

Reduction of Phosphorus Trifluoride & Phosphoryl Fluoride with Lithium Aluminium Hydride

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Received 7 May 1984; revised and accepted 5 June 1984

Phosphorus trifluoride and phosphoryl fluoride undergo reduction with lithium aluminium hydride in ether medium to produce phosphine in quantitative yield. The liberated phosphine is estimated iodometrically.

Several sulphur-fluorine compounds¹⁻⁴ and phosphorus trichloride⁵ have been found to undergo reduction with lithium aluminium hydride (LAH). In order to study the nature of phosphorus-fluorine reduction with LAH, we have presently studied the LAH reduction of phosphorus trifluoride and phosphoryl fluoride in ether medium. The results of this investigation are reported in this note.

Lithium aluminium hydride (500 mg) in ether (25 ml) was taken in a glass trap fitted with appropriate ground glass joints and vacuum stopcocks. The contents were frozen with liquid nitrogen and undissolved gases were pumped out. A known amount (~100-150 mg) of phosphorus trifluoride or phosphoryl fluoride was introduced into the reaction vessel. The coolant was withdrawn and the reaction vessel was allowed to attain room temperature and set aside for 1 hr. The reactants were frozen again with liquid nitrogen and contents allowed to warm slowly to room temperature and left overnight. The reaction vessel was connected to two bubblers B₁ and B₂, B₁ containing 20 ml of 2N potassium hydroxide (to remove unreacted PF₃ or POF₃) and B₂ containing 100 ml of 5% mercuric chloride solution (to absorb phosphine formed during the reduction)⁶. The gaseous product was swept off in a current of dry nitrogen through the bubblers. Phosphine got absorbed into the mercuric chloride solution.

The excess of LAH was destroyed by the successive addition of ethyl acetate and water. The mixture was then warmed to drive off the remaining traces of phosphine filtered and the filtrate analysed for its fluoride content⁷.

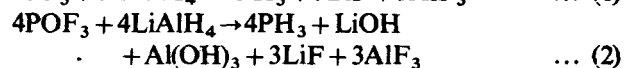
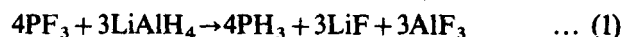
After 1 hr, when the absorption was complete, nitrogen stream was stopped and bubblers were disconnected. To the bubblers containing mercuric

Table 1—Reduction of Phosphorus Trifluoride and Phosphoryl Fluoride by Lithium Aluminium Hydride.

Amount of compd taken (mg)	Amount (mg) of PH ₃ formed		Amount (mg) of F ⁻ in soln	
	Calc	Found	Calc	Found
<i>LAH reduction of PF₃</i>				
99.20	34.85	34.26	58.42	57.64
101.20	39.10	38.75	65.55	64.76
112.30	43.39	42.96	72.74	71.23
125.60	48.53	48.05	81.35	80.96
<i>LAH reduction of POF₃</i>				
107.30	35.08	34.91	58.80	56.96
116.50	38.08	37.86	63.85	63.12
121.10	39.59	39.35	66.37	62.87
150.60	49.23	49.07	82.54	82.23
164.60	53.81	53.62	90.21	90.06

chloride solution, an excess of potassium iodide (10 g) was added, the solution acidified with 2N acetic acid and treated with a known excess of iodine solution. The excess of iodine solution was titrated against standard sodium thiosulphate solution. The phosphine content was then calculated. The analytical results are presented in Table 1.

From the analytical data (Table 1) it is observed that phosphorus trifluoride and phosphoryl fluoride undergo quantitative reduction by LAH in ether medium in accordance with the Eqs (1) and (2) respectively.



The formation of phosphine in the above reactions is further confirmed by gas phase IR spectral study (reported⁸: 2421, 2327, 1122, 992 cm⁻¹. Found: 2420, 2325, 1120, 990 cm⁻¹).

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