stants several per cent. higher than the original alcohol used, it should be reëmphasized that the solvent must be standardized against one of the pure dibromobutanes.

## Summary

Contrary to recent inferences in the literature, the reaction rate-dibromide method of analysis has been shown to give a reliable estimate of the composition of butene mixtures.

A dibromobutane mixture has been distilled at atmospheric pressure without undergoing appreciable decomposition or isomeric change.

Differences in composition of butenes obtained from the catalytic decomposition of 1-butanol are attributed to the effects of catalyst, temperature, etc., rather than to the method of analysis.

LOS ANGELES, CALIF. RECEIVED AUGUST 12, 1935

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

# Allylic Rearrangements. I. Crotyl and Methylvinylcarbinyl Bromides[1,2]

BY SAUL WINSTEIN AND WILLIAM G. YOUNG

The preparation of bromides by the action of hydrogen bromide or phosphorus tribromide on crotyl alcohol and methylvinylcarbinol has received much attention in recent years. Everyone agrees that an allylic rearrangement occurs when the latter alcohol is converted into its bromide but the extent to which it occurs has been uncertain. The existence of methylvinylcarbinyl bromide in the reaction product is not generally recognized. Some workers[3] report the isolation of pure crotyl bromide from both the primary and secondary alcohols while others[4] claim that mixtures of bromides are formed. The answer to this question is of utmost importance in the interpretation of the reactions of these bromides with water, alcohols, acetates, Grignard reagents, etc. For example, the abnormal coupling reactions reported by Prévost[5] with the 5 carbon bromide and by Van Risseghem[6] with crotyl bromide might actually be normal reactions if the bromides they used were mixtures instead of pure products as they assumed.

Baudrenghien[4a] and Gredy and Piaux[4c] have used physical methods in attacking this problem. The former attempted to fractionate his products at atmospheric pressure but could not isolate constant boiling materials. The latter have studied the Raman spectra of the bromides from crotyl alcohol and hydrogen bromide and from methylvinylcarbinol and phosphorus tribromide and have erroneously concluded that both products are identical mixtures of *cis* and *trans*-crotyl and methylvinylcarbinyl bromides. In a recent communication[7] we have shown that the problem involves not only the composition of bromides formed during their preparation but also the extent to which they rearrange during purification. The bromide preparations were found to be mixtures which could be separated into pure components by fractional distillation at low temperatures. It is the purpose of this paper to present the experimental work involving the isolation of pure crotyl and methylvinylcarbinyl bromides, the thermal rearrangement of these bromides to equilibrium mixtures, and the development of a method of analysis which may be applied to the study of the composition of bromide mixtures actually formed during the reaction of the alcohols with various reagents.

## Experimental

**Alcohols.**—Methylvinylcarbinol, prepared by Delaby's method as modified by Prévost,[3c] and crotyl alcohol, prepared by the aluminum isopropoxide[8] reduction of crotonaldehyde, were used as sources of the bromide mixture. The properties of the alcohol samples were: b. p. 96–97.5° and 120–122°, $n^{25}\text{D}$ 1.4119 and 1.4271, for methylvinylcarbinol and crotyl alcohol, respectively.

**Preparation of Mixtures of Crotyl and Methylvinylcarbinyl Bromides.**—The bromide mixtures were prepared

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[1] This work was accomplished with the aid of a grant from the Board of Research of the University of California.

[2] This paper, which was abstracted from a thesis submitted by Saul Winstein in partial fulfilment of the requirements for the degree of Master of Arts, was presented before the Organic Section at the ninetieth meeting of the American Chemical Society held in San Francisco, August 21, 1935.

(3) (a) Charon, *Ann. chim. phys.*, [7] **17**, 216 (1899); (b) Claisen and Tietze, *Ber.*, **59**, 2344 (1926); (c) Prévost, *Ann. chim.*, [10] **10**, 113, 147 (1928); (d) Juvala, *Ber.*, **63**, 1989 (1930).

(4) (a) Baudrenghien, *Bull. soc. chim. Belg.*, **31**, 160 (1922); (b) Young and Prater, THIS JOURNAL, **54**, 404 (1932); (c) Gredy and Piaux, *Bull. soc. chim.*, [5] **1**, 1481 (1934).

(5) (a) Prévost and Daujat, *Bull. soc. chim.*, [4] **47**, 588 (1930); (b) Prévost and Richard, *ibid.*, [4] **49**, 1368 (1931).

(6) Van Risseghem, *Bull. soc. chim. Belg.*, **39**, 349 (1930).

(7) Young and Winstein, THIS JOURNAL, **57**, 2013 (1935).

(8) Young, Hartung and Crossley, THIS JOURNAL, **58**, 100 (1936).

by the methods of Charon,[3a] Bouis[9] and Claisen and Tietze[3b] except that the crude preparations were generally purified by a distillation at 93 mm. instead of atmospheric pressure. The yields were 80–90%. Further details on the various preparations are not given since the crude products all had an opportunity to become equilibrium mixtures before purification. The unexpected mobility of these bromides was not observed until after they had been prepared.

**Distillations and Fractionations.**—All of the bromide preparations boiled over a large range of temperature. At atmospheric pressure the range varied from 1–12° depending on the apparatus and rate of distillation. Since redistillation of a sample always gave a different range, it was concluded that the product was unstable at temperatures in the neighborhood of 100°. Reduced pressure distillation was then employed.

Preliminary fractionation of the bromide mixtures at 93 mm. through a 100-cm. column filled with glass rings and equipped with a Hopkins reflux condenser were more successful, giving a boiling range of 31–48°, but the separation still was not as sharp as might be expected due to an appreciable amount of rearrangement even at this temperature. At this time it was noticed that the different fractions underwent a slow change in refractive index on standing at room temperature, an equilibrium value being obtained from all of them.

The equilibrium between crotyl and methylvinylcarbinyl bromides was effectively demonstrated by the slow fractionation of a mixture through the 100-cm. column at atmospheric pressure. The rate of distillation could be controlled so as to give a distilling temperature between 88–90°, the equilibrium being established so rapidly in the boiler that the secondary bromide was replaced as fast as it was removed at the top of the column. It was in this way that mixtures which were mainly secondary bromide were prepared. Thus, to illustrate, a typical experiment of this sort gave as the distillate a product boiling at 89° and possessing $n^{23}\text{D}$ 1.4636, which corresponds to 87.5% secondary and 12.5% primary bromides, whereas the starting material possessed $n^{23}\text{D}$ 1.4780, which corresponds to 13% secondary and 87% primary. This same effect took place to a much smaller extent when the efficiency of fractionation was decreased. Thus, a distillation of the same initial material through an empty 25 cm. Hempel column gave a product of $n^{23}\text{D}$ 1.4743, which corresponds to 32% secondary and 68% primary and a distillation from an ordinary distilling flask gave a distillate of $n^{23}\text{D}$ 1.4755, which gives an analysis of 26% secondary and 74% primary bromides.

Isolation of the pure primary and secondary bromides was effected by fractionation through a jacketed, all-glass, 100-cm., Claisen-head column full of glass rings and equipped with a Hopkins condenser, cold alcohol–water solution being pumped through the Hopkins condenser and column-jacket by a refrigeration unit. At the start of a fractionation when the pressure was maintained at 14 mm. and the cooling liquid at −5°, the product distilled at −2°. When the rate of distillation became low, the pressure was gradually lowered to 5 mm., the jacket temperature was changed to −1° by decreasing the rate of flow of the cold solution, and the distillation temperature rose to 2°. The fractions obtained were stored at −15°, at which temperature the rate of rearrangement was negligible. Fractionation curves for two mixtures are included in Fig. 1. Mixture I was a preparation obtained by partial fractionation of an equilibrium mixture at 93 mm. Mixture II was prepared by the slow atmospheric pressure fractionation described above. Mixture I, $n^{23}\text{D}$ 1.4788, corresponding to 8.8% secondary and 91.2% primary was found to be approximately 7 and 93%, respectively, by distillation at 0°, and mixture II, $n^{23}\text{D}$ 1.4636, 12.4% primary and 87.6% secondary by refractive index analysis, gave approximately 10 and 90%, respectively, by distillation, the variation probably being within the limits of accuracy of the distillation method.

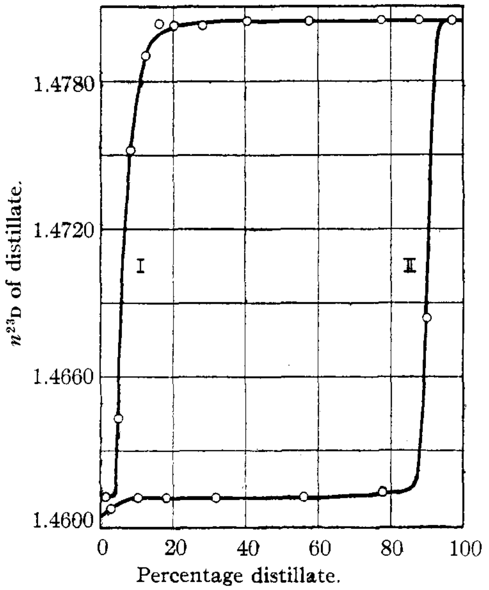

Fig. 1.—Fractionations of mixtures of crotyl and methylvinylcarbinyl bromides: Mixture I, mainly primary bromide; Mixture II, mainly secondary bromide.

**Determination of Physical Properties.**—The refractive indices were determined on Zeiss and Spencer Abbe instruments, calibrated against water and test plates. It was found that readings taken between 20–25° could be corrected to a standard temperature for comparison purposes by applying a correction of 0.0005 per degree. It was necessary to take readings as soon as possible since some of the bromide preparations rearranged more rapidly after being on the ground glass surface of the refractometer prism for a short time. The optical surface of the prism was slowly damaged by contact with these compounds.

Densities were determined with a 10-ml. cone-shaped pycnometer having a thermometer ground in the neck. The values were calculated to vacuum. As a precautionary measure the samples were checked with a refractometer before and after the density was taken.

The boiling points of the pure bromides were determined at 93 mm. by distilling 5-g. samples from a small distilling flask, the rate of rearrangement at these temperatures being low enough so that the variation in boiling points during

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(9) Bouis, *Bull. soc. chim.*, [4] **41**, 1160 (1927).

the short time of distillation was negligible. The boiling point of the methylvinylcarbinyl bromide at atmospheric pressure was determined on a thermometer placed over a 2-g. sample of the bromide in a thin-walled test-tube. The sample was brought to boiling in fifteen seconds. The thermometer recorded the temperature in fifty seconds, and then the temperature changed almost linearly with time due to the rearrangement. An extrapolation to correct for the change in boiling point during the climb of the mercury column involved a correction of less than 1° on the temperature reading after fifty seconds. The primary bromide rearranged so rapidly at its boiling point that even this latter procedure was not applicable.

The physical properties of the pure crotyl and methylvinylcarbinyl bromides and of two mixtures of them made up by weight are shown in Tables I and II.

TABLE I

THE PHYSICAL PROPERTIES OF CROTYL AND METHYLVINYLCARBINYL BROMIDES

| Isomer | Secondary | Primary |
|---|---|---|
| $n^{25}_{D}$ | 1.4602 | 1.4795 |
| $d^{25}_{4}$ | 1.2998 | 1.3335 |
| $M_D$ | 28.46 | 28.73 |
| Boiling points, °C. | −2 (14) | 2 (5) |
| | 31 (93) | 49 (93) |
| | 86.5 (760) | > 107 (760) |

TABLE II

THE ANALYSIS OF KNOWN MIXTURES OF CROTYL AND METHYLVINYLCARBINYL BROMIDES

| Mixture No. | | 1 | 2 |
|---|---|---|---|
| $n^{25}_{D}$ | Calcd. | 1.4742 | 1.4667 |
| | Exptl. | 1.4741 | 1.4667 |
| $d^{25}_{4}$ | Calcd. | 1.3242 | 1.3111 |
| | Exptl. | 1.3243 | 1.3113 |

**Equilibrium Determinations.**—For determinations of the equilibrium values at 75 and 100°, small samples of the pure bromides were sealed in 8-cm. test-tubes and placed in thermostats. At intervals, tubes were removed, quenched in an ice–HCl mixture and opened. The rearrangement was followed by refractive index measurements. The values for the equilibrium refractive index of several determinations agreed to 0.0001. The results together with the approximate times required to reach equilibrium at the several temperatures are shown in Table III.

**Carius Analyses and Molecular Weight Determinations.**—The bromide samples were analyzed for bromine by the Carius method. The extreme range of values for per cent. bromine was 59.03–59.30, theoretical being 59.20. Molecular weight determinations by the Victor Meyer method at 140° on the crotyl and methylvinylcarbinyl bromides varied from 136.1 to 136.5, theoretical being 135.0.

**Discussion of Results.**—The two bromides isolated (Fig. 1) were constant boiling at temperatures where rearrangement was negligible, they hydrolyzed rapidly, formed Grignard reagents readily, reacted readily with silver nitrate solutions and rearranged reversibly into one another, the equilibrium mixture obtained from either isomer consisting of the same two products. In view of this and the fact that their physical properties do not agree with those of the previously known bromobutenes, it is certain that the products are crotyl and methylvinylcarbinyl bromides and that a proton migration to give compounds of the type $H_3CCH{=}CBrCH_3$ does not take place in this allylic system as has been noticed in others.[10]

The crotyl bromide may theoretically exist in two modifications, *cis* and *trans*. In our work there was no evidence of more than one primary isomer. The form of the distillation curves of the mixtures (Fig. 1) and the agreement between analyses by refractive index and distillation procedures make the presence of more than one primary isomer doubtful. Gredy and Piaux[4c] by their qualitative method based on observation of intensity of Raman lines report the presence of *cis*-crotyl bromide in their mixtures, giving an upper limit of 10% for the quantity. If 10% *cis*-crotyl bromide is present, then it is necessary to conclude that the properties of the *cis* and *trans* isomers are almost identical. However, this is not the case with the *cis* and *trans* 2-bromobutenes-2.[11]

In any case, it is possible to consider the mixtures as two component systems and to analyze them for their crotyl and methylvinylcarbinyl contents by a measurement of the refractive index or density. Excellent agreement was found in the case of known mixtures, made up by weight, between the measured refractive indices and densities and those calculated on the basis of linear relations between these properties and composition (Table II).

Since the rate of rearrangement was found to be affected by mere traces of impurities, the nature of which are still uncertain, studies on the kinetics of the rearrangement have not yet been completed. For example, different bromide samples yielding good Carius analyses, and giving the same equilibrium refractive index, rearranged at different rates, and sometimes even varied in the different tubes of the same sample, possibly due to traces of adsorbed material on the walls of the glass. Because of the variation in rates, only approximate times for establishment of equilibrium

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[10] (a) Gilman and Harris, THIS JOURNAL, **53**, 3541 (1931); (b) Rambaud, *Bull. soc. chim.*, [5] **1**, 1206 (1934).

[11] Lépingle, *ibid.*, **39**, 741 (1926).

have been listed (Table III) to indicate the order of magnitude.

From the change of the equilibrium with the temperature, the difference in molal heat contents of methylvinylcarbinyl and crotyl bromides is calculated to be approximately 300 calories from the van't Hoff equation.

From the foregoing observations it is evident that the composition of bromide preparations which have been distilled at atmospheric pressure is independent of the method of preparation. Thus, the conclusion of Gredy and Piaux[4c] regarding the identity of mixtures from two different methods was unwarranted. Also, the refractive index of the one mixture for which these workers give physical properties was 1.4750 at 23° which corresponds to 28% secondary bromide. Their Raman study gave an upper limit of 10% secondary for the mixture. Evidently the mixture attained equilibrium during the interval between the refractive index determination and the Raman spectra measurements. If this is true the agreement with our equilibrium value (Table III) is even better than might be expected considering the fact that these workers did not have the pure substances on which to measure intensities of Raman lines.

TABLE III

DATA CONCERNING THE EQUILIBRIUM BETWEEN CROTYL AND METHYLVINYLCARBINYL BROMIDES

| Temp., °C. | 100 | 75 | 20 |
|---|---|---|---|
| Time | < 5 min. | 1 hour | 10 days[a] |
| $n^{25}\text{D}$ | 1.4767 | 1.4769 | 1.4770 |
| % sec. | 14.5 | 13.5 | 13.0 |
| % prim. | 85.5 | 86.5 | 87.0 |

[a] If the product has been distilled at atmospheric pressure the time may be much shorter.

It may now be explained how some investigators obtained products of narrow boiling range at atmospheric pressure. If the distillation is carried out in an ordinary distilling flask and the rate of distillation is slow enough to allow the allylic equilibrium to be maintained in the boiler, the constant temperature recorded will be that of the boiling point of the equilibrium mixture, the distillate containing considerably more secondary bromide than the equilibrium mixture. If fractionation occurs the boiling point can again be kept constant at some lower temperature, the distillate containing still more secondary bromide. On the other hand, if the distillation is so rapid that equilibrium is not maintained in the boiler a boiling range is observed.

A consideration of the properties of the product of Juvala[3d] and of the 104–107° fraction of Baudrenghien[4a] shows that these products were 29 and 25% secondary bromide, respectively, in good agreement with the compositions observed by us after distillations at atmospheric pressure with very little fractionation.

The authors are indebted to Dr. G. Ross Robertson for his helpful suggestions.

## Summary

Pure crotyl and methylvinylcarbinyl bromides have been isolated for the first time.

Both bromides rearrange to an equilibrium mixture very rapidly at 100° and at a measurable rate even at room temperature.

A method of analysis of mixtures of these bromides is given.

Conflicting reports in the literature concerning the boiling points and compositions of bromides made from crotyl alcohol and methylvinylcarbinol have been explained.

LOS ANGELES, CALIF. RECEIVED OCTOBER 4, 1935