

3. Friedelin benzoate, phenylacetate,  $\beta$ -phenylpropionate, and *p*-iodobenzoate have been prepared.

4. Friedelin and cerin have been reduced by the Clemmensen method to the same hydro-

carbon,  $C_{30}H_{52}$ .

5. Friedelin is probably a polynuclear substance containing four rings and one double bond.

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

## Action of Inorganic Bases on Isobutyl Bromide<sup>1</sup>

BY H. E. FRENCH AND W. H. WADE

In a previous communication<sup>2</sup> the action of dilute aqueous solutions of various inorganic bases on secondary and tertiary butyl bromides was discussed. This work has now been extended to cover the behavior of isobutyl bromide with the same reagents. This latter substance is of interest because of the tertiary hydrogen attached to the carbon atom adjacent to the one holding the bromine. Such hydrogens are far more reactive toward certain reagents than are primary and secondary hydrogens. Toward aqueous inorganic hydroxides, any such reactivity on the part of isobutyl bromide would result in the formation of butene. The extent of such a reaction under various conditions is of interest.

Isobutyl bromide shows a marked tendency to rearrange to the tertiary bromide. This rearrangement may take place in either the gaseous or liquid phase, often at temperatures near 100°, and is catalyzed by a number of different substances.<sup>3</sup> It therefore seemed a possibility that rearrangement might take place with the isobutyl bromide, with the rearranged product entering into the reaction with the reagent. The investigation of such questions should yield information as to the most favorable conditions for the hydrolysis of alkyl halides.

### Reagents, Apparatus and Procedure

The isobutyl alcohol was the best grade obtainable from the Eastman Kodak Company, and before use was distilled through a 90-cm. fractionating column filled with glass rings. The boiling point was 107.3°. The alcohol was converted into the bromide by the method described by Reynolds and Adkins.<sup>4</sup> Silver hydroxide was prepared as previously described, and the other reagents were of the

quality used in the previous work. The apparatus and procedure were essentially those used in the earlier investigation,<sup>2</sup> though in the present work the alcohol obtained by hydrolysis was isolated and identified in each case. This was done in the following manner. The butyl alcohol solutions obtained by distillation of the barely acidified reaction mixtures were redistilled through a 90-cm. column filled with glass rings. Isobutyl alcohol forms a constant boiling mixture with water at 89.82° at 760 mm.<sup>5</sup> In each distillation 8–10 cc. was distilled over, using a graduated tube of about 1 cm. diameter for receiver. In all cases two layers formed, but anhydrous potassium carbonate was added to decrease the solubility of the isobutyl alcohol. From 0.20 to 1.95 cc. of alcohol was obtained from the various reactions. Yields calculated from these volumes generally ran 15–20% below the theoretical yields calculated from the olefin and metallic halide determinations. In each case the alcohol was converted into the 3,5-dinitrobenzoate, and the melting point was determined.

As in the previous work, the olefin was determined by means of an Orsat gas analysis apparatus, while the metallic bromide was determined volumetrically, except for the silver bromide, which was weighed directly.

From two to three runs were made at each concentration and temperature for each of the reagents. As in the previous work, the variation in the yield of olefin between duplicate reactions never exceeded 2.2%, and was usually considerably less than that amount.

The time of reaction was usually ten hours, but in no case did reaction go to completion. There was, however, no reaction between unchanged isobutyl bromide and the water on distillation of the neutralized reaction mixtures. This was demonstrated by distilling a mixture of 12 g. of isobutyl bromide and 500 cc. of water and testing the residue for halogen. The test was negative.

### Summary of Reactions

In each case 0.087 mole of the isobutyl bromide was added to the reaction mixture. The yields are based on the amounts of the alkyl bromide which reacted, as determined from the analyses for the metallic bromide.

### Discussion

As was expected, the isobutyl bromide reacted much more slowly than did the secondary and

(1) This paper is an abstract of the thesis submitted by Mr. Wade in partial fulfillment of the requirements for the degree of Master of Arts at the University of Missouri.

(2) French, McShan and Johler, *THIS JOURNAL*, **56**, 1346 (1934).

(3) Michael, Scharf and Voigt, *ibid.*, **38**, 653 (1916); Whitmore and Lux, *ibid.*, **54**, 3448 (1932).

(4) Reynolds and Adkins, *ibid.*, **51**, 285 (1929).

(5) Young, *J. Chem. Soc.*, **81**, 727 (1902).

TABLE I  
REACTION OF ISOBUTYL BROMIDE WITH INORGANIC BASES

Base	Moles of base	Soln., cc.	Reaction temp., °C.	% Reaction in 10 hours	Yield of olefin, %
KOH	0.89	200	85	40	64.1-65.5
KOH	.89	200	60	12-13	38.9-40.9
KOH	.44	500	85	58-61	47.8-49.7
KOH	.44	500	60		34.3
NaOH	1.25	200	60		25.6-27.8
AgOH	excess	500	80		10.8-11
HOH		500	80	0 (4 hrs.)	

tertiary bromides,<sup>2</sup> which made necessary the use of higher temperatures in order to get a reasonable rate of reaction. The time of reaction for all but one of the potassium hydroxide experiments was ten hours. Among these reactions where the time factor was constant, there appear certain regularities as regards the extent of reaction. As would be expected, it increases with increase of temperature, being 40% in each of two experiments carried out at 85°, and from 12-13% in three experiments which differed in experimental conditions from the preceding two only in being run at 60°. In two experiments at 85° and in 500 cc. of solution, the extent of reaction amounted to 58 and 61%, while at the same temperature and using 200 cc. of solution, the extent of reaction in each of two reactions amounted to 40%. This increase in the rate of reaction with increase in dilution corresponds to the results of Woodburn and Whitmore,<sup>6</sup> who found the rate of hydrolysis of tertiary butyl and tertiary amyl chlorides increasing with increasing solubility in the hydrolyzing medium. In contrast to their results with tertiary halides, we found the isobutyl bromide unattacked by pure water at 80° during a period of four hours.

The formation of olefin from isobutyl bromide increases with increasing concentration of base. Increasing the concentration of potassium hydroxide from 0.44 mole in 500 cc. to 0.89 mole in 200 cc., both reactions at 85°, increased the yield of olefin by 16%, though a similar increase in concentration at 60° increased the yield of olefin by but 6%. This behavior parallels that of the secondary butyl bromide as we have previously reported.<sup>2</sup>

The formation of olefin increases with increasing temperature. At 60°, 0.89 mole of potassium hydroxide in 200 cc. of solution and 0.087 mole of isobutyl bromide gave a yield of olefin of 40%, and at 85°, a yield of 64.8%. Similarly, at 60°,

0.44 mole of potassium hydroxide in 500 cc. of solution and 0.087 mole of the bromide gave a 34.3% yield of olefin and at 85°, a 48.8% yield. All of these yields are based on the amount of the bromide which actually reacted, and not upon the amount added to the reaction mixture. This behavior does not correspond to that of the secondary and tertiary bromides previously reported upon. With those compounds the effect of temperature on olefin formation was slight.

The yield of olefin varied with the cation of the base. In reactions run at 60° with a 200 cc. volume of solution, 0.89 mole of potassium hydroxide gave a yield of 40% olefin, while 1.25 moles of sodium hydroxide in the same volume of water caused the formation of but 26.7%. Here the yields of olefin are in direct contrast to the concentration effects mentioned in the preceding paragraph. Silver hydroxide gave a surprisingly low yield of olefin, 10.9% at 80°, compared to the approximately 30% previously obtained from the secondary butyl bromide.

There appears to be no rearrangement to the tertiary bromide before reaction with the base. In the work on tertiary butyl bromide previously reported, the yields of olefin varied between 0 and 2%, with temperature changes between 30 and 60°, and with potassium hydroxide, a six-fold increase in concentration of the base. Such yields are not consistent with the much larger quantities obtained in the present work. The yields of the alcohol isolated from the various reactions were usually from 15 to 20% less than the theoretical (based on the yields of olefin and metallic bromide), probably due to the small quantities actually formed. The melting points of the 3,5-dinitrobenzoates (crystallized once) were determined. Those from reactions with sodium and potassium hydroxides melted between 80° and 83.5°. Various melting points for the dinitrobenzoate of isobutyl alcohol are reported between 83°<sup>7</sup> and 87°.<sup>8</sup> The melting point of the tertiary butyl dinitrobenzoate is given by Bryant as 142°. The alcohols from the two reactions using silver hydroxide formed esters which melted over considerable ranges of temperature, becoming completely melted only at temperatures above 100°. It seems likely that in these two instances some rearrangement might have taken place.

(7) Kamm, "Qualitative Organic Analysis," John Wiley and Sons, Inc., New York, second ed., p. 186.

(8) Bryant, THIS JOURNAL, 54, 3760 (1932).

(6) Woodburn and Whitmore, THIS JOURNAL, 56, 1394 (1934).

### 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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## Action of Inorganic Bases on Tertiary Amyl Halides<sup>1</sup>

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

In earlier publications<sup>2</sup> 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<sup>3</sup> to yield only olefin in hot solution, and chiefly olefin with cold solutions of alkalis. The present paper is concerned with the action of dilute aqueous solutions of alkalis 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.),  $n_D^{25}$  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.

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

TABLE I

METHODS OF SYNTHESIS OF TERTIARY AMYL HALIDES

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

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

<sup>a</sup> Henry, *Rec. trav. chim.*, **26**, 89 (1906). Product dried over calcium chloride.

<sup>b</sup> Wischnegradsky, *Ann.*, **190**, 328 (1878). Product dried over anhydrous potassium carbonate, then over calcium chloride.

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

<sup>d</sup> Adams and Weeks, *THIS JOURNAL*, **38**, 2518 (1916). Product dried over phosphorus pentoxide.

<sup>e</sup> Eastman Kodak Company preparation.

<sup>f</sup> Norris, Watt and Thomas, *THIS JOURNAL*, **38**, 1076 (1916).

<sup>g</sup> Faworsky, *Ann.*, **354**, 348 (1907).

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

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.

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

(2) (a) French, McShan and Jolter, *THIS JOURNAL*, **56**, 1346 (1934). (b) French and Wade, *ibid.*, **57**, 1374 (1935).

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