Quantitative Analysis of Organocalcium Halides by Double Titration

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The principle of Gilman's double titration method for organolithium compounds was applied to the quantitative analysis of organocalcium halides. Chloroform was found to be useful as a reactive halide which completely decomposed organocalcium halides, but did not react with other alkali. The method gave satisfactory analysis for methyl-, propyl- and phenylcalcium iodides.

Simple acid titration for the quantitative analysis of organocalcium halides (RCaX) usually gives too high values.[1] The quantitative analysis of organocalcium halides based on the amount of hydrocarbon (RH) evolved by the addition of water, alcohol or carboxylic acid usually gives reliable results. However, when R is a higher alkyl or aryl group, the analytical procedure gives satisfactory results only immediately after preparation of the organocalcium halides, since they react slowly with ethereal solvents to give the same hydrocarbon (RH), which remains in the system. Quantitative analysis based on the amount of carboxylic acid produced by carboxylation of organocalcium halides is not useful when R is an alkyl group, since the carboxylation does not give the corresponding carboxylic acid quantitatively.[1,2] The present work was undertaken to establish a useful, convenient, and reliable method for the quantitative analysis of organocalcium halides by application of Gilman's double titration method to organolithium compounds.[3-5] No successful result was available in the literature on quantitative analysis of organocalcium compounds by the double titration method.

Results and Discussion

In order to obtain accurate results in the Gilman's double titration method, it is necessary to completely decompose the organolithium compounds by the addition of a reactive halide before the second titration. The halide should not react with alkali other than the organolithium compounds. Thus the first problem was to find a suitable halide which rapidly reacts with organocalcium halides but not with other alkali. Benzyl chloride is not adequate for this purpose, since it reacts very slowly with organocalcium halides.[6] Bryce-Smith and Skinner[1] reported that preliminary attempts to use benzyl chloride in a double titration procedure for organocalcium halides gave no promising results. We attempted to use a variety of organic halides which were more reactive than benzyl chloride toward organocalcium halides.

First we carried out a double titration on a supernatant layer of phenylcalcium iodide in diethyl ether using carbon tetrachloride, chloroform, dibromomethane, and 1,2-dibromoethane. These halides were allowed to react with phenylcalcium iodide for 5—10 min at room temperature before the second titration. The standard molarity was determined based on the amount of benzoic acid obtained by carboxylation. Vapor phase chromatographic analysis showed neither benzophenone nor triphenylmethanol in the products of carboxylation indicating the adequacy of the above molarity as a standard. Chloroform gave satisfactory results which are given in Table 1. Carbon tetrachloride gave a too high value, probably due to the reaction of the chloride with alkali other than phenylcalcium iodide. On the other hand, dibromomethane and 1,2-dibromoethane gave too low values, apparently due to slow reactions of these halides with phenylcalcium iodide.

TABLE 1. ANALYSIS OF PHENYLCALCIUM IODIDE SOLUTION IN DIETHYL ETHER[a]

Organic halide	Molarity: Total alkali	Molarity: By double titration	Molarity: Standard[b]	Error (%)
CCl_4	0.501	0.369	0.292	+26
$CHCl_3$	0.501	0.291	0.292	0
CH_2Br_2	0.501	0.189	0.292	−35
$BrCH_2CH_2Br$	0.501	0.189	0.292	−35

a) Phenylcalcium iodide was prepared by the reaction of 5.0 mmol of iodobenzene with 6.5 mmol of calcium metal in 10 ml of diethyl ether. The analysis was carried out for a supernatant layer of phenylcalcium iodide in diethyl ether at room temperature, and the reaction with organic halides was carried out for 5—10 min at room temperature before the second titration. b) The standard molarity was determined from the amount of benzoic acid evolved by carboxylation.

The mode of titration in a uniform suspension of phenylcalcium iodide in diethyl ether was similar to that in solution (Table 2). Although excess calcium metal was used in the preparation of phenylcalcium iodide, chloroform gave satisfactory results. Probably the reaction of the halide with excess calcium metal was

TABLE 2. ANALYSIS OF PHENYLCALCIUM IODIDE SUSPENSION IN DIETHYL ETHER[a]

Organic halide	Molarity: Total alkali	Molarity: By double titration	Molarity: Standard[b]	Error (%)
$CBrCl_3$	0.583	0.302	0.216	+40
CCl_4	0.583	0.276	0.216	+28
$CHCl_3$	0.583	0.227	0.216	+5
CH_2Br_2	0.583	0.151	0.216	−30

a) See footnote (a) in Table 1. b) See footnote (b) in Table 1.

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negligibly slow under the conditions. Thus, the double titration method can be satisfactorily applied to suspensions in diethyl ether, although experimental error would be more significant since it is not easy to take out a homogeneous sample.

Chloroform gave satisfactory results for a supernatant layer of phenylcalcium iodide in tetrahydrofuran (Table 3).

TABLE 3. ANALYSIS OF PHENYLCALCIUM IODIDE SOLUTION IN TETRAHYDROFURAN[a)]

Organic halide	Molarity			Error (%)
	Total alkali	By double titration	Standard[b)]	
$CHCl_3$	0.223	0.157	0.163	−4
$CHCl_3$	0.821	0.490	0.485	+1
CH_2I_2	0.223	0.120	0.163	−26
CH_2I_2	0.821	0.390	0.485	−20
CH_2ClI	0.223	0.105	0.163	−26
CH_2ClI	0.821	0.350	0.485	−28

a) See footnote (a) in Table 1. b) See footnote (b) in Table 1.

Two series of experiments were carried out on a uniform suspension of phenylcalcium iodide in tetrahydrofuran (Table 4). In series A, excess iodobenzene was used in the preparation of phenylcalcium iodide. Chloroform gave satisfactory results. In series B, excess calcium metal was used in the preparation of phenylcalcium iodide. Each titration gave too high values, probably due to the reaction of the halides with calcium metal which remained unchanged in the suspension of phenylcalcium iodide. Thus, the double titration method can be satisfactorily applied to suspensions in tetrahydrofuran in the absence of unchanged calcium metal.

TABLE 4. ANALYSIS OF PHENYLCALCIUM IODIDE SUSPENSION IN TETRAHYDROFURAN[a)]

Organic halide	Molarity			Error (%)
	Total alkali	By double titration	Standard[b)]	
Series A[c)]				
$CHCl_3$	0.776	0.512	0.502	+2
CH_2I_2	0.776	0.417	0.502	−17
CH_2ClI	0.776	0.379	0.502	−25
Series B[d)]				
$CHCl_3$	0.834	0.625	0.490	+28
CH_2I_2	0.834	0.614	0.490	+25
CH_2ClI	0.834	0.598	0.490	+22

a) The analysis was carried out for a uniform suspension of phenylcalcium iodide in tetrahydrofuran at room temperature, and the reaction with organic halides was carried out for 5—10 min at room temperature before the second titration. b) The standard molarity was determined from the amount of benzoic acid evolved by carboxylation. c) Phenylcalcium iodide was prepared by the reaction of 7.0 mmol of iodobenzene with 6.5 mmol of calcium metal in 10 ml of tetrahydrofuran. d) Phenylcalcium iodide was prepared by the reaction of 5.0 mmol of iodobenzene with 6.5 mmol of calcium metal in 10 ml of tetrahydrofuran.

Chloroform gave satisfactory results for suspensions of methylcalcium iodide in diethyl ether (Table 5). The standard molarity was determined from the amount of methane evolved by the addition of acetic acid. Carbon tetrachloride also showed satisfactory results in contrast to the case of phenylcalcium iodide. The reaction of carbon tetrachloride with alkali other than methylcalcium iodide seems to be insignificant. Dibromomethane and 1,2-dibromoethane gave better results when allowed to react with methylcalcium iodide at room temperature for a period of time before the second titra-

TABLE 5. ANALYSIS OF METHYLCALCIUM IODIDE SUSPENSION IN DIETHYL ETHER[a)]

Organic halide	Molarity			Error (%)
	Total alkali	By double titration[b)]	Standard[c)]	
$CBrCl_3$	0.895	>0.895(5)	0.657	>+36
CCl_4	0.895	0.611(10)	0.657	−8
CCl_4	0.659	0.482(10)	0.497	−3
$CHCl_3$	0.659	0.435(5)	0.497	−12
CH_2Br_2	0.659	0.459(45)	0.497	−8
$BrCH_2CH_2Br$	0.659	0.419(35)	0.497	−16
$BrCH_2CH_2Br$	0.453	0.097(5)	0.331	−71

a) Methylcalcium iodide was prepared by the reaction of 5.0 mmol of methyl iodide with 6.5 mmol of calcium metal in 10 ml of diethyl ether. The analysis was carried out for a uniform suspension of methylcalcium iodide in diethyl ether at room temperature. b) The number in parentheses indicates the time in min of the reaction of methylcalcium iodide with organic halides at room temperature before the second titration. c) The standard molarity was determined from the amount of methane evolved by the addition of acetic acid.

TABLE 6. ANALYSIS OF METHYLCALCIUM IODIDE SUSPENSION IN TETRAHYDROFURAN[a)]

Organic halide	Molarity			Error (%)
	Total alkali	By double titration	Standard[b)]	
$CHCl_3$	0.394	0.306	0.299	+2
$CHCl_3$[c)]	0.422	0.254	0.196	+30
CH_2I_2	0.394	0.276	0.299	−8
CH_2ClI	0.394	0.243	0.299	−19
CH_2Br_2	0.394	0.255	0.299	−15

a) Methylcalcium iodide was prepared by the reaction of 7.0 mmol of methyl iodide with 6.5 mmol of calcium metal in 10 ml of tetrahydrofuran. The analysis was carried out for a uniform suspension of methylcalcium iodide in tetrahydrofuran at room temperature, and the reaction with organic halides was carried out at room temperature for 5—10 min before the second titration. b) The standard molarity was determined from the amount of methane evolved by the addition of acetic acid. c) Methylcalcium iodide was prepared by the reaction of 5.0 mmol of methyl iodide with 6.5 mmol of calcium metal in 10 ml of tetrahydrofuran.

tion. Bromotrichloromethane gave a too high value. In this case, the reaction mixture of the halide with methylcalcium iodide was already acidic before the second titration.

Chloroform gave satisfactory results for a uniform suspension of methylcalcium iodide in tetrahydrofuran in the absence of unchanged calcium metal (Table 6).

In a double titration on a uniform suspension of propylcalcium iodide in diethyl ether, propylcalcium iodide was prepared in diethyl ether. Most of the solvent was removed by evaporation under reduced pressure at room temperature and replaced by cyclohexane. The analysis was carried out for the suspension of propylcalcium iodide. The standard molarity was determined based on the amount of propane evolved by the addition of acetic acid. The replacement of diethyl ether by cyclohexane was carried out in order to make the standard molarity more accurate by decreasing the amount of propane dissolved in the solvent and that of vaporized solvent. Cyclohexane can easily be frozen. Another aliquot of the suspension was taken out and added to diethyl ether containing reactive organic halides at room temperature. The reaction of propylcalcium iodide with the halides was carried out at room temperature for 10 min before the second titration. The results are given in Table 7. Chloroform and dibromomethane gave satisfactory results.

Chloroform gave satisfactory results for a uniform suspension of propylcalcium iodide in tetrahydrofuran (Table 8).

From the results, the reactivity of organic halides toward organocalcium halides appears to be in the order bromotrichloromethane>carbon tetrachloride>chloroform>dibromomethane>1,2-dibromoethane>benzyl chloride. Of these halides we recommend chloroform for the double titration, since it gave satisfactory results for methyl-, propyl-, and phenylcalcium iodides. Only 5—10 min was sufficient to destroy the organocalcium halides at room temperature, the coloration during the course of titration not being significant.

Table 7. Analysis of propylcalcium iodide suspension in diethyl ether[a)]

Organic halide	Molarity: Total alkali	Molarity: By double titration	Molarity: Standard	Error (%)
CCl_4	0.693	0.112	0.129	−13
$CHCl_3$	0.693	0.121	0.129	−6
CH_2Br_2	0.693	0.126	0.129	−2
$BrCH_2CH_2Br$	0.693	0.050	0.129	−61

a) Propylcalcium iodide was prepared by the reaction of 5.0 mmol of propyl iodide with 6.5 mmol of calcium metal in 10 ml of diethyl ether, most of the solvent being removed by evaporation under reduced pressure at room temperature and replaced by cyclohexane. The standard molarity was determined from the amount of propane evolved by the addition of acetic acid to the suspension. The double titration was carried out for the suspension in diethyl ether at room temperature. The reaction of propylcalcium iodide with organic halides was carried out at room temperature for 10 min before the second titration.

Table 8. Analysis of propylcalcium iodide suspension in tetrahydrofuran[a)]

Organic halide	Molarity: Total alkali	Molarity: By double titration	Molarity: Standard[b)]	Error (%)
$CHCl_3$	0.487	0.242	0.240	+1
$CHCl_3$	0.259	0.080	0.086	−7
CH_2I_2	0.487	0.229	0.240	−5
CH_2I_2	0.259	0.064	0.086	−26
CH_2ClI	0.487	0.178	0.240	−26
CH_2ClI	0.259	0.043	0.086	−50

a) Propylcalcium iodide was prepared by the reaction of 8.0 mmol of propyl iodide with 6.5 mmol of calcium metal in 10 ml of tetrahydrofuran. The analysis was carried out for a uniform suspension of propylcalcium iodide in tetrahydrofuran at room temperature, and the reaction with organic halides was carried out at room temperature for 5—10 min before the second titration. b) The standard molarity was determined from the amount of propane evolved by the addition of acetic acid.

The double titration method using chloroform as a reactive halide gave good results for a solution of phenylcalcium iodide. The method can be applied to uniform suspensions of methyl-, propyl-, and phenylcalcium iodides in tetrahydrofuran in the absence of unchanged calcium metal, and to those in diethyl ether even in the presence of some amount of unchanged calcium metal, although experimental error would be significant because of the difficulty to take out a uniform sample.

Thus, double titration using chloroform would be useful as a method for quantitative analysis for organocalcium halides, although its accuracy would compare unfavorably with the Gilman procedure for organolithium compounds, since many organocalcium halides are poorly soluble in organic solvents and we must use suspensions instead of solutions.

Experimental

Vapor phase chromatographic analysis was performed on a Shimadzu GC-4A gas chromatograph using columns of Chromosorb 101 (80—100 mesh), active charcoal (60—80 mesh) and polyethylene glycol 20 M on Celite 545 (60—80 mesh) for benzoic acid, methane and propane, and other products, respectively.

Materials. Calcium metal of higher purity (Mitsuwa Chemicals, Ltd., Osaka) was rasped in dry liquid paraffin. Particle size of the rasped calcium was 0.1—0.3 mm. Organocalcium halides were prepared in diethyl ether or in tetrahydrofuran. The organocalcium halides were immediately subjected to double titration, or left to stand at room temperature for several days before analysis. Organic halides were purified by distillation after being dried with calcium chloride or phosphorus pentoxide. Purification of diethyl ether, tetrahydrofuran, cyclohexane, and nitrogen was carried out as described.[7,8)] Carbon dioxide was dried with concentrated sulfuric acid and molecular sieves.

Analytical Procedure. A 2 or 3 ml aliquot of the solution or suspension of organocalcium halides to be analyzed was taken out with a hypodermic syringe and hydrolyzed with 30

ml of distilled water in a 100 ml beaker and acidified with excess standard 0.5 M hydrochloric acid, and titrated with standard 0.1 M sodium hydroxide solution using phenolphthalein as an indicator to give the total alkali present. A second aliquot was taken out and added to 10 ml of diethyl ether or tetrahydrofuran containing 1 ml of the organic halide in a 100 ml Erlenmeyer flask under a nitrogen atmosphere. The mixture was stirred at room temperature for the prescribed time, after which it was hydrolyzed with distilled water, acidified with excess standard 0.5 M hydrochloric acid and titrated with a standard 0.1 M sodium hydroxide solution, phenolphthalein being used as the indicator. In the second titration, the end point sometimes became obscure due to the coloration of the system, but the coloration was not significant when chloroform was used.

The standard molarity of phenylcalcium iodide was determined from the amount of benzoic acid evolved after carboxylation. Carboxylation was carried out at −30 °C for 2 h, and acidified by the addition of 6 M hydrochloric acid. The amount of evolved benzoic acid was determined by vapor phase chromatography.

The standard molarity of methylcalcium iodide and propylcalcium iodide was determined from the amount of methane and propane evolved by the addition of acetic acid at −70 and −10 °C, respectively. The total amount of evolved gas was determined by a gas burette, the gas being analyzed by vapor phase chromatography. The gas usually contained a small amount of hydrogen.

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