Journal of Organometallic Chemistry
Elsevier Publishing Company Amsterdam
Printed in The Netherlands

THE DETERMINATION OF GRIGNARD REAGENT CONCENTRATION BY AN ACIDIMETRIC DOUBLE TITRATION METHOD

T. VLISMAS AND R. D. PARKER
Analytical Research Section, Midland Silicones Limited, Barry, Glamorgan (Great Britain)

(Received April 20th, 1967)

Grignard reagent solutions (RMgX) usually contain compound of the general type ROMgX and HOMgX unless extreme care has been taken to exclude moisture and oxygen. These titrate in an equivalent manner to RMgX in the acid–base titration method of Gilman *et al.*[1] for the quantitative determination of Grignard reagent. Consequently the results given by this method are higher than those obtained by methods which involve a specific and directly measurable reaction with the active Grignard species. Two methods of this latter class have been developed by D'Hollander and Anteunis[2]. One is based on the reaction of the Grignard compound with excess acetone, followed by the determination of the unreacted acetone with hydroxyammonium formate. The other method they reported involves the reaction of the Grignard compound with an excess of benzophenone and the determination of this excess quantity spectrophotometrically. The two methods have disadvantages, however. The acetone method is lengthy, and the spectrophotometric method is limited to aliphatic non-tertiary derivatives. Gilman *et al.*[1] reported a gasometric method based on the measurement of the volume of hydrocarbon produced when the Grignard reagent is decomposed by a compound containing "active hydrogen", particularly water. This method is restricted to those RMgX compounds giving a hydrocarbon that is gaseous at ordinary temperatures. The gas chromatography method of Guild *et al.*[3] is applicable to arylmagnesium compounds. This method has the advantage of determining the amount of free aromatic hydrocarbon which may be present as a hydrolysis product in the original solution. The analytical procedure, however, is rather involved, and expensive equipment is required.

The acidimetric titration procedure, already referred to, has the advantages of being quick and simple, but clearly a correction must be made for non-Grignard basicity in order to obtain a reliable estimate of the concentration of active Grignard compound.

A similar situation exists in the case of organolithium compounds, and a double acidimetric titration method was developed in which benzyl chloride was used to destroy the RLi compound[4]. This method was subsequently modified by substituting other organic halides for benzyl chloride in order to improve the accuracy of the method[5].

This present paper reports work which was carried out in order to develop a double titration method for the determination of Grignard compounds. The Grignard compound was reacted with an organic halide to give a neutral product. An acidimetric titration of this reaction product was performed thus giving the amount of non-

Grignard basicity to be applied as a correction to an acidimetric titration of the original Grignard solution.

The new procedure developed has been compared with other quantitative methods.

EXPERIMENTAL

Reaction between alkyl halides and Grignard compounds

The initial stage of the investigation was devoted to a search for a suitable alkyl halide for the decomposition of Grignard compound. The reaction between Grignard reagent and a number of alkyl halides was studied by determining the residual basicity after various reaction times.

A 4–5 g quantity of Grignard solution was mixed with 1 ml of alkyl halide in 10 ml of dry diethyl ether. The residual basicity was determined by adding a known amount of 0.25 *N* sulphuric acid, and titrating the excess acid with 0.25 *N* sodium hydroxide solution.

These residual basicity values were compared with the calculated values, the results being given in Tables 1 and 2.

TABLE 1

REACTIONS OF METHYLMAGNESIUM IODIDE WITH ALKYL HALIDES

Analysis of methylmagnesium iodide solution: Moles/1000 g of Grignard compound (determined by acetone method[2]), 0.55. Total basicity of original solution (equivs./1000 g), 0.82. Calculated residual basicity (equivs./1000 g), 0.27.

Halide	*Reaction time (min)*	*Residual basicity (equivs. basic Mg/1000 g)*
Methyl iodide	60	0.80
Ethyl iodide	60	0.80
1,2-Dibromoethane	30	0.73
1,2-Dibromoethane	120	0.50
Chloroform	30	0.61
Carbon tetrachloride	5	0.45
Carbon tetrachloride	15	0.30
Carbon tetrachloride	30	0.29

TABLE 2

REACTIONS OF PHENYLMAGNESIUM CHLORIDE WITH ALKYL HALIDES

Analysis of phenylmagnesium chloride solution: Moles/1000 g of Grignard compound (determined by acetone method), 1.20. Total basicity of original solution (equivs./1000 g), 2.07. Calculated residual basicity (equivs./1000 g), 0.87.

Halide	*Reaction time (min.)*	*Residual basicity (equivs. basic Mg/1000 g)*
Ethyl iodide	60	1.87
1,2-Dibromoethane	15	1.79
1,2-Dibromoethane	30	1.57
1,2-Dibromoethane	120	1.33
Chloroform	60	1.6
Carbon tetrachloride	5	0.89
Carbon tetrachloride	30	0.89

With the exception of carbon tetrachloride, the experimental results indicated incomplete neutralization of the Grignard compound. The reaction with carbon tetrachloride was apparently complete in 15 min and the residual basicity values agreed well with those calculated when assuming complete neutralization of the Grignard compound.

Carbon tetrachloride was therefore chosen as the most suitable alkyl halide for the decomposition stage. However, since the products of the reaction are deep yellow in colour, it was necessary to employ a potentiometric finish to the titration.

Double titration method

Total basicity titre. A 4–5 ml weighed aliquot of the sample was hydrolysed with 10 ml of deionised water. To this was added 25 ml of standard 0.25 *N* sulphuric acid and the excess acid titrated potentiometrically with standard alkali using a glass electrode with a standard calomel reference electrode.

Correction titre. A further 4–5 ml weighed aliquot of the sample was transferred to a flask containing 10 ml of diethyl ether and 1 ml of carbon tetrachloride. The solution in the stoppered flask was stirred for 15 min after which it was hydrolysed with 10 ml of deionised water. Sulphuric acid (25 ml of standard 0.25 *N*) was added to the hydrolysate and the excess acid titrated potentiometrically with standard alkali using the electrode system as described above.

RESULTS AND DISCUSSION

In evaluating the double titration procedure, comparison was made with the acetone and gasometric methods.

Table 3 shows satisfactory agreement between the three methods, in particular between the double titration and acetone methods. A statistical comparison of these latter two methods showed no divergence between the results respectively obtained.

TABLE 3

COMPARISON OF THREE METHODS FOR DETERMINATION OF GRIGNARD REAGENTS

Grignard	*Moles Grignard compound/1000 g solution*		
	Double titration method	*Acetone method*	*Gasometric method*
CH_3MgBr	1.93	1.90	
CH_3MgI	0.52	0.55	0.54
C_2H_5MgBr	0.43	0.42	0.37
C_2H_5MgI	2.28	2.25	2.40
$CH_3Si(H_2)CH_2MgCl$	0.57	0.56	
$CH_3Si(H_2)CH_2MgBr$	0.99	0.99	0.98

Analytical data given in Table 4 for a solution of phenylmagnesium bromide give confirmatory evidence for the validity of the double titration procedure. The free benzene, as would be expected is in equimolar proportion to the non-Grignard basicity.

TABLE 4

ANALYSIS OF PHENYLMAGNESIUM BROMIDE SOLUTION

Theoretical Grignard concentration[a]:	1.16 moles/1000 g
Grignard concentration determined by the "double titration" method:	1.00 moles/1000 g
Uncorrected acidimetric titre:	1.18 equivs./1000 g
Correction titre:	0.18 equivs./1000 g
Free benzene in solution[b]:	0.18 moles/1000 g

[a] Calculated assuming complete conversion of bromobenzene into phenylmagnesium bromide. [b] This was determined by vapour phase chromatography.

ACKNOWLEDGEMENTS

The authors are indebted to the Directors of Midland Silicones Ltd. for their permission to publish this paper, and also to the Chief Analyst, Mr. J. F. LEES, for his support and advice.

SUMMARY

An acidimetric double titration method for the determination of Grignard compound has been developed which compensates for the free basicity present in the solution. The active Grignard compound present in solution was reacted with carbon tetrachloride to produce neutral magnesium chloride, allowing free basic magnesium to be subsequently determined by titration. A correction was thus applied to an acidimetric titration on the original Grignard solution to give a reliable determination of the concentration of active Grignard compound in solution.

REFERENCES

1 H. GILMAN, P. D. WILKINSON, W. P. FISHEL AND C. H. MEYERS, *J. Am. Chem. Soc.*, 45 (1923) 150.
2 R. D'HOLLANDER AND M. ANTEUNIS, *Bull. Soc. Chim. Belges*, 72 (1963) 77.
3 L. V. GUILD, C. A. HOLLINGSWORTH, D. H. MCDANIEL AND J. H. WOTIZ, *Anal. Chem.*, 33 (1961) 1156.
4 H. GILMAN AND A. H. HAUBEIN, *J. Am. Chem. Soc.*, 66 (1944) 1515.
5 H. GILMAN AND F. K. CARTLEDGE, *J. Organometal. Chem.*, 2 (1964) 447.