collected in ether, the ether was evaporated and the residue was recrystallized from benzene. About 0.1 g. of a product of m. p. 80° was obtained. The melting point of this product was not depressed by mixing it with a sample of 2,3,4,5-tetramethylphenol prepared from prehnitene.[7] Limpach gives the melting point of this phenol as 80–81°.[8]

Summary

1. The cyclization of substituted divinylacetylenes has been extended to 3,6-dimethyloctadiene-2,6-ine-4 and 3,6-diethyloctadiene-2,6-ine-4. The reaction could not be applied to the disubstituted divinylacetylene, 2,5-dimethylhexadiene-1,5-ine-3.

2. The structure proposed for the ring compounds and the mechanism of the cyclization reaction have been established by converting the cyclohexane derivatives obtained from 3,6-dimethyloctadiene-2,6-ine-4 to known derivatives of tetramethylbenzene.

[7] Cummings, Hopper and Wheeler, "Systematic Organic Chemistry," Constable and Co., London, 1931, pp. 323, 210.

[8] Limpach, *Ber.*, **21**, 645 (1888).

URBANA, ILLINOIS

RECEIVED JUNE 19, 1933
PUBLISHED OCTOBER 6, 1933

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

Dehalogenation of Aliphatic Bromo Acids. The Bromo and Dibromo Olefins*

BY G. BRYANT BACHMAN

Dehalogenation of cinnamic acid dibromide may lead to the formation of cinnamic acid, α-bromocinnamic acid, α-bromoallocinnamic acid or ω-bromostyrene or mixtures of all of these depending upon the conditions of dehalogenation and particularly on the nature of the dehalogenating base used. In the aliphatic series the dehalogenation of α,β-dibromo acids has been less thoroughly studied and although the bromoolefins analogous to ω-bromostyrene have been detected among the products in some cases, attention has generally been centered on the relative yields of α-bromo and α-bromoisoolefinic acids. No systematic efforts have been made to isolate the 1-bromo-1-olefins formed and determine their physical and chemical properties and their yields.

There are apparently two other well-defined methods available for the preparation of 1-bromo-1-olefins (1) the dehalogenation of olefin dibromides

$$2RCHBrCH_2Br + \text{Alc. KOH} \longrightarrow \begin{array}{l} RCH{=}CHBr \\ +RCBr{=}CH_2 \end{array} + 2KBr + 2H_2O \qquad (1)$$

and (2) a method recently devised by Kirrmann.[1] Neither of these meth-

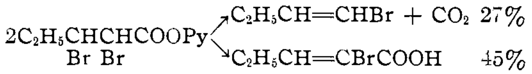
---

* Presented before the Organic Section at the Chicago Meeting of the American Chemical Society, September, 1933.

[1] Kirrmann, *Bull. soc. chim.*, **41**, 316–323 (1926).

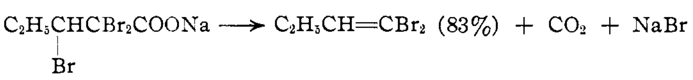
ods is entirely satisfactory—the first yielding a mixture of isomers which is difficult to separate completely into the pure components and the second being rather roundabout and applicable only with difficulty to some members of the series. In view of the fact that these bromoolefins might be expected to serve as unexcelled intermediates for the preparation of normal acetylenes, it seemed desirable to study their formation through the decomposition of a series of aliphatic olefinic acid dibromides.

It has been found that the organic as well as the inorganic salts of the α,β-dibromo acids from butyric acid through pelargonic acid decompose when heated to give 1-bromo-1-olefins in from 20 to 35% yields depending among other things on the base used. Thus when α,β-dibromovaleric acid dissolved in pyridine is heated the following reactions occur



$$\underset{\text{Br}\ \ \text{Br}}{2C_2H_5CHCHCOOPy}\left\langle\begin{array}{l}\nearrow C_2H_5CH{=}CHBr + CO_2\ \ 27\% \\ \searrow C_2H_5CH{=}CBrCOOH\ \ \ 45\%\end{array}\right. + 2Py{\cdot}HBr \qquad (2)$$

The 1-bromo-1-olefins thus formed, when isolated, are exceptionally pure, colorless, pleasant odored liquids, and are uncontaminated with the isomeric 2-bromo-1-olefins or more highly brominated products. The above decomposition may be explained most simply perhaps on the assumption that there are two simultaneous competitive reactions occurring, the more rapid one being a simple dehalogenation in which the β-bromine atom and the α-hydrogen atom are removed together with the resulting formation of an α-bromoolefinic acid, the second reaction giving rise to the bromoolefin.[2] In the aromatic series, *i. e.*, when the β-carbon is substituted by a phenyl group, this latter reaction predominates. In the aliphatic series, however, it is subordinate. The nature of the substituent groups therefore exerts a marked influence on the relative rates of these two reactions. This would lead one to predict that even higher yields of bromoolefins would result from the decomposition of acids containing a still greater number of electronegative atoms or groups. This was found to be the case—the α,α,β-tribromo acids decompose to give 1,1-dibromo-1-olefins in excellent yields.



$$C_2H_5\underset{\substack{|\\ \text{Br}}}{C}HCBr_2COONa \longrightarrow C_2H_5CH{=}CBr_2\ (83\%) + CO_2 + NaBr \qquad (3)$$

It should also be pointed out, of course, that here a simple dehalogenation reaction of the previously illustrated type is impossible since there is no α-hydrogen atom available. Without competition from this reaction then the formation of the dibromoolefin proceeds practically completely. Beta-gamma dehalogenation does not seem to occur to an appreciable extent.

---

(2) Two different mechanisms have been proposed to account for this second type of reaction. The earlier one of Erlenmeyer, *Ber.*, **13**, 303 (1880), assumes the intermediate formation of β-lactones. More recently Johansson, *ibid.*, **48**, 1262 (1915), and **55**, 647 (1922), proposes the simultaneous elimination of carbon dioxide and the bromide ion. Further research is in progress to determine which of these mechanisms explains most satisfactorily the present work.

Of the 1,1-dibromo-1-olefins only 1,1-dibromo-1-propene has been mentioned previously in the literature.[3] Unfortunately it was inadequately described. The compounds prepared by the writer were found to be colorless, pleasant odored, mobile but dense liquids, which on standing in the air absorbed oxygen and took on an acid bromide odor. 1,1-Dibromo-1-propene absorbed oxygen especially quickly and had a pungent odor within fifteen minutes after preparation. Sealed tubes containing this compound were found to be under diminished pressure after standing for only a week. This reaction is being further investigated for comparison with the oxidation of 1,1-dibromoethylene by atmospheric oxygen.[4] If the reactions are analogous, α-bromopropionyl bromide should result

$$2CH_3CH{=}CBr_2 + O_2 \longrightarrow 2CH_3CHBrCOBr \qquad (4)$$

The series of α-bromoolefinic acids formed by reaction (2) and the α,α,β-tribromo acids prepared by their bromination are new except α-bromocrotonic and α,α,β-tribromobutyric acids. Although several different kinds of salts of α,β-dibromo acids were decomposed, the pyridine salts were found to be most satisfactory since the α-bromo acids resulting were purer and furthermore were not contaminated with the corresponding α-bromo iso acids or bromohydroxy acids.[5] Dehalogenation of the α,β,β-tribromo acids was accomplished more conveniently with dilute sodium carbonate solution since side reactions were found to be inconsiderable, and practically the only products were dibromoolefins.

Experimental Part

Olefinic Acids.—These acids were prepared in excellent yields by the condensation of the appropriate aldehydes with malonic acid in the presence of pyridine.[6] Hexaldehyde was prepared in 60% yields by the reaction of 1 mole of *n*-amylmagnesium bromide with 1 mole of orthoformic ester, a method apparently not hitherto used for its preparation. The following constants were obtained: b. p. (747 mm.), 126–128°; n^{20}_{D} 1.4068; d^{20}_{4} 0.8176. Several unsuccessful attempts were made to dehydrogenate *n*-hexyl alcohol with metallic copper according to the procedure of Sabatier and Mailhe. Although some aldehyde was formed, its preparation by this method was found to be impracticable. The catalytic oxidation of alcohols in the presence of copper bronze and nitrobenzene recommended by Rosenmund[7] was also tried. It proceeded too slowly to be of value when considerable quantities of hexaldehyde were desired.

Of the olefinic acids α-octenic acid is new. The following constants were noted. b. p. (22 mm.) 154° (corr.); n^{20}_{D} 1.4587; d^{20}_{4} 0.9807. The acid was analyzed in the form of its *p*-bromophenacyl ester, m. p. 92.5°.

Anal. Calcd. for $C_{16}H_{19}O_3Br$: Br, 23.6. Found: Br, 23.4, 23.5.

α,β-Dibromo Acids.—The carefully fractionated olefinic acids were brominated in carbon disulfide with a small excess of bromine at 5°. Direct sunlight has a most marked influence on the speed of this reaction. On dull days several hours are required for com-

---

(3) Valentin, *Ber.*, **28**, 2664 (1895).

(4) Demole, *ibid.*, **11**, 316 (1878).

(5) Pfeiffer, *ibid.*, **43**, 3039 (1910).

(6) Auwers, *Ann.*, **432**, 46 (1923).

(7) Rosenmund, *Ber.*, **54**, 2033 (1921).

pletion of a bromination that is completed within twenty minutes when the sun is shining directly on the reaction flask. The α,β-dibromo acids used in this investigation have all been described except α,β-dibromoheptanoic and α,β-dibromooctanoic acids.

Acid	M. p., °C.	Analyses for bromine, % Calcd.	Found	
$C_4H_9CHBrCHBrCOOH$	74.5	55.5	55.2	55.2
$C_5H_{11}CHBrCHBrCOOH$	Oil	53.0	53.6	53.4
$C_6H_{13}CHBrCHBrCOOH$	44	50.6	50.9	50.8

The reported melting point of α,β-dibromononanoic acid is 35°.[8]

The 1-Bromoolefins.—If the above α,β-dibromo acids are treated with an equivalent amount of dilute (5 or 10%) sodium carbonate the solutions formed appear to be stable at room temperatures for several days. If heated, however, they evolve carbon dioxide, become turbid and rapidly separate an oily layer, which partially distils with the steam when the mixture is boiled. Similar results were obtained by heating the ammonium, pyridinium, silver and potassium salts in aqueous solution. The table shows the comparative percentage yields of 1-bromo-1-octene from α,β-dibromopelargonic acid.

Salt	K	Na	Py	NH_4	Ag
Yield, %	30	30	26	20	20

With anhydrous pyridine dried and fractionated over barium oxide a different procedure was necessary. One mole of acid was dissolved in 3 moles of pyridine and the solution heated on the steam-bath. Within one-half hour a separation of pyridine hydrobromide occurred with an accompanying darkening of the solution and an evolution of carbon dioxide. Heating was continued for three hours, the brown solution cooled and poured into an excess of concentrated hydrochloric acid mixed with an equal weight of crushed ice. The lower oily layer was separated and distilled with water. The bromoolefins distil rapidly with the first few cubic centimeters of water. After drying over calcium chloride they are nearly pure and boil almost completely within a two degree range.

1-BROMOOLEFINS

	Yield, %	B. p., °C. (corr.)	Press., mm.	d^{20}_{20}	n^{20}_{D}	Analyses for bromine, % Calcd.	Found	
1-Propene[a]	28	58–60	747	1.4181	1.4560	66.1	65.9	65.7
1-Butene[b]	28	87–89	747	1.3123	1.4536	59.3	59.0	59.1
1-Pentene[c]	32	113–115	747	1.2391	1.4572	53.7	53.3	53.5
1-Hexene[d,e]	27	138–140	747	1.1910	1.4584	49.1	49.0	48.7
1-Heptene[c,d]	35	161–163	747	1.1553	1.4594	45.2	44.7	44.8
1-Octene[f]	26	178–180	750	1.1342	1.4602	41.9	41.7	41.7

[a] "Int. Crit. Tables," Vol. I, p. 182. [b] Lépingle, *Bull. soc. chim.*, **39**, 748 (1926). [c] Kirrmann, *ibid.*, **41**, 316 (1926). [d] Welt, *Ber.*, **30**, 1494 (1897). [e] Hecht and Strauss, *Ann.*, **172**, 70 (1874). [f] Rubien, *ibid.*, **142**, 298 (1867).

1-Bromo-1-octene gave a 70% yield of 1-octine, b. p. 123–126°, on dehalogenation with potassium hydroxide and mineral oil at 175°. The monobromoolefins react readily with one mole of bromine in carbon disulfide to yield colorless tribromides having a mild camphor-like odor. These products were not further investigated.

An attempt was made to prepare pure 1-bromo-1-octene through dehalogenation of 1,2-dibromooctane. A small sample of very pure 1-octene[9] was brominated in carbon disulfide at 0°. After isolation and purification the 1,2-bromooctane had the constants

---

[8] Harding and Weizmann, *J. Chem. Soc.*, **97**, 301 (1910).

[9] Kindly supplied by Professor C. E. Boord of this institution.

b. p. (12 mm.) 117°; n_D^{20} 1.4942. It was recovered unchanged after boiling for three hours with pure dry pyridine or with an ethyl alcohol solution of pyridine. With alcoholic potassium hydroxide a mixture was obtained which on account of the small amount available could not be separated completely into its components. The liquid gave a test for an acetylene (octine) with alcoholic silver nitrate and contained some 1-bromo-1-octene as well as 2-bromo-1-octene and a vinyl ether, all of which products are known to result from this type of reaction.

Alpha Bromo Acids.—The oils remaining after removal of the bromoolefins and acidification were separated and distilled under diminished pressure except in the case of the first member of the series. α-Bromocrotonic acid is soluble in water. It was therefore extracted with ether and recrystallized from hot water. Of the remaining acids those which were solid at room temperatures were recrystallized from petroleum ether.

α-BROMOOLEFINIC ACIDS

	M. p., °C.	B. p., °C.	Press., mm.	Analyses for bromine, % Calcd.	Found		Yield, %
Crotonic	106–107						55
α-Pentenoic	49–50	122–124	15	44.7	44.4	44.5	45
α-Hexenoic	37–38	143–145	15	41.4	41.3	41.2	40
α-Heptenoic	Oil	153–156	15	38.6	38.6	38.7	38
α-Octenoic	Oil	165–167	15	36.2	36.0	35.8	40
α-Nonenoic	Oil	176–179	15	34.0	33.5	33.4	35

α,α,β-Tribromo Acids.—The carbon disulfide solutions of the α-bromoolefinic acids readily absorbed one mole of bromine in the presence of direct sunlight to give practically quantitative yields of the corresponding tribromo acids. Less heat was evolved than in the bromination of the olefinic acids. The products except the eight and nine carbon atom acids formed masses of large hard white crystals upon evaporation of the solvent. After one recrystallization from petroleum ether they were pure. The oily tribromocaprylic and tribromopelargonic acids were left in a vacuum desiccator over solid potassium hydroxide for several days before analyzing.

α,α,β-TRIBROMO ACIDS

	M. p., °C.	Analyses for bromine, % Calcd.	Found	
Butyric	117.5			
Valeric	90.5–91	70.8	70.7	70.6
Caproic	102.5	68.0	67.7	67.8
Enanthic	72	65.4	65.4	65.3
Caprylic	Oil	63.0	63.3	63.2
Pelargonic	Oil	60.8	60.8	60.6

1,1-Dibromoolefins.—The tribromo acids were dissolved in a small excess of dilute aqueous sodium carbonate and the solutions heated to boiling. Turbidity appeared,

1,1-DIBROMOOLEFINS

	Yield, %	B. p., °C.	Press., mm.	d_{20}^{20}	n_D^{20}	Analyses for bromine, % Calcd.	Found	
1-Propene[a]	88	127.4	750	1.9803	1.5260	80.0	79.6	79.8
1-Butene	83	53–55	22	1.8348	1.5168	74.8	74.4	74.6
1-Pentene	79	72–74	22	1.7013	1.5097	70.2	69.8	69.7
1-Hexene	75	90–92	22	1.6047	1.5050	66.1	65.9	65.7
1-Heptene	74	105–107	22	1.5130	1.5009	62.5	62.2	62.3
1-Octene	70	120–122	22	1.4448	1.4978	59.3	59.0	58.9

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

carbon dioxide was evolved and oily layers formed which distilled with the water vapor. The products were dried over calcium chloride and distilled. The decreased yields found among the higher members of the series as indicated in the table below are probably the result of partial hydrolysis by water. Longer heating with water is necessary to steam distil these higher boiling substances than is necessary with the members of lower molecular weight.

With bromine the 1,1-dibromoolefins form tetrabromides which are colorless oils and which have an intense camphor-like odor. These products were not further investigated.

Summary

The decompositions of α,β-dibromo and α,α,β-tribromo aliphatic acids with alkaline reagents yield the corresponding 1-bromoolefins and α-bromoolefinic acids in the first case and 1,1-dibromoolefins in the second case.

The 1-bromo-1-olefins may serve as intermediates in the preparation of normal acetylenes in good yields. The 1-bromoolefins as well as the 1,1-dibromoolefins add one mole of bromine to yield oils having camphor-like odors.

COLUMBUS, OHIO

RECEIVED JUNE 19, 1933
PUBLISHED OCTOBER 6, 1933

[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF WASHINGTON]

Phosphoric Acid in Organic Reactions

BY WILLIAM M. DEHN AND KIRBY E. JACKSON

Phosphoric acid is superior to sulfuric acid as a catalyst in certain organic reactions of hydrolysis,[1] dehydration and isomerization. Its chief advantages are disclosed in its lesser tendency to carbonize or otherwise to react with the organic materials, hence these processes can be made to deliver larger yields of desired products. Furthermore, the phosphoric acid can be recovered from the reaction mixtures practically pure for repeated use.

We have found that it is the ideal catalyst for ketonic hydrolyses of alkyl acetoacetates, having obtained 95% yields of the ketones and no fatty acids, whereas sulfuric acid and the alkalies give less than 70% yields of the ketones. The advantages here result from lesser carbonization, from lesser quantities of water used, and in the simple method of reprocessing fractions containing unchanged acetoacetates. Because either acids or alkalies hydrolyze the acetoacetates, the mechanism of reaction seems to be conditioned by the capacity of the reagent to add to the reactant before hydrolysis results.

---

(1) For the use of phosphoric acid to prepare olefins, see Newth, *J. Chem. Soc.*, **79**, 915 (1901); Adams, Kamm and Marvel, THIS JOURNAL, **40**, 1951 (1918); German Patent 66,866.