[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE COLLEGE]

# RELATIVE REACTIVITIES OF ORGANOMETALLIC COMPOUNDS. XV. ORGANOALKALI COMPOUNDS

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## INTRODUCTION

*Historical.*—No systematic study of the relative reactivities of organoalkali compounds has been reported. One of a series of broad generalizations concerning the relative reactivities of all organometallic compounds[1] postulates that the organoalkali compounds will be found to fall in the following order of increasing reactivities: RLi, RNa, RK, RRb, RCs. It might be stated forthwith that the results reported at this time give adequate support to the generalization mentioned.

There are scattered references to the relative reactivities of RLi, RNa and RK compounds. Benzyllithium does not decompose diethyl ether, but benzylsodium decomposes ether in a very short time.[2] Ethyllithium may be prepared in a benzene solution[3] in which it is stable for a long time; however, ethylsodium and ethylpotassium metalate benzene to give phenylalkali and *o*- and *p*-phenylenedialkali compounds.[4] In the metalation of dibenzofuran it was observed that RNa and RK compounds reacted more rapidly than RLi compounds[5a]; and that dimetalation proceeds smoothly with RNa and RK compounds, but does not go at all with RLi compounds.[5b]

In a study of very weak acids, $\alpha$-naphthyldiphenylmethylsodium reacted erratically with triphenylmethane in periods of a few minutes to several months, whereas the corresponding RK compound reacted smoothly and instantaneously.[6] Organopotassium compounds add more readily than organolithium compounds to the olefinic linkage of some ethylenes.[2]

It is pertinent to observe that organolithium compounds are distinctly more reactive than the corresponding organomagnesium compounds.[7]

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[1] GILMAN AND NELSON, *Rec. trav. chim.*, **55**, 518 (1936).

[2] ZIEGLER AND CO-WORKERS, (*a*) *Ann.*, **473**, 1 (1929); (*b*) *Ber.*, **64**, 448 (1931).

[3] SCHLENK AND HOLTZ, *Ber.*, **50**, 269 (1917).

[4] (*a*) SCHORIGIN, *ibid.*, **41**, 2711 (1908); (*b*) MORTON AND HECHENBLEIKNER, *J. Am. Chem. Soc.*, **58**, 1024 (1936); (*c*) GILMAN AND KIRBY, *ibid.*, **58**, (October, 1936).

[5] (*a*) GILMAN AND YOUNG, *ibid.*, **56**, 1415, (1934); (*b*) *ibid*, **57**, 1121 (1935).

[6] CONANT AND WHELAND, *ibid.*, **54**, 1212 (1932).

[7] GILMAN AND KIRBY, *ibid.*, **55**, 1265 (1933).

*Phenylacetenylalkali compounds and benzonitrile.*—One of the compounds used to compare the relative reactivities of organoalkali compounds was benzonitrile. This compound was selected for several reasons: (1) it was used in studies of relative reactivities of other RM compounds previously reported in this series; (2) it reacts slower than most organic compounds having a functional group reactive to RM compounds;[8] and (3) it undergoes reaction with a minimum of secondary transformations.

The phenylacetenyl radical was selected because it was known from earlier observations that $C_6H_5C{\equiv}CM$ types are of a relatively low order of reactivity, particularly in addition reactions to some unsaturated functional groups.[9] Slow-reacting combinations were desirable in order to measure with some accuracy the time required to use up the highly reactive organoalkali compound when a definite excess of benzonitrile was used. The color test[10] was used to determine the disappearance of RM compound.

The use of the color test involves the periodic removal of small samples of the reaction mixture. This made it desirable to avoid special all-glass-sealed containers, like Schlenk tubes, which have been used so effectively in studies of organoalkali compounds. Although the organoalkali compounds are the most reactive organometallic compounds it seemed likely that special apparatus could be dispensed with, and that with reasonable care these RM compounds could be manipulated in the conventional three-necked, round-bottomed flasks provided with a mercury-sealed stirrer. The chief reason for the use of special sealed tubes is to exclude atmospheric oxygen, moisture and carbon dioxide. However, the Grignard reagents as well as other moderately reactive RM compounds are highly sensitive to these deleterious substances, and yet can be prepared and manipulated with only ordinary precautions in the more conventional apparatus. Furthermore, organolithium compounds can be prepared and used in accordance with RMgX technique, and this is also true of some organosodium compounds.[11] The chief prerequisite to such operations is a stream of dry and pure nitrogen or other inert gas. Even the highly inflammable rubidium and cesium can be transferred by means of regular pipettes. All that is necessary is to cover the upper and lower surfaces of these liquid metals in the pipette with a layer of petroleum ether, and this is done simply and easily when the metals are drawn up into the pipettes. Actually these most reactive metals are

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[8] ENTEMANN AND JOHNSON, *ibid.*, **55**, 2900 (1933). RM is used as a general formula for organometallic compounds.

[9] GILMAN AND CO-WORKERS, *Rec. trav. chim.*, **55**, (October, 1936).

[10] GILMAN AND SCHULTZE, *J. Am. Chem. Soc.*, **47**, 2002 (1925).

[11] GILMAN, ZOELLNER AND SELBY, *ibid.*, **54**, 1957 (1932).

in many ways easier to manipulate, from the viewpoint of getting a definite quantity, than are lithium, sodium and potassium, because of the high accuracy of pipettes for measuring desired quantities.

Apparently, phenylacetenylsodium is the only member of this series reported, and it was prepared by the action of sodium on phenylacetylene in ether[12] and by metalation of phenylacetylene by indenylsodium.[6] We prepared all of the phenylacetenylalkali compounds, with the exception of the lithium compound, by the action of alkali metal on phenylacetylene in ether. Phenylacetenyllithium did not form in this way under our conditions, and was prepared from phenylacetylene and *n*-butyllithium. The organoalkali compounds could be prepared in consistently good yields as evidenced by the yields of phenylpropiolic acid obtained by carbonation.

TABLE I

TIME (IN HOURS) REQUIRED FOR REACTION OF $C_6H_5C{\equiv}CM$ WITH BENZONITRILE

| | |
|---|---|
| $C_6H_5C{\equiv}CMgBr$ | 87, 85 |
| $C_6H_5C{\equiv}CLi$ | 57, 63 |
| $C_6H_5C{\equiv}CNa$ | 6.5, 7.0 |
| $C_6H_5C{\equiv}CK$ | 4.3, 4.5 |
| …… | …… |
| $C_6H_5C{\equiv}CK$ | 5.3, 5.1 |
| $C_6H_5C{\equiv}CRb$ | 4.8, 4.9 |
| $C_6H_5C{\equiv}CCs$ | 3.8, 3.9 |

$$C_6H_5C{\equiv}CM + CO_2 \xrightarrow{HOH} C_6H_5C{\equiv}CCO_2H$$

It is interesting that there was no significant reaction of these organoalkali compounds with the ether in the time required to complete addition to benzonitrile.

Table I records the relative times required for reaction with benzonitrile. Phenylacetenylmagnesium bromide is included for purposes of comparison. The experiments with the first four compounds were carried out on a comparatively larger scale and with slightly greater concentrations than those involving the more expensive rubidium and cesium compounds. To make the relative rates of reaction of these last two members of the series comparable with those of the first four, phenylacetenylpotassium was run under conditions and with concentrations like those of phenylacetenylrubidium and -cesium.

*Metalation by ethylalkali compounds.*—A series of experiments was carried out on the metalation of dibenzofuran by several ethylalkali compounds.

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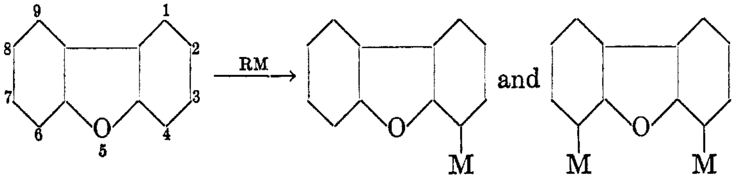
[12] GLASER, *Ann.*, **154**, 161 (1870).

Ethylalkali compounds of lithium, sodium and potassium are known; however, ethylrubidium and ethylcesium have only been prepared as complexes with diethylzinc.[13] We prepared the ethyllithium, -sodium, and -potassium compounds by interaction of a definite excess of alkali metal with diethylmercury in petroleum ether. This reaction is reversible,[14]

$$(C_2H_5)_2\,Hg + M \rightleftarrows 2C_2H_5M + Hg\ (\text{or } Hg\cdot M)$$

but the use of an excess of metal drives the reaction to essential completion. The need of an excess of metal discouraged, at this time, the preparation of ethylrubidium and -cesium.

Dibenzofuran was selected, and it is known that this compound metalates in the 4- and 4,6- positions.



It was first shown that at the end of 15 days, when reaction had reached completion, the quantities of acids resulting subsequent to carbonation (and composed of the 4-acid or the 4-acid and 4,6-diacid) were essentially alike, as determined by the quantity of standard alkali required for neutralization of the acid product. Then the reaction with each of the three ethylalkali compounds was interrupted at the end of two and one-half hours, the mixture carbonated, and the resulting dibenzofuran acids titrated with alkali. The quantity of acids determined in this manner is a measure of the extent of metalation, and the values given in Table II were obtained in this way.

Although the mechanism of such metalations has not been established, and may involve preliminary addition to an olefinic linkage, it is clear that the relative reactivities fall in the same increasing order established in the $C_6H_5C \equiv CM + C_6H_5CN$ reactions: RLi, RNa, RK. Supporting evidence for this order of reactivity in the metalation studies are the facts that (1) ethyllithium gives only monometalation under the experimental conditions; (2) ethylsodium and -potassium give both mono- and dimetalation; and (3) ethylpotassium gives more dimetalation than does ethylsodium. Similar observations were reported recently in the metalation of benzene, where ethyllithium gave no metalation and the sodium and

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[13] von Grosse, *Ber.*, **59**, 2646 (1926).

[14] Ziegler, *ibid.*, **64**, 445 (1931).

potassium analogs gave coincident mono- and dimetalation, ethylpotassium giving the greater quantity of dimetalation products.[4b, c]

The case for polymetalation as a criterion of the relative reactivities of RM compounds is not decisive. If metalation proceeds stepwise, which is a reasonable assumption, then the rate of polymetalation may be determined not only by the inherent reactivity of the metalating agent, but also by the labilizing effect on the nucleus of the initially introduced metal. In short, the monopotassium-dibenzofuran may undergo nuclear substitutions more rapidly than the monosodium-dibenzofuran.

In the ethylalkali experiments it was assumed that the extent of decomposition of the several compounds was essentially alike. It is known that methyl- and ethylsodium and methylpotassium are thermally labile, and that some decomposition occurs at room temperature.[15] In some random observations it was noticed that ethylsodium and -potassium underwent some decomposition (as evidenced by gas evolution) during their preparation; but they appeared to be essentially stable, or to undergo only slight change at room temperature, subsequent to the initial decomposition. No exact measurements were made. To reduce such decomposition, the ethylalkali compounds were prepared without the application of heat, and any rise in temperature during preparation was checked by rapid cooling with a water bath.

TABLE II

RELATIVE QUANTITIES OF DIBENZOFURANCARBOXYLIC ACIDS RESULTING AFTER METALATION BY $C_2H_5M$ COMPOUNDS

| | |
|---|---|
| $C_2H_5Li$ | 0.1, 0.05 |
| $C_2H_5Na$ | 4.5, 4.7, 4.5 |
| $C_2H_5K$ | 14.1, 12.6, 15.0 |

The Experimental Part describes some orienting observations on the relative reactivities of 4-dibenzofurylalkali and triphenylmethylalkali compounds.

*Formation of organopotassium compounds from sodium-potassium alloy.*— Sodium-potassium alloy has been used extensively in reactions culminating in the formation of organoalkali compounds. Inasmuch as there exists some uncertainty concerning the nature of the product or products, we thought it advisable to examine typical reactions to learn whether the product was an RNa or RK compound or a mixture of these two. The first use of the alloy for the preparation of RM compounds involved the

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[15] CAROTHERS AND COFFMAN, *J. Am. Chem. Soc.*, **51**, 588 (1929); *ibid.*, **52**, 1254 (1930).

cleavage of some mixed ethers and some ethanes.[16] Other reactions and references to sodium-potassium alloy may be found in the excellent review by Wooster[17] on organoalkali compounds and in the recent monograph by Schmidt[18] on organometallic compounds. The compounds examined were such that they could yield either sodium or potassium compounds soluble and stable in anhydrous ether. In each case we found that an RK and not an RNa compound was formed. The illustrative reactions follow:

$$C_6H_5C(CH_3)_2OCH_3 + Na\cdot K \rightarrow C_6H_5C(CH_3)_2K$$
$$(C_6H_5)_3COC_2H_5 + Na\cdot K \rightarrow (C_6H_5)_3CK$$
$$(C_6H_5)_2CHOCH_3 + Na\cdot K \rightarrow (C_6H_5)_2CHK$$
$$(C_6H_5)_2CHCH(C_6H_5)_2 + Na\cdot K \rightarrow (C_6H_5)_2CHK$$
$$(C_6H_5)_2C{=}C(C_6H_5)_2 + Na\cdot K \rightarrow (C_6H_5)_2C(K)C(K)(C_6H_5)_2$$
$$(C_6H_5)_3CH + Na\cdot K \rightarrow (C_6H_5)_3CK$$

The ultimate formation of RK rather than RNa compounds is in accordance with a generalization concerning the preparation and relative reactivities of organometallic compounds.[19] For example, all organometallic compounds can be prepared from any selected organometallic compound by one or both of two general reactions. If we select the Grignard reagent as the starting RM compound, *more* reactive RM compounds can be prepared from it by means of the metal of the more reactive compound:

$$RMgX + Li \rightarrow RLi$$

And *less* reactive RM compounds can be prepared from it by means of salts, particularly the halides, of the less reactive metal:

$$RMgX + CdCl_2 \rightarrow R_2Cd \text{ or } RCdX$$

On such a basis, if an RNa compound be formed initially in preparations involving sodium-potassium alloy, the metallic potassium would be expected to react with the RNa compound to give an RK compound:

$$RNa + K \rightarrow RK + Na$$

Actually, triphenylmethyllithium and sodium-potassium alloy gave triphenylmethylpotassium:

$$(C_6H_5)_3CLi + Na\cdot K \rightarrow (C_6H_5)_3CK$$

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[16] Ziegler and Thielman, *Ber.*, **56**, 1740 (1923).

[17] Wooster, *Chem. Rev.* **11**, 1 (1932).

[18] Schmidt, "Organometallverbindungen," Wissentschaftliche Verlagsgesellschaft, Stuttgart, **1934**, Vol. II.

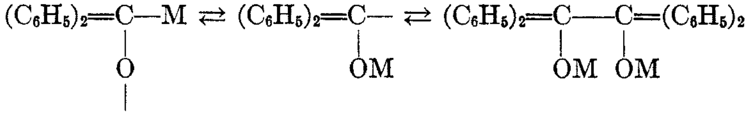
[19] Gilman and Straley, *Rec. trav. chim.*, **55**, 821, 1936.

*Addition of alkali metals to tetraphenylethylene.*—The addition of sodium to tetraphenylethylene is a well-known reaction:[20]

$$(C_6H_5)_2C{=}C(C_6H_5)_2 + 2Na \rightarrow (C_6H_5)_2C(Na)C(Na)(C_6H_5)_2$$

It appears that this reaction is essentially peculiar to sodium. Under corresponding conditions, lithium does not add. This is not altogether surprising in view of the lesser general reactivity of lithium. However, potassium alone likewise appeared not to add, and the reaction previously given with sodium-potassium alloy may have been due to initial addition of sodium followed by replacement of the two sodium atoms by potassium. It was quite surprising to note that neither rubidium nor cesium appears to add. The apparent lesser reactivity of these otherwise extremely reactive metals may be due to steric factors; in the case of tetraphenylethylene we are dealing with a highly sterically hindered olefinic linkage, and this together with the relatively huge atomic volumes of rubidium and cesium may combine to frustrate addition. Special conditions permit reaction of rubidium and cesium, but the course of reaction has not yet been established. Significantly, although rubidium alone does not add, a sodium-rubidium alloy adds to give the RRb compound. Here, again, it is probable that sodium first adds and is then replaced by the more reactive rubidium. This is in accordance with the generalization that steric factors have a much greater retarding effect on addition than on substitution reactions. Addition, in general, is not excluded, for 1,1-diphenylethylene dimerizes and adds rubidium.

*Metal ketyls and* n-*butyl chloride.*—The relative reactivities of *n*-butyl chloride with the benzophenone alkali compounds of potassium, rubidium and cesium showed the order of increasing reactivity to be: K, Rb, Cs. This is the order one would expect, on the basis of the other results presented at this time, if the metal were attached to carbon. The carbon-alkylation may proceed through the -OM type. What the order would be if the metal were definitely attached to oxygen in a compound like $R_2CHOM$ or $R_3COM$ remains to be established. The following equilibria or their electronic modifications appear valid, depending somewhat on the solvent:[21]



$$(C_6H_5)_2{=}\underset{\underset{|}{\overset{|}{O}}}{C}{-}M \rightleftarrows (C_6H_5)_2{=}\underset{\overset{|}{OM}}{C}{-} \rightleftarrows (C_6H_5)_2{=}\underset{\overset{|}{OM}}{C}{-}\underset{\overset{|}{OM}}{C}{=}(C_6H_5)_2$$

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[20] Schlenk, Appenrodt, Michael, and Thal, *Ber.*, **47**, 473 (1914); Schlenk and Bergmann, *Ann.*, **463**, 1 (1928); Blum-Bergmann, *ibid.*, **484**, 26 (1930).

[21] Schlenk and Weickel, *Ber.*, **44**, 1182 (1911); Bachmann, *J. Am. Chem. Soc.*, **55**, 1179 (1933); Wooster and Dean, *ibid.*, **57**, 112 (1935). See, however, Bent and Keevil, *ibid.*, **58**, 1367 (1936).

Like the triphenylmethylalkali studies described in the Experimental Part, the relative reactivities may be influenced by the varying positions of equilibria dependent on the nature of the metal.

Should the reaction involve predominatingly the -OM form, it suggests the use of RRb or RCs compounds for establishing the mechanisms of some reactions, particularly that of RM compounds with esters which probably involves preliminary addition to the carbonyl* to give an -OM linkage.

*Carbonation of organoalkali compounds.*—The carbonation of RM compounds does not always lead to the facile formation of carboxylic acids. For example, Grignard reagents give not only the acid, but also varying quantities of ketone and tertiary alcohol. These chief by-products arise largely from secondary reactions between the Grignard reagent and the RCOOMgX salt which is first formed. The secondary reactions can be effectively depressed by carbonating in the cold or by the use of solid carbon dioxide. Under usual conditions of carbonation the otherwise secondary reactions may become chief reactions with a compound like phenyllithium which gave but a trace of benzoic acid[22] and an excellent yield (upward of 70 per cent.) of benzophenone. With solid carbon dioxide, the yield of benzoic acid from phenyllithium is 60 per cent., and only 15 per cent. of benzophenone is formed.[23] It has been suggested that the relatively low yields of acid and high yields of ketone by carbonation of an aryllithium compound are due, in part, to the greater reactivity of RLi compounds over the corresponding RMgX compounds.[23]

We have found that not only RNa compounds, but also the RK, RRb and RCs compounds give highly satisfactory yields of acids when carbonated in boiling ether. In contrast, the carbonation of phenyllithium in boiling ether gave but 1.6 per cent. of benzoic acid and 76 per cent. of benzophenone. The explanation for these significant differences may reside in the varying solubilities of the salts.

*Some methods for the determination and postulation of the relative reactivities of organoalkali compounds.*—There is no question concerning the pronounced polar characteristics of organoalkali compounds. All RM compounds are to be considered as salts derived from the weakly acidic RH compounds. As such, the organoalkali compounds should be the most polar RM types inasmuch as they are prepared, directly or indirectly, from the strongest bases. If relative reactivities are to be correlated with

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* This finds support by analogy with the mechanism of reaction of Grignard reagents and thio-esters. In such cases the -SM linkage is more readily converted to an -SEthyl linkage than is the case of the -OM→ -OEthyl conversion.

[22] ZIEGLER AND COLONIUS, *Ann.*, **479**, 135 (1930).

[23] GILMAN AND VAN ESS, *J. Am. Chem. Soc.*, **55**, 1258 (1933).

the salt-like or polar characteristics of the RM compounds, it should be possible to use conductivity measurements to establish relative reactivities. Unfortunately the less reactive RM types have not lent themselves to such measurements. The more reactive types, of which the organoalkali compounds are distinguished examples, have been examined rather closely. Some of the findings are very pertinent and a particularly happy illustration is contained in Table III, which is taken from some of the studies by Hein and co-workers.[24] For comparative purposes the molar conductance values of 0.1 $N$ solution of the corresponding alkali metal hydroxide at 18° are also given.[25]

The splendid correlation between conductivities of the RM compounds and relative reactivities promises a high utility for this method of comparing relative reactivities. However, there are two general reasons for a restricted applicability of the method. First, even though the organoalkali compounds are the best conductors and, with the exception of RM types of the alkaline-earth metals, the only types that conduct adequately for the purposes in hand, they cannot generally be examined in this way. Their thermal instability precludes measurements in the fused state, and their insolubility, together with high reactivity, markedly restricts appropriate solvents. Second, the promise held out by the ethylalkali compounds is not sustained generally because of disturbing anomalous results. For example, phenylsodium in diethylzinc does not conduct at all, whereas phenyllithium which is distinctly less reactive chemically does conduct. Also, the order of conductivity of a given series with a selected metal (like the RLi types) but with different R groups, does not always follow either the order of chemical reactivity or the order established by conductometric methods for corresponding radicals attached to another metal

TABLE III

MOLAR CONDUCTANCES OF $C_2H_5M$ AND MOH

| MOLAR CONDUCTANCES OF $C_2H_5M$ SOLVATES OF $(C_2H_5)_2Zn$ | | MOLAR CONDUCTANCES OF MOH | |
|---|---|---|---|
| $C_2H_5Li$ | 0.13 | LiOH | 74.5 |
| $C_2H_5Na$ | 4.01 | NaOH | 195.3 |
| $C_2H_5K$ | 6.49 | KOH | 213 |
| $C_2H_5Rb$ | 9.39 | RbOH | 213.3 |

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[24] (*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).

[25] *International Critical Tables*, McGraw-Hill Book Co., New York, **1929**, Vol. VI, pp. 246–253.

(like the RMgX types). It should be stated that equivalent conductance measurements of triphenylmethylsodium and -potassium in pyridine show the RK compound to be more polar.[26]

A method for arriving at relative reactivities of RM compounds is to postulate a correlation with the electromotive series of the metals, the more electropositive metals forming the more polar and more reactive RM compounds. In a general way there is a correlation, but some of the exceptions are notorious. Table IV lists the alkali metals and calcium in an order of decreasing voltage.[27]

It is at once evident that lithium is entirely out of line in the sense that the above series might lead one to expect that RLi compounds would be the most reactive of the organoalkali compounds whereas they actually are the least reactive. Also, the organocalcium compounds should be more reactive than the organosodium compounds, but they are less reactive than either the organosodium or organolithium compounds;[28] and diethylcalcium has been reported as completely non-conducting in diethylzinc,[24b] whereas ethylsodium is a good conductor.

TABLE IV

E.M.F. SERIES OF SOME METALS

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

All that can be said at this time is that the broad rule formulated on the simple basis of groups and families of the periodic table[1] is most useful because it has fewest exceptions. Undoubtedly more exceptions (see Experimental Part) will be found with further studies, for in the field of organometallics exceptions can be the rule as much as in other fields of organic chemistry.

It should be emphasized, also, that the order of increasing activities of organoalkali compounds (RLi, RNa, RK, RRb, RCs) is dependent both on the metal and the R group. The series can be transposed with different R groups. For example, phenyllithium is decidedly more reactive than phenylacetenylcesium. Also, there is no regular decrease in activity[1]

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[26] ZIEGLER AND WOLLSCHITT, *Ann.*, **479**, 123 (1930).

[27] *International Critical Tables*, McGraw-Hill Book Co., New York, 1929, Vol. VI, p. 332.

[28] GILMAN, KIRBY, LICHTENWALTER AND YOUNG, *Rec. trav. chim.*, **55**, 79 (1936).

(using like R groups), for the difference between RLi and RNa is decidedly greater than that between RNa and RK compounds. Finally, it now appears that when RM compounds shall have been prepared from Element 87 these will prove to be the most reactive types. In contrast, it also appears that organoplatinum compounds may prove to be the least reactive RM types.

## EXPERIMENTAL PART

*General.*—The several reactants were purified prior to use by crystallization, distillation, or combinations of these procedures. Ziegler's[2a] method was used for the purification of ether, and this consists essentially in a preliminary drying over sodium wire, followed by distillation under nitrogen from a mixture of sodium-potassium alloy and benzophenone. The nitrogen was purified by bubbling through two Milligan wash bottles containing strongly alkaline pyrogallol solutions; then through two gas towers containing concentrated sulfuric acid; and, finally, by passage over phosphorus pentoxide. It is quite important to have effective scrubbing towers like Milligan bottles for removal of traces of oxygen.

The solid alkali metals 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 provided a convenient and rapid method to measure them. Because of the spontaneous inflammability of rubidium and cesium they were covered during transfer by a small layer of high-boiling petroleum ether, and sucked into the pipette in such a manner as to provide a thin layer of petroleum ether at the bottom of the metal contained in the pipette. The petroleum ether (b.p. 115–150°) used to protect the metals from the atmosphere was dried for several days over sodium-potassium alloy.

Most of the rate reactions were carried out in a 150-cc. three-necked balloon flask provided with a mercury-sealed stirrer, reflux condenser, and ground-glass stopper. All joints to the flask were ground-glass. Flexibility of the three ground-glass joints was increased by lubricating the upper part of the joints with vaseline. Check runs, to be described later, were carried out in similar conventional flasks having rubber stoppers and no ground joints. After flushing the apparatus with nitrogen, the flask and contents were always protected by admitting nitrogen under a small, positive pressure.

*Phenylacetenylalkali reactions.*—The phenylacetenyl compounds of magnesium and lithium were prepared in ether from phenylacetylene and phenylmagnesium bromide and phenyllithium, respectively. The acid obtained by carbonation was phenylpropiolic acid free of benzoic acid.

Phenylacetenylsodium and -potassium were prepared from 3.06 g. (0.03 mole) of phenylacetylene in 30 cc. ether and 0.02 g. atom of the alkali metal cut into small pieces. Reaction was allowed to proceed at room temperature with constant stirring until all the metal was used up, as evidenced by absence of hydrogen evolution when a few drops of the suspension was added to an equal volume of water. Reaction with sodium is complete in 8 hours, but potassium requires about 48 hours. The times were checked in five preparations. Under similar conditions lithium and magnesium do not react to give any significant quantity of RM compound (negative color test), although the metals are slightly coated.

In the second series (see Table I) of preparations, 2.04 g. (0.02 mole) of phenylacetylene in 25 cc. of ether was added to 0.01 g. atom of metal. Reaction was completed with potassium in about 40 hours, with rubidium in about 12 hours and with cesium in about 25 hours. The suspended phenylacetenylalkali compounds varied progressively in color from a dark tan for cesium and rubidium, to a light tan for potassium, and to colorless for the sodium and lithium compounds. Each compound was carbonated, the lithium compound by means of solid carbon dioxide and the others with carbon dioxide gas at room temperature, which was frequently at the boiling point of ether. The yields of phenylpropiolic acid were: RLi, 68%; RNa, 74%; RK, 71%; RRb, 74%; RCs, 78%.

Reactions with benzonitrile were carried out at room temperature and with vigorous stirring. In the first series of experiments (Table I), 4.12 g. (0.04 mole) of benzonitrile in 10 cc. of ether was added to the 0.02 mole of RM compound. In the second series (RK, RRb and RCs compounds), 2.06 g. (0.02 mole) of benzonitrile was added to 0.01 mole of RM compound in 25 cc. of an ether suspension. The general procedure for making color tests to determine the reaction rates has been described adequately in earlier papers of this series.

The following times in hours were noted when rate studies were carried out in the flasks provided exclusively with rubber stoppers: RK, 5.1; RRb, 5.2; RCs, 3.7. These experiments were not checked.

When the reaction between phenyllithium and benzonitrile was run under conditions like those used in the corresponding experiments with phenylacetenylpotassium, -rubidium, and -cesium, the time required for completion of reaction was less than 0.05 hour.

*Ethylalkali compounds and dibenzofuran.*—The ethylalkali compounds were prepared in a 250-cc. flask by adding 0.04 g. atom of the metal cut into small pieces to a solution of 2.59 g. (0.01 mole) of diethylmercury in 25 cc. of petroleum ether (b.p., 68–77°). The mixture was stirred rapidly for 4 days with lithium, 1.5 days with sodium and 2 days with potassium. The times mentioned in the preparation of the ethylalkali compounds are the approximate times required for completion of reaction, as evidenced by a cessation of gas evolution during the preparation of ethylsodium and potassium. No attempt was made to determine the amount or rate of gas evolution from the preparation of ethyllithium, and 4 days was arbitrarily selected as adequate for the completion of this preparation.

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 cc. 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 mixture 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 cc. of cold water, and the solution subsequently heated to boiling. The hot solution was filtered, and the residue was extracted with 50 cc. 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 ethyllithium, -sodium and -potassium with dibenzofuran were then compared by titrating them with 0.1380 *N* sodium hydroxide. The titrations were carried out by dissolving the acids in 50 cc. of a 50% water-acetone solution that had been previously neutralized with the base. Phenolphthalein was used as an indicator. The titration values, in cc. of standard sodium hydroxide, are: $C_2H_5Li$, 25.6; $C_2H_5Na$, 29.7; $C_2H_5K$, 30.9.

In the rate studies the ethylalkali compounds were prepared in the same manner, and after allowing reaction with dibenzofuran to proceed for 2.5 hours, the mixture was carbonated by pouring upon solid carbon dioxide. The results are given in Table II, and the values given there are in terms of cc. of standard sodium hydroxide.

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 cc. and 90 cc. of gas were evolved. Similar experiments with ethylpotassium yielded 84 cc. and 280 cc. of gas. These volumes of gas were obtained from 0.10 mole of diethylmercury reacting with 0.04 g. 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.

An attempted metalation of benzene by ethyllithium was carried out in a Schlenk tube, in which the air was displaced by nitrogen. To 50 cc. of benzene, contained in this tube, was added 3.45 g. (0.5 g. 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.

*Formation of organopotassium compounds from sodium-potassium alloy.*—The sodium-potassium alloy was prepared from a mixture of 1 part of sodium and 5 parts of potassium by weight.[2a] 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. To 150 cc. of absolute diethyl ether was added 2 g. (0.013 mole) of 2-phenylisopropyl methyl ether,[2a] and 2 cc. 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 organoalkali compound was obtained. Fifty cc. of this clear red solution was hydrolyzed by pipetting it into about 25 cc. 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. Also 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.

In like manner, reactions were carried out with the alloy and triphenylmethyl ethyl ether, diphenylmethyl methyl ether, tetraphenylethane (over a 36 hour period), tetraphenylethylene, and triphenylmethane. In the tetraphenylethylene experiments the reaction with sodium-potassium alloy (1.0 cc.) 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. Tetraphenylethylene (1.66 g. or 0.005 mole) in 75 cc. of ethyl ether and a sodium-rubidium alloy prepared from 0.1 g. sodium and 0.8 g. rubidium were stirred at room temperature for 43 hours. Within one hour the mixture assumed a dark brown color. Carbonation by carbon dioxide gas at room temperature gave tetraphenylsuccinic acid. The insolubility of the RM compound in ether, prior to carbonation, indicates that the organometallic compound contained rubidium and not sodium inasmuch as the sodium compound is soluble in ether.

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.

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

In the triphenylmethane experiment, chlorobenzene was found very useful, functioning perhaps in accordance with the very suggestive metal-halyl concept of Morton.[29] To a solution of 2.44 g. (0.01 mole) of triphenylmethane dissolved in 125 cc. of absolute ether was added 1 cc. of sodium-potassium alloy. No reaction could be observed in 30 hours. When one cc. 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.

To 200 cc. of a red ether solution containing about 0.02 mole of triphenylmethyllithium, was added 2 cc. of liquid sodium-potassium alloy, and the mixture was allowed to stir for 40 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 an aliquot portion of the clear ether solution with solid carbon dioxide yielded a small amount of triphenylacetic acid.

On the basis of observations in this study, the RK compounds are generally distinctly less soluble than the corresponding RNa compounds in diethyl ether. This

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[29] Morton and Stevens, *J. Am. Chem. Soc.*, **54**, 1919 (1932).

is, of course, as one would expect because of the more polar characteristics of RK compounds.

*Alkali ketyls and* n-*butyl chloride.*—The ketyls were prepared by adding 0.005 g. atom of the metal to 0.92 g. (0.005 mole) of benzophenone in ethyl ether. The mixture was stirred at room temperature for 18 hours, and at the end of this time no metal was observed to be suspended in the mixture. Then 2.8 g. (0.03 mole) of *n*-butyl chloride was added and stirring was continued at room temperature to the disappearance of the blue color of the several ketyls. The average times in hours were:

| | |
|---|---|
| Benzophenonepotassium | 16.5 |
| Benzophenonerubidium | 7.5 |
| Benzophenonecesium | 4.6 |

*Carbonation of organoalkali compounds.*—The results of some carbonations have already been given. Carbonation of phenylacetenyl-sodium and -potassium by means of solid carbon dioxide gave phenylpropiolic acid in 60% and 57% yields, respectively. These single experiments may be anomalous, for not only is there no present reason for expecting a *lower* yield in these cases when solid carbon dioxide is used, but 4-dibenzofurylsodium gave almost the same yield (65%) of 4-dibenzofurancarboxylic acid when carbonated either with gaseous carbon dioxide at room temperature or with solid carbon dioxide.

*Some reactions of 4-dibenzofurylalkalis.*—In orienting experiments made at the beginning of this study, the 4-sodium and 4-potassiumdibenzofuran compounds were prepared in ether from dibenzofuran and a selected excess of di-*n*-butylmercury and alkali metal. These preparations were not suitable for reasonably accurate rate studies for two reasons: (1) the RM compounds were only slightly soluble in ether and difficult to separate from the excess of metal; and (2) the RM compounds apparently cleaved ethyl ether to an appreciable extent. This latter difficulty was indicated when the ether solutions were titrated by the acid method[30] and by Ziegler's[2a] *n*-butyl bromide titration procedure. For example, some ether solutions of the RNa compound were shown to be 0.041 normal by the acid analysis and 0.001 normal by the *n*-butyl bromide titration.

The low concentrations together with admixed compounds may account for some of the apparently anomalous results. The clear ether solutions were transferred by pipettes, the rubber tubing used for sucking up the solutions being filled as usual with dry nitrogen. The color test technique was used in experiments with 50 cc. of a 0.001 normal ether solution of RM compound together with a definite excess of phenyl halide or *o*-tolunitrile. The average time in minutes for using up the RM compounds follows:

| | *RNa* | *RK* |
|---|---|---|
| $C_6H_5F$ | 22 | 19 |
| $C_6H_5Cl$ | 29 | 35 |
| *o*-$CH_3C_6H_4CN$ | 0 | 0 |

That is, reactions with the nitrile were immediate; the RK compound was more reactive than the RNa compound with fluorobenzene; and the reverse was true with chlorobenzene. Most surprising is the apparent greater reactivity of fluorobenzene over chlorobenzene.

Recent studies by Bergstrom and co-workers [J. ORG. CHEM; 170 (1936)] indicate that catalysts may be responsible for some of the anomalous results.

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[30] GILMAN, WILKINSON, FISHEL AND MEYERS, *J. Am. Chem. Soc.*, **45**, 150 (1923).

*Some reactions of triphenylmethylalkali compounds.*—The triphenylmethylalkali compounds formed, hitherto, the only representative series of the organoalkalis comprising all five of the metals.[13] The attractiveness of a complete series was diminished somewhat by three facts. (1) The RNa and RK compounds, unlike the RLi compound, give no color test with Michler's ketone because of ketyl formation:

$$(C_6H_5)_3CNa \rightleftarrows (C_6H_5)_3C + Na$$
$$R_2C{=}O + Na \rightleftarrows R_2C{-}ONa$$

No tests were carried out with $R_3Rb$ and $R_3CCs$ compounds, but undoubtedly they would behave like the $R_3CNa$ and $R_3CK$ compounds. (2) All of these triphenylmethylalkali compounds dissociate and to degrees not yet established so that there would be no exact measure of the concentration of RM compound available. (3) The more polar RM compounds are only sparingly soluble in ether.

To make their preparation comparable with the metalation reaction used with dibenzofuran, they were made (in good yields) as follows:—

$$(C_6H_5)_3CH + M \xrightarrow{(n-C_4H_9)_2Hg} (C_6H_5)_3CM + Hg{\cdot}M$$

The $R_3CLi$ compound was also prepared by metalation with *n*-butyllithium.

The clear ether solutions were standardized by the acid titration method, for these RM compounds are essentially stable in ether. Also, carbonation by solid carbon dioxide of the RNa and RLi compounds gave triphenylacetic acid in 90% and 82% yields, respectively. Triphenylmethylpotassium yielded an ether solution of such low concentration that it could not be used in these experiments.

The end-point of the several reactions was the disappearance of the characteristic red color of the organoalkali compound. The average times in hours when 0.008 mole of halide or nitrile was added to 100 cc. of a 0.04 molar ether solution follow.

| | $(C_6H_5)_3CLi$ | $(C_6H_5)_3CNa$* |
|---|---|---|
| $C_6H_5Cl$ | 16 | 40+ |
| $C_6H_5Br$ | 10 | 40+ |
| *o*-$CH_3C_6H_4CN$ | 0.04 | 0.02 |

It will be noted that here also the halides give anomalous results, the RLi compound being more reactive than the RNa compound. However, the relative reactivities towards the nitrile are about as one might have expected, although much greater differences in time would have been predicted. The aryl halides may possibly react differently in different media, for triphenylmethylsodium with phenyl halides in liquid ammonia gives good yields of tetraphenylmethane.[31]

*Dibenzyl and potassium-rubidium alloy.*—In connection with studies now in progress on cleavage reactions by the more reactive alkali-alloys, 1.8 g. or 0.01 mole of dibenzyl in 25 cc. petroleum ether and the alloy from 0.2 g. potassium and 0.8 g. of rubidium reacted and gave after carbonation *sym.*-diphenylsuccinic acid. The reaction was allowed to proceed for six days in a Schlenk tube. In general, such tubes are most convenient for extended slow reactions.

Dibenzyl is not cleaved by sodium-potassium alloy or the amalgams of sodium and potassium.[32]

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* In the reactions of triphenylmethylsodium with the phenyl halides no observations were made after 40 hours.

[31] KRAUS AND KAWAMURA, *J. Am. Chem. Soc.*, **45**, 2756 (1923).

[32] CONANT AND GARVEY, *ibid.*, **49**, 2599 (1927).

Incidental to cleavage reactions it is interesting to note that phenyllithium is readily cleaved by hydrogen. This may provide a means for comparing the carbon-metal bonds in organoalkali compounds.[33]

Phenylisopropylsodium in quite satisfactory yields from cumene by metalation with ethylsodium.

## SUMMARY

1. The order of increasing activity of organoalkali compounds is: RLi, RNa, RK, RRb, RCs.

These results were obtained by an examination of (a) the reaction rates of $C_6H_5C{\equiv}CM$ with benzonitrile; (b) metalation of dibenzofuran by $C_2H_5M$ compounds; and (c) reaction of ketyls with *n*-butyl chloride.

2. In reactions of sodium-potassium alloy, RK and not RNa compounds result.

3. Only sodium adds to tetraphenylethylene to give $(C_6H_5)_2C(Na)C(Na)(C_6H_5)_2$. Potassium will add when sodium-potassium alloy is used, and this is probably due to the prior addition of sodium followed by replacement by potassium. It is suggested that the non-addition of rubidium and cesium may be due to steric factors associated with the large atomic volumes of these metals.

4. The organoalkali compounds other than these of lithium are satisfactorily and preferably carbonated at room temperature. The RLi like the RMgX compounds are better carbonated at low temperatures or with solid carbon dioxide.

5. Attention is directed to some limitations of conductometric methods and the electromotive series for predicting relative reactivities of RM compounds.

6. The organoalkali compounds were prepared, and reacted, in conventional apparatus and not in sealed all-glass containers.

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[33] ZARTMAN AND ADKINS, *ibid.*, **54**, 3398 (1932).