

The data are presented in Table I. Because of the difficulty of reproducing on a small scale a plot of temperature *vs.* composition when the liquid and vapor are so nearly alike, this plot has been omitted. On a large-scale plot all of the points fall on smooth curves with no deviations as large as those given above. It is evident from these data that this system behaves in the normal manner for systems exhibiting a minimum boiling mixture. The azeotropic mixture contains 58.2 mole per cent. carbon tetrachloride and boils at 71.56° under 685 mm. pressure.

In Table II are given the various data available on the azeotropic constants for this system at different pressures. The values attributed to Tyrer were obtained after a careful consideration of his data and do not agree with those given in the International Critical Tables.<sup>3</sup>

Inspection of Table II shows that the rate of change of composition of the azeotrope with pressure is decreasing as the pressure decreases. This behavior is just the reverse of that found in numerous other systems which have been investigated over a range of pressures.<sup>4</sup> Because of this

(3) "International Critical Tables," McGraw-Hill Book Co., Inc., New York, N. Y., 1928, Vol. III, p. 312.

(4) (a) Wade and Merriman, *J. Chem. Soc.*, **99**, 997 (1911). (b) Merriman, *ibid.*, **103**, 628, 1790 (1913); (c) Vrevsky, *Z. physik. Chem.*, **81**, 1 (1912); **83**, 551 (1913).

TABLE II

AZEOTROPIC DATA AT DIFFERENT PRESSURES

P, mm.	B. p., °C.	Mole % CCl <sub>4</sub>	Observer
760	74.75	43	Young, <sup>5</sup> Lecat <sup>6</sup>
745	74.04	51.0 ± 0.5	Tyrer <sup>1</sup>
685.0	71.56	58.2	This paper
318.8	49.99	67.4	Zawidzki <sup>7</sup>

apparent difference in behavior, this system is being investigated over a wide pressure range in order to verify this difference with a single set of data.

The refractive index-composition curve falls just slightly below the straight line joining the indices of the two pure components. The maximum deviation comes at 50 mole per cent., and the curve appears to be symmetrical about this point.

### Summary

The system carbon tetrachloride-ethyl acetate has been investigated at 685 mm. and found to behave as expected for a system having a minimum boiling mixture, contrary to indications from other data.

(5) Young, "Distillation Principles and Processes," Macmillan and Company, London, 1922, p. 52.

(6) Lecat, "L'azeotropisme," Lamertin, Brussels, 1918, p. 136.

(7) Zawidzki, *Z. physik. Chem.*, **35**, 129 (1900).

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## The Peroxide Effect in the Addition of Reagents to Unsaturated Substances. XXII. The Addition of Hydrogen Bromide to Trimethylethylene, Styrene, Crotonic Acid, and Ethyl Crotonate

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Recently we described an abnormal addition of hydrogen bromide to 2-bromo-2-butene under peroxidic conditions in dilute pentane solution, and commented upon the efficacy of this method of obtaining the abnormal addition of this reagent.<sup>2</sup> Further interesting results, with the aid of this technique, now have been obtained with several more olefins.

**Addition of Hydrogen Bromide to Trimethylethylene.**—In 1904 Ipatieff and Dechanov<sup>3</sup> observed that, while treatment of trimethylethylene with hydrogen iodide or aqueous hydrobromic acid yielded exclusively the tertiary halide, addi-

tion of hydrogen bromide in 60% acetic acid gave 10–25% of *s*-isoamyl bromide (2-methyl-3-bromobutane). A similar result was reported by Michael and Zeidler.<sup>4</sup> Recently, however, Smith<sup>5</sup> has indicated that *t*-amyl bromide is the sole product of the addition of hydrogen bromide to this olefin and that peroxides are without effect upon the course of the reaction, but unfortunately he does not describe the experimental conditions employed. The latter conclusion is contradicted by the results of this investigation, as shown in Table I. In the absence of a solvent and air and in the presence of an inhibitor, a

(1) Du Pont Fellow 1938–1939.

(2) Walling, Kharasch and Mayo, *This Journal*, **61**, 1711 (1939).

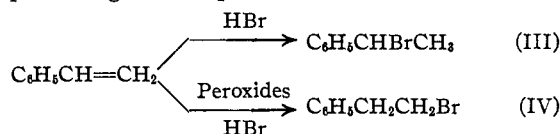
(3) Ipatieff and Dechanov, *Chem. Zentr.*, **76**, 11, 961 (1904).

(4) Michael and Zeidler, *Ann.*, **385**, 271 (1911).

(5) Smith, *Chemistry and Industry*, **67**, 561 (1938).



However, when the normal reaction is retarded by working in dilute pentane solution and peroxides are added, products may be isolated which contain as much as 80% of  $\beta$ -phenylethyl bromide (IV). There seems to be no reason to doubt that greater dilution and the slower addition of the halogen acid would result in an even greater percentage of this product.



**Addition of Hydrogen Bromide to Crotonic Acid and Ethyl Crotonate.**—Preliminary investigation in this Laboratory has found only one product (the usual  $\beta$ -bromo derivative) in the addition of hydrogen bromide to acrylic, crotonic and bromocrotonic acids<sup>14</sup> in both the presence and absence of oxygen and peroxides. Furthermore, no reversal of addition has been obtained with bromomaleic,<sup>15</sup> bromofumaric,<sup>15</sup> and tetrolic acid,<sup>16</sup> although in the latter case there is evidence that the products obtained in the presence of peroxides are stereoisomeric with those obtained in the absence of these materials.

We can now report that even in the presence of a peroxide, illumination, and dilution with a solvent such as pentane, the only products of the addition of hydrogen bromide to crotonic acid and ethyl crotonate are the  $\beta$ -bromo derivatives.

### Discussion

It is well established and is further shown in this paper that the normal addition of hydrogen bromide to olefins in which the double bond is not at the end of a hydrocarbon chain or is conjugated with a benzenoid nucleus proceeds with great rapidity. The present work shows that when these addition reactions are carried out in dilute pentane solution the normal reaction is retarded, and considerable abnormal addition of hydrogen bromide is observed. The previous paper in this series reached a similar conclusion in the case of 2-bromo-2-butene.

However, even though these conditions markedly retard the addition of hydrogen bromide to crotonic acid and its ethyl ester, no reversal of the direction of addition could be observed under even the most favorable conditions; neither do peroxides markedly accelerate the addition of hydro-

gen bromide to these substances in dilute pentane solution as they do in the case of other olefins.<sup>17</sup> This fact may indicate that the chain mechanism postulated for abnormal addition<sup>18</sup> is inoperative in the case of ethylenic bonds conjugated with a carboxyl or similar group. However, the alternative explanation cannot be excluded, that the mechanisms of both normal and abnormal addition lead, in the case of these compounds, to the formation of the same product. Indeed this explanation is to some extent supported by the reaction of tetrolic acids cited previously.

### Experimental

**Trimethylethylene and Hydrogen Bromide.**—Trimethylethylene was prepared from Eastman *t*-amyl alcohol. Four hundred grams was placed in a distilling flask equipped with an efficient condenser and a "cold finger" in the neck of the flask to minimize the distillation of alcohol. Thirty cubic centimeters of concentrated sulfuric acid was added, and the flask heated on a steam-bath. Distillation of the product (together with a little alcohol and water) began almost at once, and the reaction was practically complete in two hours. The distillate was washed with sodium carbonate solution, dried over calcium chloride, and distilled through a 1.5-meter packed column. Two fractionations yielded 114 g. (36%) of trimethylethylene, b. p. 37.6–38.0° (744 mm.).

Addition of hydrogen bromide was carried out as indicated in Table I. Seven grams (0.1 mole) of trimethylethylene was used in all experiments. The pentane employed was a 30–35° fraction free from unsaturated material obtained from the Skelly Oil Company, Tulsa, Oklahoma. Hydrogen bromide was passed in (at room temperature except in vacuum experiments) and seemed to react as rapidly as it was added. After the removal of solvent the products were distilled at 100 mm. through a Podbielniak column. The yield recorded in the table is the amount of distillate collected at 47–52°. In the experiment in nitrobenzene the addition products were quickly distilled from the reaction mixture at reduced pressure and then fractionated.

Preliminary experiments on a redistilled sample of Kahlbaum *t*-amyl bromide,  $n_D^{20}$  1.4420, indicated that it was hydrolyzed to the extent of 95% in fifteen minutes at 100° in 80% aqueous acetone, and that under the conditions of the experiment this amount presumably represented an equilibrium, as longer heating produced no fur-

(17) As an example, 0.1 mole of crotonic acid in 1.2 moles of pentane kept saturated with hydrogen bromide at about 20° reacted only to the extent of 40% in six hours, despite strong illumination and the presence of 0.0025 mole of lauroyl peroxide. In absence of solvent, crotonic acid, if warmed to start the reaction, will absorb the theoretical amount of hydrogen bromide in a few minutes. Propylene, by way of contrast, is subject to abnormal addition, and, while it undergoes the normal reaction in absence of solvent at a rate roughly comparable with crotonic acid, it reacts completely with hydrogen bromide in a few minutes in dilute pentane solution in the presence of only traces of peroxides (Mayo and Savoyias, kinetic investigation now in progress in this Laboratory).

(18) Kharasch, Engelmann and Mayo, *J. Org. Chem.*, **2**, 288 (1937).

(14) Kharasch and McNab, unpublished work.

(15) Kharasch, Mansfield and Mayo, unpublished work.

(16) Grigorieff, Ph.D. Dissertation, University of Chicago, 1939.

ther hydrolysis. Similarly, when the products of experiments I, II, and V were combined and carefully fractionated into four portions, the third and fourth fractions (which presumably contained the greatest proportion of 2-methyl-3-bromobutane) were hydrolyzed by this procedure to the extent of 17.9 and 5.7%, respectively. As it seemed likely that even the highest boiling fraction contained some *t*-amyl bromide, it was assumed for purposes of calculation that 2-methyl-3-bromobutane was not measurably hydrolyzed under these conditions. Accordingly, 0.3 g. of the addition products was weighed out into Pyrex tubes of about 10 cc. capacity, and 5 cc. of 80% aqueous acetone added. The tubes were then sealed and placed in boiling water for fifteen minutes. After cooling and opening, the liberated acid was titrated with standard base.

As an additional check, the indices of refraction of all products were determined, and the percentage of normal and abnormal product calculated. Although results by both methods are included in Table I, we consider those obtained by hydrolysis to be the more accurate. The index of refraction of 2-methyl-3-bromobutane was found to be  $n_D^{20}$  1.4453 by extrapolation.

**Styrene and Hydrogen Bromide.**—Styrene used in this investigation was obtained from the Bakelite Corporation, Bloomfield, New Jersey. As it contained hydroquinone to prevent polymerization, it was distilled *in vacuo* shortly before use. Experiments were performed as indicated in Table II. In all experiments, 10.4 g. of styrene was used; 9 g. of hydrogen bromide was passed in (at room temperature in all except vacuum experiments) and in no case did addition appear to require more than a few minutes. The products were worked up by distillation through a Podbielniak column at a pressure of 9 mm. of mercury. The yield recorded in Table II is based upon the weight of the fraction collected. In cases of addition in pentane, the solvent was removed before distillation by evaporation at atmospheric pressure.

For analysis, 0.2 g. of the product was weighed out into a Pyrex tube of about 10 cc. capacity, and 5 cc. of 80% aqueous acetone added. After sealing and heating for two hours in boiling water, the liberated acid was titrated with standard base. Experiments with samples of known composition indicated that, under these conditions, hydrolysis proceeded to the extent of 95% with  $\alpha$ -phenylethyl bromide as compared with less than 2% with  $\beta$ -phenylethyl bromide.

As a further check, the addition product of experiment I (Table II) were treated with alcoholic potassium hydrosulfide,<sup>19</sup> and the potassium salts of the resulting mercaptans allowed to react with 2,4-dinitrochlorobenzene according to the procedure of Bost, Turner, and Norton.<sup>20</sup> From the reaction mixture,  $\beta$ -phenylethyl 2,4-dinitrophenyl sulfide was obtained in yellow pearly plates (m. p. after crystallization from alcohol 87–88°). Similar treatment of the product from experiment II yielded  $\alpha$ -phenylethyl 2,4-dinitrophenyl sulfide (orange crystals, m. p. after crystallization from alcohol 108–109°).

**Addition to Crotonic Acid and Ethyl Crotonate.**—Two sets of conditions were chosen as favoring the abnormal reaction. (a) One-tenth mole of crotonic acid or ethyl

crotonate, 0.0025 mole of lauroyl peroxide, and 1.0 to 1.2 moles of pentane were placed in a Pyrex bomb tube and cooled to  $-80^\circ$ . One-eighth mole of hydrogen bromide was passed in, the tube sealed, and allowed to warm to room temperature. After standing overnight, the tubes were opened, the solvent evaporated off, and the products distilled under reduced pressure. (b) Hydrogen bromide (0.14–0.16 mole) was condensed in a Pyrex tube cooled to  $-80^\circ$ . By carefully raising the tube from the cooling-bath, a very slow stream of hydrogen bromide could be obtained. This was bubbled very slowly through another Pyrex vessel containing 0.1 mole of the unsaturated material and 0.0025 mole of lauroyl peroxide in 1.2 moles of pentane. During the addition the vessel was illuminated by a 500-watt incandescent lamp at a distance of 15 cm. and cooled to about  $20^\circ$  by a stream of water. After three to six hours the product was worked up as described under (a). Under these conditions, crotonic acid added hydrogen bromide to the extent of 40% in six hours, while in the case of ethyl crotonate the reaction was virtually complete in three hours.

Fifteen-hundredths gram of the crotonic acid addition product was weighed into a flask, and 2.00 ml. of 1.942 *N* potassium hydroxide solution added. After standing for one hour at room temperature the mixture was diluted with water and titrated with standard acid. Under these conditions hydrogen bromide was liberated from known  $\alpha$ - and  $\beta$ -bromobutyric acids to the extent of 3 and 98%, respectively. By this method all samples obtained by the addition of hydrogen bromide to crotonic acid contained over 95% of the  $\beta$ -bromo acid. A different method of analysis was used for the ester addition products on account of the partial hydrolysis of the esters. Three-tenths gram of the addition product was weighed out and 2.0 cc. of 1.8 *N* alcoholic potassium hydroxide added. After one minute the mixture was diluted with water and acidified with nitric acid. After addition of an excess of standard silver nitrate solution, the mixture was back titrated with ammonium thiocyanate solution. Under these conditions the  $\alpha$ - and  $\beta$ -bromo esters liberated 1.3 and 99.3%, respectively, of the theoretical bromide ion. By this method, all samples obtained by addition of hydrogen bromide to ethyl crotonate contained 97% or more of ethyl  $\beta$ -bromobutyrate.

### Summary

1. Trimethylethylene adds hydrogen bromide in the absence of oxygen and peroxides to give *t*-amyl bromide. Under conditions of peroxide catalysis the product contains as much as 64% of the abnormal product, 2-methyl-3-bromobutane.
2. Styrene adds hydrogen bromide in the absence of oxygen and peroxides to give  $\alpha$ -phenylethyl bromide. Under conditions of peroxide catalysis and in the presence of solvent the product contains as much as 80%  $\beta$ -phenylethyl bromide.
3. In presence or absence of peroxides, crotonic acid and ethyl crotonate yield only  $\beta$ -bromobutyric acid and ethyl  $\beta$ -bromobutyrate, respectively.

(19) Sontag, *Ann. Chim.*, (11) 1, 428 (1934).

(20) Bost, Turner, and Norton, *This Journal*, 54, 1985 (1932).