Summary

1. An investigation has been made of the complex structure of the third harmonic O–H bands of ethylene chloro and bromohydrin, methyl cellosolve, trimethylene chloro and bromohydrin, propylene chlorohydrin, and *sym*-glycerol dichlorohydrin. These substances were all studied in the vapor state. In all cases except trimethylene chloro and bromohydrin the substitution of a halogen or a methoxy group in the alcohol has given rise to one or more new O–H bands.

2. Photometric studies have been made of the effect of temperature on the relative intensities of the components of the O–H bands in *o*-chlorophenol, propyl alcohol and ethylene chlorohydrin. It is found that in the vapor state at 180° the energy and free energy of the *trans* form of *o*-chlorophenol exceed those of the *cis* form by 3.9 ± 0.7 and 2.8 ± 0.5 kgcal., respectively.

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

Allylic Rearrangements. X. The Reproducibility of the Standard Methods for the Preparation of Butenyl Bromide Mixtures[1]

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As a result of a recent study[2] of the composition of butenyl bromide mixtures obtained from crotyl alcohol and methylvinylcarbinol by the action of various solutions of hydrogen bromide *under controlled conditions*, a mechanism was proposed for the reaction[3] in which two simultaneous processes were considered. Process 1 assumed an opportunity for resonance of the reacting oxonium ion of the alcohol and hence for the formation of the same mixture of bromides from either the primary or secondary alcohols. Process 2, a normal substitution without resonance, gives only primary bromide from the primary alcohol and secondary bromide from the secondary alcohol. Since the values calculated for M (the fraction of alcohol reacting by Process 2), N_r (the refractive index of the bromide mixture formed by Process 1) and P_r (the percentage of primary bromide in the bromide mixture formed by Process 1 due to resonance) are dependent on the accuracy with which the composition of the butenyl bromide mixtures (prepared by the various standard methods) can be determined, it is highly desirable to test the reproducibility of the standard methods; especially since we have continually pointed out the difficulties encountered by other workers due to the extreme mobility of the bromides.

The results of the present investigation are summarized in Table I along with the results previously reported.[2,3] In general, the average deviation of the refractive index of the butenyl bromide mixture obtained from the same alcohol with a given standard method is ±0.0001 although with the standard method 3 (saturated hydrobromic acid at 0°) the mean deviation is ±0.00016. Two cases were observed where the previous results were in error. The action of hydrogen bromide gas at −20° on methylvinylcarbinol gave a bromide mixture with a refractive index 0.0010 unit lower than that previously reported, showing that a small amount of rearrangement had occurred in the previous case in spite of the special precautions which were taken to avoid it. The discrepancy observed between the results obtained by method 7 (the action of glacial acetic acid saturated with hydrogen bromide at 0°) on crotyl alcohol were traced to a different cause. A preliminary run proved that insufficient time had been allowed for the reaction (twenty-five min.). Hence the product contained traces of unreacted alcohol. This was indicated by a low Carius analysis (Br = 57.7% instead of 59.2%). As a result, the rearrangement of the sample at 100°, to get the corrected refractive index, caused the formation of dibutenyl ether which lowered the refractive index of the sample. Proof of this was found when a mixture of butenyl bromides was contaminated with a quantity of crotyl alcohol comparable with that suspected to be present in the bromide mixture prepared in

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[1] This work, which was accomplished with the aid of a grant from the Board of Research of the University of California, was presented before Section C of the Pacific Division of the American Association for the Advancement of Science at Stanford University, June 29, 1939.

[2] Young and Lane, THIS JOURNAL, **59**, 2051 (1937).

[3] Young and Lane, *ibid.*, **60**, 847 (1938).

TABLE I

SUMMARY OF COMPOSITIONS OF BUTENYL BROMIDES OBTAINED FROM CROTYL ALCOHOL AND METHYLVINYLCARBINOL UNDER CONTROLLED CONDITIONS

Standard experimental method	Butenol used	n^{25}D of bromide mixture (cor.)		Compn. of bromide mixture,[a] %		Diff. in % primary bromide from primary and secondary alcohols
		Young and Lane[2,3]	Young and Nozaki	Primary bromide	Secondary bromide	
1. 48% HBr at −15°	Primary	1.4768 1.4768	1.4767 1.4769	86.0	14.0	2.8
	Secondary	1.4763 1.4762	1.4763	83.2	16.8	
2. 48% HBr + H_2SO_4 at −15°	Primary	1.4764	1.4764	84.0	16.0	4.2
	Secondary	1.4755	1.4757	79.8	20.2	
3. Saturated HBr at 0°	Primary	1.4755 1.4752	1.4756 1.4758 1.4756	79.3	20.7 ± 1.5	5.6
	Secondary	1.4746 1.4745	1.4742	73.7	26.3 ± 1.0	
4. HBr gas at −20°	Primary	1.4761	1.4763	82.9	17.1	12.2
	Secondary	1.4749	1.4739 1.4738	(70.7)	(29.3)	
7. Glacial AcOH satd. HBr gas at 0°	Primary	1.4763	1.4767	(85.5)	(14.5)	13.7
	Secondary	1.4740	1.4741	71.8	28.2	

[a] All percentages are the average of the results of both determinations except those enclosed in parentheses which are based on the present work only.

acetic acid by standard method 7. After rearrangement the contaminated bromide possessed a refractive index 0.0003 unit lower than it should, showing that ether had been formed. Consequently the time allowed for reaction by standard method 7 was increased to forty-five minutes. Using the modified procedure, both crotyl alcohol and methylvinylcarbinol gave bromide mixtures free from alcohol (Br = 59.23%). The revised values for the compositions of the bromide mixtures (columns 5 and 6) and for the differences in % primary bromide in the bromide mixtures obtained from the primary and secondary alcohols (column 7) are averages of the results of both investigations except for the two cases discussed above where the results of the present investigation are shown to be more reliable.

The Thermal Rearrangement of the Butenyl Bromides.—One objection to the previous work done in correlating the compositions of butenyl bromide mixtures produced from the butenols (by resonance process 1B) with those of the equilibrium mixtures produced by thermal rearrangement of the primary and secondary bromides under the same conditions, was that the thermal rearrangements were carried out in two-phase systems. Further work on the rearrangement of butenyl bromides (this time dissolved in a solution of hydrogen bromide in glacial acetic acid) gives a product having a refractive index qualitatively in agreement with N_r calculated[3] from the data obtained under the same conditions (standard method 7). When attempts were made to rearrange the primary and secondary butenyl bromides at room temperature in glacial acetic acid saturated with hydrogen bromide, it was discovered that addition of hydrogen bromide occurred faster than rearrangement. As a result the product was a mixture of dibromobutanes. However, at 15° in the presence of a trace of benzoyl peroxide it was possible to obtain a thermal equilibrium of the bromides before too large a quantity of dibromobutane had been formed. Although the last two runs listed in Table II show a qualitative agreement between the equilibrium refractive index of n^{25}D 1.4765 and calculated value n^{25}_{r} 1.4764, it is recognized that the interpretation may be debatable. It should be recognized, however, that the accuracy of the work was limited in two ways. First, it was difficult to allow sufficient time to establish equilibrium without producing large quantities of dibromobutane; second, it was necessary to effect a quantitative separation of the mono and dibromides at low temperatures to avoid rearrangement of the butenyl bromide portion. Runs 1 and 2 are of little value since they were carried out with short reaction times and obviously had not come to equilibrium.

TABLE II

THE THERMAL REARRANGEMENT OF BUTENYL BROMIDES AT 15° IN GLACIAL ACETIC ACID SATURATED WITH HYDROGEN BROMIDE

Run	Butenyl bromide	$n^{25}\mathrm{D}$ of crude bromide before fractionation	$n^{25}\mathrm{D}$ of butenyl bromide fraction	$n^{25}\mathrm{D}$ after rearrangement at 100°	$n^{25}\mathrm{D}$ of butenyl bromide mixt. (corrected)[2]
1	Primary	1.4900	1.4779	1.4774	1.4772
2	Secondary	1.4820	1.4761	1.4766	1.4762
3	Primary	1.4890	1.4768	1.4771	1.4764
4	Secondary	1.4920	1.4771	1.4772	1.4766

Experimental Part

Alcohols.—Crotyl alcohol, b. p. 121–122°, was prepared by the aluminum isopropoxide method.[4,5] Methylvinylcarbinol, 96–97°, $n^{25}\mathrm{D}$ 1.4110, was supplied by the Shell Development Company, through the courtesy of Dr. E. C. Williams.

Pure Butenyl Bromides.—Crotyl bromide, and methylvinylcarbinyl bromide were prepared as previously described.[6]

The Synthesis of Butenyl Bromide Mixtures from Crotyl Alcohol and Methylvinylcarbinol by Standard Methods.—The reproducibility of the standard methods reported by Young and Lane,[2,3] for preparing butenyl mixtures under controlled conditions, has been tested. The exact directions described by them for synthesizing and purifying the bromide mixtures have been followed except in the case of method 3 (saturated hydrobromic acid at 0°), and method 7 (glacial acetic acid saturated with hydrogen bromide at 0°) where the total reaction times were extended twenty minutes. This was done to assure completion of the reaction since in a preliminary run with method 7 the bromide mixture contained traces of crotyl alcohol which reacted with the bromide during the rearrangement at 100° and consequently interfered with the determination of the corrected refractive index. After this modification had been made the bromide preparations always contained the correct amount of bromine by Carius analysis.

The Rearrangement of Pure Butenyl Bromides in Glacial Acetic Acid Saturated with Hydrogen Bromide.—Since preliminary attempts to rearrange the butenyl bromides at 25° gave only 2,3-dibromobutane, while runs at 0° gave too slow rearrangement, it was necessary to add benzoyl peroxide[7] to speed up the rearrangement and to choose a temperature at which equilibrium of the bromide could be attained without excessive amounts of dibromides being formed. The final procedure adopted is given below: thirty-five grams of glacial acetic acid was placed in a glass-stoppered oil sample bottle and saturated with hydrogen bromide at 10°. After 8.0 g. of pure primary or secondary butenyl bromide, 0.4 g. of benzoyl peroxide and 1.5 ml. of water were added, the bottle was stoppered and the mixture shaken for fifteen to twenty minutes at 15°. The mixture was then cooled rapidly to 0° and poured over 100 g. of crushed ice and 35 g. of sodium bicarbonate in a 500-ml. separatory funnel. As soon as the initial effervescence had subsided, 35 g. of bicarbonate and more ice were added. The neutralization of the acid took nearly an hour but the ice and salt mixture present maintained a temperature several degrees below zero. The bromide layer was next washed twice with cold bicarbonate solution, then with ice water and placed over anhydrous calcium chloride at −15° for several hours. The resulting crude, dry bromide mixture was partially purified by evaporation at 2 mm. pressure. The butenyl bromide portion was then separated from dibromides by fractionation at 3 mm. pressure through a 20-cm. column which was filled with glass helices and equipped with a Hopkins condenser and an ice-filled jacket. The experimental results are shown in Table II.

Summary

The standard methods developed by Young and Lane[2] for preparing butenyl bromide mixtures from butenols under controlled conditions have been tested with both crotyl alcohol and methylvinylcarbinol. The compositions of the bromide mixtures produced are in good agreement with those previously reported except for two cases which have been explained.

The thermal rearrangement of pure primary and secondary butenyl bromides in glacial acetic acid saturated with hydrogen bromide produces equilibrium mixtures which possess refractive indices qualitatively in agreement with the calculated value of n_r or the bromide mixture produced from the butenols by process 1[3] involving resonance.

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[4] Young, Hartung and Crossley, THIS JOURNAL, **58**, 100 (1936).

[5] The crotonaldehyde used in preparing the crotyl alcohol was kindly furnished by the Niacet Chemicals Corporation, through the courtesy of Mr. G. M. Bramann.

[6] (a) Young and Lane, THIS JOURNAL, **59**, 2054 (1937); (b) Winstein and Young, *ibid.*, **58**, 104 (1936).

[7] Kharasch, Margolis and Mayo, *J. Org. Chem.*, **1**, 397 (1936).