[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

Allylic Rearrangements. VII. The Action of Metals on Crotyl and Methylvinylcarbinyl Bromides[1]

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Some time ago an attempt was made to prepare *trans*-2-butene from crotonaldehyde by the following steps: *trans*-crotonaldehyde ⟶ crotyl alcohol ⟶ crotyl bromide ⟶ crotylmetallic bromide ⟶ *trans*-2-butene. According to the classical concepts of organic chemistry this procedure should have offered no outstanding difficulties. However, it was found that the final butene product consisted of a mixture of 1-butene, *cis*-2-butene and *trans*-2-butene.[2] Since the starting material, crotonaldehyde, had been prepared by the dehydration of aldol—a process which could, theoretically, give rise to a mixture of three isomeric aldehydes—it was at first thought that such a mixture was the cause of the butene mixture finally obtained. Subsequent studies of the absorption spectra[3] and oxidation[4] reactions of crotonaldehyde indicate, however, that this material is a pure *trans* isomer rather than a mixture. Likewise, unpublished experiments in this Laboratory and those by Gredy and Piaux[5] have demonstrated that the ordinary preparation of crotyl alcohol is also a pure substance containing at most only a trace of the *cis* isomer. On the other hand, investigation of the next step in the above-mentioned synthesis of butenes has shown conclusively that crotyl alcohol yields mixtures of crotyl and methylvinylcarbinyl bromides when treated with several different reagents[6] even under controlled conditions and that these butenyl bromide mixtures tend to rearrange thermally to an equilibrium mixture during the isolation and purification process unless special precautions are used.[7] Furthermore, it is now known that the formation and hydrolysis of the butenyl metallic complexes of magnesium or zinc[8] produce a mixture of the three above-mentioned butenes the composition of which is independent of the composition of the butenyl bromide mixture from which they are prepared. Summarizing, we find that in the original preparation of butene from crotonaldehyde there were at least three separate allylic rearrangements involved, namely, during (a) the formation, (b) isolation of the butenyl bromides, and (c) the conversion of the bromides into butenes. The last step in the synthesis, the conversion of the butenyl bromides into butenes, has required careful consideration. It was important to determine whether or not the composition of the butene mixture was dependent on the character of the metal and solvent or on the temperature at which the butenes were generated. Preliminary experiments[9] having shown that butenes could be liberated from butenyl bromides by several metals, the present paper shows that the composition of a butene mixture obtained with the aid of a metal varies decidedly with the character of the metal, but is independent of the nature of the butenyl bromide mixture.

Discussion of Results

When mixtures of crotyl and methylvinylcarbinyl bromides are treated with aluminum amalgam, zinc, chromium, cadmium or tin in 80% ethanol to form butene mixtures an allylic rearrangement occurs in each case. This is shown by the fact that the compositions of the butene mixtures obtained with any of the metals do not correspond even remotely to the compositions of the butenyl bromides used. Although widely different compositions of butenyl bromides were used the butene mixtures from any given metal varied in composition only by amounts to be expected from the procedure of converting the butenes into dibromobutanes and applying the reaction-rate method of analysis.[10] An allylic equilibrium is thus indicated. From the experimental results summarized in Tables I and II it may be seen that this allylic equilibrium is different for each metal used. The striking effect which the character of the metal has in determining the proportion of the butenyl forms is shown in Table II where the ratio 1-butene/2-butene

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[2] Young and Prater, THIS JOURNAL, **54**, 404 (1932).

[3] Blacet, Young and Roof, *ibid.*, **59**, 608 (1937).

[4] Young, *ibid.*, **54**, 2498 (1932).

[5] Gredy and Piaux, *Bull. soc. chim.*, [5] 1, 1481 (1934).

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

[7] (a) Young and Winstein, *ibid.*, **57**, 2013 (1935); (b) Winstein and Young, *ibid.*, **58**, 104 (1936).

[8] (a) Young, Winstein and Prater, *ibid.*, **58**, 289 (1936); (b) Young and Winstein, *ibid.*, **58**, 441 (1936).

[9] Young, Lane, Loshokoff and Winstein, *ibid.*, **59**, 2441 (1937).

[10] (a) Dillon, Young and Lucas, *ibid.*, **52**, 1953 (1930); (b) Young and Winstein, *ibid.*, **58**, 102 (1936).

and the ratio *cis*-2-butene/*trans*-2-butene are listed. Just what property of the metal determines the character of the allylic equilibrium is not yet known with certainty. Since the reaction involves an oxidation of the metal it is possible that the molal reduction potential may be involved. It is recognized that the absolute values of molal reduction potential are of no particular significance since they pertain only to aqueous solutions and we are dealing with an 80% ethanol solution in which the concentrations of the metallic ions are continually changing as the reaction proceeds. Nevertheless, when the molal reduction potential is plotted against the mean percentage of 1-butene in the mixtures (Fig. 1) an interesting correlation is observed.

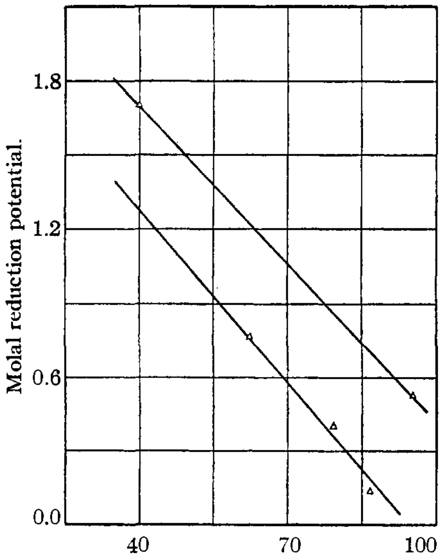

Fig. 1.—Composition of butene mixture as a function of the molal reduction potential of the metal.

The points for the divalent metals fall upon a straight line while those for the trivalent metals fall upon another. Unfortunately only two trivalent metals have been found which liberate butenes from the butenyl bromides. Chromium is considered trivalent in this case since the color of the reaction mixture corresponds to that of chromic rather than chromous bromide in alcohol. Likewise, if the molal reduction potentials are plotted against the ratio *cis*-2-butene/*trans*-2-butene (Fig. 2) all of the points lie upon a smooth curve. Since the *trans*-2-butene content cannot be determined with precision in small concentrations, the curve is not too significant. Nevertheless, it seems to be more than a coincidence that the ratios calculated from the mean *cis*- and *trans*-2-butene compositions all fall upon a smooth curve. At any rate, it appears that the same property of the metal which determines the character of the molal reduction potentials may determine the character of the allylic forms produced.

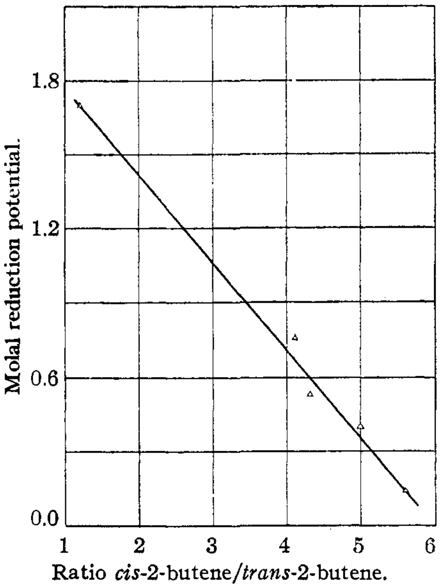

Fig. 2.—Composition of *cis*- and *trans*-2-butene mixture as a function of the molal reduction potential of the metal.

In a previous communication,[8b] five explanations were suggested to account for the formation of the same mixture of butenes when different mixtures of crotyl and methylvinylcarbinyl bromides were allowed to react with zinc or magnesium. The first and fifth explanations could be ruled out, leaving only the following for consideration. Retaining the same numbers of the previous communication: (2) the formation of the same mixture of alkenyl metallic bromides from any bromide mixture at the instant the bromide reacts with the metal due to resonance between the primary and secondary forms of the intermediate positive ion, $CH_3CH{=}CHCH_2^+$ and $CH_3^+CHCH{=}CH_2$; (3) the establishment of equilibrium between primary and secondary alkenyl metallic bromides after the butenyl bromide has reacted with the metal; (4) the rearrangement to equilibrium during hydrolysis of the alkenyl metallic bromides.

With the aid of the experimental work presented in the present paper, it is now possible to reconsider these alternate explanations more effectively. Number 4, always considered improbable, is now dropped from consideration since it would lead to the conclusion that the composition of the butene mixtures would be independent of the character of the metal used. Such a conclusion would not be justified by the data in Table II. This leaves only numbers 2 and 3 as possibilities.

Although number 2 postulated the establishment of the allylic equilibrium by resonance of the intermediate positive butenyl ions, it is not necessary for these ions to exist independently in the solution. The following mechanism would suffice to explain the experimental facts: as the butenyl bromide molecule approaches the envelope of electrons on the metal surface the bromine atom starts to move away from the adjoining carbon atom, taking the covalent electrons with it. When the carbon–bromine distance becomes sufficiently great resonance sets in. In this activated condition the butenyl bromide molecule may coördinate with the valence electrons of an atom of the metal at either carbon atom number 1 or 3 allowing the bromide ion to leave the molecule. The proportion of the molecules forming the primary and secondary butenyl metallic complex is determined by the character of the metal and of the resonating molecule, but this proportion will be independent of the structure of the butenyl bromide molecule at the start of the reaction.

If the allylic equilibrium is established according to explanation number 3 the resonance may involve the different modifications of the negative butenyl ions as well as several forms of the metallic complex. However, if this is the case it should be possible to alter the proportion of the butenyl forms by introducing into the reaction mixture other metallic ions than those produced during the reaction of a given metal with the butenyl bromides. This would bring about a competition between the two metallic ions in coördinating with the resonating negative butenyl ions, giving rise to a different mixture of butenes than would be expected from either metallic ion alone. Experiments of this character are being carried out at the present time.

Experimental Part

Metals.—Commercial "C. P." preparations of the metals were used. The cadmium, chromium and zinc were fine powders; the tin was 50 mesh and the aluminum was a thin sheet 0.005 inch (0.13 mm.) thick. The aluminum was cut into small pieces and amalgamated as previously described.[9]

Butenyl Bromides.—Two types of butenyl bromide mixtures were used in generating butenes with the aid of the various metals. One mixture was essentially crotyl bromide with a small amount of methylvinylcarbinyl bromide and the other mixture was mainly methylvinylcarbinyl bromide with some crotyl bromide. The first mixture was obtained from the fractional distillation of an equilibrium mixture of the two bromides at 90 mm. pressure. The second mixture was prepared by the high temperature fractionation of the equilibrium mixture using the modification suggested by Jasaitis.[6] No attempt was made to prepare the pure primary and secondary bromides since previous experiments with zinc[3b] had demonstrated that the composition of the butene mixture obtained was independent of the composition of the butenyl bromide mixture from which they were prepared. However, the refractive index and composition of the butenyl bromide mixtures used in each experiment are included in Table I.

Generation of the Butene Mixtures.—The reduction of the butenyl bromides to butenes with the aid of various metals was carried out in the apparatus used by Young and Winstein.[8] The bromides were dropped into a suspension of the metal in boiling 80% ethanol. The butenes were purified and converted into dibromobutane mixtures as before.[3b] In all experiments except the ones with aluminum amalgam, three gram atoms of metal, 135 ml. of 95% ethanol and 30 ml. of water were used per mole of butenyl bromide mixture. In the case of aluminum amalgam it was difficult to maintain rapid stirring of the reaction mix-

TABLE I

THE ACTION OF METALS ON MIXTURES OF CROTYL AND METHYLVINYLCARBINYL BROMIDES IN BOILING 80% ETHANOL

Metal	Chromium		Tin		Cadmium		Aluminum (amalgam)	
Run number	1	2	1	2	1	2	1	2
n^{25}_{D} of butenyl bromide mixture	1.4742	1.4630	1.4742	1.4625	1.4735	1.4650	1.4742	1.4625
Crotyl bromide, %	72.5	14.5	72.5	11.9	68.9	24.9	72.5	11.9
Methylvinylcarbinyl bromide, %	27.5	85.5	27.5	88.1	31.1	75.1	27.5	88.1
B. p. (50 mm.) of dibromobutane mixture, °C.	80.3–81.0	80.0–81.3	79.5–81.3	79.0–81.0	78.0–80.9	78.1–81.6	75.0–80.9	75.5–80.5
d^{25}_{4} of dibromobutane mixture	1.7868	1.7865	1.7866	1.7861	1.7858	1.7858	1.7826	1.7824
Reaction rate, K_2, of dibromobutane mixture	0.0747	0.0746	0.0708	0.0702	0.0678	0.0675	0.0556	0.0545
1,2-Dibromobutane (1-butene), %	95.9	94.6	87.9	84.4	78.6	79.4	41.2	38.1
dl-2,3-Dibromobutane (*cis*-2-butene), %	3.5	4.19	12.2	11.4	16.1	19.0	31.8	33.8
meso-2,3-Dibromobutane (*trans*-2-butene), %	0.6	1.2	−0.1	4.15	5.32	1.6	27.0	28.1

ture due to the formation of a thick gel of aluminum hydroxide. This difficulty was obviated by the use of a double quantity of ethanol and water. The dibromobutanes were distilled at 50 mm. pressure through the column described by Lucas, Dillon and Young[11] or the column described by Weston[12] depending on the size of the sample. The boiling points and densities of the various dibromobutane mixtures are listed in Table I.

Analysis of the Dibromobutane Mixtures.—The reaction rate determinations necessary for the analysis of the dibromobutane mixtures were carried out according to the directions of Dillon, Young and Lucas.[10] Since the number of runs which could be made with each metal was limited by the supply of butenyl bromides available, it seemed advisable to carry out the analysis of each dibromobutane sample with special care. Consequently duplicate rate determinations were made on each sample by at least two of the co-authors using a different supply of methanol as a solvent. Each solvent was standardized as recommended by Young and Winstein[10b] against pure 1,2-dibromobutane and another sample of dibromobutanes, the composition of which was known from previous work. The constants, K_2, listed in Table I for each dibromobutane mixture are the average of all the runs made with the different supplies of solvent.

In connection with this work one supply of synthetic methanol was purchased containing an impurity which used up iodine slowly over a period of sixty hours at 75°. The total iodine used at any time depended on the concentration of the iodine present in the solvent during the run. Consequently this methanol was discarded since it was not possible to determine a reliable iodine correction which could be applied during a run with a dibromobutane sample because of the manner in which the blank run differed from the run using dibromobutane mixtures. The blank runs start with an appreciable iodine concentration which diminishes with time. On the other hand, in the actual rate runs the iodine concentration starts at zero and increases with time. All other supplies of methanol which had been used in the analysis of dibromobutane mixtures have required the application of a small iodine correction. However, in each case the iodine was used up rapidly so that a constant correction could be applied.

TABLE II

SUMMARY OF RESULTS

Metal	Mean butene composition 1-butene, %	*cis*-2-butene, %	*trans*-2-butene, %	Ratio *cis*-2-butene / *trans*-2-butene	Ratio 1-butene / 2-butene
Chromium	95.2 ±0.6	3.9 ±0.4	0.9 ±0.3	4.3	19.8
Tin	86.1 ±1.7	11.8 ±0.4	2.1 ±2.0	5.6	6.2
Cadmium	79.0 ±0.4	17.6 ±1.5	3.5 ±1.8	5.0	3.8
Zinc[a]	62.1 ±1.9	30.5 ±0.5	7.5 ±2.4	4.1	1.6
Aluminum (amalgam)	39.6 ±1.5	32.8 ±1.0	27.5 ±0.5	1.2	0.65

[a] Results of Young and Winstein.[7b]

The following procedure may be followed in determining whether or not a given supply of methanol is acceptable for use as a solvent in analyzing dibromobutane mixtures by the reaction rate method. Amounts of iodine and potassium iodide equivalent to those encountered in the actual rate measurements are dissolved in the solvent. Tubes containing 20 ml. of this mixture are then placed in the thermostat at 75° and titrated against 0.02 *N* sodium thiosulfate at intervals. If the iodine consumption reaches a constant value of not more than 0.5 ml. in a short time, three to five hours, the solvent is acceptable. In the actual rate measurements on the dibromobutane samples the reaction is allowed to proceed for fifteen to eighteen hours before the first tubes are removed and titrated. This procedure allows sufficient time for all of the impurity in the solvent to react with the iodine and thus makes it possible to apply a constant correction. The two samples of methanol used in the present work possessed iodine corrections corresponding to 0.14 and 0.30 ml. of 0.02 *N* sodium thiosulfate per 20 ml. of solvent. Although it is possible to remove the impurity before using the solvent, the process of purifying large batches is burdensome. Reaction rate constants obtained with a highly purified solvent and those obtained using an iodine correction agree within 0.5%.

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Summary

An allylic rearrangement to an equilibrium has been shown to occur when different mixtures of crotyl- and methylvinylcarbinyl bromides are reduced with various metals in 80% ethanol to form butenes. The composition of the butene mixtures varies decidedly with the character of the metal, but is independent of the composition of the butenyl bromide mixture. There appears to be a correlation between the molal electrode potential of the metals and the composition of the butene mixtures.

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[11] Lucas, Dillon and Young, THIS JOURNAL, **52**, 1949 (1930).

[12] Weston, *Ind. Eng. Chem., Anal. Ed.*, **5**, 179 (1933).