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

# Allylic Rearrangements. II. Crotyl and Methylvinylcarbinylmagnesium Bromides[1]

BY WILLIAM G. YOUNG, SAUL WINSTEIN AND ARTHUR N. PRATER

The possibility of the occurrence of allylic rearrangements during the formation and hydrolysis of the Grignard reagent from mixtures of crotyl and methylvinylcarbinyl bromides was reported some time ago,[2] but at that time it was not possible to determine accurately in which reaction and to what extent rearrangements occurred in going from crotyl alcohol or methylvinylcarbinol to butene mixtures. Because of recent developments in our knowledge of the composition of these bromobutene mixtures,[3] it is now possible to show that an allylic rearrangement to an equilibrium does occur when these bromides are converted into Grignard reagents and then into butenes.

We have converted different mixtures of crotyl and methylvinylcarbinyl bromides into Grignard reagents, have hydrolyzed the latter with dilute acid and have analyzed the resulting butene mixtures by the dibromobutane reaction rate method.[4] Regardless of the composition of the starting bromide, the same mixture of the three normal butenes was obtained.

## Discussion of Results

The variations from a mean value in the compositions of the butenes obtained from the various bromide mixtures were, in general, of the order of magnitude usually obtained from the method of analysis[4] when a distillation of the dibromobutanes is necessary. The mean composition of the mixtures was 56.4 ± 2.0% 1-butene, 26.5 ± 1.4% *cis*-2-butene and 17.2 ± 3% *trans*-2-butene, whereas mixtures varying from 10% 1-butene and 90% 2-butene to 80% 1-butene and 20% 2-butene would have been obtained if no allylic rearrangements were involved in the transformation of the mixtures of $\alpha$- and $\gamma$-methylallyl bromides into butenes. Further evidence of the rearrangement is shown by the fact that both *cis*- and *trans*-2-butenes are formed whereas the crotyl bromide consisted at most of only a few per cent. of *cis* isomer.[3,5]

The results cannot be due to a rearrangement either of the initial bromide mixtures or the final butenes. The bromides were present in the ether solution only a very short time after being dropped into the reaction mixture due to the very rapid reaction to form the Grignard reagent. The contact time of the liberated butenes on the pasty solid from which they were liberated was very short, the temperature was low, and the butene composition disagrees with the few facts which are known about butene equilibria.[6] It is certain that an allylic rearrangement to an equilibrium has taken place either in the preparation or hydrolysis of the Grignard reagent or at both steps, but it is desirable to analyze the situation further.

When both the primary and secondary forms of a Grignard reagent may be isolated it is possible to show whether or not a rearrangement occurs in the reaction of the Grignard reagent with other materials and to classify these materials as normal or abnormal reactants as was done in the case of the benzyl and *o*-tolylmagnesium chloride system.[7] In our case, as with the cinnamylmagnesium chloride system,[8] information is available only on the over-all reaction.

Although more work must be done to locate the exact reaction or reactions in which the rearrangement occurs it is possible to give qualitative evidence at this time. If we assume that no rearrangement occurs during hydrolysis of the Grignard reagent, then the butene composition is a measure of the composition of the Grignard reagent. Since the equilibrium composition of the $\alpha$- and $\gamma$-methylallyl bromide mixture is known[3] and that of the Grignard is assumed to correspond to that of the butene mixture, namely, 56% primary and 44% secondary, it is possible to predict the composition of the hydrocarbons obtained when the bromide and Grignard reagent are allowed to couple. The ratio of primary to secondary radicals in the coupling product is predicted to be 66:34 assuming that the coupling reaction is normal.[9] This prediction is in good agreement

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

[3] Winstein and Young, *ibid.*, **57**, 2013 (1935).

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

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

[6] Hurd and Goldsby, THIS JOURNAL, **56**, 1812 (1934).

[7] Austin and Johnson, *ibid.*, **54**, 647 (1932).

[8] Gilman and Harris, *ibid.*, **53**, 3541 (1931).

[9] The coupling reaction of allyl bromide with benzylmagnesium chloride has been shown to be normal.[7]

TABLE OF RESULTS

| Run number | 1[a] | 2 | 3 | 4 | 5 | 6[a] | Mean butene composition |
|---|---|---|---|---|---|---|---|
| $n^{23}$D of bromide mixture | | 1.4772 | 1.4771 | 1.4750 | 1.4738 | 1.4650 | |
| % Crotyl bromide | 90 | 82.9 | 82.4 | 71.5 | 65.3 | 19.7 | |
| % $\alpha$-Methylallyl bromide | 10 | 17.1 | 17.6 | 28.5 | 34.7 | 80.3 | |
| $n^{25}$D of $C_4H_8Br_2$ mixture | 1.5118 | 1.5121 | 1.5118 | 1.5121 | 1.5121 | 1.5118 | |
| Calcd. $n^{25}$D of $C_4H_8Br_2$ mixture | 1.5119 | 1.5121 | 1.5118 | 1.5120 | 1.5120 | 1.5118 | |
| Reaction rate, $K_2$, of $C_4H_8Br_2$ mixture | 0.0596 | 0.0611 | 0.0605 | 0.0599 | 0.0601 | 0.0604 | |
| $d^{25}_4$ of $C_4H_8Br_2$ mixture | 1.7836 | 1.7845 | 1.7837 | 1.7842 | 1.7843 | 1.7835 | |
| % 1,2-$C_4H_8Br_2$ (1-butene) | 53.7 | 60.4 | 55.2 | 57.0 | 57.7 | 54.2 | 56.4 ± 2.0[b] |
| % *dl*-2,3-$C_4H_8Br_2$ (*cis*-2-butene) | 27.0 | 26.8 | 24.8 | 28.4 | 28.2 | 24.1 | 26.5 ± 1.4 |
| % *meso*-2,3-$C_4H_8Br_2$ (*trans*-2-butene) | 19.4 | 13.0 | 20.2 | 14.8 | 14.0 | 21.8 | 17.2 ± 3.3 |

[a] The authors were assisted in these runs by Mr. John Lane. [b] In preliminary experiments[2] traces of solvent persisted in the dibromobutane samples, as has already been explained, causing the density to be low. On the basis of reaction rate measurements alone it was evident that at least 10% 1-butene must have been present even though it was assumed that the product was mainly *trans*-2-butene. When it became possible to use both the rates and densities in the calculations it was found that *cis*-2-butene was also present thus causing the original estimate of the 1-butene content to be much too low.

with the composition of the hydrocarbon mixture obtained by Lespieau and Heitzmann[10] from the action of magnesium on his so-called crotyl bromide and with the results of Prévost on the similar 5-carbon system.[11] It therefore appears that the rearrangement actually takes place during the formation of the Grignard reagent and that we have determined the composition of this reagent. Further work is now being done which should test the validity of the foregoing assumptions.

## Experimental Part

**Alcohols.**—The following alcohols were used as sources of the mixtures of crotyl and methylvinylcarbinyl bromides: crotyl alcohol (which contained 30% butyl alcohol) from Charon's method;[12] pure crotyl alcohol from the aluminum isopropoxide method;[13] and methylvinylcarbinol from Delaby's method as modified by Prévost.[14] The properties of the alcohols in the order named above were: b. p. 117-121, 120-122 and 96-97.5°; $n^{25}$D 1.4190, 1.4271 and 1.4119.

**Bromide Mixtures.**—Mixtures of crotyl and methylvinylcarbinyl bromides were prepared in yields of 80-90% by the methods previously described.[3] The compositions of the bromide mixtures at the time of use, as shown in the table of results, were determined by refractive index measurements.[3] In the one case where the refractive index was low due to the presence of butyl bromide arising from the butyl alcohol present in Charon's crotyl alcohol, the composition was estimated by comparison with other mixtures having undergone a similar treatment. Carius analyses on the mixtures gave values for per cent. bromine varying from 59.03 to 59.30, the theoretical being 59.20.

**Preparation and Hydrolysis of the Grignard Reagent.**—The Grignard reagents were prepared in 80-85% yields in diethyl ether from approximately 1 mole quantities of bromide mixtures by the procedure outlined in a previous paper.[15] After the Grignard reagents were prepared, the solutions of the reagents in ether were decanted from the excess magnesium, and the ether was distilled off through a 40-cm. column with the aid of a water-bath at 40-50°, the last portion being removed at reduced pressure.

The well-cooled and well-stirred Grignard reagents were then hydrolyzed by slow dropwise addition of 2 *N* sulfuric acid. The evolved butene passed through a 100-cm. spiral reflux condenser, a safety bottle, a spiral gas washer containing 23% perchloric acid, and a soda lime-calcium chloride tube into a brominating flask held at −15°, where pure, dry bromine was added at a rate such that any excess did not impart more than faint color to the dibromobutane already formed. The dibromobutane was washed with solutions of sodium bisulfite, then sodium carbonate, and finally with water and dried over calcium chloride. The butyl constituent in the case of the one mixture which contained butyl bromide was almost entirely eliminated at this stage as butane which did not react with the bromine.

**Purification of the Dibromobutanes.**—In preliminary experiments it was found that dibromobutanes prepared from the Grignard reagent were not completely freed from ether by the distillation procedure ordinarily used in preparing the dibromides for analysis. In order to remove this ether and, in one case, butane from the preparation, the crude dibromobutane samples were brought to boiling at 50 mm. pressure under a 70-cm. fractionating column. The volatile material was trapped out with solid carbon dioxide and the heating was stopped when the first drop of dibromobutane distilled. This treatment removed the bulk of the volatile materials. The dibromobutane preparations were further purified by dropping them upon twice the theoretical amount of zinc dust in boiling alcohol, the regenerated butenes again being passed through the above-described purification-bromination train. The resulting dibromobutanes were washed and

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(10) Lespieau and Heitzmann, *Compt. rend.*, **200**, 1077 (1935).

(11) Prévost and Richard, *Bull. soc. chim.*, [4] **49**, 1368 (1931).

(12) Charon, *Ann. chim. phys.*, [7] **17**, 216 (1899).

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

(14) Prévost, *Ann. chim.*, [10] **10**, 147 (1928).

(15) Young, Prater and Winstein, THIS JOURNAL, **55**, 4908 (1933).

dried as above; 95% yields were obtained in the regenerations.

The dibromobutane samples were then distilled at 50 mm. pressure through the column described by Lucas, Dillon and Young.[16] The first part of the distillation was conducted slowly to strip out the last possible residual traces of low-boiling impurities, the first distillate being collected in several small fractions, of which the first one or two were discarded. Refractive indices of the fractions indicated that the impurities when present were removed in the first part of the distillate. That no change in composition is wrought by the purification procedure used already has been definitely shown.[17]

The boiling ranges of the dibromobutane mixtures through the apparatus used were all approximately 76.2–79.4°. Carius analyses were in the range 73.80–74.18% Br, theoretical 74.03.

**Analysis of the Dibromobutane Mixtures.**—The reaction rate determinations necessary for the analysis of the dibromobutanes were carried out exactly as described by Dillon, Young and Lucas.[4] The methyl alcohol preparations in this work were those used by Young and Winstein.[17] Duplicate rate runs were always made. Eight tubes, titrated successively at two to two and one-half hour intervals after a lapse of sixteen to twenty hours, constituted a run. The results of duplicate runs never differed by more than 0.0003.

The average corrected pseudo-specific reaction rate constants, the densities corrected to vacuum and the compositions of the mixtures appear in the table of results. As a further check on the analyses a comparison of the calculated and observed refractive indices is also included.

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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 converted into Grignard reagents and then decomposed to form butenes. The rearrangement apparently occurs only during the formation of the Grignard reagent.

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

[17] Young and Winstein, *ibid.*, **58**, 102 (1936).

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[CONTRIBUTION FROM THE CHEMICAL LABORATORY OF THE WASHINGTON SQUARE COLLEGE OF NEW YORK UNIVERSITY]

# The Grignard Reaction on Alpha-Pinene Oxide

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The action of Grignard reagents upon alpha-pinene oxide (I) has been investigated recently by Prileshaev and Vershuk.[2] These authors stated that the reaction proceeds in a complicated manner with methyl, ethyl and isopropylmagnesium halides with the formation in each case of gaseous products and an alcohol (IV). Isobutyl and phenylmagnesium halides, however, appeared to act normally to form saturated alcohols (V).

We have repeated and extended this work, and have now secured evidence which indicates that the alcohol formed from alpha-pinene oxide and methylmagnesium iodide is methylcampholenol (III). The newly assigned structure is based upon the fact that campholenic aldehyde (II), prepared by isomerization of alpha-pinene oxide with anhydrous zinc bromide according to the method of A. Arbuzov[3] reacts with methylmagnesium iodide to yield methylcampholenol (III) identical with that obtainable directly from alpha-pinene oxide by the action of the same reagent. The products of the action of a series of Grignard reagents upon alpha-pinene oxide seem to be analogous to methylcampholenol, and probably possess the same type of structure.

It has been found recently by Arbuzov[3] that the Reformatzky reaction upon alpha-pinene oxide likewise involves a simultaneous isomerization to campholenic aldehyde (II). It may be noted also that products of ring isomerization in Grignard reactions with other cyclic olefin oxides have been observed occasionally.[4]

The volumes of gases evolved in these reactions were found to diminish greatly, and the yield of alcohol to increase correspondingly, when the reaction is allowed to take place for a longer period and at an elevated temperature. Even so, not inconsiderable amounts of gas are obtained, although the quantity is small in comparison with the yield of alcohol. The gases apparently arise

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[1] This paper is based upon a portion of the Dissertation submitted by Mr. Russell to the Graduate School of New York University in December, 1935, in partial fulfilment of the requirements for the Ph.D. degree.

[2] Prileshaev and Vershuk, *J. Russ. Phys.-Chem. Soc.*, **61**, 473 (1929).

[3] A. Arbuzov, *Ber.*, **68**, 1430–1435 (1935).

[4] Bedos, *Compt. rend.*, **189**, 255 (1929); Godchot and Conquil, *ibid.*, **186**, 375, 954 (1928); Godchot, Conquil and Bedos, *Bull. soc. chim.*, **43**, 521 (1928); Vavon and Metchavetch, *Compt. rend.*, **186**, 702 (1928).