In order to circumvent the possibility of aldol condensation products, analogous experiments were made with one mole of benzaldehyde in benzene. Yields of benzyl alcohol were 28 and 55%, respectively, for the ethoxide and isopropoxide. In each case some benzoic acid or benzyl benzoate was obtained.

### Chloromagnesium Alkoxides

Chloromagnesium ethoxide, according to Meerwein and Schmidt, gave 60% yields of crotyl alcohol. The details are not given for the reduction of crotonic aldehyde, but their description with cinnamaldehyde was followed. It is to be noted that these investigators used 2 g. of metallic magnesium (0.083 mole) to reduce 100 g. of cinnamaldehyde (0.76 mole). In a typical experiment, following the same procedure, but with methylacrolein (crotonaldehyde) replacing the phenylacrolein (cinnamaldehyde) of Meerwein and Schmidt, the following results were obtained: 300 ml. of crotonaldehyde was reduced with the chloromagnesium ethoxide from 6 g. of magnesium. Distillation after hydrolysis gave 33 g. of crude crotyl alcohol (13%), 25 g. of esters of crotonic acid, 23 g. of a product containing dipropenyl glycol and 200 g. of resinous material.

The magnesium dissolves incompletely and with difficulty in isopropyl alcohol containing hydrogen chloride. Consequently, no parallel experiments were made with chloromagnesium isopropoxide.

It is quite apparent from these results that the mechanism of the reaction is not a simple adaptation of the Cannizzaro reaction, as Meerwein and Schmidt propose, although crossed Cannizzaro reactions are known to be promoted by aluminum ethoxide.[14]

## Summary

Aluminum isopropoxide has been found effective for the reduction of aldehydes to the corresponding alcohols; other products are esters, aldol derivatives and resinous material.

The reaction mechanism is shown to be more complicated than previously reported.

[14] (a) Nord, *Biochem. Z.*, **106**, 275 (1920); (b) Davidson and Bogert, THIS JOURNAL, **57**, 905 (1935).

LOS ANGELES, CALIFORNIA
PHILADELPHIA, PENNA. RECEIVED AUGUST 12, 1935

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

# The Dibromide Method of Analysis of Butene Mixtures[1]

BY WILLIAM G. YOUNG AND SAUL WINSTEIN

The general procedure of identifying butene mixtures by converting them into the corresponding dibromobutanes has been criticized sharply by workers using high precision fractionating columns.[2] The differences in composition of butene mixtures observed in various laboratories during the catalytic decomposition of 1-butanol have been attributed mainly to faults in the dibromide method of analysis rather than to the effect of catalyst, temperature, efficiency of fractionation, etc.

In view of the fact that many laboratories interested in butene analysis do not possess special costly fractionating columns, it seems desirable to present further evidence that the dibromide method of analysis does give a reliable estimate of the composition of butene mixtures when conducted with the proper care; further, that the amount of decomposition and isomeric change accompanying the distillation of dibromobutanes at atmospheric pressure has been greatly over-emphasized; and finally that the results obtained by the dibromide method of analysis by different workers on the decomposition of 1-butanol with phosphoric acid catalysts fall almost without exception within the limits of variation reported by investigators using the butene distillation method of analysis.

**Discussion.**—The objections which have been raised against the dibromide method of analysis were originally considered and met by Dillon, Young and Lucas[3] in the development of the reaction-rate dibromide method.

Their method of analysis was originally shown to give a reliable estimate of the composition of dibromobutane mixtures made by mixing the pure dibromobutanes in known proportions. We have now demonstrated that the process of converting butene mixtures into dibromobutane mixtures and preparing the sample for analysis does not cause an appreciable change in composition of the mixture. Known mixtures of dibromobutanes have been converted into butenes by treatment with zinc and alcohol and back into dibromobutanes without changing their composition. In this process the butenes being generated were converted into dibromides which were

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[1] The research included in this paper was accomplished with the aid of a grant from the Board of Research of the University of California.

[2] (a) Komarewsky, Johnstone and Yoder, THIS JOURNAL, **56**, 2705 (1934); (b) Pines, *ibid.*, **55**, 3892 (1933).

[3] Dillon, Young and Lucas, *ibid.*, **52**, 1953 (1930).

washed, dried and distilled in the same manner as would be used in applying the reaction-rate method of analysis. The results of these experiments are shown in Table I, which gives the properties of each mixture before and after the treatment described above. In order to indicate what the observed changes in physical properties mean in terms of composition of the mixture we have calculated the composition of mixture 3, which showed the greatest deviation in properties. The results are 57.3% of 1,2, 28.3% of rac.-2,3 and 14.4% of meso-2,3 dibromobutanes before regeneration and 54.1% of 1,2, 29.8% of rac.-2,3 and 16.2% of meso-2,3 dibromobutanes after regeneration. In every case the change in composition of the mixture is within the limits of error originally claimed for the method.

TABLE I

SUMMARY OF RESULTS SHOWING THE LACK OF REARRANGEMENT DURING DIBROMOBUTANE–BUTENE–DIBROMOBUTANE TRANSFORMATIONS

| Material | Second order rate with KI Before | Second order rate with KI After | Density *in vacuo*, $d^{25}_4$ Before | Density *in vacuo*, $d^{25}_4$ After |
|---|---|---|---|---|
| 1,2-Dibromobutane | 0.0765 | 0.0765 | | |
| Mixture 1 | .0430 | .04310 | 1.7781 | 1.7779 |
| Mixture 2 | .0435 | .0435 | 1.7784 | 1.7783 |
| Mixture 3 | .0600 | .0590 | 1.7842 | 1.7840 |
| Mixture 4 | | | 1.7854 | 1.7853 |

A comparison of the results reported by Young and Lucas[4] on the low temperature decomposition of 2-butanol with sulfuric acid, with those reported recently by investigators using precision fractionating columns affords a further test of the reliability of the dibromide method of analysis. This example has been chosen in order to avoid the confusing effects of purity of catalyst, rate of isomerization, etc., which must be considered in catalytic decompositions at high temperatures. The values reported by Young and Lucas[4] of 41.6% *cis* and 58.4% *trans* 2-butene are in good agreement with the values of 38% *cis* and 62% *trans* found by Hurd and Goldsby,[5] and of 43% *cis* and 57% *trans* as calculated from the distillation curves of Kistiakowsky and co-workers.[6]

**The Catalytic Decomposition of 1-Butanol.**—In spite of the fact that the dibromide method of analysis has been reported to be unreliable, we find that the analyses obtained by this procedure on butene mixtures arising from the decomposition of 1-butanol with phosphoric acid catalysts at high temperatures by different workers[2a,4,7] fall almost without exception within the limits of variation reported with the butene distillation method.

Likewise, attributing the variation in results[4,7a,b,d,8] obtained by the catalytic decomposition of 1-butanol on $Al_2O_3$ to the method of analysis is hardly justified, especially when one considers the effect of the acidic nature of the catalyst and temperature on the composition of butenes obtained.[7a,8b,9]

**The Distillation of Dibromobutanes at Atmospheric Pressure.**—In view of the recent work of Komarewsky, Johnstone and Yoder[2a] it seemed advisable to determine whether the normal dibromobutanes actually do undergo isomeric change during distillation, it being recalled that the rearrangements reported by Faworsky[10] were done at 210–230° and required long periods of heating. We, therefore, slowly distilled a mixture of dibromobutanes at 760 mm. through a 70-cm. bead column in order to approximate the conditions of Lépingle[7b] and Matignon.[8b] The entire product distilled between 159–165°. No high-boiling residue was obtained. The properties of the 111.5 g. of original material were $n^{25}_D$ 1.5118, reaction-rate constant 0.0600, and $d^{25}_4$ 1.7835; those of the 109.0 g. of final product were $n^{25}_D$ 1.5118, reaction-rate constant 0.0598, and $d^{25}_4$ 1.7828. The absence of change in the reaction-rate constant shows that no isomerization had occurred. Traces of decomposition products due to the loss of hydrogen bromide were the cause of the slight change in density but a distillation at reduced pressure would undoubtedly restore the density to its previous value.[11]

In connection with the use of the reaction-rate-dibromide method of analysis, it should be noted that the original rate constants of Dillon, Young and Lucas[3] give better results than the new constants of Dillon.[12] In view of the fact that the synthetic methanol now available gives rate con-

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[4] Young and Lucas, THIS JOURNAL, **52**, 1964 (1930).

[5] Hurd and Goldsby, *ibid.*, **56**, 1812 (1934).

[6] Kistiakowsky, Ruhoff, Smith and Vaughan, *ibid.*, **57**, 878 (1935).

[7] (a) Ipatieff, Pines and Schaad, THIS JOURNAL, **56**, 2697 (1934); (b) Lépingle, *Bull. soc. chim.*, **39**, 741 (1926); (c) King, *J. Chem. Soc.*, **115**, 1404 (1919); (d) Coffin and Maass, THIS JOURNAL, **50**, 1429 (1928).

[8] (a) Davis, *ibid.*, **50**, 2779 (1928); (b) Matignon, Moureu and Dode, *Compt. rend.*, **196**, 973, 1561 (1933).

[9] After this manuscript was prepared, an article appeared which likewise attributed the above-mentioned variations to the effect of catalyst and temperature rather than to the method of analysis; see Matignon, Moureu and Dode, *Bull. soc. chim.*, [5] **2**, 1169 (1935).

[10] Faworsky, *Ann.*, **354**, 370 (1907).

[11] See the "Purification of Dibromobutanes," Young and Lucas, THIS JOURNAL, **52**, 1967 (1930).

[12] Dillon, *ibid.*, **54**, 952 (1932).

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).