

## Summary

1. The preparation and properties of compounds arising from the reaction between piperazine and derivatives of monochloroacetic acid have been described.

2. *n*-Hexyl chloroacetate has been synthesized and its physical constants reported.

3. The reaction between piperazino-1,4-bis-(ethanenitrile) and hydrogen peroxide is being studied.

GAINESVILLE, FLORIDA

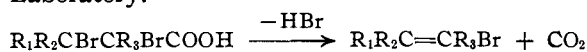
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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE OHIO STATE UNIVERSITY]

## The Dehalogenation of $\alpha,\beta$ -Dibromo Acids. II. The Influence of the Acid Structure on the Yields of Bromoolefins

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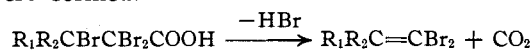
Dehalogenation of  $\alpha,\beta$ -dibromo acids has been shown by many investigators to yield a large variety of products. In most cases these workers have interested themselves principally in the  $\alpha$ -bromoolefinic acids which usually make up the major portion of the products, and they have determined not only the yields of these acids but also the ratio in which their stereoisomeric forms arise. More recently a definite study of the preparation and properties of the bromoolefins which also arise in such dehalogenations under suitable conditions has been undertaken in this Laboratory.<sup>1</sup>



As a part of this program it was decided to investigate the effect of varying the structure of the dibromo acid on the yield of bromoolefin. The importance of such a study becomes readily apparent if one considers as an example the difference in behavior of cinnamic and crotonic acid dibromides upon dehalogenation with aqueous sodium carbonate. The former yields bromostyrene in 65% yields; the latter gives only a trace of bromopropene. The only difference between these two acids lies in the nature of the hydrocarbon radical attached to the  $\beta$ -carbon atom of the acid. Even if attention is confined to the aliphatic series alone, striking differences are manifested. Thus  $\alpha,\alpha,\beta$ -tribromobutyric acid gives 1,1-dibromopropene in 88% yields while  $\alpha,\beta$ -dibromopelargonic acid gives 1-bromooctene in only 30% yields when dehalogenated under the same conditions as the two acids mentioned above.

If one considers the basic skeleton of these dibromo acids as  $\begin{array}{c} | \quad | \\ -C-C-COOH \\ | \quad | \\ Br \quad Br \end{array}$ , there are ob-

viously three points at which different groups may be introduced into the molecule—one on the  $\alpha$ -carbon atom, and two on the  $\beta$ -carbon atom of the chain. In the present work most of the possible  $\alpha,\beta$ -dibromo acids of the aliphatic series up to and including those containing six carbon atoms have been studied. Whenever the structure of the acid permitted it, the corresponding  $\alpha,\alpha,\beta$ -tribromo acids were also prepared and their dehalogenation studied. In such cases dibromoolefins were formed.



In order to make comparisons valid all dehalogenations were carried out by standardized procedures, using pyridine or 20% aqueous sodium carbonate as the bases. The reasons for this selection of bases are discussed in the first paper of this series. More detailed descriptions of the procedures are given in the experimental part. In the following table (I) are shown the results. A few yields obtained in previous work are also included since they are pertinent to the general discussion.

It is apparent that the nature and position of the groups introduced, strongly influence the yield of bromoolefins obtained. With hydrogen in all three positions the yield of bromoolefin is practically zero and the principal product is the corresponding  $\alpha$ -bromoolefinic acid or its polymer.<sup>2</sup> Replacement of one hydrogen by a bromine atom in the alpha position or by an alkyl group in the alpha or beta positions gives acids which yield about 30% of bromoolefins. The nature of the alkyl group introduced does not exert much influence on the yield of bromoolefin. Thus it will be noted that a methyl, ethyl, propyl

(2) An odor suggestive of bromoethylene was noted but none of this compound could be isolated.

(1) Bachman, *THIS JOURNAL*, **55**, 4279 (1933).

TABLE I  
 RESULTS OF THE DEHALOGENATION OF DI- AND TRIBROMO ACIDS

| Acid                                                                     | M. p.,<br>°C. | Product                                                             | Yield,          |                                      | B. p.,<br>°C. | $d_{20}^{25}$ | $n_D^{20}$ | Anal. for Br |       |
|--------------------------------------------------------------------------|---------------|---------------------------------------------------------------------|-----------------|--------------------------------------|---------------|---------------|------------|--------------|-------|
|                                                                          |               |                                                                     | pyri-<br>dine   | %<br>Na <sub>2</sub> CO <sub>3</sub> |               |               |            | Calcd.       | Found |
| CH <sub>2</sub> BrCHBrCOOH                                               | 51            | CH <sub>2</sub> =CHBr                                               | 0               | 0                                    | .....         | ...           | ....       |              |       |
| CH <sub>3</sub> CHBrCHBrCOOH                                             | 87-88         | CH <sub>3</sub> CH=CHBr                                             | 28 <sup>e</sup> | 0                                    | "             | "             | "          |              |       |
| CH <sub>2</sub> BrC(CH <sub>3</sub> )BrCOOH                              | 46-48         | CH <sub>2</sub> =CBrCH <sub>3</sub>                                 | 32              | ..                                   | 48-49         | 1.382         | 1.4426     |              |       |
| C <sub>2</sub> H <sub>5</sub> CHBrCHBrCOOH                               | 56            | C <sub>2</sub> H <sub>5</sub> CH=CHBr                               | 28 <sup>e</sup> | ..                                   | 87-89         | 1.312         | 1.4536     |              |       |
| (CH <sub>3</sub> ) <sub>2</sub> CBrCHBrCOOH                              | 106-107       | (CH <sub>3</sub> ) <sub>2</sub> C=CHBr                              | 81              | 88                                   | 90-91         | 1.338         | 1.4625     |              |       |
| CH <sub>3</sub> CHBrC(CH <sub>3</sub> )BrCOOH                            | 84-86         | CH <sub>3</sub> CH=C(CH <sub>3</sub> )Br                            | 71              | 41                                   | 108-110       | 1.277         | 1.4580     |              |       |
| <i>n</i> -C <sub>8</sub> H <sub>7</sub> CHBrCHBrCOOH                     | 70-71         | <i>n</i> -C <sub>8</sub> H <sub>7</sub> CH=CHBr                     | 32 <sup>e</sup> | ..                                   | "             | "             | "          |              |       |
| (CH <sub>3</sub> ) <sub>2</sub> CHCHBrCHBrCOOH                           | 124-126       | (CH <sub>3</sub> ) <sub>2</sub> CHCH=CHBr <sup>a</sup>              | 28              | 28                                   | 99-101        | 1.227         | 1.4482     | 53.7         | 53.0  |
| C <sub>2</sub> H <sub>5</sub> CHBrC(CH <sub>3</sub> )BrCOOH              | 97-98         | C <sub>2</sub> H <sub>5</sub> CH=C(CH <sub>3</sub> )Br <sup>b</sup> | 75              | ..                                   | 108-110       | 1.277         | 1.4580     | 53.7         | 53.6  |
| CH <sub>3</sub> CHBrC(C <sub>2</sub> H <sub>5</sub> )BrCOOH              | 80-81         | CH <sub>3</sub> CH=C(C <sub>2</sub> H <sub>5</sub> )Br <sup>a</sup> | 73              | ..                                   | 110-111       | 1.273         | 1.4628     | 53.7         | 53.8  |
| (CH <sub>3</sub> ) <sub>2</sub> CBrC(CH <sub>3</sub> )BrCOOH             | 222           | (CH <sub>3</sub> ) <sub>2</sub> C=C(CH <sub>3</sub> )Br             | 45              | 84                                   | 118-120       | 1.289         | 1.4738     | 53.7         | 53.6  |
| CH <sub>2</sub> BrCBr <sub>2</sub> COOH                                  | 90-91         | CH <sub>2</sub> =CBr <sub>2</sub>                                   | ..              | 30 <sup>d</sup>                      | 91-92         | ...           | ....       |              |       |
| CH <sub>3</sub> CHBrCBr <sub>2</sub> COOH                                | 117-118       | CH <sub>3</sub> CH=CBr <sub>2</sub>                                 | 80 <sup>e</sup> | 88 <sup>e</sup>                      | "             | "             | "          |              |       |
| C <sub>2</sub> H <sub>5</sub> CHBrCBr <sub>2</sub> COOH                  | 90-91         | C <sub>2</sub> H <sub>5</sub> CH=CBr <sub>2</sub>                   | ..              | 83 <sup>e</sup>                      | "             | "             | "          |              |       |
| (CH <sub>3</sub> ) <sub>2</sub> CBrCBr <sub>2</sub> COOH <sup>a</sup>    | 230           | (CH <sub>3</sub> ) <sub>2</sub> C=CBr <sub>2</sub> <sup>a</sup>     | 81 <sup>c</sup> | 81                                   | 156-157       | 1.866         | 1.5300     | 74.8         | 74.6  |
| <i>n</i> -C <sub>8</sub> H <sub>7</sub> CHBrCBr <sub>2</sub> COOH        | 102-103       | <i>n</i> -C <sub>8</sub> H <sub>7</sub> CH=CBr <sub>2</sub>         | ..              | 79 <sup>e</sup>                      | "             | "             | "          |              |       |
| (CH <sub>3</sub> ) <sub>2</sub> CHCHBrCBr <sub>2</sub> COOH <sup>a</sup> | Oil           | (CH <sub>3</sub> ) <sub>2</sub> CHCH=CBr <sub>2</sub> <sup>a</sup>  | ..              | 70                                   | 159-160       | 1.664         | 1.5037     | 70.2         | 70.0  |

<sup>a</sup> New compound. <sup>b</sup> Lieben and Zeisel, *Monatsh.*, **4**, 10 (1883), report this compound but give no physical constants and no analysis. <sup>c</sup> This reaction occurred rapidly without external heating and was complete within a few minutes. <sup>d</sup> Determined as the dibromide. <sup>e</sup> Determined in previous work.

or isopropyl group in the beta position yields about 30% bromoolefin. With two substituents other than hydrogen better than 70% yields result. The best yields are obtained when there are two alkyl groups in the beta position or two bromine atoms in the alpha position (except with CH<sub>2</sub>BrCBr<sub>2</sub>COOH). In such cases the bromo or dibromoolefins are obtained in 70-90% yields, those acids of lower molecular weight giving the higher yields. Strangely enough when all three hydrogens are replaced by alkyl groups the yield with pyridine drops to 45%. In most cases, pyridine and sodium carbonate gave practically the same yields; in some cases, however, radically different yields of bromoolefin were obtained with the same acid. Whether the latter difference is due to the relative alkalinity of these two reagents or to some other cause is not clear as yet. Other work which will be published shortly indicates that a tertiary nitrogen atom in a ring influences the course of dehalogenation of  $\alpha,\beta$ -dibromo acids even in the presence of other stronger bases.

### Experimental Part

**The Acrylic Acids.**—The substituted acrylic acids used in this work were prepared by three general methods: (a) condensation of aldehydes with malonic acid, (b) dehydration of hydroxy acids, (c) dehydrohalogenation of halogen acids. The syntheses of type (a) were quite satisfactory, *i. e.*, yields of 50-85% of the theoretical were obtained using anhydrous pyridine as a catalyst. The syntheses of type (b) usually involved the Reformatsky

reaction as a preliminary step. With aldehydes this was entirely satisfactory; with ketones, less satisfactory. Dehydration of the resulting  $\beta$ -hydroxy acids was accomplished with thionyl chloride. The  $\alpha$ -hydroxy acids which may also be used in some cases are likewise dehydrated with thionyl chloride<sup>3</sup> although the yields are generally not as high as from the  $\beta$ -hydroxy acids. In syntheses of type (c) the procedure consists in the removal of the elements of hydrogen bromide from  $\alpha$ -bromo acids. Quinoline<sup>4</sup> is a satisfactory base for this purpose although dimethylaniline<sup>5</sup> and alcoholic potassium hydroxide<sup>6</sup> have also been used. Special methods of syntheses are available in a few cases. Thus  $\beta,\beta$ -dimethylacrylic acid may be obtained very pure and in excellent yields by the oxidation of mesityl oxide,<sup>7</sup> and  $\alpha$ -methylacrylic acid is most easily synthesized by the action of aqueous sodium carbonate on citrobromopyrotartaric acid.<sup>8</sup>

**$\alpha,\beta$ -Dibromo Acids.**—The bromination of  $\alpha,\beta$ -unsaturated acids usually proceeds readily at 0° in carbon disulfide in the direct sunlight. A 5% excess of bromine should be used. Recrystallization of the products is best carried out in petroleum ether. Cooling the solution in liquid ammonia to induce crystallization is frequently advantageous. All of these acids crystallize rather slowly.  $\alpha,\beta$ -Dibromopropionic acid was prepared by the oxidation of the dibromide of allyl alcohol.<sup>9</sup>

Perkin<sup>10</sup> reports the melting point of  $\alpha,\beta$ -dibromo- $\alpha,\beta$ -dimethylbutyric acid to be 190-191°. We found that this acid begins to decompose slowly above 180° and that the

(3) Lauer and Stodola, *THIS JOURNAL*, **56**, 1216 (1934).

(4) Staudinger and Ott, *Ber.*, **44**, 1635 (1911).

(5) Weinig, *Ann.*, **280**, 252 (1894).

(6) Goodwin and Perkin, *Proc. Chem. Soc.*, **10**, 64 (1894).

(7) Barbier and Leser, *Bull. soc. chim.*, [3] **33**, 917 (1905).

(8) Autenrieth and Pretzell, *Ber.*, **36**, 1271 ((1903).

(9) Kohler, *Am. Chem. J.*, **42**, 381 (1909).

(10) Perkin, *J. Chem. Soc.*, **69**, 1480 (1896).

melting point therefore depends upon the rate of heating. The instantaneous decomposition point was found to be  $222^\circ$  (corr.). Below this temperature several seconds are required to obtain complete liquefaction. At  $222^\circ$ , however, a fresh sample liquefies instantly and is partially ejected from the melting point tube by the gas which is evolved.

**Bromoolefins.** (a) **Procedure with Pyridine.**—The acid was dissolved in six moles of anhydrous pyridine and heated on the steam-bath under a reflux condenser for five hours. The resulting mixture of solution and solid was poured into a small excess of concentrated hydrochloric acid and sufficient ice to prevent the temperature from rising above room temperatures. The bromoolefins were separated by steam distillation, washed with dilute acid and water, dried and distilled.

(b) **Procedure with Sodium Carbonate.**—The acid, 1 mole, was dissolved in a 20% solution of sodium carbonate containing 1.5 moles. This solution was heated to boiling and the bromoolefin distilled with the water. The product was purified as in procedure (a). The yields shown in the table are based in all cases on the undistilled material.

**$\alpha$ -Bromoolefinic Acids.**—The aqueous solution in procedure (a) above after removal of the bromoolefin was extracted with ether. The aqueous solution in procedure (b) after removal of the bromoolefin was acidified and extracted with ether. The ether solution in either case was then dried and evaporated. The solid bromoolefinic acids so obtained were distilled and/or recrystallized from petroleum ether. The yields of  $\alpha$ -bromoolefinic acids were not always as high as might be expected due to side reactions and in some cases to the fact that other products were formed. Above  $100^\circ$  pyridine condenses with  $\alpha$ -bromoolefinic acids rapidly to form substances the nature of which is now being investigated. Even at steam-bath temperatures this type of side reaction occurs to some extent. With sodium carbonate dehalogenation proceeds at least partially as though the dehalogenating agent were a metal like zinc. Two bromine atoms are removed and the original acrylic acids result. The role of the base in these dehalogenations will be discussed more fully in a later paper.  $\alpha$ -Bromo- $\beta$ -isopropylacrylic acid is new. It boils at  $152^\circ$  (23 mm.) and melts at  $80.5^\circ$ ; yield, 31%.

*Anal.* Calcd. for  $C_6H_9O_2Br$ : Br, 41.4. Found: Br, 41.3, 41.5.

**Tribromo Acids.**—The  $\alpha$ -bromoolefinic acids were brominated in carbon disulfide solution at  $0^\circ$  in the presence of direct sunlight.  $\alpha$ -Bromo- $\beta$ -isopropylacrylic acid brominated with difficulty. A glass-stoppered bottle containing this acid, carbon disulfide, and a 5% excess of bromine was placed out-of-doors for ten days. The temperature over this period averaged  $0^\circ$  and never rose above  $5^\circ$ . At the end of this time hydrogen bromide was

being evolved although addition was still not quite complete. The  $\alpha,\alpha,\beta$ -tribromo- $\beta$ -isopropylpropionic acid was obtained by evaporation of the solvent and the excess bromine under diminished pressure. It is an oil; yield, 90%.

*Anal.* Calcd. for  $C_6H_9O_2Br_3$ : Br, 68.0. Found: Br, 67.8.

$\alpha,\alpha,\beta$ -Tribromopropionic acid was prepared by several methods, the most successful and convenient being that of Berlande<sup>11</sup> in which acrolein is converted successively into  $\alpha$ -bromoacrolein, tribromopropionaldehyde, and finally tribromopropionic acid. In the last step better yields (80%) were obtained by oxidizing the aldehyde with a mixture of equal quantities of concentrated and fuming nitric acid. Niemilowicz<sup>12</sup> preparation of this acid could not be duplicated. Although several attempts were made we were unable to convert glycerol into tribromopropionaldehyde by reaction with hydrobromic and sulfuric acids according to his directions. The preparation of  $\alpha,\alpha,\beta$ -tribromopropionic acid by the bromination of  $\alpha$ -bromoacrylic acid is a satisfactory method but is not to be recommended because of the difficulty of preparing  $\alpha$ -bromoacrylic acid and preserving it from polymerization.

$\alpha,\alpha,\beta$ -Tribromo- $\beta$ -methylbutyric acid is new. It begins to decompose above  $180^\circ$  and shows an instantaneous decomposition temperature of  $230^\circ$ .

*Anal.* Calcd. for  $C_6H_7O_2Br_3$ : Br, 70.8. Found: Br, 70.8.

**Dibromoolefins.**—These substances were obtained by the action of pyridine or aqueous sodium carbonate on the corresponding tribromo acids according to procedures (a) and (b) under the monobromoolefins.

The 1,1-dibromoethylene formed by the dehalogenation of tribromopropionic acid polymerizes rapidly to a solid. Consequently it was brominated immediately and the 1,1,1,2-tetrabromoethane so formed purified by distillation and weighed to determine the yield.

## Summary

1. A series of aliphatic  $\alpha,\beta$ -dibromo- and  $\alpha,\alpha,\beta$ -tribromo acids has been prepared. Dehalogenation of these acids with anhydrous pyridine and with aqueous sodium carbonate has led to the corresponding bromo- and dibromoolefins.
2. Conclusions have been drawn as to the effect of the nature, the number, and the position of substituents on the yields of bromoolefins obtainable.

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(11) Berlande, *Bull. soc. chim.*, [IV] **37**, 1385 (1925).

(12) Niemilowicz, *Monatsh.*, **11**, 87 (1890).