THE ANALYSIS OF ORGANIC-SUBSTITUTED GROUP IVB LITHIUM COMPOUNDS

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There has been considerable recent attention in the literature directed toward the preparation and properties of the R_3ELi (E = Si, Ge, Sn, Pb) compounds*. Excellent procedures for a variety of these reagents have now been described[1-3], making it of great value to have available a general analytical procedure for solutions of these compounds.

A number of procedures for the analysis of organolithium compounds have been described[4]. The simple hydrolysis of an aliquot and titration with acid[4a] gives results which are uniformly high. This is due to the unavoidable presence of metal oxides and alkoxides in the solution. The most widely used method of analysis for alkyllithium compounds has been that which consists of a double titration using benzyl chloride[4c]. The method is convenient to use; however, it is not applicable to the analysis of methyllithium or aryllithium compounds, and evidence has accumulated indicating that the titration shows an RLi content lower than the true value[4e,5]. These drawbacks led us to reinvestigate the double titration procedure. This reinvestigation brought the conclusion that allyl bromide[4g,3d,6] is a better RLi-consuming reagent than benzyl chloride, and thus gives a more accurate analysis when employed in the double titration of alkyllithium compounds[7].

A previous report from this Laboratory has described a quantitative estimation of organosilylmetallic compounds[8]. The method proposed was the initial reaction of the R_3SiLi compound with *n*-butyl bromide followed by determination of the amount of bromide ion released using a Volhard titration procedure. However, the earlier success with the more convenient double titration procedure using allyl bromide suggested that the method might also give an improved analysis for organosilyllithium compounds.

EXPERIMENTAL

Triphenylsilyllithium[9], methyldiphenylsilyllithium[9], dimethylphenylsilyllithium[9], triphenylgermyllithium[2], and triphenyltinlithium[3c] were prepared according to published procedures in tetrahydrofuran solution. The tetrahydrofuran was purified by refluxing over sodium wire, distillation into lithium aluminum hydride, and distillation from the hydride immediately before use. The solution to be analyzed was filtered under dry, oxygen-free nitrogen through a sintered glass funnel in order

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* The preparations and properties of organosilylmetallic compounds have been thoroughly reviewed[1].

to remove insoluble material. The pipettes and flasks were baked in an oven at 140° and flushed with a stream of nitrogen until cool. The halides used in the titrations were dried over phosphorus pentoxide and then distilled. The ether employed was dried by storage over sodium wire.

Analytical procedures

The *n*-butyl bromide-Volhard method of analysis was carried out according to the published procedure[8].

For the double titrations, a 3 ml aliquot of the solution to be analyzed was withdrawn by pipette using a suction bulb and added to 10 ml of ether. The solution was hydrolyzed with 10 ml of distilled water and titrated with standard acid, using phenolphthalein as indicator, to give the total alkali present. A second 3 ml aliquot was withdrawn and added to 10 ml of ether, containing 1 ml of the halide, under an atmosphere of nitrogen. The solution was swirled gently and allowed to stand for 2 min, after which it was hydrolyzed with distilled water and titrated immediately with standard acid, again using phenolphthalein as indicator.

In titrating the latter solution the end point is easily overstepped, since the aqueous layer decolorizes before the ether layer. Vigorous shaking near the end point is recommended. There is the possibility of interference from hydrolysis of the halide, so that the titration should be carried out within a reasonable length of time.

Reactions of allyl bromide with lithium ethoxide

Solutions of lithium ethoxide in ether were filtered under nitrogen. The double titration procedure using allyl bromide, as described above, was then carried out with these solutions.

Preparation of tri-n-butyltinlithium[10]

To 0.7 g (0.1 gram-atom) of finely cut lithium wire was added 6.51 g (0.02 mole) of tri-*n*-butyltin chloride in 1–2 ml of tetrahydrofuran. Stirring was begun, and an immediate exothermic reaction was noted. Tetrahydrofuran (40 ml) was then added at one time and stirring continued for 45 min. The yellow solution was filtered through glass wool, and titrations were carried out in the usual manner.

RESULTS AND DISCUSSION

In the reinvestigation of the double titration procedure for the analysis of organolithium compounds[7], a series of nineteen different substituted benzyl halides, allyl halides, and polyhaloalkanes was employed as potentially better RLi-consuming reagents than benzyl chloride. The first significant results were those with phenyllithium. In that case the double titration values with several halides were compared with the amount of tetraphenyltin formed on treatment with triphenyltin chloride. It was concluded that among the halides so far investigated the titration values obtained with 1,1,2-tribromoethane were in closest agreement with the actual concentrations, with allyl bromide giving values several percent lower[7]. The investigation was then extended to alkyllithium compounds.

It is difficult to assess a method of analysis when solutions of known concentration cannot be prepared. The closest one can come with reactive organometallic compounds is to prepare solutions of alkyllithium compounds in hydrocarbon solvent under conditions rigorously controlled to exclude oxygen and moisture. In this case the amount of base from alkoxide sources is controlled by the lack of solvent cleavage and also by the low solubility of lithium alkoxides in hydrocarbons, making C–Li almost the sole contributor to the total basic content. Under these conditions the titration of an aliquot reacted with a halide should show very little base, a condition fulfilled very well by allyl bromide[7].

Recently it has been shown from competitive reactions[11] that the coupling reaction of triphenylsilyllithium with monohalosilanes is more facile than those of *n*-butyllithium or phenyllithium. Although this system is different from that existing in the double titrations, it seems reasonable to suppose from the evidence above that the reaction of an organic halide with triphenylsilyllithium should go to completion if the same reaction is complete or very nearly so with *n*-butyllithium and phenyllithium. It has been shown that the reactions of triphenylsilyllithium with alkyl bromides proceed largely through halogen–metal interconversion, followed by a coupling reaction[1]; however, the destruction of Si–Li should be complete in any case.

Following the above conclusions, the present investigation was begun using the better of the titrating reagents previously tried. A given preparation of an R_3ELi compound was analyzed using several different halides in the double titration procedure as well as by the *n*-butyl bromide-Volhard method. The results of some of these comparisons are shown in Table 1.

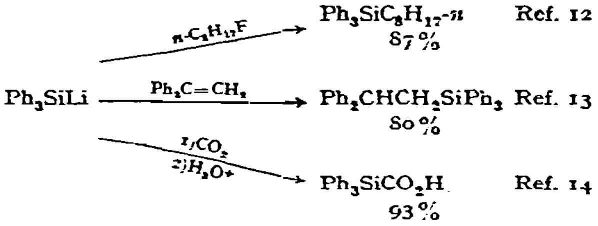
TABLE 1

COMPARISON OF DIFFERENT METHODS OF ANALYSIS OF R_3ELi COMPOUNDS

Solutions of R_3ELi compounds were analyzed by the *n*-butyl bromide-Volhard method and by double titration with various halides. The results are expressed as percentage yield of R_3ELi compound in the preparation, and are average values of two or more determinations.

R_3ELi *Compound*	*Percentage Yield of R_3ELi*						
	Double Titration Halide Used						*Volhard Analysis*
	None	C_3H_5Br	$PhCH_2Cl$	$BrCH_2CH_2Br$	$PhCCl_3$	Br_2CHCH_2Br	
Ph_3SiLi	128.0	94.2	82.2	> 100	118.0	—	95.2
Ph_3SiLi	112.4	95.6	87.5	—	—	—	88.2
Ph_3SiLi	134.8	89.6	—	107.3	—	—	86.2
Ph_3SiLi	123.9	96.7	—	—	—	—	84.8
$Ph_2MeSiLi$	119.3	85.7	—	—	—	—	83.5
$Ph_2MeSiLi$	113.0	92.0	—	100.8	—	—	74.6
$PhMe_2SiLi$	91.2	52.7	—	70.0	—	—	—
Ph_3GeLi	117.7	80.0	—	—	—	—	84.6
Ph_3SnLi	117.2	94.2	89.5	90.3	—	—	86.1
Ph_3SnLi	118.3	94.1	75.0	81.9	110.2	86.9	74.7

It should first be noted that there is considerable reason to believe that the preparations of the R_3ELi compounds are accomplished in good yield. The particular case of triphenylsilyllithium has been investigated most thoroughly. It is common for products of reactions with triphenylsilyllithium to be isolated in 80% yield or better[1], as illustrated in the following reactions. A particularly good method for forming derivatives of silyllithium compounds is the reaction with a trialkyl phosphate[15]. With this reaction yields of greater than 85 % are normally obtained, and in one case a yield of 97 % has been reported[15]. Another observation pointing to the



same conclusion is that hexaphenyldisilane is not isolated in reactions of triphenylsilyllithium prepared from the disilane unless it can be produced from the silyllithium compound by some route. This is of particular significance because hexaphenyldisilane has low solubility in tetrahydrofuran, making it difficult to overlook and

$$\mathrm{Ph_3SiLi} + (n\text{-}\mathrm{C_4H_9O})_3\mathrm{PO} \longrightarrow \underset{97\,\%}{\mathrm{Ph_3SiC_4H_9}\text{-}n}$$

very easy to isolate. There is reason to believe that preparations of other R_3ELi compounds are equally good. In one study[3b] the Ph$_3$ELi (E = Si, Ge, Sn, Pb) reagents were prepared by lithium cleavage of the Ph$_3$E–EPh$_3$ compounds and also by direct reaction of lithium with the appropriate chloride, and the resulting solutions treated with benzyl chloride. The yields of benzyl derivatives were all good, with triphenylsilyllithium giving the lowest yield, probably because of halogen-metal interconversion followed by formation of hexaphenyldisilane. The reaction conditions were not rigorously controlled in this study, nor was any attempt made to maximize the yields of the preparations, but the results are strongly indicative of a high yield in all the preparations. A further fact of some importance is that decomposition of R_3SiLi compounds through reaction with the solvent is reasonably slow[8].

The observations above lead to the conclusion that titrations of fresh R_3ELi preparations may be expected to show yields consistently above 90 %, with yields above 95 % being quite possible. The data in Table 1 show high yields in most cases, and in general the observed yield is higher with the allyl bromide double titration than with the n-butyl bromide-Volhard analysis. The single preparation of triphenylgermyllithium represents an exception. In other preparations, with which comparative analyses were not made, double titration with allyl bromide has shown yields of 96.7 %, 96.6 %, 98.0 % and 96.0 %. Also, preparations of dimethylphenylsilyllithium have given analyses corresponding to 86.5, 86.1 and 85.8 % yields.

It will be noticed from Table 1 that the titration with no halide present give values corresponding to considerably more than 100 % of the theoretical R_3ELi content. It has been suggested in the case of silyllithium compounds[8] that this may be due in large part to lithium alkoxide; however, the reagents are prepared in good yield, and cleavage of the solvent is slow[8]. It is possible that the extra basic content may be due to very finely divided lithium metal, which would interfere with the titration if it reacted with the halide used to form an alkyllithium compound which subsequently coupled with the excess halide. This may be occurring with some of the halides used in the double titration, for some of the yields shown in Table 1 are in excess of 100 %. It seems unlikely, however, that anything of this nature takes place with allyl bromide, for in the period of more than two years during which the allyl bromide method of assay has been in regular use in this Laboratory and elsewhere[3d], no anomalous results have been encountered in a large number of preparations, principally of various silyllithium compounds*.

As cleavage of the solvent proceeds, the increasing concentration of lithium alkoxide is a major potential source of interference. It has been suggested[18] that there is no reaction between allyl bromide and lithium alkoxide under the conditions of the double titration. In the present work, lithium ethoxide solutions in diethyl ether were treated in the same manner as R_3ELi solutions to be analyzed. The results given in Table 2 indicate that a reaction took place to the extent of about 2 % or less. This is slight enough to be negligible unless alkoxide concentrations become very high. The extent of this reaction in hydrocarbon solvent has been measured to be 1.8 % under the conditions of the titration[17].

TABLE 2

REACTIONS OF ALLYL BROMIDE WITH LITHIUM ETHOXIDE

Clear solutions of lithium ethoxide in diethyl ether were reacted with allyl bromide under the conditions used in the double titration.

	ml LiOEt	*ml C_3H_5Br*	*Molarity*
Run 1	2	0	0.097
Run 1	2	1	0.095
Run 1	2	1	0.095
Run 2	2	0	0.169
Run 2	2	1	0.166
Run 2	3	1	0.166

The precision which may be expected with the allyl bromide double titration is indicated in Table 3. The results are all for solutions of triphenyltinlithium, but they are typical for the other R_3ELi compounds as well. As is shown, deviations of the order of 0.5 % are to be expected when using the titration method.

TABLE 3

TITRATIONS OF TRIPHENYLTINLITHIUM PREPARATIONS

Preparations of triphenyltinlithium were analyzed by the double titration procedure using allyl bromide. In each case two determinations were made and translated into percentage yield of the preparation.

Preparation	*M*	*Yield, %*	*Deviation, %*
1	0.533, 0.535	96.0, 96.2	0.2
2	0.399, 0.400	93.5, 93.7	0.2
3	0.282, 0.281	97.0, 96.6	0.4
4	0.298, 0.296	95.5, 95.0	0.5
5	0.288, 0.286	94.4, 93.6	0.8

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* Another conceivable source of interference is the reaction of allyl bromide with R_3EH compounds. For a study of the reaction with triorganosilanes see Ref. 16.

In addition to the results so far discussed, titrations of tetrahydrofuran solutions of triphenylleadlithium[3b,c] were also attempted, but the method has not yet proven satisfactory. In titrations of hydrolyzed aliquots without halide added, the end point is not clearly defined by the phenolphthalein indicator. Also, the reaction of triphenylleadlithium with allyl bromide produces a highly colored solution which masks the indicator change.

Another reagent which has been titrated is tri-*n*-butyltinlithium[3d]. Although little is known at the present time about the reactivity of this reagent and an estimation of the yield to be expected in its preparation would be difficult, there is no apparent reason to expect the allyl bromide titration to be inapplicable. By using the preparative procedure described above, the yields of tri-*n*-butyltinlithium, as determined by titration, varied from 55 to 66%. On theoretical grounds one might expect the trialkyltinlithium reagents to be more reactive than triphenyltinlithium, so that the relatively low yields obtained in the present case are probably attributable to the method of preparation and not to the method of analysis.

The analytical procedure using allyl bromide has had great utility in this Laboratory. Of some interest is the stability of the various R_3ELi compounds in tetrahydrofuran, and this study will be reported at a later time.

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SUMMARY

A method for the quantitative analysis of triorganosilyl-, -germyl-, and -tinlithium compounds, involving a double titration using allyl bromide, has been investigated and compared with other methods of analysis. The new procedure is considered to be more accurate and convenient than previous methods.

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