[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF IOWA STATE UNIVERSITY]

A Quantitative Estimation of Organosilylmetallic Compounds

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The available methods of analysis for organometallic compounds have been evaluated in relation to their suitability for estimation of organosilylmetallic compounds. It was found that organosilylmetallic compounds reacted with *n*-butyl bromide to give an equivalent amount of metal bromide which could conveniently be estimated by a Volhard titration. A study has been made of the stability of the various available organosilyllithium compounds in tetrahydrofuran.

Various methods have been devised for the quantitative estimation of organometallic compounds. Those concerned with organomagnesium halides have been discussed in standard reference works.[1,2] Some of these methods have been used for the estimation of organoalkali metal compounds.[3] The method first studied for organomagnesium halides[4] was based on a reaction described by Bodroux.[5] This method involves the determination of the amount of iodine consumed according to equation 1:

$$RMgX + I_2 \longrightarrow RI + MgXI \qquad (1)$$

It has been found, however, that this is not the only possible reaction taking place[1,6] although it does seem to be the only one in the specific case of phenyllithium.[7] The competing reaction shown in (2) causes the consumption of only half the amount of iodine consumed by Equation 1

$$2\,RMgX + I_2 \longrightarrow R{-}R + 2\,MgXI \qquad (2)$$

Because of the interfering reaction (2) this method is not generally recommended.[1,6,8] Estimation of organometallic compounds in solvents which are not cleaved to any appreciable extent may be performed by hydrolysis and titration with acid of the total base liberated.[3,6,8,9] This method is not applicable to organometallic compounds which react with the solvent, as cleavage of an ether type solvent, for example, would yield alkoxides which would tend to increase the assay of the solution above the true value.

A double titration has been devised for this class of compounds.[10] This involves the determination of total base as described above. A second aliquot is reacted with benzyl chloride, which causes the consumption of the organometallic compounds; the alkoxides are then determined by a simple acid titration. This method has recently[11] been studied in detail. A gasometric method is useful in a limited number of cases involving low molecular weight organometallic compounds.[6]

Organoalkali metal compounds have been analyzed by a method involving their reaction with *n*-butyl bromide (3) followed by determination of the liberated alkali metal bromide according to the Volhard procedure.[12] This method is useful only for organo-metallic compounds of high reactivity (R—Li). A procedure was described for the use of this method for the estimation of less reactive organometallic compounds (R′—Li). In this procedure, dibenzylmercury was added dropwise to a mixture of the organometallic reaction and *n*-butyl bromide. Dibenzylmercury reacted with the less active organometallic compound to give a benzylmetallic intermediate (by Equation 4) which coupled readily with the *n*-butyl bromide present (Equation 5). The alkali metal halide liberated was titrated as above.

$$R{-}Li + n\text{-}C_4H_9Br \longrightarrow n\text{-}C_4H_9{-}R + LiBr \qquad (3)$$

$$R'{-}Li + (C_6H_5CH_2)_2Hg \longrightarrow C_6H_5CH_2Li + R'HgCH_2C_6H_5 \qquad (4)$$

$$C_6H_5CH_2Li + n\text{-}C_4H_9Br \longrightarrow n\text{-}C_4H_9{-}CH_2C_6H_5 + LiBr \qquad (5)$$

Halogen-metal interconversion reactions cannot be excluded, but do not interfere with these determinations as excess *n*-butyl bromide is present. It was likewise established that alkoxides did not react rapidly enough with *n*-butyl bromide to

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(1) M. S. Kharasch and O. Reinmuth, *Grignard Reactions of Nonmetallic Substances*, Prentice-Hall, N. Y., 1954, p. 92–98.

(2) F. Runge, *Organo-metallverbindungen*, Wissenschaftliche Vlgs., Stuttgart.

(3) Houben-Weyl, E. Müller ed., "Methoden der Organischen Chemie," Vol. II, *Analytische Methoden*, G. Thieme, Stuttgart, 1953, p. 326.

(4) P. Jolibois, *Compt. rend.*, **155**, 219 (1912).

(5) F. Bodroux, *Compt. rend.*, **135**, 1350 (1902).

(6) H. Gilman, P. D. Wilkinson, W. P. Fishel, and C. H. Meyers, *J. Am. Chem. Soc.*, **45**, 150 (1923); H. Gilman and C. H. Meyers, *Rec. trav. chim.*, **45**, 314 (1926).

(7) A. F. Clifford and R. R. Olsen, *Anal. Chem.*, **32**, 544 (1960).

(8) H. J. S. Winkler and H. Gilman, unpublished study.

(9) H. Gilman, J. A. Beel, C. G. Brannen, M. W. Bullock, G. E. Dunn, and L. S. Miller, *J. Am. Chem. Soc.*, **71**, 1499 (1949); H. Gilman, W. Langham, and F. W. Moore, *J. Am. Chem. Soc.*, **62**, 2327 (1940); H. Gilman, E. A. Zoellner, and J. B. Dickey, *J. Am. Chem. Soc.*, **51**, 1576 (1929).

(10) H. Gilman and A. H. Haubein, *J. Am. Chem. Soc.*, **66**, 1515 (1944); H. Gilman, A. H. Haubein, and H. Hartzfeld, *J. Org. Chem.*, **19**, 1034 (1954).

(11) C. W. Kamienski and D. L. Esmay, *J. Org. Chem.*, **25**, 115 (1960); see also, K. C. Eberly, *J. Org. Chem.*, **26**, 1309 (1961).

(12) K. Ziegler, F. Crössmann, H. Kleiner, and O. Schäfer, *Ann.*, **473**, 31 (1929).

liberate excess halide which would interfere with the determination.

An oxidimetric method of analysis of aliphatic organolithium compounds has recently been reported.[13] This method is based on the reduction of vanadium pentoxide by the organometallic reagent followed by a potentiometric titration of the reduced vanadium, using potassium permanganate or preferably a cerium (Equation IV) salt as the oxidizing agent.

It was the purpose of the present study to develop a quantitative method for organosilylmetallic compounds in the presence of alkoxides. The total base method has been used for the estimation either of complete cleavage of symmetrical disilanes in the formation of organosilylmetallic compounds (Equation 6) or in the direct preparation of these from halosilanes (7)[15]:

$$R_3Si{-}SiR_3 + 2\,Li \longrightarrow 2\,R_3SiLi \qquad (6)$$

$$R_3Si{-}X + 2\,Li \longrightarrow R_3SiLi + LiX \qquad (7)$$

The values obtained by this method exceed the theoretical by 30-50% depending on extraneous factors. The high alkoxide content of the solutions may be assumed to have caused this error.

For this reason, the double titration has been utilized in one instance,[16] but the values were low as also shown in the present study. The values shown in Table I indicate this trend to give assays 10-20% lower than those obtained by the n-butyl bromide method.

TABLE I

COMPARISON OF n-BUTYL BROMIDE AND DOUBLE TITRATION VALUES FOR TRIPHENYLSILYLLITHIUM

Number	M by n-C_4H_9 Method	M by Double Titration Method	Theory
1	0.319	0.262	0.320
2	0.377	0.325	0.390
3	0.343	0.301	^{a,b}
4	0.287	0.186	^{a,c}

[a] These analyses were performed on the same sample as was used in No. 2. [b] After the solution had been standing for 48 hr. [c] After standing for 72 hr.

An attempt to use the iodine method[8] failed to give results as high as those obtained by the n-butyl bromide method (Table II).

TABLE II

COMPARISON OF n-BUTYL BROMIDE AND IODINATION VALUES FOR TRIPHENYLSILYLLITHIUM

Number	Hours of Standing	M by n-C_4H_9 Method	% Yield by n-C_4H_9 Method	M by Iodination Method	% Yield by Iodination Method
1	24	0.314	81	0.214	55
2	48	0.323	84	0.228	59
3	72	0.256	66[a]	0.235	61
4	—	0.204	53		
5	92	0.222	57[a]	0.237	61
6	—	0.143	37	0.213	55

[a] The solution was filtered before analysis.

These values indicate that the iodination method gives results for freshly prepared samples which are 20-30% lower than those obtained by the n-butyl bromide method. It should be noted that the triphenylsilyllithium content did not decrease according to the iodination method, whereas the assay decreases considerably as determined by the n-butyl bromide method. The solution which had been filtered was more stable than that which had not (Nos. 3-6).

The failure of the iodination method may be attributed to the extensive reaction of type (2). That this reaction does take place was established by isolation of hexaphenyldisilane from the reaction of triphenylsilyllithium with bromine by normal or inverse addition (hexaphenyldisilane was isolated in 42 and 54% yields, respectively).

$$2\,(C_6H_5)_3SiLi + Br_2 \longrightarrow (C_6H_5)_3Si{-}Si(C_6H_5)_3 + 2LiBr$$

No reduction of vanadium pentoxide by triphenylsilyllithium was observed. If any had taken place it would have been possible to detect a potentiometric end-point. Using potassium permanganate as the oxidizing agent there was obtained a smooth millivolts *vs.* milliliter plot with no inflection point within a reasonable range near the end-point expected from theory.

The method involving reaction of the silyllithium compound with n-butyl bromide and subsequent determination of lithium bromide by the Volhard procedure was investigated. The Volhard procedure is very accurate for bromides,[17] and the end-point is clearly distinguishable even in the presence of organic compounds. The reaction of triphenylsilyllithium with n-butyl bromide is known to take place with halogen-metal interconversion to a large extent.[18] The following reactions proceed to consumption of all the organosilylmetallic and organometallic compounds as evidenced by a negative Color Test[19]:

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[13] D. L. Esmay and P. F. Collins, private communication. See P. F. Collins, C. W. Kameinski, D. L. Esmay, and R. B. Ellestad, *Anal. Chem.*, **33**, 468 (1961).

[14] H. Gilman and G. D. Lichtenwalter, *J. Am. Chem. Soc.*, **80**, 608 (1958).

[15] H. Gilman, D. J. Peterson, and D. Wittenberg, *Chem. & Ind.*, 1479 (1958); M. V. George, D. J. Peterson, and H. Gilman, *J. Am. Chem. Soc.*, **82**, 403 (1960).

[16] A. G. Brook and H. Gilman, *J. Am. Chem. Soc.*, **76**, 278 (1954).

[17] I. M. Kolthoff and V. A. Stenger, *Volumetric Analysis*, Vol. II, Interscience Publ., N. Y., 1947, p. 272.

[18] H. Gilman and D. Aoki, *J. Org. Chem.*, **24**, 426 (1959).

[19] H. Gilman and F. Schulze, *J. Am. Chem. Soc.*, **47**, 2002 (1925).

$$(C_6H_5)_3SiLi + n\text{-}C_4H_9Br \longrightarrow (C_6H_5)_3SiBr + n\text{-}C_4H_9Li \quad (9a)$$

$$(C_6H_5)_3SiLi + (C_6H_5)_3SiBr \longrightarrow (C_6H_5)_3Si\text{—}Si(C_6H_5)_3 + LiBr \quad (9b)$$

$$(C_6H_5)_3SiBr + n\text{-}C_4H_9Li \longrightarrow n\text{-}C_4H_9\text{—}Si(C_6H_5)_3 + LiBr \quad (9c)$$

$$(C_6H_5)_3SiLi + n\text{-}C_4H_9Br \longrightarrow n\text{-}C_4H_9\text{—}Si(C_6H_5)_3 + LiBr \quad (9d)$$

$$n\text{-}C_4H_9Li + n\text{-}C_4H_9Br \longrightarrow n\text{-}C_8H_{18} + LiBr \quad (9e)$$

The extent of the individual reactions may be indicated by the yields of hexaphenyldisilane (60%) and n-butyltriphenylsilane (10%), isolated in these laboratories during previous investigations.[18] The fact that there is such a large amount of halogen-metal interconversion does not interfere with the method of analysis, as the organometallic compound is consumed by one or more of the possible reactions. It may be expected, however, that 9d proceeds to a larger extent under the conditions of analysis than under the preparative conditions, as under the former the concentration of n-butyl bromide exceeds that of the latter. That part of the triphenylsilyllithium reacts by halogen-metal interconversion and that the bromotriphenylsilane thus formed reacts further by the very rapid coupling reaction (reaction 9b) is evident from the isolation of hexaphenyldisilane as the major product of the reaction. In the event that trace amounts of bromotriphenylsilane should have evaded either of the very fast coupling reactions (9b or 9c), liberation of the bromide ion, necessary for estimation, would have been effected by hydrolysis.

Two different procedures have been used in this study. The less expedient procedure involves the addition of an aliquot of the organosilylmetallic solution to excess n-butyl bromide. The amount of base is determined by standardized sulfuric acid using phenolphthalein indicator, and the organic layer is extracted with portions of water which are combined and diluted to volume in a volumetric flask. Aliquots of this solution are then withdrawn and their content of bromide determined by the Volhard procedure (this method will be referred to as the "extraction method").

The more expedient procedure (referred to as the "direct method") involves the same steps as above including the titration with standardized sulfuric acid. The extraction is not carried out, and the total amount of bromide is determined in the presence of the organic layer.

It was established in individual experiments, performed under the conditions of the analyses, that neither lithium silanolates (R_3SiOLi) which are formed on contact of silyllithium compounds with air,[20] nor lithium alkoxides, formed by cleavage of tetrahydrofuran by silyllithium compounds,[21] interferes with the determination.

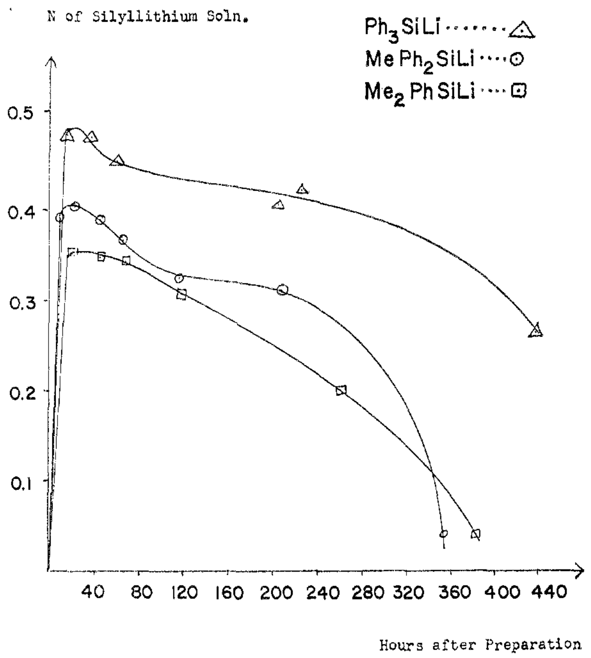

Fig. 1. Stabilities of organosilyllithium compounds in tetrahydrofuran

Figure 1 shows the results of analyses for solutions of triphenylsilyllithium, methyldiphenylsilyllithium, and dimethylphenylsilyllithium kept in volumetric flasks under a nitrogen atmosphere. The decrease in silyllithium content was paralleled by an increase in alkoxide content. The alkoxide content of the solutions of methyldiphenylsilyllithium and dimethylphenylsilyllithium had risen to 0.490 and 0.500N, respectively, whereas the solution of triphenylsilyllithium was 0.264N in alkoxide after 440 hours. It may be seen that the decrease in silyllithium content is more rapid for the more alkylated silyllithium compound, whereas the solution triphenylsilyllithium was considerably more stable. This increase in reactivity has been established in reactions of silyllithium compounds with silicon-silicon bonds.[22]

The analytical results of various solutions at the times indicated are shown in Table III with the deviation of the determinations by the particular method used. Normalities in Table III for which deviation values are given represent the average of several titrations made by one or several workers as indicated.

From the data given in Table III it is evident that the analyses obtained by the "extraction method" are consistently lower than those obtained by the "direct method" (Nos. 6, 7, and 10). This does not necessarly mean that the extraction

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[20] M. V. George and H. Gilman, *J. Am. Chem. Soc.*, 81, 3288 (1959).

[21] D. Wittenberg and H. Gilman, *J. Am. Chem. Soc.*, 80, 2677 (1958).

[22] H. Gilman and G. D. Lichtenwalter, *J. Am. Chem. Soc.*, 81, 5320 (1959).

TABLE III

QUANTITATIVE ESTIMATION OF SILYLLITHIUM COMPOUNDS

No.	Silyllithium Compound	Normality	Time of Analysis, Hours after Prep.	Deviation, %	Per Cent Yield
1	$(C_6H_5)_3SiLi$	0.313[a]	24	4	97
2	$(C_6H_5)_3SiLi$	0.302[a,c]	24	1	94
3	$(C_6H_5)_3SiLi$	0.443[b]	24	3	90
4	$(C_6H_5)_3SiLi$	0.456[b,c]	24	2	91
5	$(C_6H_5)_3SiLi$	0.269[b,c]	24	2	95
6	$(C_6H_5)_3SiLi$	0.294[a]	24	—	74
		0.317[b]	24	—	79
		0.294[a]	48	—	74
		0.302[b]	48	—	75
		0.267[a]	72	—	67
		0.278[b]	72	—	70
7	$CH_3(C_6H_5)_2SiLi$	0.340[a]	24	—	88
		0.341[b]	24	—	88
		0.310[a]	48	—	81
		0.321[b]	48	—	84
8	$CH_3(C_6H_5)_2SiLi$	0.239[b]	18	1	75
		0.237[b,c]	24	4	74
		0.231[b,c]	48	4	72
9	$(CH_3)_2C_6H_5SiLi$	0.251[b]	24	3	94
10	$(CH_3)_2C_6H_5SiLi$	0.294[a]	24	—	74
		0.317[b]	24	—	79
		0.294[a]	48	—	74
		0.302[b]	48	—	76

[a] Extraction method. [b] Direct method. [c] Determined by different workers.

method gives analyses lower than theory. On the contrary, this method is considered of higher accuracy than the "direct method" which is accompanied by additional sources of error caused by adsorption phenomena.

The yields given in the last column are in good agreement with the yields of various derivatives obtained from these silyllithium compounds by reactions with chlorosilanes or tri-*n*-butyl phosphate.[23]

EXPERIMENTAL[24]

Materials. Hexaphenyldisilane, *sym*-dimethyltetraphenyldisilane, and *sym*-tetramethyldiphenyldisilane were prepared in accordance with previously reported directions.[25] The tetrahydrofuran used in the preparation of the silyllithium compounds was distilled from sodium wire into a flask containing lithium aluminum hydride. The tetrahydrofuran was redistilled from the lithium aluminum hydride as needed to insure dryness and absence of alcohols. The *n*-butyl bromide (Matheson, Coleman & Bell, reagent grade) was distilled under nitrogen through a heated, 75 cm. long helices column before use.

Direct method of analysis. Solutions of organosilylithium compounds were prepared by cleavage of the symmetrically substituted disilanes.[14] The pipettes and flasks used for the analyses were dried in an oven at 140° and flushed in a rapid stream of dry nitrogen until cool. A 5-ml. sample of the solution to be analyzed was transferred to a flask containing 5 ml. of *n*-butyl bromide under an atmosphere of dry nitrogen. The tip of the pipette was placed immediately above the surface of the *n*-butyl bromide and the organosilyllithium solution was allowed to flow freely into the *n*-butyl bromide with gentle swirling. After standing for 2 min., the solution was hydrolyzed by the addition of 5 ml. of *ca.* 0.1*N* standardized sulfuric acid, and phenolphthalein indicator was added. The excess base was neutralized by titration with the standardized sulfuric acid. It is important to note the point at which the aqueous layer becomes colorless. At this point the mixture should be shaken vigorously and the titration should be completed under slow addition of acid and good shaking. The lithium bromide content was determined by a standard Volhard procedure adding an excess of standardized silver nitrate solution and back-titrating with thiocyanate to a ferric alum end-point. The addition of a few drops of nitrobenzene may aid in the coagulation of the silver bromide but is not necessary.

Extraction method of analysis. This procedure is carried out in the same manner as the "direct method" up to and including the neutralization by standardized sulfuric acid. At this point the organic layer is extracted three times with distilled water, and the aqueous extracts are combined and diluted to volume in a 200-ml. volumetric flask. Aliquots are removed with 50-ml. pipettes and titrated for their bromide content as described under the Direct Method of Analysis.

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[23] D. Wittenberg and H. Gilman, *Quart. Revs.* (*London*), **13**, 119 (1959); M. V. George, B. J. Gaj, and H. Gilman, *J. Org. Chem.*, **24**, 624 (1959).

[24] All preparations and analyses were carried out in an atmosphere of dry, oxygen-free nitrogen.

[25] H. Gilman and G. E. Dunn, *J. Am. Chem. Soc.*, **73**, 5077 (1951); A. G. Smith, M.S. thesis, Iowa State University, 1953.