

A Study of the Preparation of the Lower Alkyl Iodides

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The present study of the lower alkyl iodides was undertaken when a literature survey revealed disagreement in the ratio of chemicals, procedure, purification, and storage of these compounds¹. While the majority of laboratory manuals recommend the use of red phosphorus,

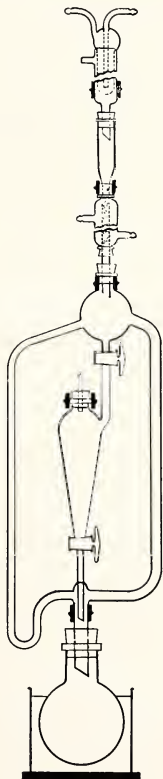


Fig. 1.

iodine, and the proper alcohol, *Organic Syntheses* recommends equal amounts of red and yellow phosphorus, iodine, and the proper alcohol². A series of experiments was conducted to determine the effect of the ratio of red to yellow phosphorus upon the yield of the iodide. Ethyl iodide was prepared in these experiments and the results are indicated in Table I³.

¹ Data collected from laboratory manuals by R. F. Duncan of Purdue University.

² *Organic Syntheses*. 13, 61.

³ The experimental data listed in this table were obtained by B. J. Freedman under an NYA assignment.

TABLE I.

Run No.	Iodine g.	Alcohol ml.	Phosphorus		Iodide %
			red	yellow	
1	75	90	7.50	0.00	86.5
2	75	90	7.50	0.00	86.0
3	75	90	7.50	0.00	87.0
4	75	90	6.25	1.25	88.1
5	75	90	6.00	1.50	88.7
6	75	90	6.00	1.50	88.3
7	75	90	3.75	3.75	89.5
8	75	90	3.75	3.75	88.2
9	75	90	3.75	3.75	88.8
10	75	90	1.50	6.00	90.2
11	75	90	1.50	6.00	88.0
12	75	90	1.50	6.00	88.5
13	75	90	0.00	7.50	91.0
14	75	90	0.00	7.50	90.5
15	75	90	0.00	7.50	90.0

The results in Table I indicate that the yields of iodide are increased when yellow phosphorus is introduced into the reaction, but these increases do not justify the hazard encountered in handling yellow phosphorus. Furthermore, red phosphorus reacts less violently, and a more controllable reaction ensues.

The apparatus used is a modified type of that recommended in *Organic Syntheses* as indicated in Figure 1. Five hundred fifty milliliters of the absolute alcohol is poured into the reaction flask. This flask is then charged with 50 g. of red phosphorus per pound of iodine to be added. The reaction flask is attached to the apparatus as indicated in Figure 1 and heated with an oil bath until the apparatus is operating under full reflux. The bath temperatures for the respective iodides may be found in Table II. Meanwhile, 100 ml. of the absolute alcohol, followed with 25 g. of iodine, is added to the dropping funnel. When full reflux is attained, the solution in the dropping funnel is introduced dropwise into the reaction flask, and the condensed liquid is allowed to flow into the dropping funnel. As soon as the solution in the dropping funnel is clear or nearly so, another 25 g. of iodine

TABLE II.

Iodide	Boiling Point °C.	Boiling Point of alcohol °C.	Bath Temperature	Addition rate of I ₂ min./lb.
Methyl	42.5	64.6	105	62
Ethyl	72.2	78.5	130	62
Isopropyl	89.5	82.5	130-5	63
n-Propyl	102.4	97.2	150-60	61
n-Butyl	131.0	117.7	180-200	70

is placed in the funnel. The average time of addition for the first pound of iodine is listed in Table II. The addition rate is constant above one pound of iodine. (The apparatus is designed to use three pounds of iodine.) The contents of the reaction flask are allowed to reflux until the condensed liquid becomes colorless.

The contents of the reaction flask are distilled from the flask directly into ice water, and the iodide and alcohol are separated by selective solution. Data for this separation may be found in Table III. The iodide is washed several times with water and stored in amber bottles over anhydrous calcium chloride.

TABLE III.

Iodide	Solubility in Water		Yield %
	Iodide	Alcohol	
Methyl	1.4	∞	90
Ethyl	0.4	∞	90-5
Isopropyl	i	∞	95
<i>n</i> -Propyl	i	∞	90-5
<i>n</i> -Butyl	i	8.3	90-5

i=insoluble

Summary

The use of red phosphorus is conducive to a smooth reaction and eliminates the hazards encountered in handling yellow phosphorus. The procedure and apparatus recommended present the advantages gained in handling smaller quantities of reagents, permitting the condensed liquids to return to the reaction flask without encountering the ascending vapors and allowing the iodine to be added more rapidly and in smaller quantities.