

THE PREPARATION OF ALKYL BROMIDES FROM THE CORRESPONDING ALCOHOLS BY THE USE OF BROMINE IN THE PRESENCE OF PHOSPHORUS¹

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The yields obtained by the use of the hydrogen bromide and phosphorus tribromide methods for the preparation of alkyl bromides from the corresponding alcohols are illustrated in Table I.

Since the phosphorus-iodine method has proven very successful for the preparation of alkyl iodides, it was deemed advisable to test the possible use of a corresponding method for the preparation of the bromides. A procedure was developed for the preparation of ethyl bromide from ethyl alcohol and bromine in the presence of a mixture of red and yellow phosphorus.

As a starting point, ethyl alcohol was treated with bromine and varying amounts of red and yellow phosphorus under different conditions. These separate experiments are tabulated in Table II.

TABLE I. Yields obtained by using hydrogen bromide and phosphorus tribromide.

Alcohol	Ratio of ROH/HBr	% Yield on Basis of ROH	% Yield on Basis of Br ₂	Worker
Methyl.....	1/3	50	16	Norris ²
Ethyl.....	1/3	71	22	Norris ²
Ethyl.....	1/3.5	81	22	Norris ²
Ethyl.....	1/4	86	20	Norris ²
Ethyl.....	1/1. 2?	90-95	77	O.S. ³
Propyl.....	1/2	59	27	Norris ²
Propyl.....	1/4	84	20	Norris ²
Propyl.....		95	82.5	O.S.(PBr ₂) ⁴
Iso-propyl.....	1/3	89	28	Norris ²
Iso-propyl.....		68	59	O.S.(PBr ₃) ⁴
Butyl.....	1/1. 2?	95	76	O.S. ³
Iso-butyl.....	1/3	30-55	9-17	Norris ²
Iso-butyl.....		60	52	O.S.(PBr ₃) ⁴
Sec.-butyl.....	1/3	95	29	Norris ²
Sec.-butyl.....		80	69.5	O.S.(PBr ₃) ⁴
Tert.-butyl.....	1/1	50	46	Norris ²
Tert.-butyl.....	1/2	91	42	Norris ²
Iso-amyl.....	1/1	37	34	Norris ²
Iso-amyl.....	1/2	78	36	Norris ²
Iso-amyl.....	1/3	85	26	Norris ²
Iso-amyl.....	1/1. 2?	88-90	70-72	O.S. ³
Tert.-amyl.....	1/3	95	29	Norris ⁵

¹Preliminary report presented before Organic Division of A. C. S., San Francisco, 1935.

²Norris, 1907. Am. Chem. J. 38:627.

³Org. Syn. 1:1. 1921.

⁴Org. Syn. 13:20. 1933.

⁵Norris, 1916. J. Am. Chem. Soc. 38:1071.

7.	19	363	25	36	377	16	3	80-90 65-110 85-115	-	s		2	160 g. CCl ₄ +377 Br ₂ , 80-90°C. Then add 363g. EtOH, 110-65°C. Attempt to introduce Br ₂ below EtOH. Br ₂ introduced below EtOH layer. Br ₂ introduced below EtOH layer. Br ₂ , EtOH mixed below 20°C., sucked back into flask. 8.c.1 repeated. Stirred during reaction. y. and r. Phos. decreased. r. Phos. decreased. y. Phos. decreased. Repetition of 8.g.1. Stirred during addition of Br ₂ . r. Phos. decreased. y. Phos. decreased.
8.a.	18	363	25	36	377	428	83	85-115	-	s	6.b	3	
b(1.	20	363	25	36	377	433	84	85-115	-	3	8.a	3	
(2.	26	363	25	36	377	458	89	90-100	-	s	8.b.1	3	
c(1.	24	163 (200)	25	36	(377)	331	64?	90-110	-	s	8 b	3	
(2	25	163 (200)	25	36	(377)	426	83	90-110	-	s	8.c.1	3	
d.	27	163 (200)	25	36	(377)	410	80	90-110	+	s	8.c.2	3	
e.	28	363	20	30	377	454	88	90-110	-	3	8.b.2	3	
f.	29	363	20	25	377	450	88	90-110	-	3	8.e	3	
g(1.	30	363	15	25	377	465	90	90-110	-	3	8.f	3	
(2.	33	363	15	25	377	464	90	90-110	-	3	8.g.1	3	
h.	34	363	15	25	377	457	89	90-110	+	3	8.g.1	3	
i.	31	363	15	20	377	460	90	90-110	-	3.5	8.g.1	3	
j.	32	363	10	20	377	449	87	90-110	-	2.5	8.i	3	
9.a.	35	363	0	40	377	419	82	90-115	-	3.5		3	
b	36	363	0	40	377	426	83	90-110	-	3		3	
c.	37	363	40	0	377	449	87	90-110	-	3.5		3	
d.	38	363	40	0	377	437	85	90-115	-	3		3	

66" a" indicates use of absolute alcohol; 95% alcohol was used elsewhere. Quantities of alcohol and bromine shown in parenthesis were mixed below 30° C., then this mixture added to the alcohol-phosphorus mixture. Apparatus I consisted of a bolt-head, reflux condenser, dropping funnel and stirrer. Apparatus II was a modified alkyl (Adams) iodide unit, and Apparatus III was similar to Apparatus I, but distillation was carried out during the reaction. All yields have been calculated on the amount of bromide used.

The procedure for ethyl bromide, as finally adopted, is as follows:

Place 363 g. of 95% ethyl alcohol, 25 g. of red phosphorus, and 15 g. of yellow phosphorus in a three-neck distilling flask.⁷ Fit the flask

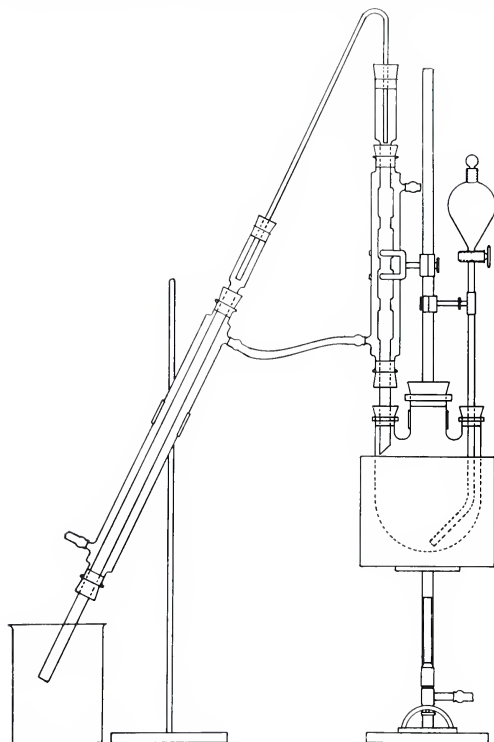


FIG. 1. Apparatus for preparation of ethyl bromide.

with an Ahlin⁸ condenser. By means of a bend of glass tubing connect the top of the Ahlin condenser to a Liebig condenser which dips beneath the surface of ice water in a beaker. The tip of the dropping funnel should be adjusted so that it extends beneath the surface of the phosphorus layer (Fig. 1).

The mixture is heated on a water or oil bath until a good reflux is obtained (bath at 100-110° C.). Then 377 g. of bromine is slowly added through the dropping funnel. Vigorous reaction, with some bumping and the formation of white vapors, accompanies the first additions. As the amount of the vapors decreases, the rate of addition of the bromine may be increased to the extent that some of the white vapors are carried over into the Liebig condenser. About three hours are required for the reaction and the bath is allowed to cool slowly to about 90° C.

When the bromine addition has been completed the mixture is allowed to cool and the flask is connected directly to the Liebig condenser.

⁷The data in the tables indicate that yellow phosphorus, used alone, gives yields nearly as good as those obtained with the red-yellow phosphorus mixture. With the mixture, however, a much smoother and more readily controllable reaction is obtained.

⁸The lower end of the Ahlin condenser should be cut at an angle to prevent flooding.

Distillation is carried out at the rate of forty to fifty drops per minute up to a temperature of about 94° C. (bath at about 155° C.). This distillate is collected with the previous portion beneath the surface of ice water. Then the entire distillate is washed with 20 c.c. of 5% potassium hydroxide, then with 50 c.c. of water and dried over calcium chloride.

TABLE III. Yields from butyl alcohols, glycol, and glycerol.

Alcohol	Grams	y. Phos.	r. Phos.	Time Min.	Bro- mide grams	%	Remarks
<i>n</i> -butyl. . .	278	7.5	12.5	120	211	66	90-135°, bath temp.
<i>n</i> -butyl. . .	138	4	6	90	150	93	165-175° bath temp.
<i>n</i> -buytl. . .	69	0	5	60	57	71	20-25° (H ₂ O bath) Alc. added to PBr _x with stirring.
<i>sec.</i> -butyl. .	138	4	6	30	132	82	125-128° bath temp.
<i>sec.</i> -butyl. .	138	4	6	40	137	85	140-150° bath temp.
<i>t</i> -butyl. . .	278	7.5	12.5	120	56	17	90-105° bath temp.
<i>t</i> -butyl. . .	138	4	6	20	10	7	0° (ice-water) bath temp.
<i>t</i> -buytl. . .	69	0	5	60	34	42	Water bath 16-20°. Alc. added to PBr _x with stirring.
Glycol. . .	58	4	6	60	63	57	Heated with burner.
Glycol. . .	58	4	6	75	52	47	190-210°, bath temp.
Glycerine. .	85.8	6	9	120	56?	34	130-150° Vacuum distilled reaction mixture at 45-55 mm. and vacuum distilled product at 18-20 mm.

(The residue in the flask should be disposed of by pouring it into the hood sink.) The dried product is fractionated and the 37-40° C. fraction collected in a dry receiver packed in an ice-salt mixture. Yield, 455-465 g. or 88-90%.

Similar preparations were made from butyl alcohol, secondary butyl alcohol, tertiary butyl alcohol, glycol, and glycerol, and the following results obtained as shown in Table III.

Apparatus III, with omission of the Liebig condenser, is used for the preparation of the butyl bromides. In the flask are placed 138 g. of butyl alcohol, 6 g. of red phosphorus, and 4 g. of yellow phosphorus.⁷ The flask is placed in an oil bath which is brought to a temperature of 175°. Bromine (94 g.) is then added slowly through the dropping funnel, the rate of addition being adjusted so that the dense white vapor which forms remains near the top of the condenser. As the reaction proceeds, the rate of addition is increased and the temperature of the bath is allowed to decrease slowly to 165°. The time required for the reaction is about one hour.

When the bromine addition is complete, the reaction mixture is slowly fractionated through a Vigreux column by heating with an oil bath to a temperature of about 210° C. When the rate of distillation becomes very slow, 25 c.c. of water may be added to carry over the last traces of the product as a constant boiling mixture.

The product is fractionated to remove alcohol, dried with CaCl₂, and distilled, giving 150 g. or 93.2% yield of butyl bromide, b.p. 97-99.5°.

The procedure in the case of secondary butyl bromide is similar to that used in the preparation of n-butyl bromide, except that the bromine is added at a bath temperature of 140-150°, and that the distillate from the reaction mixture is washed with water and dried with Na₂SO₄ before redistilling. The yield, b.p. 86-87°, is 137 g., or 85.10%.

Tertiary butyl bromide may be prepared as follows: In a 500 c.c. flask are placed 5 g. of red phosphorus, and 47 g. of bromine are added slowly over a period of 1 to 2 hours, while the flask is cooled with cold water. A mechanical stirrer is then inserted through the large neck of the flask and 69 g. of tertiary butyl alcohol are added slowly (1 hr.) through the dropping funnel.

When the addition of the alcohol is completed, the bromide is distilled through a Vigreux column by heating with an oil bath at a temperature of 70-80°. A slow rate of distillation is maintained by adjusting the pressure, which is gradually decreased to 20 to 24 mm. The product is washed with water, dried with CaCl₂, and distilled to give 34.0 g., or 42.2% yield of tertiary butyl bromide, b.p. 69-72°.

The procedure used in the preparation of 1,2-dibromoethane and 1, 2, 3-tri-bromopropane is similar to that used in the preparation of secondary butyl bromide. It should be noted, however, that in the preparation of 1, 2, 3-tri-bromopropane a decreased pressure is used in the distillation of the reaction mixture and in the final distillation of the product.

Hence it appears that this method is applicable to the preparation of primary, secondary or tertiary bromides.

Summary: A method has been developed for the preparation of (1) alkyl bromides from the corresponding alcohols by the use of bromine in the presence of a red and yellow phosphorus mixture, and (2) the method gives satisfactory results for the preparation of primary, secondary and tertiary alkyl bromides.