[CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY AND PHYSICS OF THE PENNSYLVANIA STATE COLLEGE]

The Hydrolysis and Rearrangement of Certain Olefin Dibromides Containing a Tertiary Bromine

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This rearrangement was discovered by Eltekow who heated isobutylene dibromide with twenty volumes of water and obtained isobutyraldehyde.[1] Later using lead oxide Ipatiew hydrolyzed the dibromide from tertiary amyl alcohol and bromine and obtained methyl isopropyl ketone and methylethylacetaldehyde.[2] Later Froebe and Hochstetter studied the formation of ketones by the hydrolysis of dihalides.[3] The preparation of the dibromides from tertiary alcohols and bromine has been studied by many workers.[2,4]

In this Laboratory it was found that the use of high temperatures and pressures or of lead oxide is unnecessary in the hydrolysis of the dibromide of isobutylene and of trimethylethylene. The products isobutyraldehyde and methyl isopropyl ketone could be distilled out as formed by the use of an effective column. This method was used for converting tertiary amyl alcohol to the large amounts of methyl isopropyl ketone needed in some rearrangement studies.[5] In view of the success with the two lower members of this series of dibromides repeated attempts have been made during several years to extend this reaction to higher tertiary alcohols as a general means of preparing ketones of the type, RR′CHCOR″. Of thirteen tertiary alcohols or related dibromides containing more than five carbons, which were studied, only four gave identifiable products. The others gave mainly tars. In a few cases indications of the formation of conjugated dienes and of allenes were obtained. 2,3-Dibromo-2-methylpentane gave a 25% yield of 2-methylpentanone-3; 2,3-dibromo-3-methylpentane gave a 20% yield of 3-methylpentanone-2; 2,3-dibromo-3-ethylpentane gave a small yield of 3-ethylpentanone-2; and 2,3-dibromo-2-methylhexane gave a 33% yield of 2-methylhexanone-3. The most complex dibromides studied were 1,2-dibromo-2,3,3-trimethylbutane and 2,3-dibromo-2-methyltridecane.

Both the positive and negative results obtained are interesting from the point of view of rearrangements.[6] In the two cases which give good yields,

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(1) Eltekow, *J. Russ. Phys.-Chem. Soc.*, **10**, 215 (1878); *Chem. Zentr.*, 516 (1878); *cf.* Krassuski, *ibid.*, I, 628 (1902).

(2) Ipatiew, *J. prakt. Chem.*, [2] **53**, 266 (1896).

(3) Froebe and Hochstetter, *Monatsh.*, **23**, 1075 (1902).

(4) Étard, *Compt. rend.*, **114**, 755 (1892); Albizky, *J. Russ. Phys.-Chem. Soc.*, **69**, 304 (1897); Henry, *Bull. acad. roy. Belg.*, **1906**, 424; *Rec. trav. chim.*, **26**, 116 (1907); Mereschkowski, *J. Russ. Phys.-Chem. Soc.*, **45**, 1940 (1913).

(5) Whitmore and Evers, THIS JOURNAL, **55**, 812 (1933).

(6) *Cf.* Whitmore, *ibid.*, **54**, 3274 (1932).

the removal of the tertiary bromine with its complete octet of electrons leaves the fragments

$$(CH_3)_2C^+—CH_2Br \text{ and } (CH_3)_2C^+—CHBr—CH_3$$

These unstable systems might undergo a shift of an electron pair with its attached atom or group or the loss of a proton to give unsaturated compounds. The tendency for the latter in the case of methyl groups is small.[7] The shift of an electron pair with a proton would give the following

$$(CH_3)_2CH—C^+HBr \text{ and } (CH_3)_2CHC^+Br—CH_3$$

which would hydrolyze at once to give isobutyraldehyde and methyl isopropyl ketone. When larger groups than methyl are involved, the tendency to lose protons to give olefins and diolefins increases. These would tend to polymerize in the presence of the acid formed in the hydrolysis.

Experimental

1,2-Dibromo-2-methylpropane.—Preliminary experiments indicated that tertiary butyl alcohol and bromine do not react appreciably at 20° but that near the boiling point of the alcohol a rapid reaction occurs with the production of a colorless dibromide boiling mainly at 140–150°. It was finally found best to keep the alcohol at 60–70° and to add the bromine with stirring at such a rate that no unreacted bromine accumulated and the temperature did not rise. The product consisted of two layers. The upper layer contained water and hydrobromic acid. In six runs involving a total of 1.4 kg. of tertiary butyl alcohol and 3.1 kg. of bromine the yield of dibromide, b. p. 143–150° (735 mm.), was 68–75%. From 10 to 16% of the bromine appeared as hydrobromic acid. Considerable amounts of polybromides and smaller amounts of tertiary butyl bromide were also formed.

The isobutylene dibromide was hydrolyzed in 2-mole lots by heating with 2 liters of water in a flask equipped with a 90 × 1.5 cm. packed column. At first heat was applied to give refluxing without any distillation. Later the heat was increased to distil off the isobutyraldehyde as formed (59–64° at top of column). After fifty hours the dibromide layer had disappeared and 185 g. of crude product had distilled. This was treated with hydroquinone and distilled through an efficient 45 × 1 cm. column to give 108 g. of isobutyraldehyde, b. p. 58–65° (740 mm.), a yield of 75%. The time of hydrolysis and distillation for a one-mole run of the dibromide was cut from fourteen to three hours by the use of an efficient stirrer.

It was found possible to make isobutyraldehyde directly from the crude bromination mixture from tertiary butyl alcohol in 50–55% yields. Distillation of the water layer gave about 80% of the bromine as constant boiling hydrobromic acid.

2,3-Dichloro-2-methylbutane, b. p. 134–138° (735 mm.), refluxed with water and with disodium phosphate solution for thirty hours gave only 10% hydrolysis. Refluxing with 1 mole of sodium hydroxide solution for twenty-four hours gave 17% hydrolysis. Methyl isopropyl ketone was identified.

1,2-Dibromo-2-methylbutane.—Secondary butylcarbinol,[8] b. p. 125–127.5° (735 mm.), was treated with constant boiling hydrobromic acid and sulfuric acid to give a 40% yield of 1-bromo-2-methylbutane, b. p. 117–118.4° (732 mm.). A considerable amount of tertiary amyl bromide was also formed. Attempts to convert the 1-bromo

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[7] *Cf.* Whitmore and Woodburn, THIS JOURNAL, **55**, 361 (1933); Whitmore and Williams, *ibid.*, **55**, 406 (1933).

[8] Supplied by the Sharples Solvents Corp. of Philadelphia.

TABLE I

Carbinol	G.	Dbromide	G.	Yield %	B. p., °C.	Mm.	n_D^{20}	Hydrolysis product identified	B. p., °C.	Mm.	n_D^{20}	Yield, %
Dimethyl-propyl-[a]	204	2,3-Dibromo-2-methylpentane	313	64	66–68	15	1.4975	Ethyl isopropyl ketone (semicarbazone m. p. 93.5–94°)[b]	111–115	...	1.4000	25[c]
Dimethyl-butyl-[a]	232	2,3-Dibromo-2-methylhexane	337	71	75–78	6	1.5024[e]	Propyl isopropyl ketone (semicarbazone[d] m. p. 118–118.5°)	130–133	738	1.4086	33
Dimethyl-undecyl-	75	2,3-Dibromo-2-methyltridecane	118[g]					Partial hydrolysis. No product[u]				
Dimethyl-isobutyl-[f]	59	2,3-Dibromo-2,4-dimethylpentane	117[g]					Charred, tar[h]				
Methyl-di-ethyl-[i]	102	2,3-Dibromo-3-methylpentane[j]	122	50	48–50 72–74	5 15	1.5085	Methyl *sec.*-butyl ketone (semicarbazone m. p. 94-95°)[k]	114–117	732	1.4010	20
Methylethyl-butyl-	65	Much charring	11		56–64	4						
Triethyl-[l]	125	2,3-Dibromo-3-ethylpentane	190	63	73–77	4	1.5098[m]	3-Ethylpentadiene-1,3[n]	97–99	735	1.4508	30
								3-Ethylpentanone-2 (semicarbazone m. p. 93–94°)[o]	132–135	734	1.4140	10
Methylethyl-isopropyl[a]	232	2,3-Dibromo-2,3-dimethyl-pentane[t]	133	51	60–85	10	1.496	Methyl tertiary amyl ketone (semicarbazone m. p. 135.5–137°)[s]	129–130.5	733	1.4150	10
Methyl-di-butyl-	79	4,5-Dibromo-5-methylnonane	52	34	100–107	2.2		Partial hydrolysis. No product[u]				
Methylbutyl-isopropyl-[a]		2,3-Dibromo-2,3-dimethylheptane[q]						Unsaturated[p]	45–52	25		
Methylamyl-isopropyl-[a]	15	2,3-dibromo-2,3-dimethyloctane[r]	36[g]					None[u]				
Dimethyl-*tert.*-butyl-		1,2-Dibromo-2,3,3-trimethyl-butane[q]						Trace of aldehyde[u]				

[a] For the preparation of these carbinols see Whitmore and Evers, THIS JOURNAL, **55**, 812 (1933).

[b] Fournier, *Bull. soc. chim.*, [4] **7**, 840 (1910), gives m. p. 95°.

[c] The high boiling fractions gave indications of a bromohydrin with strong lachrymatory properties.

[d] Meerwein, *Ann.*, **419**, 140 (1919), gives m. p. 119°.

[e] n_D^{18} 1.5035; n_D^{19} 1.5029; d_4^{25} 1.5184.

[f] To prevent charring, it was necessary to brominate this carbinol at 0°. It required 103 hrs.

[g] The crude dibromide was not distilled.

[h] The only volatile products were 6 g., b. p. 83–101°, and 9 g., b. p. 101–127°. These contained bromine.

[i] Prepared in 60% yield by the action of ethylmagnesium bromide with ethyl acetate, b. p. 40–43° (25 mm.), n_D^{20} 1.4168. Pariselle and Simon, *Compt. rend.*, **173**, 86 (1922), give b. p. 121°, n_D^{20} 1.418.

[j] Bromination in carbon tetrachloride solution at 65–75°.

[k] Zelinsky, *Ber.*, **34**, 2865 (1901), gives the b. p. of the ketone as 118° (760 mm.) and its n_D^{18} as 1.4002; Courtot, *Bull. soc. chim.*, [3] **35**, 981 (1906), gives the m. p. of the semicarbazone as 95–96°.

[l] Prepared in 79% yield from diethyl carbonate and ethylmagnesium bromide [Moyer and Marvel, "Organic Syntheses," 1931, Vol. XI, p. 99], b. p. 136–139.5° (740 mm.), 52° (17 mm.), n_D^{20} 1.4290.

[m] n_D^{15} 1.5120.

[n] Carbon and hydrogen and molecular weight determinations indicated the formula C_7H_{12}. Heating with sodium gave no acetylene derivative such as would be expected from an allene. On standing in a closed bottle for three months it changed to a viscous polymer which only partly distilled at 260°.

[o] Tiffeneau, *Compt. rend.*, **143**, 127 (1906), gives the b. p. as 137–138° and the m. p. of the semicarbazone as 98° while Blaise, *Ann. chim. phys.*, [8] **17**, 371 (1909), gives the m. p. as 92°.

[p] Bromine and potassium permanganate tests. No semicarbazone.

[q] Prepared from the olefin made by dehydrating the carbinol with iodine.

[r] The bromination was at −3° to prevent charring; time, 110 hrs.

[s] Meerwein, *Ann.*, **396**, 255 (1913), gives the b. p. as 130.6° (760 mm.), and the m. p. of the semicarbazone as 136–138°.

[t] Considerable amounts of mono- and polybromides were obtained.

[u] When hydrolysis with water alone gave no satisfactory result, the experiment was repeated with lead oxide and water.

compound to the 1,2-dibromo compound by bromination in the presence of ferric bromide gave mainly polybromides. The monobromide was then treated with potassium hydroxide in methyl alcohol to give a 45% yield of 2-methylbutene-1, b. p. 33–35.5° (740 mm.). This was treated with bromine in carbon tetrachloride to give an 80% yield of the desired dibromide, 1,2-dibromo-2-methylbutane, b. p. 60–62° (15 mm.).

Seventy grams (0.30 mole) of this dibromide was refluxed with 700 cc. of distilled water in a 1-liter flask provided with a 50-cm. column. The distillate on redistillation gave only 7 g. of material of b. p. 94–98° (735 mm.). This had an aldehyde odor, reduced ammoniacal silver nitrate and gave a semicarbazone, m. p. 85–93° which could not be purified by recrystallization. The product of the hydrolysis was thus impure methylethylacetaldehyde.

2,3-Dibromo-2-methylbutane.—This bromide was best prepared from tertiary amyl alcohol (b. p. 100–102° (740 mm.)[8] and bromine at 60–65°. The yield of material of

b. p. 56–60° (20 mm.) was 75%.[9] The bromide was also prepared by the direct addition of bromine at 5° to trimethylethylene prepared by dehydrating tertiary amyl alcohol with 15% sulfuric acid. The use of a solution of bromine in aqueous sodium bromide solution was also tried. Neither of these methods had any advantage over the direct treatment of tertiary amyl alcohol with pure bromine. The dibromide (1740 g.) was hydrolyzed with stirring, first refluxing and later distilling off the methyl isopropyl ketone. The product on redistillation through a 90 × 1.5 cm. packed column weighed 477 g., b. p. 90–93.4° (734 mm.), n_D^{20} 1.3880, yield 55% based on the tertiary amyl alcohol used. A small amount of high boiling material, b. p. 69–82° (29 mm.), n_D^{20} 1.4630. 42.6% bromine, with strong lachrymatory power was obtained.

The results with the other twelve dibromides are summarized in Table I.

Summary

1. The hydrolysis and rearrangement of isobutylene dibromide and trimethylethylene dibromide are practical methods of converting tertiary butyl and tertiary amyl alcohols to isobutyraldehyde and methyl isopropyl ketone in good yields.

2. The hydrolysis of thirteen other dibromides prepared from aliphatic tertiary alcohols has been studied. With seven of these the rearranged aldehyde or ketone has been obtained in poor yield. With the others, polymerizations occur apparently due to the formation of substituted butadienes and other unsaturated products.

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[9] Full details of the preparation of the dibromide and of its hydrolysis to methyl isopropyl ketone will appear in "Organic Syntheses," Vol. XIII, 1933.

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Researches on Pyrimidines. CXXXI. The Reduction of 1,2,3,4-Tetrahydropyrimidines

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Several new members of a hitherto little studied class of tetrahydropyrimidines were described in a recent publication from this Laboratory.[2] These were represented by the general formula, I, in which R designates an alkyl, aryl or arylalkyl group. Inasmuch as the investigation of these compounds was primarily to ascertain whether they were of pharmacological interest, it was desirable to hydrogenate a few of them to the hexahydropyrimidine derivative, II, if possible, and then to determine the effect on the physiological activity. Furthermore, these hexahydropyrimidines possessing an ureide structure could probably be hydrolyzed to substituted β,β-diamino-isobutyric acids, III, which in themselves would be interesting substances and otherwise difficult to obtain.

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[1] Squibb and Sons Research Fellow in Organic Chemistry.

[2] Folkers, Harwood and Johnson, THIS JOURNAL, 54, 3751 (1932).