in the preparation of organoalkali compounds. Their reaction involved the cleavage of some mixed ethers and ethanes by this alloy, and they reported good yields of the organopotassium compounds. These reactions are illustrated by Equation A and B.



The organic radicals represented by "R" in Equations (A) and (B) are generally phenylated methyl groups, and "R'" in equation (A) is usually a simple aliphatic radical, such as ethyl- or methyl-. The ether cleavage is not unique with

(88) Lecher, Ber., 48, 527 (1915).

sodium-potassium alloy. Schorigin (89) was able to cleave ethers with sodium metal at higher temperatures, before the introduction of the alloy-cleavage method by Ziegler and Thielman. Schlenk and Bergmann (90) have also demonstrated that powdered sodium or potassium may, many times, be substituted for this alloy with good results.

The cleavage of phenylated ethanes by use of the alkali metals was discovered by Schlenk and Marcus (32) who were able to cleave hexaphenylethane with a 1% sodium amalgam, and they obtained triphenylmethylsodium. Schlenk and Marcus were unable to cleave tetraphenylethane; but by the use of sodium-potassium alloy, Ziegler and Thielman were able to accomplish this and obtained benzohydrylpotassium. With these facts in mind, Conant and Garvey (25) determined the relative stability of the carbon-carbon bond in a number of phenylated ethanes. Their general technique involved treatment of the hydrocarbon with sodium-potassium alloy, 40% sodium amalgam, and 1% sodium amalgam, in ether and benzene solutions. The most stable bond in their series was that of dibenzyl which resisted the action of sodium-potassium alloy in benzene, and the most labile bond was found with hexaphenylethane which was cleaved by 1% sodium amalgam in ether.

Other reactions of and references to sodium-potassium alloy may be found in the reviews by Wooster, and Schmidt (14).

(89) Schorigin, Ber., 56, 176 (1923).

(90) Schlenk and Bergmann, Ann., 464, 35 (1928).

The extensive uses of sodium-potassium alloy have made it an important tool in the chemistry of organoalkali compounds; but despite its wide application, the nature of the reacting metal has never been investigated. The general trend has been to write the compounds as derivatives of potassium, but no direct evidence has been found in the literature to prove the nature of the metal in these compounds.

From predictions made by Gilman and Nelson (2), the organoalkali compounds prepared with sodium-potassium alloy should exist as the organopotassium compound, since potassium should be more reactive than sodium, and Gilman and Straley (39) have predicted that a more reactive metal (in this case, potassium) will react with an organometallic compound derived from a lesser reactive metal (in this case sodium), to form the organometallic compound of the more reactive metal. From this it may be seen that if an organosodium compound were formed by the reaction of sodium-potassium alloy, it would immediately be replaced by potassium to yield the organopotassium compound.

To test this hypothesis, and to elucidate the exact nature of the metal in the compounds prepared from sodium-potassium alloy, a series of reactions was run involving sodium-potassium alloy, and some common reagent. The reagents chosen for these experiments were such, that they could yield either sodium or potassium compounds, that are soluble and stable in anhydrous diethyl ether.

The experiments were all carried out with absolute diethyl ether as the solvent, and in 250 c.c. 3-necked balloon flasks,



equipped with reflux condenser, mercury-sealed stirrer, and with facilities for working in an atmosphere of purified nitrogen. The sodium-potassium alloy was prepared from a mixture of 1 part of sodium and 5 parts of potassium by weight (6). The mixture may be heated in anhydrous xylene, or in high boiling (b.p. 115-150°) petroleum ether, until the sodium and potassium have melted. The molten metals should then be carefully mixed together with a glass rod, and care should be taken to keep the metal in one large globule to facilitate handling. When cooled to room temperature, the alloy will remain liquid, and may be easily transferred by means of clean, dry pipettes. Care should be exercised in handling this alloy, and it must be kept under a suitable hydrocarbon all of the time. It is spontaneously inflammable in the air.

Reaction of 2-Phenyl-iso-propyl Methyl Ether with Sodium-Potassium Alloy. Test for Sodium and Potassium Ions.

The mixed ether was prepared by the method described by Ziegler and co-workers (6), and the cleavage reaction was carried out as follows (all reactions under nitrogen): To 150 c.c. of absolute diethyl ether was added 2 g. (0.013 mole) of 2-phenyl-iso-propyl methyl ether, and 2 c.c. of liquid sodium-potassium alloy. The reaction started immediately, and the solution became intensely red. After 30 hours of stirring, the reaction was allowed to settle and a clear, red solution of the organo-alkali compound was obtained. Fifty c.c. of this clear, red

solution was hydrolyzed by pipetting it into about 25 c.c. of distilled water. The ether was evaporated, and the solution was neutralized with 10% hydrochloric acid. Ordinary tests employed in qualitative analysis, were then made on the resulting aqueous solution. The test for the sodium ion was made with a concentrated aqueous solution of uranylzinc acetate, and the test for potassium was made with an aqueous solution of sodium cobaltinitrite. The solution gave a positive test for the potassium ion, and a negative test for the sodium ion. Further experimenting with the flame test indicated a negative test for sodium and a positive test for potassium. Carbonation of a portion of the clear, red ether solution with solid carbon dioxide yielded dimethylphenylacetic acid. The reaction was checked with similar results.

Reaction of Triphenylmethyl Ethyl Ether with Sodium-Potassium Alloy. The cleavage reaction of the triphenylmethyl ethyl ether with sodium-potassium alloy was carried out in a manner identical with that described above. To 150 c.c. of anhydrous diethyl ether was added 2.8 g. (0.01 mole) of triphenylmethyl ethyl ether, and 2 c.c. of liquid sodium-potassium alloy. The reaction immediately colored and was allowed to proceed for 24 hours. The ether solution was then allowed to settle and 100 c.c. of the clear, red ether solution was hydrolyzed and analyzed by the procedure described above. Both of the tests described above were positive for potassium

and negative for sodium. Carbonation of a portion of the clear, red ether solution with solid carbon dioxide yielded triphenylacetic acid (mixed m.p.). A check run was made of this reaction with the same results.

Reaction of Diphenylmethyl Methyl Ether with Sodium-

Potassium Alloy. The reaction was carried out in a manner identical with that described for triphenylmethyl ethyl ether. The same molecular proportions were used, and similar results were obtained only the potassium ion could be found, and carbonation of a portion of the clear light red ether solution with solid carbon dioxide yielded diphenylacetic acid (mixed m.p.). The diphenylmethylpotassium is only slightly soluble in ether and gave a weaker, but definitely positive test for potassium, and no sodium ions could be found.

The Reaction of Tetraphenylethane with Sodium-Potassium

Alloy. The reaction was carried out in a manner identical with that described for the cleavage reaction of the ethers. To 150 c.c. of a diethyl ether solution containing 1.67g. (0.005 mole) of tetraphenylethane was added 2 c.c. of sodium-potassium alloy. The reaction was slow, and was allowed to proceed for 36 hours. The clear, light red ether solutions of benzohydrilalkali compound were hydrolyzed, neutralized and tested as previously described. Only potassium ions could be found in the solution. Carbonation of the benzohydrilpotassium at room temperature, yielded the corresponding diphenylacetic

acid (mixed m.p.) \*

Reaction of Triphenylmethyl-Lithium with Sodium-Potassium

Alloy. The triphenylmethyl-Lithium was prepared as previously described (91). To 200 g. of a red ether solution containing about 0.02 mole of triphenylmethyl-Lithium, was added 2 g. of liquid sodium-potassium alloy, and the mixture was allowed to stir for 48 hours. At the end of this time the solution was a deeper shade of red, and a red precipitate had formed. The solution was allowed to settle for 6 hours, and was then tested by the methods previously described for sodium and potassium, and an additional test was made for lithium. The aqueous solution was evaporated on the water bath and in a platinum crucible with a small amount of hydrofluoric acid. The residue was treated with a little dilute ammonium hydroxide and completely dissolved. Under these conditions, if lithium is present, it will precipitate as a white gelatinous mass of lithium fluoride. Potassium is the only ion that could be found in the solutions. Carbonation of a aliquot portion of the clear ether solution with solid carbon dioxide yielded a small amount of triphenylacetic acid (authenticated by a mixed melting point). No check run was made.

Reaction of Tetraphenylethylene with Sodium and Sodium-

Potassium Alloy. To 150 g. of an anhydrous diethyl ether

of 0.66 g. (0.002 mole) of tetraphenylethylene was added

0.09 g. (0.004 mole) of sodium cut in very fine pieces.

(91) See page 45 of this thesis.

The reaction started promptly, and the reaction gave a very deep red solution of the disodium addition product. Hydrolysis of this product yielded tetraphenylethane, (mixed m.p.), and carbonation at room temperature yielded 58% of the theoretical amount of tetraphenylsuccinic acid.

When lithium or potassium was substituted for sodium the reaction would not proceed, and the metals remained unchanged after a period of 48 hours of constant stirring. No reports of the lithium or potassium addition product of tetraphenylethylene were found in the literature.

The reaction with sodium-potassium alloy (1.0 c.c.) proceeded slowly, and yielded, instead of a deep red ether solution, a red precipitate. No direct analysis of the precipitate could be made for sodium and potassium because it was contaminated with the alloy. Carbonation of the red precipitate at room temperature yielded 50% of the theoretical amount of tetraphenylsuccinic acid. The tetraphenylethylenedisodium has been found to be soluble in ether, and the red precipitate, which yields the same product upon carbonation is insoluble, so it is reasonable to assume that the red solid obtained from the action of sodium-potassium alloy on tetraphenylethylene, is tetraphenylethylenedipotassium.

Metalation of Triphenylmethane. To a solution of 2.44 g. (0.01 mole) of triphenylmethane dissolved in 125 c.c. of absolute ether was added 1 c.c. of sodium-potassium alloy. No

reaction could be evidenced in 30 hours. When one c.c. of chlorobenzene was added to the solution, a red coloration appeared immediately, and a red precipitate formed in about three hours. After 24 hours of stirring, the solution was allowed to settle and analysis of the clear red ether solution showed only the presence of the potassium ion. Carbonation of a portion of the clear, red solution with solid carbon dioxide yielded triphenylacetic acid.

DISCUSSION OF RESULTS

The results of these experiments indicate that the action of sodium-potassium alloy in the synthesis of organoalkali compounds leads to the formation of the organopotassium compound, and no trace of the organosodium compound could be found with the compounds studied.

The course of the reaction is not definitely known. The alloy may be more reactive due to its nature (liquid), and not to any specific chemical property of the mixture of the metals. On the other hand, the sodium may play an important part in some of the reactions, and an organosodium compound may be formed momentarily, and then it may be replaced by the lesser reactive potassium compounds. From observations in the laboratory, it may be said that organopotassium compounds are generally much less soluble in diethyl ether than their corresponding sodium analogs.

## II. CARBONATION OF ORGANOSODIUM COMPOUNDS

### INTRODUCTION AND EXPERIMENTAL PART

The reaction of organoalkali compounds with carbon dioxide is well known, and is a valuable method that is employed to obtain carboxylic acids. The yield of acid may vary enormously, from only very small to almost quantitative yields. During an investigation of the reactions of organolithium compounds with carbon dioxide, Gilman and Van Ess (92) were able to increase the yields of benzoic acid, obtained by the carbonation of phenyl-lithium, from 5% reported by Ziegler and Colonius (45), to 60% by the use of solid carbon dioxide. This reagent is one of choice for the carbonation of organomagnesium and -lithium compounds.

The low yields of acids obtained in carbonating organo-metallic compounds, is generally due to side reactions that yield ketones and tertiary alcohols (92). Solubility effects may influence these secondary reactions, and if an insoluble organoalkali compound is allowed to react with carbon dioxide to form an insoluble metallic salt of the acid; the insolubility of both the organoalkali compound and salt of the acid might prevent further action, and the reaction may stop at the acid without any appreciable amount of ketone and carbinol formation. Soluble organoalkali compounds might also be predicted to give good yields of acid if the metallic salt of the acid is insoluble to the extent that it does not react (92) Gilman and Van Ess, J. Am. Chem. Soc., 55, 1258 (1933).



with the organoalkali compound. Gilman and Peterson (93) have demonstrated that the ether insoluble salt, sodium bicarbonate, containing a carbonyl and an active hydrogen group will not react with the Grignard reagent. Carbonation of organosodium compounds is commonly reported in the literature, but very little data is given regarding the conditions of the reaction. Accordingly, several organosodium compounds were prepared and carbonated at room temperature, with gaseous carbon dioxide, and in each case excellent yields of the corresponding acid were obtained.

Carbonation of Phenylethynylsodium, -potassium, -rubidium, and -cesium. Preparation of phenylethynylsodium, -potassium, -rubidium, and -cesium is described elsewhere in this thesis (94). The solutions of these compounds were standardized by carbonation at room temperature, and the results were previously described (95). Carbonation of phenylethynylmagnesium bromide, and -lithium was not carried out at room temperature, because of the tendency of these organoalkali compounds to yield ketones and tertiary carbinols (92). Carbonation of phenylethynylsodium and -potassium with solid carbon dioxide, gave 60 and 57% yields respectively, of the phenylpropionic acid, which was

(93) Gilman and Peterson, Rec. trav. chim., 48, 247 (1929).

(94) See page 74 of this thesis.

(95) See page 76 of this thesis.

about 15% lower than that from room temperature carbonation. Very little heat was liberated during the reaction of the phenylethenylalkali compounds with gaseous carbon dioxide.

Carbonation of 4-Dibenzofurylsodium. 4-Dibenzofurylsodium was prepared as previously described (96). The mixture was carbonated by passing in gaseous carbon dioxide at room temperature, and yielded 64% of the theoretical amount of the corresponding acid. The reaction was not checked. Carbonation with solid carbon dioxide gives yields varying from 61-68% of the theoretical amount. A small amount of heat was liberated during room temperature carbonation, and the ether solution refluxed gently.

Preparation and Carbonation of Phenylsodium. The reaction was carried out in a 250 c.c. 3-necked balloon flask equipped with reflux condenser, mercury-sealed stirrer, and facilities for working under an atmosphere of purified nitrogen. To 35 c.c. of anhydrous benzene was added 1.4 g. (0.06 atom) of sodium and 4.71 g. (0.015 mole) of di-n-butylmercury. The reaction was allowed to stir for 18 hours at room temperature, and was then carbonated by passing in gaseous carbon dioxide. The mixture became warm, and the benzene gently refluxed. When the reaction had subsided, it was found to contain 2.2 g. of benzoic acid, which was 60% of the theoretical amount.

(96) See page 33 of this thesis.

No comparison was made with low temperature carbonation experiments.

Carbonation of Tetraphenylethylenedisodium. The tetraphenylethylenedisodium was prepared by the method previously described (97). The clear, red ether solution was carbonated by gaseous carbon dioxide at room temperature. Very little heat was liberated during this reaction, and 58% of the theoretical amount of tetraphenylsuccinic acid was formed. The yield of tetraphenylsuccinic acid was not checked with low temperature carbonation.

(97) See page 86 of this thesis.

### DISCUSSION OF RESULTS

The results indicate that carbonation of some organosodium compounds may be carried out at room temperature without materially affecting the yield of acids. This simplifies the carbonation procedures for these compounds, and shows the marked difference between organosodium and -lithium compounds. Organolithium compounds can only be effectively carbonated to produce acids at very low temperatures, preferably with solid carbon dioxide (92). The difference in the behavior of organosodium and -lithium compounds may be due to solubility effects, either of the original organosodium and -lithium compound, or the resulting salt of the acid that is formed from the carbon dioxide, or both. Soluble organosodium compounds may yield sodium salts of acids that are almost entirely insoluble in the reaction media, while the soluble organolithium compounds may produce lithium salts of acids that are appreciably soluble in the media. The increased solubility of lithium salts of acids may then make them available for further reaction, with the subsequent formation of ketones and carbinols, while the sodium salts will be unaffected. If the organometallic compound is insoluble in the reaction media, it will only be available for reaction with the carbon dioxide, and similarly only the sodium salt of the acid will be formed. Further experimentation will be necessary to confirm this assumption.

## V. SUMMARY

The relative reactivities of 4-dibenzofurylsodium and -potassium with fluorobenzene, chlorobenzene, and *o*-tolu-nitrile were studied. The low concentrations of the solutions of the organoalkali compounds, and the high velocity of the reactions, made an accurate determination of their relative reaction rates impossible under the conditions employed. It was observed that fluorobenzene reacted more rapidly than chlorobenzene with the 4-dibenzofurylalkali compounds.

The relative reaction velocities of triphenylmethylsodium and -lithium were studied. The reactions with chlorobenzene, bromobenzene, and *o*-tolunitrile were carried out, and triphenyl-methyl-lithium reacted more rapidly than the sodium analog. The results were considered anomalous, in view of the many abnormal reactions of triphenylmethylsodium.

Reactions of ethylpotassium, -sodium, and -lithium were carried out with dibenzofuran. It was found that the relative order of decreasing reactivity of the ethylalkali compound was ethylpotassium, -sodium, -lithium. Dimetalation of dibenzofuran occurred to the greatest extent with ethylpotassium, and was not present with ethyl-lithium. Dimetalation was considered as a possible criterion of relatively high reactivity of an organoalkali compound.

Relative reaction velocities of the phenylethynylalkali compounds with benzonitrile were studied. It was found that

the order of their relative decreasing reactivity was phenyl-ethynylcesium, -rubidium, -potassium, -sodium, -lithium, and -magnesium. Experimentation with various types of apparatus indicated that the equipment and technique ordinarily used with organomagnesium and -lithium compounds could be applied to many organoalkali compounds with good results.

Reactions of sodium-potassium alloy, that lead to the formation of organoalkali compounds, produced only the organopotassium compounds with the reagents studied, and no trace could be found of organosodium compounds.

Carbonation of some organoalkali compounds, -lithium compounds excepted, can be effected at room temperature, with the formation of high yields of the corresponding acids. The results were ascribed to solubility effects of the organoalkali compounds, and the alkali metal salts of the acids.