

# The Preparation of Acetyl Bromide from Acetic Acid and Bromine in the Presence of Red and Yellow Phosphorus

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The use of red phosphorus in the bromination of aliphatic acids is not new. Gal<sup>1</sup> and Hanriot<sup>2</sup> used this method for the preparation of acetyl bromide. Various later workers have used red phosphorus either in catalytic or molar quantities for the preparation of acid bromides, alpha-bromo acids, or alpha-bromo acid bromides.

It was stated by Hell<sup>3</sup> that the presence of small amounts of phosphorus resulted in large amounts of acetyl bromide whereas molar amounts tended to yield mainly bromoacetyl bromide. The mechanism of the reaction as postulated by Zelinsky<sup>4</sup> and Volhard<sup>5</sup> was the complete conversion to the acid bromide followed by alpha bromination. This explanation was abandoned by Hell<sup>6</sup> since it was found that alpha-bromination could occur with catalytic quantities of phosphorus. Later experiments by Ward<sup>7</sup> confirm the earlier conclusion that large quantities of phosphorus favor acid bromide formation.

The yields obtained by the use of bromine and red phosphorus for the preparation of acetyl bromide from glacial acetic are illustrated in Table I.

TABLE I. Illustrative Yields Obtained by the Use of Red Phosphorus and Bromine on Glacial Acetic Acid

No.	Gm. Br.	gm. p (red)	gm. AcOH	Temp.	Time	% Yield	Remarks
1*	80	10	60	85	2	12	Stood 24 hours.
2*	100	10	60	95	1	8	Refluxed.
3*	160	4	30	?	?	10	Method of Hanriot.
4	240	33	90	?	?	47	Reported by Gal.**
5†	100	13.7	37.4	?	2½	23	Method of Gal.
6†	100	13.7	37.4	?	2½	38	Method of Gal.
7†	100	13.7	37.4	?	2½	36	Method of Gal.

\* Experiment carried out by author.

† Experiment carried by D. Herman on NYA assignment.

\*\* Gal, 1863. *Annalen* **129**, 53.

The successful use of a mixture of red and yellow phosphorus for the preparation of ethyl bromide from ethyl alcohol and bromine<sup>8</sup>

<sup>1</sup> Gal, 1863. *Annalen* **129**, 53.

<sup>2</sup> Hanriot. *Ann. Chimie et Physique* (5) **17**, 83.

<sup>3</sup> Hell, 1881. *Berichte* **14**, 891.

<sup>4</sup> Zelinsky, 1887. *Berichte* **20**, 2026.

<sup>5</sup> Volhard, 1888. *Annalen* **242**, 141.

<sup>6</sup> Hell, 1888. *Berichte* **21**, 1726.

<sup>7</sup> Ward, 1922. *Journ. Chem. Soc.* **121**, 1161.

<sup>8</sup> Degering, Ed. F., and Goshorn, R. H., 1936. *Proc. Indiana Acad. Sci.* **45**, 139-144.

suggested the use of a similar mixture for the preparation of acetyl bromide.

Glacial acetic acid was treated with bromine in the presence of varying amounts of red and yellow phosphorus and under differing experimental conditions. The data on these experiments are recorded in Table II.

TABLE II.—Summary of Experiments Conducted Using a Mixture of Red and Yellow Phosphorus

No.	Gm.Br	Gm.P		Gm.AcOH	Temp. °C.	Time	Yield %	Remarks
		red	yellow					
1	80	5	5	60	below 45	1½	35	Stood 22 hrs. after Br addition.
2	85	5	7	60	15-30	1½	41	Stood 22 hrs. after Br addition.
3	45	2	4	30	below 25	1½	57	Stood 48 hrs. after Br addition.
4	85	5	6½	60	10-20	3½	64	1st heated to 90°, Br dropped in.
5	80	5	5	60	below 30	1	52	Dist. at once.
6	160	4	5	60	10-20	3¼	32	Br dropped in.
7	100	3	5	60	20-40	2	52	Dist. at once, excess Br.
8	100	2	7	60	30-45	3¼	49	P didn't all react.
9	100	3	6	60	20±	3½	49	1st heated to 45°.
10	100	4	5	60	60±	2	37	No external cooling.
11	80	4	5	60	40-45	2½	53	Refluxed till Br reacted.
12	100	4	5	60	35-50	1¾	63	Refluxed till Br reacted.
13	100	4	5	60	35-45	1	65	Refluxed till Br reacted, (70°).
14	100	4	5	60	150-170	½	59	Refluxed till Br reacted.
15	100	4	5	60	175-190	½?	27	Refluxed till Br reacted.

\*% Yields are based on the amount of bromine used assuming the following equation to be correct:  
 $4\text{CH}_3\text{CO}_2\text{H} + \text{P} + 2\frac{1}{2}\text{Br}_2 = 4\text{CH}_3\text{COBr} + \text{PO}(\text{OH})_3 + \text{HBr}$ .

The following procedure was adopted: Place 60 g. of glacial acetic acid, 5 g. of yellow phosphorus, and 4 g. of red phosphorus in a 250 ml. round-bottom flask. Fit the flask with a thermometer, a reflux condenser and a dropping funnel, the tip of which must extend below the surface of the liquid in the flask. Place 100 g. of bromine in the dropping funnel and introduce it into the reaction mixture at such a rate as to require approximately one hour for the addition. Maintain the temperature at 35-50°C. by occasional shaking and external cooling if necessary. After the addition of bromine is complete, reflux the reaction mixture until the red color due to bromine disappears.

Substitute a Liebig condenser (set for distillation) for the reflux condenser and distil the mixture under anhydrous conditions, collecting everything which comes over below 130°. Redistil the distillate so obtained through a Vigreux or similar column, making sure that anhydrous conditions obtain. Collect the fraction boiling 74-80°. Yield is 78-80 g., 63-65% of the theoretical.

### Summary

1. Experiments were conducted for the preparation of acetyl bromide from glacial acetic acid and bromine in the presence of a mixture of red and yellow phosphorus.

2. A procedure was developed which gives a 63-65% yield as compared with a reported 47% yield obtained by the use of red phosphorus alone.