saturated molecule and one silver ion with two unsaturated molecules. In the case of two hydrocarbons, *viz.*, biallyl and dicyclopentadiene, solid silver complexes were obtained.

Equilibrium constants have been obtained for the reactions of silver ion with all of the unsaturated compounds mentioned (except dicyclopentadiene) at 25°, and with trimethylethylene, cyclohexene and phenol at 0°. For trimethylethylene and cyclohexene it has been found that $\Delta H = -6.0$ kcal.

Neither *cis*-2-butene nor *trans*-2-butene isomerizes in the presence of silver ion.

In aqueous solution the following ions fail to form complexes with an olefin: Cd^{++}, Co^{++}, Cr^{+++}, Cu^{++}, Fe^{+++}, Ni^{++}, Pb^{++}, Tl^{+}, Zn^{++}.

A structure is proposed for the ethylenic silver ion complex, according to which the ethylenic compound is able to occupy one of the two coördination positions of silver by acting as the donor of an electron pair. A covalence joins the silver atom to one of the two carbon atoms, and a positive charge appears on the other. Resonance involving two such bonded forms and an unbonded form is believed to account for the stability of the complex.

It is believed that many other coördination complexes have similar structures; for example, those of unsaturated compounds with platinum salts, anhydrous aluminum, ferric and zinc chlorides, iron carbonyl residues and nitro compounds. It is possible that complexes of a still lower order of stability such as those with oxygen, protons and positive bromine atoms, have similar structures.

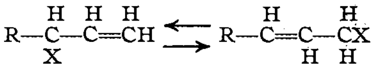
PASADENA, CALIF. RECEIVED NOVEMBER 29, 1937

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

Allylic Rearrangements. V. The Mechanism of the Reaction of Crotyl Alcohol and Methylvinylcarbinol with Solutions of Hydrogen Bromide[1,2]

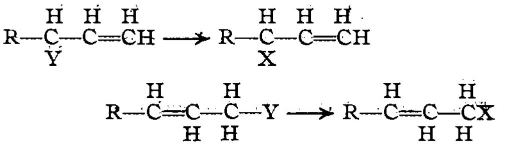
BY WILLIAM G. YOUNG AND JOHN FERO LANE

The application of the electronic theory of valence has thrown considerable light upon the nature of allylic rearrangements. Recognition by Ingold and co-workers that allylic (anionotropic) systems are special cases of tautomerism has been largely responsible for the progress which has been made.[3] Using the concepts developed to correlate reactions of prototropic systems, these workers have been able to show that the mobility of the allylic system



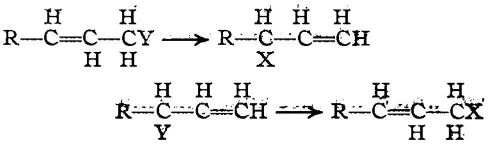
$$\mathrm{R-\underset{X}{\overset{H}{C}}-\overset{H}{C}=\overset{H}{C}H \rightleftarrows R-\overset{H}{C}=\underset{H}{C}-\underset{H}{\overset{H}{C}}X} \qquad \text{(I)}$$

is dependent on the nature of R and X and on the dielectric constant of the solvent. Prévost[4] and Meisenheimer and Link[5] also have been partially successful in developing concepts which correlate the experimental facts at hand. Unfortunately, the successful application of any of these concepts has been handicapped by the presence in the literature of many conflicting experimental data. In studying allylic rearrangements it is of vital importance to recognize that transformations of the type II



$$\mathrm{R-\underset{Y}{\overset{H}{C}}-\overset{H}{C}=\overset{H}{C}H \longrightarrow R-\underset{X}{\overset{H}{C}}-\overset{H}{C}=\overset{H}{C}H}$$
$$\mathrm{R-\overset{H}{C}=\underset{H}{\overset{H}{C}}-\underset{H}{C}-Y \longrightarrow R-\overset{H}{C}=\underset{H}{C}-\underset{H}{\overset{H}{C}}X} \qquad \text{(II)}$$

may be complicated by the occurrence of a thermal rearrangement of the type I, which takes place subsequent to the type II reaction, thus giving the impression that a reaction of type III is also involved.



$$\mathrm{R-\overset{H}{C}=\underset{H}{\overset{H}{C}}-\underset{H}{C}Y \longrightarrow R-\underset{X}{\overset{H}{C}}-\overset{H}{C}=\overset{H}{C}H}$$
$$\mathrm{R-\underset{Y}{\overset{H}{C}}-\overset{H}{C}=\overset{H}{C}H \longrightarrow R-\overset{H}{C}=\underset{H}{C}-\underset{H}{\overset{H}{C}}X} \qquad \text{(III)}$$

Such a thermal rearrangement may be the result of the technique used in carrying out the type II reaction or in the isolation and purification of the reaction product. The failure of many workers

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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.

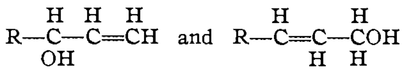
(2) This paper was abstracted from a dissertation submitted by John Fero Lane in partial fulfilment of the requirements for the degree of Master of Arts.

(3) Burton and Ingold, *J. Chem. Soc.*, 904 (1928); see also 1. W. Baker's "Tautomerism," Routledge, London, 1934, for an excellent summary of the work on anionotropy.

(4) Prévost, *Compt. rend.*, **185**, 132, 1283 (1927); **187**, 1052 (1928); and *Ann. chim.*, [10] **10**, 117 (1928).

(5) Meisenheimer and Link, *Ann.*, **479**, 211–277 (1930).

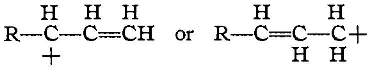
to appreciate this has resulted in the accumulation of a large amount of data which are of doubtful value. The literature on the alkenyl halides presents a good example of this unfortunate situation. Some workers claim that the two isomers



$$\mathrm{R{-}\underset{OH}{\overset{H}{C}}{-}\overset{H}{C}{=}\overset{H}{C}H} \quad \text{and} \quad \mathrm{R{-}\overset{H}{C}{=}\underset{H}{C}{-}\underset{H}{\overset{H}{C}}OH}$$

form only the primary bromide while others report that mixtures of the primary and secondary bromides are produced.[6] Furthermore, the alkenyl bromides have been converted into hydrocarbons, esters, ethers, amino acids and alcohols and conclusions have been drawn regarding the amount of rearrangement which accompanies the various reactions. In most of the work done by others, conditions were used which are now known[6] to cause thermal rearrangement of the starting materials.

In dealing with compounds which may give rise to reactions of types II and III, it is of the utmost importance to determine the nature of the reaction product RC_3H_4X, that is, whether it is a pure compound or a mixture. If a mixture results, it is important to know whether its composition is the same when prepared from both the primary and secondary isomers, RC_3H_4Y. The theory advanced by Prévost[4] requires that reactions involving the formation of either of the cations



$$\mathrm{R{-}\underset{+}{\overset{H}{C}}{-}\overset{H}{C}{=}\overset{H}{C}H} \quad \text{or} \quad \mathrm{R{-}\overset{H}{C}{=}\underset{H}{C}{-}\underset{H}{\overset{H}{C}}{+}}$$

should give the same mixture of products and that the composition of these products should be independent of the character of the anions leaving the molecule.

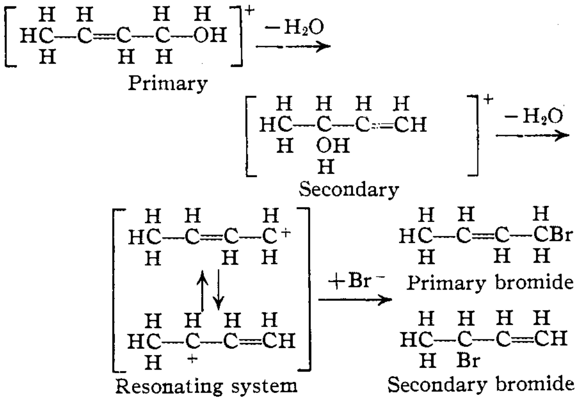
As a result of carefully controlled experiments by Meisenheimer and Link[5] and by workers in this Laboratory,[7] it is now well established that in certain cases the same mixtures of products are formed regardless of the starting material while in others the primary and secondary isomers give rise to different mixtures of products. Consequently, the concept advanced by Prévost[4] is inadequate to account for all of the facts.

It is the purpose of this paper to present a mechanism which will account quantitatively for the results obtained recently in the preparation of butenyl bromide mixtures from crotyl alcohol and methylvinylcarbinol by several standard methods.[7b] We recognize that the complete verification of this theory will require many more controlled experiments on several types of compounds, but in view of the painstaking work which is necessary in the preparation and study of the compounds needed, it seems advisable to present a *preliminary* account of the work at this time.

A Mechanism for the Reaction of Crotyl Alcohol and Methylvinylcarbinol with Hydrogen Bromide in Various Media.—The experiments on the conversion of crotyl alcohol and methylvinylcarbinol into butenyl bromide mixtures,[7b] which are summarized briefly in Table I of this paper, indicate that by any given method there is a well-defined difference in the crotyl bromide content of the products obtained from the two alcohols. Nevertheless, the similarity in composition of the bromide mixtures obtained from the two alcohols indicates that an equilibrium of some sort is involved.

The most logical interpretation of the results is to consider that the mechanism of the reaction consists of two simultaneous processes. In order to simplify the discussion, it is convenient to consider that the predominating process (process 1a) involves an ionic mechanism. Thus we should imagine that the positively charged oxonium ions, formed from the reaction of the alcohols with the strongly acidic media, decompose to form an equilibrium (resonating) mixture of primary and secondary butenyl cations which may then coördinate with the bromide ion to produce a mixture of primary and secondary butenyl bromides. The composition of the resulting bromide mixture will therefore be determined by the character of the resonating system and of the medium in which it is produced and not by the alcohol from which it arises.

Process 1a



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(6) See Winstein and Young, THIS JOURNAL, **58**, 104 (1936).

(7) (a) Young and Winstein, *ibid.*, **58**, 289, 441 (1936); (b) Young and Lane, *ibid.*, **59**, 2051 (1937).

TABLE I

THE COMPOSITION OF BUTENYL BROMIDES OBTAINED FROM CROTYL ALCOHOL AND METHYLVINYLCARBINOL UNDER CONTROLLED CONDITIONS

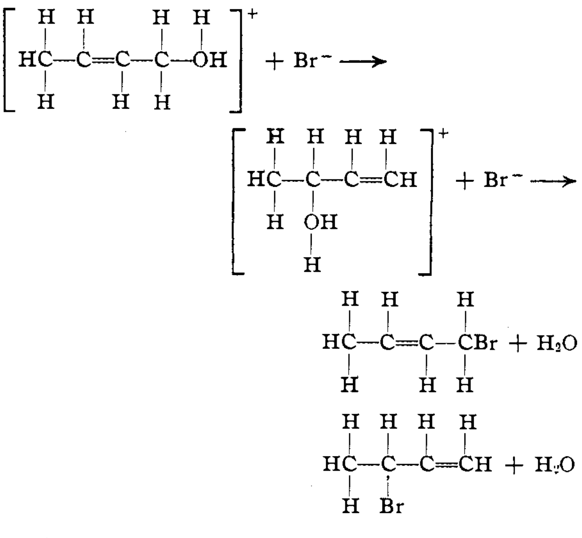
Standard experimental method[b]	Alcohol used	$n^{25}D$ of bromide mixture (corr.)	Composition of product Primary bromide, %	Secondary bromide, %	Av. diff. in % primary bromide from the primary and secondary alcohols (100 M)
1. 48% hydrobromic acid at −15°[a]	Primary	1.4768	86.0	14.0	2.9
	Primary	1.4768	86.0	14.0	
	Secondary	1.4763	83.4	16.6	
	Secondary	1.4762	82.9	17.1	
2. 48% hydrobromic acid + H_2SO_4 at −15°[a]	Primary	1.4764	84.0	16.0	4.7
	Secondary	1.4755	79.3	20.7	
3. Saturated hydrobromic acid at 0°[a]	Primary	1.4755	79.3	20.7	4.7
	Primary	1.4752	77.7	22.3	
	Secondary	1.4746	73.6	26.4	
	Secondary	1.4745	74.1	25.9	
4. Hydrogen bromide gas at −20°[a]	Primary	1.4761	82.4	17.6	6.2
	Secondary	1.4749	76.2	23.8	
7. Hydrogen bromide in glacial acetic acid at 0°	Primary	1.4763	83.4	16.6	11.9
	Secondary	1.4740	71.5	28.5	

[a] Results by Young and Lane.[7b] [b] Standard methods 5 and 6 have been omitted from this table since they involved a different type of reagent.[7b]

Process 1b.—Although a complete rupture of the molecule to give ions was assumed in process 1a in order to emphasize the concept of resonance, we recognize that the most likely mechanism for process 1 involves an exchange reaction of the type which Olson[8] and Polanyi[9] have assumed to account for Walden inversions during substitution reactions. It is not necessary that the carbon–oxygen linkage be completely broken. If the oxygen atom has moved out a sufficient distance to allow resonance to set in before a bromide ion coördinates with the molecule, then coördination may occur at either the primary or secondary position. This would produce a mixture of primary and secondary bromides. On the other hand, if the bromide ion coördinates with the molecule when the oxygen–carbon distance is insufficient to allow resonance to set in, then only the normal substitution product would be formed as described in process 2 (below). The important point is that with either process 1a or 1b, the conversion of the oxonium salt into the bromide affords an opportunity for resonance to occur. Hereafter no distinction will be made between 1a and 1b. They will be referred to as process 1 (resonating).

Process 2, which accounts for only a small portion of the reaction, is considered to be a molecular process in which the oxonium salt reacts with the bromide ion without resonance being involved. Thus the primary alcohol gives only primary bromide and the secondary alcohol gives only secondary bromide.

Process 2



If process 1 predominates, we would expect the bromide mixtures from both alcohols to have similar compositions. However, due to the occurrence of process 2, we would expect the product from the primary alcohol to contain more primary bromide than the mixture which would result if only process 1 were operating. Likewise, the product from the secondary alcohol would contain

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(8) (a) Olson, *J. Chem. Phys.*, **1**, 418 (1933); (b) Olson, THIS JOURNAL, **56**, 1294 (1934).

(9) Bergmann, Polanyi and Szabo, *Z. physik. Chem.*, **B20**, 161 (1933).

less primary bromide than the product resulting only from process 1.[10]

If the proposed mechanism is valid, equations may be constructed which will make it possible to calculate not only the extent to which processes 1 and 2 take place, but also the composition of the bromide mixture formed as a result of process 1 in any given standard method. Let

P_r = the percentage of primary bromide in the bromide mixture formed by process 1 due to resonance
n_r = the refractive index at 25° of the bromide mixture formed by process 1
n^0_p = the refractive index at 25° of pure primary bromide
n^0_s = the refractive index at 25° of pure secondary bromide
n_p = the refractive index at 25° of the product prepared from the primary alcohol as a result of processes 1 and 2
n_s = the refractive index at 25° of the product prepared from the secondary alcohol as a result of processes 1 and 2
P_p = the percentage of primary bromide in the product from the primary alcohol
P_s = the percentage of primary bromide in the product from the secondary alcohol
I = the fraction of alcohol reacting by process 1 (resonating)
M = the fraction of alcohol reacting by process 2 (non-resonating)

Since it has been demonstrated that the butenyl bromides form perfect solutions[6] we may write

$$M + I = 1 \qquad (1)$$
$$n^0_p M + n_r I = n_p \qquad (2)$$
$$n^0_s M + n_r I = n_s \qquad (3)$$

From equations (2) and (3) we find that

$$M = \frac{n_p - n_s}{n^0_p - n^0_s} = \frac{n_p - n^0_s}{n^0_p - n^0_s} - \frac{n_s - n^0_s}{n^0_p - n^0_s} = \frac{P_p}{100} - \frac{P_s}{100} \qquad (4)$$

In other words, the percentage of the alcohol which reacts by process 2 is given by the difference between the percentages of primary bromide in the products obtained from primary and secondary alcohols, respectively. The last column of Table I, then, lists values of 100 M for each standard method.

The value of n_r in terms of directly measurable experimental quantities is obtained by solving equations (1), (2) and (3) simultaneously. Then

$$n_r = n^0_s + \frac{(n_s - n^0_s)(n^0_p - n^0_s)}{(n^0_p - n^0_s) + (n_p - n_s)} = 1.4602 + \frac{0.0193\,(n_s - 1.4602)}{0.0193 + (n_p - n_s)} \qquad (5)$$

where $n^0_s = 1.4602$ and $n^0_p = 1.4795$. Substituting $P_p = 100\,\frac{n_p - n^0_s}{n^0_p - n^0_s}$ and $P_s = 100\,\frac{n_s - n^0_s}{n^0_p - n^0_s}$ in equation (5), we obtain

$$P_r = \frac{P_s}{1 - \frac{P_p - P_s}{100}} = \frac{P_s}{1 - M} \qquad (6)$$

Thus using equations (4), (5), (6) we may calculate values of M, P_r and n_r from the data in Table I. The results of these calculations for each of the standard methods of synthesis are summarized in Table II.

It is recognized that all of these results are consequences of the assumptions used in constructing the picture (for example, *M and I were assumed to be the same with each alcohol*). They would attain considerable significance, however, were it possible to determine independently one of the three variables, say, n_r or P_r. Since Burton[11] has demonstrated that the thermal rearrangement of allylic isomers involves the intermediate formation of ions which correspond in our nomenclature to the resonating butenyl cations of process 1a,[12] it is apparent that the thermal rearrangement of the pure primary and secondary butenyl bromides in contact with a given medium may give the same mixture of bromides as that formed from process 1 by the coördination of bromide ion with the resonating butenyl ions in that medium. Consequently, it is possible to determine both n_r and P_r experimentally by rearranging the pure primary and secondary butenyl bromides at 25° in contact with the same media used in synthesizing the bromides by the standard methods. The experimentally determined values of n_r and P_r are listed in Table III along with the calculated values from Table II.

In the first column are listed the media used. In the second are the refractive indices and composition of the pure isomeric bromides which were used in each determination. The third column gives the corrected refractive index, n_r, of the purified mixture which resulted after the

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(10) Meisenheimer and Link[5] considered the possibility that part of the reaction goes normally and part abnormally but they discarded the notion because it did not account for the results obtained from the reaction of the primary and secondary pentenols with thionyl chloride. It is questionable, however, whether hydrogen chloride and thionyl chloride should be expected to react by the same mechanism.

(11) Burton, *J. Chem. Soc.*, 1650 (1928).

(12) It is not necessary that this thermal rearrangement involves complete rupture of the carbon–bromine bond. An exchange reaction similar to that described in process (1b) involving resonance will give the same effect.

TABLE II

DATA ON THE MECHANISM OF FORMATION OF BUTENYL BROMIDES FROM THE BUTENOLS THROUGH THE AGENCY OF HYDROGEN BROMIDE, CALCULATED FROM THE RESULTS OF TABLE I

Method used in preparing the butenyl bromides	Av. % of primary bromide from primary alcohol, P_p	Av. % of primary bromide from secondary alcohol, P_s	% of alcohol reacting by process 2 100 M or $P_p - P_s$	Calcd. % of primary bromide in the mixture arising from process 1 $P_r = \frac{P_s}{1 - M}$	Calcd. refr. index of the equilib mixture arising from process 1 n_r = Eq. (5)
1. 48% hydrobromic acid at −15°	86.0	83.1	2.9	85.6	1.4767
2. 48% hydrobromic acid + H_2SO_4 at −15°	84.0	79.3	4.7	83.2	1.4763
3. Saturated hydrobromic acid at 0°	78.5	73.8	4.7	77.8	1.4752
4. Gaseous hydrobromic acid at −20°	82.4	76.2	6.2	81.2	1.4759
7. Hydrogen bromide in glacial acetic acid at 0°	83.4	71.5	11.9	81.2	1.4759

TABLE III

COMPARISON OF CALCULATED AND EXPERIMENTAL DATA ON THERMAL EQUILIBRIUM OF BUTENYL BROMIDES IN CONTACT WITH DIFFERENT MEDIA

Medium	Composition of bromide sample before treatment $n^{25}D$	% primary bromide	Corr. $n^{25}D$ of equil. mixture, (expt.)[a]	Av. % primary bromide in equil. mixt. (expt.)	Calcd. $n^{25}D$ of equilibrium mixture	Calcd. % primary bromide in equil. mixt.
1. 48% hydrobromic acid at 25°	1.4795	100	1.4767	85.0	1.4767	85.6
	1.4602	0	1.4765			
	1.4602	0	1.4766			
2. 48% hydrobromic acid + H_2SO_4 at 25°	1.4795	100	1.4763	82.9	1.4763	83.2
	1.4602	0	1.4762			

[a] The corrected refractive index was obtained in the manner described by Young and Lane.[7b]

bromides were rearranged in the presence of the media. In the fourth column appears the average value of P_r the percentage of primary bromide corresponding to the average of the experimental values of n_r computed by the relation, P_r (obsd.) = $[n_r \text{ (exp.)} - 1.4602]/0.0193 \times 100$. The last two columns list the calculated values of n_r and P_r for these methods, repeated from Table II for purposes of comparison.

In these two cases where it has been possible to determine the thermal equilibrium of the butenyl bromides in contact with the reaction media, the observed values for the refractive index of the rearranged products agree remarkably well with the values of n_r calculated. That a new equilibrium position was reached in each case is evidenced by the fact that the rearrangement products from the primary bromide in contact with a medium at 25° contained more secondary bromide than the equilibrium mixture obtained by rearranging the pure bromide in the absence of the medium.[6]

The experimental determination of the thermal equilibrium in contact with the media used in standard methods 3, 4, 7 (Table II) would afford an excellent test of the theory proposed above, since the calculated values of n_r are remarkably different from the normal equilibrium value of $n^{25}D$ 1.4770. Unfortunately, the conditions needed to cause thermal rearrangement of the bromides in contact with these media also cause rapid addition of hydrogen bromide to the double bond thus giving rise to mixtures of dibromobutanes and butenyl bromides. Since the method of purification developed for this work will not separate the addition products from the butenyl bromides it is impossible to use these media until a different technique is developed.

Although the results presented are most encouraging, they should be considered to be of a *preliminary nature*. The accuracy of the values calculated for M, n_r and P_r is naturally dependent on the composition of the butenyl bromides prepared from the crotyl alcohol and methylvinylcarbinol by the standard methods previously described.[7b] In spite of the fact that the butenyl bromides were prepared under carefully controlled conditions, we are not unmindful of the difficulties encountered by other workers due to the extreme mobility of the bromides, and that on one or two occasions unexpected mobility has been observed in this Laboratory under supposedly controlled conditions. Consequently, the reproducibility of the standard methods is being tested by other workers in this Laboratory.

Even though the theory presented above enables us to calculate the composition of the butenyl bromide mixture, P_r, arising from process 1 it is possible that the thermal rearrangements of butenyl bromides in contact with the required media might not afford an experimental check of the calculated values. For example, the bromides are formed in the aqueous phase due to coördination of the bromide ions with the resonating system, while the thermal rearrangement of the bromides, due to the polar character of most of the media, is of necessity carried out in a two-phase system. In order to eliminate this difficulty we are investigating the possibility of using media in which the synthesis and thermal rearrangement of the bromides may be done in a one-phase system so that the calculated and experimental values of P_r may be obtained under comparable conditions. The theory is also being tested in the case of several other alkenyl bromides.

The Action of a Saturated Solution of Hydrogen Bromide in Glacial Acetic Acid on Crotyl Alcohol and Methylvinylcarbinol.—The experiments, summarized in Table I, on the synthesis of butenyl bromides by Standard Methods 1–4, indicated that the percentage of the alcohol which reacts by process 2 (non-resonating) could be varied by changing the character of the reaction medium. It was desirable to find conditions which would favor a higher percentage of process 2 and thus afford a better test of the mechanism developed above. Accordingly controlled experiments were made with saturated solutions of hydrogen bromide in glacial acetic acid. It was found that the percentage of alcohol (100 M) reacting by process 2 increased to 12%. These experiments are included in Table I and the calculated values of n_r and P_r are listed in Table II.

Experimental Part

Materials.—The crotyl alcohol, crotyl bromide, methylvinylcarbinol and methylvinylcarbinyl bromide were prepared according to the procedures described in previous communications.[6,7b]

The Thermal Equilibrium of Butenyl Bromides in Various Reaction Media.—As a result of the theoretical considerations advanced above it was possible to calculate the composition of the equilibrium mixtures of butenyl bromides which should be formed by the thermal rearrangement of either crotyl or methylvinylcarbinyl bromides in the presence of the reagent or reaction media used in the standard methods of synthesis previously developed. The following experiments were performed to check experimentally the validity of the calculations. Ten-gram samples of pure crotyl and methylvinylcarbinyl bromides were separately sealed with paraffin in glass-stoppered oil-sample bottles together with 50 cc. of the reagent. The bottles were shaken for sixty hours in a thermostat at 25°. The resulting mixtures of bromides were then separated from the reaction media and washed first with a mixture of crushed ice and dilute sodium bicarbonate solution and then with ice water. After the resulting product had been dried for several hours over calcium chloride at −15°, it was distilled completely and without fractionation at 3 mm. pressure to free it from tarry materials. At this stage the bromides were analyzed by the Carius method and found to contain the correct percentage of bromine. The refractive index was then measured and small samples of the material were rearranged at 100° to determine the correction to be applied to the observed refractive index.[13] The following reaction media were used: (1) 48% hydrobromic acid; (2) a mixture of 7.2 cc. of concentrated sulfuric acid with 72 cc. of 48% hydrobromic acid; (3) hydrobromic acid saturated with hydrogen bromide at 0°; (4) a saturated solution of hydrogen bromide in glacial acetic acid (m. p. 16.5°) at 0°.

The results obtained with reagents 1 and 2 are summarized in Table III. Those with reagents 3 and 4 are not recorded since these reagents favored addition of hydrogen bromide to the butenyl bromide, thus forming a mixture of butenyl bromides and dibromobutanes which would not be separated by the standard procedures being employed. These reagents are being studied further.

Standard Method 7. Synthesis of Butenyl Bromides from Crotyl Alcohol and Methylvinylcarbinol by the Action of a Saturated Solution of Hydrogen Bromide in Glacial Acetic Acid at 0°.—In continuing the study of butenyl bromides prepared under *controlled* conditions, the following standard method was developed: 100 g. of pure glacial acetic acid was placed in a 250-cc. glass-stoppered Erlenmeyer flask and saturated with approximately 75 g. of pure dry hydrogen bromide at 0°. The flask was then placed in a mixture of salt and ice and 0.3 mole of the crotyl alcohol or methylvinylcarbinol cooled to −25° was added slowly through a dropping funnel. The rate of addition was such that the temperature of the reaction mixture remained between ±1° (ten minutes). The addition completed, the mixture was shaken thoroughly and allowed to stand for fifteen minutes at 0°. A single phase resulted in which a slight turbidity appeared toward the end of the fifteen-minute interval.

The mixture was then poured over a mixture of about 300 g. of crushed ice and 100 g. of sodium bicarbonate in a one-liter separatory funnel. After the initial effervescence had subsided about 100 g. more of sodium bicarbonate was added until the bulk of the acid was neutralized. The resulting ice-salt mixture produced a low temperature at all times. The heavy bromide layer was then removed and washed twice with a mixture of ice and dilute sodium carbonate solution and three times with pure ice water.

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[13] Details of the method of correcting the refractive index of bromide samples are given in a previous paper.[7b]

The remainder of the purification was similar to that described above for the purification of the bromides from the thermal equilibrium experiments. The results of these experiments are included in Table I, which also contains a summary of previous experiments with standard procedures.

The authors are indebted to Professors Linus Pauling and Howard J. Lucas and Mr. Saul Winstein for valuable discussions during the preparation of the manuscript.

Summary

A mechanism is proposed to account quantitatively for the differences in composition of the butenyl bromide mixtures which are observed when crotyl alcohol and methylvinylcarbinol are allowed to react with hydrogen bromide by standardized methods under controlled conditions.

The reaction is considered to be composed of two simultaneous processes. Process 1, involving resonance, gives the same mixture of bromides from both alcohols. Process 2, a normal substitution reaction without resonance, gives only primary bromide from the primary alcohol and secondary bromide from the secondary alcohol. The net result is a difference of 3–12% in the primary bromide content of the butenyl bromide mixtures prepared from the two alcohols by the standard methods.

Mathematical equations have been developed which make it possible to calculate (1) the percentage of alcohol which reacts by processes 1 and 2; (2) the refractive index, n_r, and hence the composition, P_r, of the bromide mixture produced due to a reaction by process 1. The calculated and experimentally determined values of n_r and P_r agree within experimental error for cases reported.

The use of a saturated solution of hydrogen bromide in glacial acetic acid in the preparation of butenyl bromide mixtures is described.

LOS ANGELES, CALIF. RECEIVED NOVEMBER 29, 1937

[CONTRIBUTION FROM THE MELLON INSTITUTE OF INDUSTRIAL RESEARCH]

alpha-Naphthaldehyde and Certain of its Derivatives

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Most of the numerous methods reported in the literature for the preparation of α-naphthaldehyde were found to be too inconvenient and too costly for the preparation of relatively large quantities required for another project. It was found that the treatment of α-chloromethylnaphthalene with hexamethylenetetramine in 60% alcohol solution was most satisfactory in giving constant yields of 59–60% α-naphthaldehyde.[3] The necessary α-chloromethylnaphthalene was prepared in 68–70% yields by treating naphthalene with 40% formaldehyde solution and hydrochloric acid followed by treatment with concentrated sulfuric acid.[4] The modification of this method suggested by Rupe and Brentano[3c] (no details are given) together with several important precautions stressed in the experimental part have resulted in a trustworthy procedure for preparing α-chloromethylnaphthalene.

A number of α-naphthaldehyde derivatives prepared in the course of this work are listed in the table. These were prepared according to the usual methods. Dioxane was used in cases of difficult solubility.

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Experimental Part

Preparation of alpha-Chloromethylnaphthalene.—For this reaction, 256 g. of naphthalene, 250 cc. of 30% formaldehyde solution and 424 cc. of concentrated hydrochloric acid were combined in a three-necked Pyrex round-bottomed flask equipped with an efficient stirrer and dropping funnel. The temperature of the flask contents was brought up to 60° by means of a water-bath and was held at that temperature for seven hours, during which time 258 cc. of concentrated sulfuric acid was added with constant efficient stirring. The heating and stirring were continued for another twenty hours, the naphthalene gradually disappearing. The naphthalene which collected about the top of the flask was frequently shaken down. The flask was placed in ice water and the contents diluted

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[3] (a) Sommelet, *Compt. rend.*, **157**, 852 (1913); (b) Mayer and Stieglitz, *Ber.*, **55**, 1846 (1922); (c) Rupe and Brentano, *Helv. Chim. Acta*, **19**, 581 (1936).

[4] I. G., German Patent 533,132; *Frdl.*, **18**, 586. See also Sprague and Johnson, THIS JOURNAL, **59**, 1837 (1937).