pears to be the most active reagent in the formation of phenylhydrazones.

5. The temperature coefficient of the rate of formation of *d*-galactose phenylhydrazone has been determined under acid catalysis, as well as the specific rotation of the phenylhydrazones of *d*-glucose in the equilibrated form and of *d*-galactose.

Since this article was prepared for publication, Compton and Wolfrom[6] have published kinetic data on the acid catalyzed *d*-galactose phenylhydrazone reaction in which a monomolecular formula is used to calculate the k_1 values. In that article reference is made to observations of Bodforss[7] that the reaction between aromatic aldehydes or ketones and phenylhydrazine (in the absence of acid catalysts) is monomolecular when the concentration of the carbonyl compound is in excess of that of the base, and bimolecular when the base is in excess. Compton and Wolfrom explain their monomolecular results, obtained in experiments in which the base was at a concentration higher than that of the sugar, on the basis that the free base is the active reagent. Since the latter will then be present only as that part of the acid–base compound which is dissociated, the sugar will always be in excess of the *free* base.

While we cannot reconcile the fact that our results are in harmony with the opinion that the phenylhydrazone reaction is bimolecular while the work of Compton and Wolfrom appears to show it to be monomolecular, we would point out that our observations confirm those of Bodforss. It should be kept in mind, also, that Conant and Bartlett[3] find the reaction between semicarbazide (the exact counterpart of phenylhydrazine in its reaction with the carbonyl group) and various ketones and aldehydes to be bimolecular regardless of the ratio of the concentrations of the base and the carbonyl compound.

TORONTO, CANADA

RECEIVED MARCH 21, 1935

[6] Compton and Wolfrom, THIS JOURNAL, **56**, 1157 (1934).

[7] Bodforss, *Z. physik. Chem.*, **109**, 223 (1924).

[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

Reactions of the Bromo- and Dibromoolefins[1]

BY G. BRYANT BACHMAN

The reactions studied may be divided into two classes: (1) those in which the bromine is removed or replaced; (2) addition reactions. Reactions of class (1) have been confined to the action of bases in different solvents and of alkali metals in liquid ammonia. Reactions of class (2) include the action of a variety of reagents such as the halogens, oxygen, sulfur, etc.

Action of Bases.—Like the monobromoolefins the dibromoolefins are relatively stable toward water and weak bases. After boiling for several hours with aqueous sodium carbonate or anhydrous pyridine or aniline, they may be recovered almost quantitatively. With strong bases, however, dehalogenation occurs in both cases with the formation of acetylenes. Some oxidizing action is evident in the dehalogenation of the dibromoolefins. If reaction with potassium hydroxide takes place in alcoholic solution acetic acid is one of the products;[2] in other cases the most easily oxidized substance present is attacked. Thus dehalogenation of 1,1-dibromopropene with sodium ethyl mercaptide in alcoholic solution proceeds as follows

$$CH_3CH{=}CBr_2 + 2NaSC_2H_5 \longrightarrow CH_3C{\equiv}CH + C_2H_5SSC_2H_5 + 2NaBr$$

The low yields of acetylenes from the dehalogenation of 1,1-dibromoolefins in mineral oil[3] can probably be explained on this basis as due to the oxidation of some of the product.

Sodium in Liquid Ammonia.—The action of sodium on the monobromoolefins in inert solvents such as ether has already been investigated by Nef[4] and by others, and in liquid ammonia by Kirrmann,[5] Vaughn[6] and Chablay.[7] In the present work the following substances were added separately to sodium dissolved in liquid ammonia until the blue color of the solution just vanished: 1,1-bromopropene, 1-bromooctene, 1,1-dibromo-

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[1] Presented before the Organic Section of the Midwest Regional meeting of the American Chemical Society held in Kansas City, May 3–5, 1934.

[2] Valentin, *Ber.*, **28**, 2664 (1895).

[3] Bachman and Hill, THIS JOURNAL, **56**, 2730 (1934).

[4] Nef, *Ann.*, **308**, 267 (1894).

[5] Kirrmann, *Compt. rend.*, **181**, 671 (1925).

[6] Vaughn, THIS JOURNAL, **56**, 2064 (1934).

[7] Chablay, *Ann. chim.*, [9] **1**, 469 (1914).

propene and 1,1-dibromooctene. From a quantitative examination of the products formed it appears likely that the above reactions follow closely the general theory of metallic reductions in liquid ammonia formulated by Kraus.[8]

The monobromoolefins give principally the corresponding acetylenes and olefins, in a ratio, *A/O*, which increases with increasing electronegativity of the hydrocarbon radical. Under similar conditions the dibromoolefins also yield acetylenes and olefins, but high molecular weight polymers are formed at the same time and make up a considerable portion of the products. The ratio *A/O* is larger for the dibromoolefins than for the corresponding monobromoolefins and also increases with increasing electronegativity of the hydrocarbon radical. Small amounts of saturated hydrocarbons arise in all cases due to reduction of the olefins and acetylenes by the hydrogen formed in the reaction.

Halogens.—Both the bromo and dibromoolefins add chlorine and bromine but not iodine. Addition of free chlorine proceeds easily and with but little substitution, but sulfuryl chloride does not react in any way even at steam-bath temperatures with either the mono or dibromoolefins. This is in contrast to the behavior of unhalogenated olefins such as heptene-1 which give better yields of dichlorides with sulfuryl chloride than with chlorine itself.

Oxygen.—The dibromoolefins absorb oxygen from the air and are converted into α-bromo acid bromides.

$$RCH{=}CBr_2 + O \longrightarrow RCHBrCOBr$$

This very interesting "oxydative rearrangement" in which a bromine atom shifts from the α- to the β-carbon, parallels the corresponding reactions of the halogen derivatives of ethylene itself first observed by Demole.[9] The reaction, which is strongly exothermic, has been found to proceed readily in hydrocarbon solvents or in the absence of solvents, slowly in the presence of water, and practically not at all in alcohol or aniline solution. If the oxygen gas used is not thoroughly dry the acid bromide formed is partially hydrolyzed and the liberated hydrogen bromide adds to the unreacted dibromoolefin to form a tribromo saturated hydrocarbon of the type $RCHBrCBr_2$. Apparently none of the isomeric compound RCH_2CBr_3 is formed.

Other Reagents.—Diazomethane, nitrosyl chloride and benzyl mercaptan either do not react or react in very small amounts only. Attempts to reduce the dibromoolefins with hydrogen under moderate pressures in the presence of a platinum catalyst were likewise unsuccessful.

Experimental

The bromoolefins used in the following experiments were prepared by the action of pyridine on the corresponding α,β-dibromo acids; the dibromoolefins by the action of 20% sodium carbonate solution on the corresponding α,α,β-tribromo acids.[10]

Reaction of 1,1-Dibromoheptene-1 with Sodium Ethylate.—Ten grams of 1,1-dibromoheptene-1 was refluxed for eight hours with a solution of 2 g. of sodium in 20 cc. of absolute ethanol. Water was added and the brown oil which separated was dried over calcium chloride and distilled. There was obtained 3.0 g. (yield 70%) of a colorless, characteristically odored liquid, b. p. 110–112°, which proved to be heptyne-1. It gave a mercury salt[11] of m. p. 60–61°. The water solution was evaporated to dryness, ethyl alcohol and sulfuric acid added and the ethyl acetate formed identified by its odor and boiling point.

Reaction of 1,1-Dibromopropene-1 with Sodium Ethyl Mercaptide.—To a solution of 10 g. of sodium in 150 cc. of absolute ethanol were added first 25 g. of carefully dried ethyl mercaptan and then 41 g. of 1,1-dibromopropene-1. The mixture was refluxed for fifteen hours, the sodium bromide (38 g.) removed by filtration, and the resulting clear solution poured into water. The oil which separated was extracted with ether, the ether solution dried and distilled. There was obtained 9.0 g. of diethyl disulfide, b. p. 55–57° (20 mm.).

Anal. Calcd. for $C_4H_{10}S_2$: S, 52.4. Found: S, 52.0.

The gaseous product of the reaction, propyne, was not determined quantitatively but was identified through the fact that it formed a silver salt with ammoniacal silver nitrate solution and yielded a mercury derivative,[11] m. p. 203°, with alkaline mercuric iodide solution.

Reaction of 1-Bromopropene-1 with Sodium in Liquid Ammonia.[12]—The reactions of the bromo and dibromoolefins with sodium in liquid ammonia are extremely rapid and the products if gaseous are evolved instantly. The addition of the halide was always carried out slowly to avoid accident and to ensure complete reaction. Before starting the reaction the apparatus was thoroughly swept out with ammonia.

The results obtained in these experiments are shown below in tabular form.

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[8] Kraus, *Chem. Rev.*, **8**, 251 (1931).

[9] Demole, *Ber.*, **11**, 315, 1302, 1307, 1710 (1878); **12**, 2245 (1879); *Bull. soc. chim.*, [ii] **34**, 201 (1880); see also Swarts, *Bull. acad. roy. Belg.*, [3] **36**, 532–52 (1898); Henry, *ibid.*, [3] **36**, 497–504 (1899).

[10] Bachman, This Journal, **55**, 4279 (1933).

[11] Johnson and McEwen, *ibid.*, **48**, 470 (1926).

[12] The writer is greatly indebted to his colleague, Dr. W. C. Fernelius, for his able assistance and valuable suggestions in the liquid ammonia work here described. The apparatus used was essentially the same as that of Johnson and Fernelius, *J. Chem. Ed.*, **6**, 445 (1929), except that provision was made for the drop by drop introduction of liquids into the mixture at the bottom of the reaction tube.

TABLE I

Substance	Moles Used	Sodium	Acetylene	Olefin	Acetylene / Olefin
1-Bromopropene-1	0.167	0.202	0.006	0.818	0.012
1-Bromooctene-1	.167	.221	.034	.075	.45
1,1-Dibromopropene-1	.167	.389	.050	.070	.71
1,1-Dibromooctene-1	.167	.374	.052	.029	1.80

The olefins formed were identified as their dibromides: 1,2-dibromopropane, b. p. 140° (760 mm.); $d^{20}{}_4$ 1.934; 1,2-dibromooctane, b. p. 126° (21 mm.); $n^{20}{}_D$ 1.4963. The acetylenes were converted into their mercury derivatives with alkaline mercuric iodide:[11] dipropynyl mercury of m. p. 203°, dioctynyl mercury of m. p. 80.5°. In the cases of the propene derivatives the propene was obtained directly from the reaction mixture in 49% yields, the evolved gas being 95% pure propene, contaminated by a few per cent. of a mixture of hydrogen and propane. The propyne was liberated from its sodium salt when the reaction mixture was hydrolyzed with concentrated aqueous ammonium hydroxide. In the cases of the octene derivatives the products were hydrolyzed after all of the ammonia had evaporated. Not more than 50 cc. of gaseous product was formed and this proved to be hydrogen. The brown oils which separated in the reaction tube were dried and distilled until the boiling point reached 130°. The percentages of acetylene in the distillates were then determined by the method of Hill and Tyson.[13] The distillates were shaken for twelve hours with an excess of aqueous silver nitrate solution (10%) and the mixture filtered and extracted with ether. Upon fractionation of the ether extract the octene was obtained as a colorless oil of b. p. 122–124° (760 mm.).

Halogen Derivatives of 1-Bromopropene-1 and 1,1-Dibromopropene-1.—Halogenation with chlorine and bromine was carried out in carbon tetrachloride solution at −5°. The products formed together with their properties and analyses are shown in the table.

	CH_3CHCl-$CHClBr$[a]	CH_3CHCl-$CClBr_2$	$CH_3CHBrCBr_3$[b]
B. p., °C. (mm.)	154.5 (760)	84 (16)	122 (15)
$n^{20}{}_D$	1.5022	1.5500	1.6187
$d^{20}{}_4$	1.702	2.082	2.679
Yield, %	70	68	75
Analyses........	Wt. AgBr + AgCl, g.	Wt. AgBr + AgCl, g.	Br, %
Calcd.	0.6009	0.5274	88.9
Found	.6019	.5261	88.9
Sample	.2430	.2156	

[a] Linnemann, *Ann.*, **138**, 123 (1866), prepared this compound and reports its b. p. as 156–160°. His product probably contained some 1,2-dichloro-2-bromopropane.

[b] Cannot be distilled at atmospheric pressure without extensive decomposition and evolution of bromine. Cahours' [*Compt. rend.*, **31**, 291 (1850)] material is probably another substance or a mixture of substances, since it distils without decomposition at atmospheric pressure and possesses a different density than the 1,1,1,2-tetrabromopropane obtained by the author.

Reaction of 1,1-Dibromoolefins with Oxygen.—When dibromoolefins are shaken with air or oxygen they absorb the oxygen rapidly at first and the temperature rises. Later the oxygen absorption becomes slower and several days may be required to complete the addition. In one experiment 75 g. of 1,1-dibromopropene-1 was shaken continuously for forty-eight hours while a slow stream of oxygen was bubbled through the liquid. The product (weight, 73 g.) when fractionated yielded 30 g. (31% theoretical) of α-bromopropionyl bromide, b. p. 59° (15 mm.).

Anal. Calcd. for $C_3H_4OBr_2$: Br, 74.1. Found: Br, 74.0.

The α-bromopropionyl bromide was further characterized by conversion into α-bromopropionyl amide, m. p. 123°, by reaction with concentrated aqueous ammonium hydroxide. Five grams of intermediate material and 20 g. (19% theoretical) of 1,1,2-tribromopropane, b. p. 83° (6 mm.), $n^{20}{}_D$ 1.5790, $d^{20}{}_4$ 1.355 were also obtained.

Anal. Calcd. for $C_3H_5Br_3$: Br, 85.4. Found: Br, 84.7.

From the tarry residue a small amount of α-bromopropionic acid, m. p. 25°, was isolated. The physical constants of the above products correspond to those listed in Beilstein reasonably closely.

When the oxygen used was very carefully dried over phosphorus pentoxide the yield of bromo acid bromide was increased and the yield of tribromohydrocarbon decreased. Cooling the reaction mixture so that the temperature did not rise above 20° decreased the amount of tarry residue obtained in the distillation and increased the yield of products. In the presence of water the reaction was very slow and in alcohol or aniline solution absorption of oxygen ceased entirely or became immeasurably slow. In high boiling petroleum ether and in benzene the reaction proceeded normally.

Summary

1. Bromo and dibromoolefins of the types $C_nH_{2n+1}CH{=}CBr_2$ and $C_nH_{2n+2}CH{=}CBr_2$ have been treated with various reagents and their reactions studied.

2. Certain generalizations concerning the reactions of these substances with sodium in liquid ammonia have been stated.

COLUMBUS, OHIO RECEIVED MARCH 22, 1935

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[13] Hill and Tyson, THIS JOURNAL, **50**, 172 (1928).