Summary

1. Reactions have been carried out between isobutyl bromide and aqueous solutions of various metallic hydroxides, varying conditions of temperature and concentration.

2. Yields of olefin varying from 10.8 to 65.5% have been obtained.

3. The formation of olefin is favored by higher temperatures and higher concentrations of alkali.

4. The rate of reaction is greater in the more dilute solutions.

5. Rearrangement of the isobutyl bromide to the tertiary bromide does not take place during these reactions.

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF MISSOURI]

Action of Inorganic Bases on Tertiary Amyl Halides[1]

BY H. E. FRENCH AND A. E. SCHAEFER

In earlier publications[2] it was noted that, in general, the action of dilute aqueous solutions of metallic hydroxides on the butyl bromides causes increasing yields of olefin as the temperature of reaction is increased and as the concentration of the alkali is increased. The different isomers were found to follow these generalizations in varying degree, with the tertiary butyl bromide forming but little olefin under any of the conditions used. In decided contrast to this is the behavior of the corresponding tertiary butyl chloride, which was found by Woodburn and Whitmore[3] to yield only olefin in hot solution, and chiefly olefin with cold solutions of alkalies. The present paper is concerned with the action of dilute aqueous solutions of alkalies on the tertiary amyl bromide and chloride.

Reagents, Apparatus and Procedure.—The tertiary amyl alcohol used in this work was the best grade obtainable from the Eastman Kodak Company. Before use it was dried over lime and fractionally distilled through a 74-cm. column. The fraction boiling between 100.8–101.8° (731 mm.), $n^{25}\text{D}$ 1.4022, was used.

The tertiary amyl halides were prepared by several different methods, a summary of which is given in the following table. At least two runs were made with each method reported.

TABLE I

METHODS OF SYNTHESIS OF TERTIARY AMYL HALIDES

Reagent	B. p. of halide °C.	Mm.	$n^{20}\text{D}$	Yield, %
Acetyl chloride[a]	85–88.5		1.4023	
Phosphorus trichloride[b]	83–84.5	740	1.4048–1.4049	40.8
Thionyl chloride[c]	83–84.5	744	1.4048–1.4049	41.1
Oxalyl chloride[d]	83–84	744	1.4047–1.4048	18.2
Concd. HCl[e]	83–85		1.4046–1.4047	
48% HBr[f]	65–68	194–196	1.4411	
HBr gas[g]	46–49	152	1.4410	
	53–55	151	1.4420	
HBr gas + trimethylethylene[h]	56–57.5	152	1.4421	65
Phosphorus tribromide	57–58	152	1.4420	35

$n^{20}\text{D}$ for the chloride 1.4056, for the bromide 1.4421, "International Critical Tables," Vol. I, p. 277.

[a] Henry, *Rec. trav. chim.*, **26,** 89 (1906). Product dried over calcium chloride.

[b] Wischnegradsky, *Ann.*, **190,** 328 (1878). Product dried over anhydrous potassium carbonate, then over calcium chloride.

[c] Clark and Streight, *Trans. Roy. Soc. Can.*, **23,** series 3, 77 (1929). Product dried over anhydrous potassium carbonate then over phosphorus pentoxide.

[d] Adams and Weeks, THIS JOURNAL, **38,** 2518 (1916). Product dried over phosphorus pentoxide.

[e] Eastman Kodak Company preparation.

[f] Norris, Watt and Thomas, THIS JOURNAL, **38,** 1076 (1916).

[g] Faworsky, *Ann.*, **354,** 348 (1907).

[h] Olefin prepared from tertiary amyl alcohol and sulfuric acid. Norris and Reuter, THIS JOURNAL, **49,** 2630 (1927). Preparation of halide, Wischnegradsky, *loc. cit.*

Reduced pressures were found necessary in all distillations of the tertiary amyl bromide, since decomposition took place whenever distillation was attempted at atmospheric pressure, with the formation of low boiling fractions which gave the von Baeyer test for olefins. In the process of purification the chlorides were washed with ice water and dried over calcium chloride, anhydrous potassium carbonate or phosphorus pentoxide. The crude bromides were treated with anhydrous potassium carbonate, and distilled *in vacuo*. The washing with water was omitted since this treatment resulted in considerable loss through hydrolysis.

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[1] This paper is an abstract of the thesis submitted by Mr. Schaefer in partial fulfilment of the requirements for the degree of Doctor of Philosophy at the University of Missouri.

[2] (a) French, McShan and Johler, THIS JOURNAL, **56,** 1346 (1934). (b) French and Wade, *ibid.*, **57,** 1574 (1935).

[3] Woodburn and Whitmore, *ibid.*, **56,** 1394 (1934).

The apparatus and much of the procedure involved in the reactions were essentially those described in the earlier papers from this Laboratory. The reactions were carried out at either 35 or 45°, for a period of ten hours at the higher temperature and twelve hours at the lower. In each case 300 cc. of aqueous solution was used. As in the previous work, the alkaline solutions were brought to bath temperature before the halide was introduced. The temperature of the bath was controlled to less than 1°. The olefin, being a liquid under ordinary conditions of temperature and pressure, offered certain difficulties in the way of analysis, and was therefore not determined directly. In no case did the tertiary amyl chloride react to completion. The unused halide, together with the amylene, was removed by passing a slow stream of purified air through the reaction mixtures for fifty minutes at room temperature, a process found by experiment to cause no loss of the alcohol. Reactions with the tertiary amyl bromide were apparently complete, but air was passed through the reaction mixtures for twenty minutes to remove the olefin. The solutions were then neutralized with nitric acid and distilled, as described in the previous communications. Tertiary amyl alcohol forms a constant boiling mixture with water which boils at 87°,[4] and was therefore obtained in the first fraction of the distillate. The metallic halide was determined in the residue, and the alcohol was determined in the distillate by means of the refractive index, using an Abbe refractometer. From these data the yields of olefin were calculated. In analyzing the distillates for the tertiary amyl alcohol, use was made of the following new determinations of refractive index.

TABLE II

REFRACTIVE INDICES OF AQUEOUS TERTIARY AMYL ALCOHOL SOLUTIONS

% by wt.	0	1.09	1.22	2.09	2.22	3.08	3.11
n^{25}_D	1.3325	1.3338	1.3339	1.3349	1.3350	1.3360	1.3359
% by wt.	4.24	4.33	5.01	6.03	6.06	6.97	
n^{25}_D	1.3372	1.3373	1.3381	1.3391	1.3392	1.3402	

The distillates from the reactions of the chloride with sodium and potassium hydroxides were combined, as were those from reactions with calcium, barium, and silver hydroxides. From these the alcohol was fractionally distilled, dried, and redistilled, and shown to be tertiary amyl alcohol by means of the boiling point and refractive index. This procedure was also followed for the alcohols obtained from the amyl bromide.

Summary of Reactions with Tertiary Amyl Halides.—Table III gives a summary of the reactions carried out with the tertiary amyl halides. All yields are based on the amount of reaction actually taking place, as determined by the quantities of metallic halide formed. At least two reactions were run for each temperature and concentration given, those with the bromide going to completion.

TABLE III

REACTION OF TERTIARY AMYL HALIDES WITH INORGANIC BASES

$C_5H_{11}X$[a] X is	Base	Moles of base, 300 cc. of soln.	Reaction[b] temp., °C.	% Reaction	Yield of olefin, %
Cl	AgOH	0.0805	45	82–87	13.7–14.5
Cl	AgOH	.0805	35	89–91	8.4– 8.8
Cl	$Ba(OH)_2$	.061	45	76–80	16.0–16.8
Cl	$Ba(OH)_2$	.076	45	85–86	25.6–25.8
Cl	$Ba(OH)_2$	.076	35	76–82	14.0–15.0
Cl	$Ca(OH)_2$	.094	45	86–88	16.4–17.8
Cl	LiOH	.123	45	77	16.6–17.8
Cl	NaOH	.132	45	86–88	17.8–18.3
Cl	KOH	.123	45	80–81	19.3–20.8
Cl	KOH	.123	35	65	12.5–13.4
Br	AgOH	.074	45	...	8.7–10.4
Br	AgOH	.074	35	...	4.6– 5.2
Br	$Ca(OH)_2$	.069	45	...	11.3–12.0
Br	NaOH	.13	45	...	12.9–13.5
Br	KOH	.123	45	...	14.0–15.4
Br	KOH	.123	35	...	11.2–11.5
Br	$Ba(OH)_2$	.073	45	...	18.7–19.8
Br	$Ba(OH)_2$	.073	35	...	11.5–11.6

[a] When X is Cl, 0.061 mole was used; when X is Br, 0.057 mole was used.

[b] The reaction time at 35° was twelve hours, at 45° it was ten hours.

Discussion

The action of dilute aqueous solutions of inorganic bases on the tertiary amyl halides caused the formation of both alcohol and olefin in each reaction carried out. The yields of olefin were considerable (5 to 25%) although the aqueous solutions of bases were dilute, varying in concentration from 0.203 to 0.44 molar.

Earlier papers from this Laboratory[2] point out the marked increases in the yields of olefin with increasing molar concentrations of base. In the one instance in the present work where such comparison can be made, namely, in the reactions with barium hydroxide, a similar effect is found, the increase in olefin from the chloride amounting to nine per cent. for an increase in concentration of

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(4) "International Critical Tables," Vol. 3, p. 318.

base from 0.409 to 0.51 *N*, at 45°. In the work previously reported it was observed that, in reactions using similar experimental conditions and concentrations of base, potassium hydroxide caused the formation of greater quantities of olefin than did sodium hydroxide. In the present work a series of reactions was run with tertiary amyl chloride using the hydroxides of lithium, sodium, and potassium. These bases were used in the same molar concentrations, and other experimental conditions were kept constant. The variations in olefin production were slight, but their regularity, together with the fact that they correspond to the very considerable differences previously observed with sodium and potassium hydroxides, suggests a real variation in reactivity toward these bases. The yield of olefin was smallest with lithium hydroxide, greater with sodium hydroxide, and potassium hydroxide furnished the largest yield. The activity coefficients of these bases have been determined in water and in aqueous solutions of their chlorides at 25°[5] and found to increase in the order lithium hydroxide, sodium hydroxide and potassium hydroxide. The temperatures for our reactions were considerably higher than that used for these determinations, but the parallelism seems significant.

Barium hydroxide at the same normality and temperature formed slightly less olefin than did the lithium hydroxide. The highly insoluble hydroxides of silver and calcium caused the formation of olefin from both chloride and bromide in yields which were nearly as great as those formed by sodium hydroxide. Similar relatively large yields of olefin were obtained in the earlier work by the action of these heavy metal hydroxides on the butyl bromides.

Tertiary amyl alcohol was the chief product from the reactions with both the bromide and the chloride, corresponding to the behavior of the tertiary butyl bromide as previously reported. Our results are of interest in connection with those obtained by Woodburn and Whitmore,[3] who state that the "hydrolysis of tertiary chlorides with hot water or sodium carbonate solution gives olefin exclusively. With cold water or cold sodium hydroxide solution a certain amount of tertiary alcohol is formed along with the olefin." Our results are in general agreement with theirs in that we find an increased yield of olefin at the higher temperatures with lower temperatures favoring alcohol formation. The fact that they apparently obtain lower yields of alcohol with cold sodium hydroxide than we do is presumably due to their higher concentrations of base, 1.4 normal compared to the 0.44 normal which we used.

Tertiary amyl chloride consistently yields larger amounts of olefin than does the tertiary amyl bromide under comparable conditions. The difference is of the order of 5% at 45°. A parallel behavior seems to exist between the tertiary butyl chloride and bromide as pointed out above.

Increasing the temperature of reaction from 35 to 45° increased the yield of olefin. The amount of the increase varied from 4 to 10%, and corresponds to the behavior of isobutyl bromide[2b] but is in contrast to that of the secondary and tertiary butyl bromides[2a] where the temperature effect is slight.

The ease of reaction toward aqueous alkalies increases in the order primary, secondary, tertiary. Tertiary amyl chloride, however, shows a very considerable stability, since ten hours of heating to 45° with any of the reagents used in this work was insufficient to cause complete reaction. The relative stability of the tertiary chlorides has previously been reported by Woodburn and Whitmore.

There is no rearrangement of the tertiary halides during the reaction to form the alcohol. This was demonstrated by the isolation of the alcohol as described above, and the determination of its boiling point and refractive index.

Summary

1. The action of several inorganic hydroxides in dilute aqueous solution on tertiary amyl chloride and bromide was investigated.

2. The yields of olefin varied from 4.6 to 25.8%.

3. Olefin formation increased with increasing temperatures and with increased hydroxide concentrations. Slightly soluble heavy metal bases caused the formation of relatively large amounts of olefin.

4. Olefin yields increase slightly with the following change in base, lithium hydroxide, sodium hydroxide, potassium hydroxide.

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(5) (a) Harned, THIS JOURNAL, **47**, 676, 684, 689 (1925); (b) Harned and Swindells, *ibid.*, **48**, 126 (1926).