SHORT COMMUNICATION

REDUCTION OF THIOPHOSPHORYL FLUORIDE WITH LITHIUM ALUMINIUMHYDRIDE AND SODIUM BOROHYDRIDE

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ABSTRACT

Thiophosphoryl fluoride undergoes quantitative reduction both by lithium aluminiumhydride and sodium borohydride. The final products of reduction are phosphine, hydrogen sulphide and metal fluorides.

Key words: Thiophosphoryl fluoride, quantitative reduction, lithium aluminiumhydride, sodium borohydride, metal fluorides.

INTRODUCTION

Thiophosphoryl fluoride readily undergoes quantitative reduction by a suspension of lithium aluminium hydride in tetrahydrofuran and a solution of sodium borohydride in diglyme to give phosphine and a solid complex of metal-sulphur and metal-fluoride. These solids on acidification liberate hydrogen sulphide while fluoride remains in the solution. This procedure could also be employed to determine thiophosphoryl fluoride.

EXPERIMENTAL

In a reaction vessel fitted with appropriate ground glass joints and vacuum stopcocks, a small amount (150 mg) of lithium aluminium hydride in dry tetrahydrofuran (20 ml) is taken. The contents are frozen with liquid nitrogen and the uncondensable gases are pumped out. A known amount of (100 mg) thiophosphoryl fluoride is metered and introduced into the reaction vessel. The coolant is withdrawn. The reaction vessel is allowed to attain room temperature (25° C) and left to stand for about 30 minutes for the completion of the reaction.

At the end of this period, the reaction vessel is connected in series with a bubbler containing cadmium hydroxide suspension in 2N sodium hydroxide (for the absorption of hydrogen sulphide) and another bubbler containing 5% mercuric chloride solution (to absorb phosphine generated). A stream of nitrogen is flushed through the system to sweep off the gaseous products. It is observed that only traces of hydrogen sulphide is liberated, while phosphine is liberated in quantitative yield and absorbed in the bubbler containing mercuric chloride solution. Excess lithium aluminium hydride is destroyed by the addition of ethylacetate and water mixture and then it is warmed. During this process it is observed that remaining traces of phosphine also will be swept off. 20 ml of 2N hydrochloric acid is introduced into the reaction vessel and warmed. This treatment liberates hydrogen sulphide which is swept off (30 minutes) in the current of nitrogen and absorbed in the bubbler containing cadmium hydroxide. The two bubblers are disconnected. Sulphur[1] and phosphorus[2] contents in the respective bubblers are estimated iodometrically. The contents left behind in the reaction vessel are made up to a convenient volume. Aliquots are taken for the estimation of fluoride.[3]

A similar procedure could be adopted while employing sodium borohydride (150 mg) in diglyme solvent as the reducing agent. It is not necessary to use ethylacetate to destroy excess sodium borohydride. The acid added to liberate hydrogen sulphide will destroy excess sodium borohydrde.

The analytical results in a typical run are as follows:

Amount of PSF_3 taken in mg	Sulphur in mg		Phosphorus in mg		Fluoride in mg	
	Exptl.	Cald.	Exptl.	Cald.	Exptl.	Cald.
A 75·00	20·00	20·04	19·30	19·36	35·50	35·63
B 116·5	31·02	31·13	30·00	30·07	55·00	55·35

A—Lithium aluminiumhydride B—Sodium borohydride

RESULTS AND DISCUSSION

From the results, it is observed that thiophosphoryl fluoride undergoes quantitative reduction both by lithium aluminiumhydride and sodium borohydride. All the constituent elements, phosphorus, sulphur and fluoride an be estimated quantitatively. An estimate of any one constituent is ufficient for the determination of thiophosphoryl fluoride.

REFERENCES

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