has a strong tendency to coördinate with unsaturated atoms (as in the amine oxides) the 1:1 complex of aluminum chloride and dimethylaniline should be stable in the presence of olefins and should not be a catalyst for the polymerization of the latter, and this was found to be the case. More striking yet, it was found that the introduction of trimethylamine vapor during adsorption runs on acetylene, ethylene and isobutylene stopped adsorption completely. Thus it seems clear that an activated olefin molecule may cause the rupture of a C–Cl coördinate link, or even of an Al–O coördinate link, but is unable to break the much stronger Al═N link.

Summary

1. A study has been made of the reaction of aluminum chloride with acetylene, ethylene and isobutylene.

2. A study has been made of the action upon acetylene, ethylene and isobutylene of some organic complexes of aluminum chloride.

3. A theory of polymerization based on the electronic structures of aluminum chloride and olefins has been advanced.

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The Yields of Some Organolithium Compounds by the Improved Procedure

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Introduction

The valuable and elegant studies by Ziegler and Colonius[1] have pointed the way to the convenient preparation of organolithium compounds. Latterly it was shown that many of these compounds are readily accessible by the simple procedures used for the preparation of Grignard reagents, and in yields closely approximating those noted with organomagnesium compounds.[2] Incidental to other studies, some of which are reported in the following papers, it was necessary to prepare some new organolithium compounds and to determine the limits of applicability of several typical preparations. The results are given in the Experimental Part, and in the discussion of them which follows it will be observed that some organic halides which form Grignard reagents with great ease do not form any significant quantity of organolithium compound by the simplified procedure. On the other hand, some halides which react very sluggishly with magnesium enter into prompt reaction with lithium to give excellent yields of organolithium compounds.

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[1] Ziegler and Colonius, *Ann.*, **479**, 135 (1930).

[2] Gilman, Zoellner and Selby, THIS JOURNAL, **54**, 1957 (1932).

Experimental Part

The general analytical procedure is that previously described.[2] A few alterations in manipulation were introduced. First, the inverted test-tube holders for the metal are unnecessary. It is sufficient to remove the coating by scraping, and then to wash with dry ether. Second, the cutting of lithium into many fine pieces is readily effected by sharp "bandage scissors" of short blade length and long handles. These fine pieces are untarnished when the effluent inert gas (dry nitrogen) is rapid.

The results given in Table I are those obtained under three sets of conditions. In the "A-conditions," 0.05 mole of RX compound is used, 40 drops (or 0.3–0.4 g. of the solid) being used to start the reaction and the remainder in 15 cc. of ether is added over a period of 30–35 minutes (about 4–5 drops per five seconds). The 0.76 g. (0.11 atom) of lithium, cut into 30–32 pieces, is added to 15 cc. of ether contained in the graduated reaction flask. Accordingly, the total quantity of ether used is 30 cc. or 0.3 mole. The mixture is stirred at the outset, and heat is applied externally at the beginning and later also if the heat of reaction is insufficient to cause gentle refluxing. Stirring and refluxing are continued for one hour; the diluent (either ether or benzene) is added to bring the solution to the 100-cc. mark; and then, after a few minutes of stirring to get a homogeneous solution, the flask is detached and allowed to stand for thirty minutes, after which time samples are removed for titration.

The "B-conditions" are essentially those used to determine the drop in yield, when the halide is added at once in 15 cc. of ether to the cut lithium, heat being applied externally until the reaction starts, which is usually one-half to one minute. The "C-conditions" differ from the "A-conditions" only in the degree of fineness of the lithium, the 0.76 g. being cut into 165–170 rather than 30–32 pieces.

TABLE I

YIELDS OF SOME ORGANOLITHIUM COMPOUNDS

	Halide	% Yield under A-, B-, C-conditions		
		A	B	C
1	CH_3I	73.6[a]	65.5	81.5
2	$n\text{-}C_4H_9Cl$	76.1	67.5[b]	77.1
3	$n\text{-}C_4H_9Br$	59.0[c]	42.8	68.8[d]
4	$n\text{-}C_{11}H_{12}Br$	38.5	30.2	[e]
5	Cyclo-$C_6H_{11}Cl$	23.0	19.0[f]	24.3
6	C_6H_5Cl	35.4[g]	35.0	48.7
7	C_6H_5Br	95.2[h]	91.1	97.5[i]
8	C_6H_5I	80.1	80.7	82.8
9	$o\text{-}CH_3C_6H_4Br$	93.3	85.6	97.0[j]
10	$m\text{-}CH_3C_6H_4Br$	85.1	85.0	93.7[k]
11	$p\text{-}CH_3C_6H_4Br$	97.6	95.6	99.2
12	$1,4,2\text{-}(CH_3)\text{-}[(CH_3)_2CH]C_6H_3Br$	74.0	69.2	90.0[l]
13	$o\text{-}CH_3OC_6H_4Br$	84.2	86.0	87.9
14	$p\text{-}CH_3OC_6H_4Br$	75.4	66.0	87.9[m]
15	$o\text{-}C_2H_5OC_6H_4Br$	73.0[n]	75.2	82.6
16	$p\text{-}C_2H_5OC_6H_4Br$	76.7[n]	76.3	92.7
17	$p\text{-}(CH_3)_2NC_6H_4Br$	94.8[o]	95.0	96.1
18	$\alpha\text{-}C_{10}H_7Br$	79.0[p]	82.4	96.0
19	$\beta\text{-}C_{10}H_7Br$	74.0	76.3	83.1
20	$p\text{-}C_6H_5C_6H_4Br$	76.7[q]	73.9	81.5

[a] The yield is less with methyl iodide from unsealed containers. Freshly distilled methyl iodide, or methyl iodide from sealed containers, is recommended. Refluxing for 15 or 30 or 45 minutes gives about the same yield. A yield of 82% was obtained under A-conditions with 0.1 atom of lithium and 0.125 mole of methyl iodide. A patent by Ziegler and Colonius (German patent 512,882) mentions the preparation of methyllithium from methyl chloride or bromide, using methyl iodide as a catalyst. Undoubtedly the A-conditions with 10–12 molecular equivalents of ether will give yields as high as those described in the C-conditions with fine lithium. It is significant that methyllithium is stable for weeks in ether [Ziegler and Zeiser, *Ann.*, **485**, 174 (1931)].

[b] The "drop yields" are inclined here to be erratic, and the 67.5% is a minimum yield.

[c] The yield is markedly decreased without stirring, dropping in some cases to 10.5%.

[d] The finely cut lithium in the *n*-butyl bromide and methyl iodide experiments tends to aggregate into a single mass. However, when this does happen it is apparently without any significant effect on the yield.

[e] No experiment was made with very fine lithium. *n*-Laurylmagnesium bromide is obtainable in yields of 85.3%, and the decrease on rapid addition of lauryl bromide to magnesium is 11%. The average drop in yields of Grignard reagents on rapid addition of RBr compounds from *n*-butyl to *n*-octyl is about 15%.

[f] A reaction takes place with cyclohexyl bromide, but no appreciable quantity of organolithium compound was formed.

[g] Occasional erratic yields with chlorobenzene may be due to varying coatings with lithium chloride. Orienting experiments with a mixture of chlorobenzene and bromobenzene indicate that the yield of phenyl-lithium is higher than that realized from the sum of the yields when these halides are used separately. Because phenylmagnesium chloride can be obtained in excellent yields without the use of a solvent [THIS JOURNAL, **52,** 3330 (1930)] it is possible that corresponding conditions may be useful in the reaction between chlorobenzene and lithium.

To reduce the coating effect of lithium chloride, the lithium was added in three separate portions with refluxing for one hour after each addition. The yield was 51.2%.

The yield was 52% when a steel stirrer with knife edge was used to remove the coating partially; and with 310 pieces of lithium and refluxing for one and one-quarter hours, the yield was 53.5% and the solution was light yellow in color.

[h] The yield is 96.2% when the halide is added over one hour rather than thirty minutes. However, with ten instead of six equivalents of ether the yield is 98.5%, and this is due in part to the lesser precipitation of lithium bromide. Under these conditions, the yield being practically quantitative, there is no improvement when the halide is added more slowly. No experiments with intermediate quantities of ether were tried, and quantitative yields may possibly be obtained with a ratio of ether between six and ten equivalents. When more than six equivalents of ether are used it is recommended that three be used to dilute the halide and the rest be added initially to the lithium.

[i] With the fine pieces of lithium used under these conditions there is no drop in yield when the bromobenzene is added at one time.

[j] Addition of *o*-bromotoluene at one time, under these conditions, gives a 95% yield. The already high yield was not increased with ten equivalents of ether.

[k] Spontaneous refluxing ceased after twenty minutes, and at the same time the solution started to deposit lithium bromide. As in other related cases, external heat was then applied so that gentle refluxing was maintained throughout the preparation.

The yields under C-conditions are erratic at times. In the present case one yield of 88% was noted. The difficulty may be due to the varying agglomeration of the finely cut lithium. Check results within 2% are obtainable with the A- and B-conditions.

With ten molecular equivalents of ether, instead of six, under A-conditions, the yield is 98.8%.

[l] The very fine lithium is unnecessary for high yields, because 10–12 equivalents of ether in the A-conditions also gave a 90% yield.

[m] This experiment emphasizes in a striking manner the desirability of continuous refluxing throughout the preparation. If external heat is applied after the spontaneous heat of reaction has subsided, the yield is significantly decreased even though the time interval is brief. This may be due to a partial deposition of lithium halide which is subsequently removed with difficulty.

Here, also, fine lithium is unnecessary, for the yield under A-conditions with 12 equivalents of ether is 93%, and with 14 equivalents somewhat less.

[n] The effect of more ether was not studied, but it is probable that 10–12 equivalents

of ether will give yields in excess of 90%. This applies also to α- and β-bromonaphthalenes and *p*-bromodiphenyl.

[o] The high yield of *p*-dimethylaminophenyl-lithium irrespective of the rate of addition of halide or the fineness of the lithium suggested extra confirmation. With the assistance of Mr. E. B. Towne, the unused lithium was carefully assembled and shown to correspond with the high titration values. Also, derivatives like the furan analog of malachite green by Mr. R. H. Kirby, were prepared.

The recent description of this preparation by Austin [THIS JOURNAL, **54**, 3726 (1932)] directs attention to the difficulty of titration because of the colored solutions. By titrating directly in the presence of phenolphthalein he noted that the change from red to green could be observed quite satisfactorily. The present results were completed before the appearance of that paper. Subsequent to showing that neither dimethylaniline nor *p*-bromodimethylaniline was separately responsible for the blue color (and that neither one interfered essentially with the titration values), some observations revealed that the difficulty in titration was due to the action of air on *p*-dimethylaminophenyl-lithium. Accordingly, the titrations were subsequently carried out in a nitrogen atmosphere and the distilled water used was boiled to expel dissolved gases. When the air is excluded, the faint reddish tint at neutrality is not a source of inconvenience inasmuch as the subsequent addition of 2–3 drops of base gives the solution a pronounced red color. Methyl orange is apparently unsatisfactory as an indicator. Carbonation of an aliquot by Mr. P. R. Van Ess gave crystal violet, but the troublesome bluish color is not due exclusively to carbon dioxide.

[p] On standing for a moderate time there was no separation in the ether solution as is frequently observed with α-naphthylmagnesium bromide. The organolithium compound in an ether–benzene solution has an opaque purple color [see Vesely and Stursa, *Coll. Czechoslov. Chem. Comm.*, **4**, 139 (1932)].

[q] Reaction set in at once, and this is in sharp contrast with the start of reaction between *p*-bromodiphenyl and magnesium in ether. A slightly larger than usual quantity of ether was used. The solution of organolithium compound is dark blue in color.

Discussion of Results

Although the organolithium compounds were prepared under conditions closely resembling those for the synthesis of the related Grignard reagents, it is obvious that there are some marked differences between the two classes of organometallic compounds. Some RX compounds undergo more ready reaction with lithium than with magnesium. This is particularly true with compounds like chlorobenzene, *p*-chlorotoluene (which gave a 63% yield), α-chloronaphthalene,[3] *p*-bromodiphenyl and *p*-bromodimethylaniline.[4] On the other hand, some compounds which undergo ready reaction with magnesium in ether appear, under corresponding conditions, to be essentially unaffected by lithium. This is particularly true of some polyhalogen aryl types like *p*-chlorobromobenzene and *p*-dibromobenzene. *p*-Bromoiodobenzene does react to give an organolithium compound, but in some orienting experiments *p*-diiodobenzene appears to be without reaction. Fortunately, these cases admirably supplement each other and so make more readily available a larger variety of reactive organometallic compounds. There are at this time insufficient

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(3) Vesely and Stursa, *Coll. Czechoslov. Chem. Comm.*, **4**, 139 (1932).

(4) Austin, THIS JOURNAL, **54**, 3726 (1932).

data to warrant predictions as to the types of RX compounds with relatively inert halogen which will enter into reaction. This difficulty is increased by the erratic behavior of some halides in their reaction with lithium. An illustration is the reaction with β-bromonaphthalene. The β-naphthyl-lithium was not obtained recently[3] in any quantity, whereas under optimal conditions we have prepared it in excellent yields. The difficulties are not due solely to impure halides, although it is quite true that impure halides markedly affect both the starting of reaction and the yield of organolithium compound, and to an extent greater than that observed with Grignard reagents.

The general limits of usefulness of RX compounds have been defined by Ziegler and co-workers. However, methyl iodide is at least one exception to the rule that alkyl iodides are useless. Incidentally methyl iodide, as might have been predicted on the basis of anomalous behavior of first members of homologous series, behaves unlike other alkyl iodides in its reaction with magnesium. The chief difficulty in the way of using RX compounds with active halogens is the Wurtz reaction[1]

$$\mathrm{RLi} + \mathrm{RI} \longrightarrow \mathrm{R{\cdot}R} + \mathrm{LiI}$$

This reaction explains satisfactorily why alkyl chlorides are more suitable than alkyl bromides, and why alkyl iodides, in general, are of little value. A second difficulty in the way of preparing alkyl-lithium compounds in ether is their high reactivity in splitting ethers. The aryl-lithium compounds, in agreement with their lesser activity, cleave ethers to a decidedly lesser extent. Accordingly, although ether solutions of aryl-lithium compounds can be kept for some time, the alkyl-lithium compounds in ether must be used, in general, within a few hours. Fortunately, the alkyl-lithium compounds are not only quite stable in benzene, but are obtainable in better yields in this medium.[1,2] Although alkyl- and arylmagnesium *fluorides* can be prepared, it is obvious that the reaction between fluorides and lithium should take place more readily, even though it be a relatively slow reaction.

The Wurtz reaction mentioned above is hardly peculiar to alkyl halides, because the anomalous reaction[3] between lithium and β-bromonaphthalene gave di-β-naphthyl as the sole reaction product.

With continuous refluxing, applied externally if necessary, throughout a preparation, a moderate or slow rate of addition of halide generally improves the yield, but as a rule the increase in yield is not noteworthy. A greater ratio of ether than that used in most Grignard preparations distinctly improves the yield of many organolithium compounds. The yield is also improved with the increased fineness of the lithium. This does not necessarily mean that a like high yield would be realized over a longer time with coarser lithium, because the secondary Wurtz reaction may come into play to an increasing extent to use up both RLi and RX compounds. With very fine lithium, it appears that the rate of addition of halide is inconsequential. Although lithium can be conveniently cut into many small pieces for small quantitative experiments, it is probable that the next significant advance in making organolithium compounds more accessible will come with a convenient procedure for the preparation of lithium dust or granules, possibly after the method now used for the preparation of fine sodium. A technique of this kind has already been used for some organolithium compounds,[5] the molten metal being shaken under paraffin. To conserve lithium, the paraffin wax should be treated first with sodium, by dispersing it in the wax at temperatures above the melting point of lithium, and then separate the wax, refined in this manner, from the sodium, the molten globules of which should remain clear and untarnished.[6] The advantages of finely divided metal are not due exclusively to more rapid reaction *per se*, but also to a relative decrease of the coating effect of lithium halides.

On the basis of observations with Grignard reagents, it is probable that larger-sized runs will, in general, give improved yields and also reduce the relative quantity of ether.

In general, as with Grignard reagents, chlorides are more suitable than bromides, and iodides are least satisfactory. With aryl-lithium compounds, bromides are generally recommended. As yet no tertiary-organolithium compound (other than triphenylmethyl-lithium types) has been prepared. No alkali metal derivatives of vinyl or substituted vinyl radicals are known.[7] Our 34% yield by acid titration of organolithium compound from β-bromostyrene ($C_6H_5CH{=}CHBr$) is probably not an exception to this rule, because the product of carbonation is not cinnamic acid. The as yet unidentified acid may be due to the addition of lithium to a coupling product like 1,4-diphenylbutadiene-1,3. In this connection we are of the opinion that the chief mechanism of formation of organo-lithium, like other organometallic compounds,[8] is one involving free radicals.

The yield of alkyl-lithium compounds prepared in ether, decreases with the length of the chain. This decrease in yield, however, is greater than might have been predicted in view of the relatively high yields of *n*-laurylmagnesium bromide.

The authors are grateful to Mr. R. H. Kirby for assistance.

Summary

Yields have been determined of some organolithium compounds prepared in ether after the general procedure for the preparation of Grignard reagents. Optimal conditions and general limitations are discussed.

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(5) Ziegler, German patent 512,882.

(6) H. P. A. Groll, private communication; THIS JOURNAL, **52**, 2998 (1930).

(7) Wooster, *Chem. Reviews*, **11**, [1] 21 (1932).

(8) Gilman and Brown, *Rec. trav. chim.*, **50**, 184 (1931).