[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, UNIVERSITY OF ARKANSAS]

A Tracer Study of the Mechanism of the Conversion of Methallyl Alcohol to Isobutyraldehyde[1,2]

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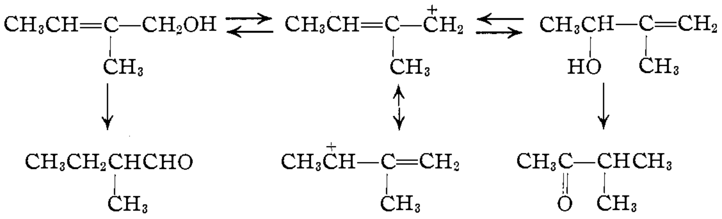
Methallyl-1-C^{14} alcohol has been prepared and converted to isobutyraldehyde by the action of 12% sulfuric acid. The isobutyraldehyde was degraded, and essentially all of the carbon-14 activity was shown to be in the carbonyl carbon. This result shows that the alcohol to aldehyde conversion takes place without intervention of a mesomeric allylic cation, since such a cation would lead to distribution of carbon-14 activity between the 1-position and the 3-position. The addition of hydrogen ion to the double bond of methallyl alcohol and subsequent conversion of the ion formed to isobutyraldehyde must be more rapid than the loss of water from the conjugate acid of methallyl alcohol.

Introduction

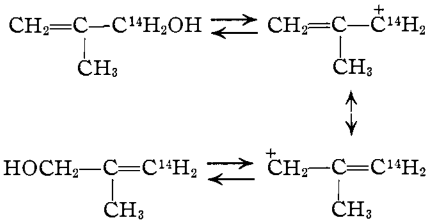
The conversion of methallyl alcohol (2-methyl-2-propen-1-ol) to isobutyraldehyde upon treatment with acid has long been known.[3] In 1941, Hearne, Tamele and Converse[4] reported on a fairly extensive study of the reaction. Yields of 96% of isobutyraldehyde were obtained upon treatment of methallyl alcohol with 12% sulfuric acid.[5] The reaction is apparently quite general for allylic alcohols. Allyl alcohol forms propionaldehyde[6] under the influence of acid, and a mixture of 3-methyl-2-butanone and 2-methyl-1-butanal is obtained upon treatment of either 2-methyl-2-buten-1-ol or 3-methyl-3-buten-2-ol with 13% sulfuric acid.[4]

In this last reaction the fact that nearly the same mixture of carbonyl compounds is obtained from either alcohol indicates that a mesomeric allylic cation is involved.



$$\begin{array}{ccccc} CH_3CH{=}\underset{CH_3}{C}{-}CH_2OH & \rightleftarrows & CH_3CH{=}\underset{CH_3}{C}{-}\overset{+}{C}H_2 & \leftrightarrows & CH_3\underset{HO}{CH}{-}\underset{CH_3}{C}{=}CH_2 \\ \downarrow & & \updownarrow & & \downarrow \\ CH_3CH_2\underset{CH_3}{CH}CHO & & CH_3\overset{+}{C}H{-}\underset{CH_3}{C}{=}CH_2 & & CH_3\underset{O}{\overset{\|}{C}}{-}\underset{CH_3}{CH}CH_3 \end{array}$$

If such a mesomeric ion were involved in the case of methallyl alcohol, it would not be detectable by ordinary chemical means, since the product of the allylic rearrangement of methallyl alcohol is still methallyl alcohol. However, if methallyl-1-C^{14} alcohol were used, such a rearrangement would show up in the distribution of carbon-14 between the 1-position and the 3-position



$$\begin{array}{ccc} CH_2{=}\underset{CH_3}{C}{-}C^{14}H_2OH & \rightleftarrows & CH_2{=}\underset{CH_3}{C}{-}\overset{+}{C}{}^{14}H_2 \\ & & \updownarrow \\ HOCH_2{-}\underset{CH_3}{C}{=}C^{14}H_2 & \rightleftarrows & \overset{+}{C}H_2{-}\underset{CH_3}{C}{=}C^{14}H_2 \end{array}$$

In order to study this reaction, we have prepared methallyl-1-C^{14} alcohol and have converted it to isobutyraldehyde in 94% yield using 12% sulfuric acid. The aldehyde has been degraded and the position of labeling determined.

Experimental

Preparation of Methallyl-1-C^{14} Alcohol.—Sodium isobutyrate-1-C^{14} was prepared from barium carbonate-C^{14} by a standard Grignard procedure[7] with minor modifications. Isobutyric-1-C^{14} acid with a suitable activity level was prepared by refluxing inactive isobutyric acid with the active salt for 1 hr.[8] Activity measurements showed that complete exchange had taken place. The isobutyric-1-C^{14} acid was converted to ethyl α-bromoisobutyrate-1-C^{14} by treatment with phosphorus and bromine and decomposition of the bromoacid bromide with ethyl alcohol.[9] The bromoester was dehydrobrominated to ethyl methacrylate-1-C^{14} by dimethylaniline using the method of Blaise and Courtot.[10]

Thirty grams of this ethyl methacrylate-1-C^{14} stabilized with hydroquinone was added dropwise with stirring to a slurry of 6 g. of lithium aluminum hydride in 300 ml. of anhydrous ether at 0°. When the addition was complete, 30 ml. of water was added to decompose the excess hydride and the product complex. The ether solution was decanted from the resulting white, granular solid and was dried and fractionated to give 10.9 g., 58% yield, of methallyl-1-C^{14} alcohol, b.p. 110–112° (730 mm.); reported[11] b.p. 114.49°. The methallyl alcohol was characterized as its 3,5-dinitrobenzoate, m.p. 77.5–78°. *Anal.* Calcd. for $C_{11}H_{10}N_2O_6$:

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[2] This paper was abstracted from the thesis submitted by Douglas Currell in partial fulfillment of the requirements for the Ph.D. degree, Department of Chemistry, University of Arkansas, 1956, and was presented before the 129th Meeting of the American Chemical Society, Dallas, Texas, April 8–13, 1956.

[3] M. Sheshukov, *J. Russ. Phys. Chem. Soc.*, **16**, 478 (1884); Z. Pogorshelski, *ibid.*, **36**, 1129 (1904); H. Groll and M. Tamele (to Shell Development Co.) U. S. Patent 2,010,076 (Aug. 6, 1935).

[4] G. Hearne, M. Tamele and W. Converse, *Ind. Eng. Chem.*, **33**, 805 (1941).

[5] Numerous other closely related compounds also give isobutyraldehyde upon heating or treatment with acid. Most of these are derivatives of isobutylene glycol, and the reaction is of the pinacol rearrangement type. Intermediates similar to that formed by the action of acid on methallyl alcohol undoubtedly are involved. See E. Linnemann and V. Zotta, *Ann.*, **162**, 33 (1872); K. Krasuskii, *J. Russ. Phys. Chem. Soc.*, **34**, 287 (1902); W. Ipatiew and W. Leontowitsch, *Ber.*, **36**, 2016 (1903); A. Behal and M. Sommelet, *Compt. rend.*, **138**, 89 (1904); *Bull. soc. chim.*, [3] **31**, 300 (1904); M. Sommelet, *Ann. chim.*, [8] **9**, 548 (1906); R. Stoermer, *Ber.*, **39**, 2288 (1906); K. Krasuskii, *Ukrainskii Khem. Zhurnal*, **4**, Sci. Pt., 61 (1929); J. Hersh and R. Nelson, THIS JOURNAL, **58**, 1631 (1936); A. Dobryanskii, R. Gutner and M. Shchigel'-skaya, *J. Gen. Chem.* (*U.S.S.R.*), **7**, 1315 (1937); M. Tamele, C. Ott, K. Marple and G. Hearne, *Ind. Eng. Chem.*, **33**, 115 (1941); T. Cairns and J. Fletcher, THIS JOURNAL, **63**, 1034 (1941); K. Johnson and E. Degering, *J. Org. Chem.*, **8**, 10 (1943).

[6] "Allyl Alcohol," Shell Development Co., San Francisco, Calif., 1946, p. 33.

[7] M. Calvin, C. Heidelberger, J. C. Reid, B. M. Tolbert and P. F. Yankwich, "Isotopic Carbon," John Wiley and Sons, Inc., New York, N. Y., 1949, p. 178.

[8] A. Fry, B. M. Tolbert and M. Calvin, *Trans. Faraday Soc.*, **49**, 1444 (1953).

[9] B. C. Saunders and G. J. Stacey, *J. Chem. Soc.*, 1773 (1948).

[10] E. E. Blaise and A. Courtot, *Compt. rend.*, **140**, 371 (1905).

[11] M. Tamele, C. Ott, E. Marple and G. Hearne, *Ind. Eng. Chem.* **33**, 115 (1941).

C, 49.62; H, 3.79; N, 10.53. Found: C, 50.57; H, 3.80; N, 10.57.

Conversion of Methallyl-1-C^{14} Alcohol to Isobutyraldehyde.[4]—Eight grams of methallyl-1-C^{14} alcohol was added to 30 ml. of 12% sulfuric acid. The resulting two-phase mixture was refluxed for 2 hr. Isobutyraldehyde was then distilled off over a period of an hour at 60–64° (730 mm.); reported[4] b.p. 64.1°. The yield was 7.5 g., 94% of theoretical. The aldehyde was identified as the 2,4-dinitrophenylhydrazone, m.p. 180–182°; reported[12] m.p. 182°; and as the methone, m.p. 153–154°; reported[13] m.p. 153–154.5°.

Degradation of Isobutyraldehyde.—In order to establish the activity distribution in the isobutyraldehyde, it was degraded by conversion to α-isopropylbenzyl alcohol followed by oxidation of the alcohol to benzoic acid and carbon dioxide.

A solution of 7.2 g. (0.10 mole) of the labeled isobutyraldehyde in 30 ml. of anhydrous ether was added dropwise to a stirred solution of 0.10 mole of phenylmagnesium bromide in 100 ml. of anhydrous ether at 0°. The resulting addition compound was decomposed with a saturated ammonium chloride solution, and the ether phase was separated, dried and fractionated. α-Isopropylbenzyl alcohol was collected at 121° (20 mm.); reported[14] b.p. 112–113° (15 mm.).

The α-isopropylbenzyl alcohol was oxidized with nitric acid in a sweep system which had been previously flushed with dry, carbon dioxide-free nitrogen. The two phase mixture of 60 ml. of 50% nitric acid and 2.0 g. (0.013 mole) of α-isopropylbenzyl alcohol was heated for 9 hr. at a temperature sufficient to produce a gentle evolution of gas. During this time, the gaseous oxidation products were swept out by a stream of nitrogen through a reflux condenser, a trap cooled to −80° and a spiral bubbler filled with carbonate-free sodium hydroxide solution. The carbon dioxide absorbed in the bubbler was determined as barium carbonate. The barium carbonate weighed 2.3 g. (0.012 mole), corresponding to approximately one mole per mole of carbinol. In other runs the amount of barium carbonate obtained varied from 0.89 to 0.94 mole per mole of carbinol.

At the end of 9 hr. the reaction flask was cooled with shaking. The crude benzoic acid which precipitated weighed 1.2 g., corresponding to a 75% yield. The acid was purified by recrystallization from water, from cyclohexane and by successive sublimations until constant activity was attained. The final product melted at 122.1–122.2°; reported[15] m.p. 122.36°.

Presumably acetic acid was also formed as a product of the oxidation, but it was not isolated.[16]

Radioactivity Determinations.—The samples whose activities were to be determined weighed from 5 to 20 mg. and were converted to carbon dioxide by a modification of the wet combustion method of Van Slyke, Folch and Plazin.[17] The carbon dioxide formed was transferred to an ionization chamber by the method of Neville,[18] and the activity measurements were made by a rate of charge method using a vibrating reed electrometer feeding into a Brown recorder. All measurements were corrected for background activity. All of the solids whose activities were determined were purified to constant activity. The activities of methallyl alcohol and isobutyraldehyde were determined both as pure liquids and as solid derivatives. It was found that the liquids tended to spatter when the combustion fluid was added in the usual manner. This difficulty was avoided by freezing the sample in liquid nitrogen or a Dry Ice–isopropyl alcohol bath before adding the combustion fluid.

Two or more activity determinations were made on each sample of each compound. The average error in duplicate activity determinations for a given sample was less than 1% for measurements made in close succession and between 1 and 2% for measurements made over intervals of several days.

Results

The results of the activity determinations on the various compounds are presented in Table I.

TABLE I

Compound	Activity, μcuries/mmole × 10^3 Run 1	Run 2	Run 3[a]
Isobutyraldehyde			26.4
Isobutyraldehyde 2,4-dinitrophenylhydrazone	16.3		
Isobutyraldehyde methone	16.1	13.1	25.7
Benzoic acid	15.5	13.1	25.3
Carbon dioxide		0.159	0.609

[a] In run 3, the molar activity of methallyl-1-C^{14} alcohol was 25.7 and of its 3,5-dinitrobenzoate, 27.1 × 10^{-3} μcuries/mmole.

These results show that the molar activity of the benzoic acid is the same as that of the isobutyraldehyde within the experimental error of about 2%. The activity of the benzoic acid is a measure of the activity of the 1-position in the isobutyraldehyde, so essentially all of the activity in the isobutyraldehyde is in the 1-position. Thus there was practically no distribution of activity away from the 1-position in the formation of the aldehyde from the alcohol. This also shows that essentially all of the activity in the methallyl alcohol is in the 1-position. These results are confirmed by the almost negligible amount of activity in the barium carbonate since the activity of the carbon dioxide produced in the oxidation of α-isopropylbenzyl alcohol is a measure of the activity in the remainder of the isobutyraldehyde molecule.

The small amount of activity in the barium carbonate may actually be the result of oxidation of the benzoic-1-C^{14} acid by nitric acid. An indication that this is true is given by the proportionately larger amount of activity in the barium carbonate when the nitric acid oxidation mixture was heated 12 hr. (run 3) than when it was heated 9 hr. (run 2). The ratio of barium carbonate activity to benzoic acid activity was 0.024 when the reaction time was 12 hr. and 0.012 when the heating time was 9 hr.

The fact that the activities of the methallyl alcohol, isobutyraldehyde and benzoic acid in run 3 are all essentially the same shows a proper material balance. In runs 1 and 2 the molar activities of the alcohol were higher than those of the aldehyde. This trouble was traced to impurities in inactive compounds used as diluents which resulted in formation of inactive isobutyraldehyde. In run 3 no dilution was made beyond the isobutyric acid stage.

Discussion

The fact that there is no appreciable distribution of carbon-14 between the 1-position and the 3-position in the isobutyraldehyde formed by the treatment of methallyl-1-C^{14} alcohol with acid demonstrates conclusively that a mesomeric allylic cation is not an intermediate in the reaction. This must necessarily mean that the aldehyde forming step proceeds more rapidly than loss of water from the conjugate acid of the alcohol.

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(12) R. L. Shriner and R. C. Fuson, "The Systematic Identification of Organic Compounds," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1940, p. 188.

(13) E. C. Horning and M. G. Horning, *J. Org. Chem.*, **11**, 95 (1946).

(14) V. Grignard, *Ann. chim.*, [7] **24**, 467 (1901).

(15) F. W Schwab and E. Wichers, *J. Research Natl. Bur. Standards*, **25**, 747 (1940).

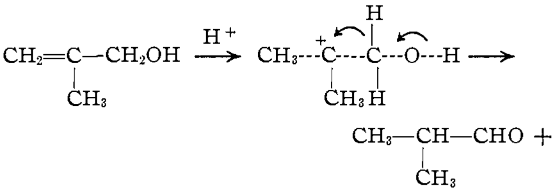
(16) Isolation and degradation of this compound and an independent degradation of the methallyl-1-C^{14} alcohol were made unnecessary by the nature of the activity results obtained. Preliminary plans for this research had included suitable schemes for these operations.

(17) D. Van Slyke, J. Folch and J. Plazin, *J. Biol. Chem.*, **136**, 509 (1940).

(18) O. K. Neville, This Journal, **70**, 3499 (1948).

The other intimate details of the aldehyde formation are not specifically covered by this work but can be inferred from this and other information.

The two points in methallyl alcohol most vulnerable to the electrophilic attack of an agent such as a proton are the double bond and the oxygen atom with its unshared pairs of electrons. Reaction of a proton with the oxygen atom could lead to the formation of an allylic cation through dissociation of the conjugate acid thus formed. This dissociation possibility is specifically ruled out by the present experimental results. Reaction of the proton with the double bond would result in the formation of a tertiary carbonium ion which could rearrange to the aldehyde by a hydride shift and proton elimination from oxygen.[19] The addition of the proton is probably the rate-determining step of the reaction. Taft[20] has shown that the rate-determining step in the hydration of isobutene in dilute nitric and sulfuric acid solutions is the addition of a proton to the double bond. One would expect similar considerations to apply in the case of methallyl alcohol.

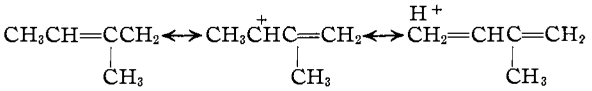


$$CH_2{=}\underset{\underset{CH_3}{|}}{C}{-}CH_2OH \xrightarrow{H^+} CH_3\cdots\overset{+}{\underset{\underset{CH_3}{|}}{C}}\cdots\overset{\overset{H}{|}}{\underset{\underset{H}{|}}{C}}\cdots O\cdots H \longrightarrow CH_3{-}\underset{\underset{CH_3}{|}}{CH}{-}CHO + H^+$$

It should be pointed out that the reversible formation of isobutylene glycol and isobutylene oxide during the reaction is not excluded and probably does occur. The reaction conditions are such that only the low boiling isobutyraldehyde is removed from the reaction mixture (see ref. 4 and 5).

The conclusion that a mesomeric allylic cation is not involved to any great extent in the conversion of methallyl alcohol to isobutyraldehyde is in striking contrast to the results of Hearne, Tamele and Converse mentioned above with 2-methyl-2-buten-1-ol and 3-methyl-3-buten-2-ol. These two alcohols differ from methallyl alcohol only in the replacement of a hydrogen in the 3-position and the 1-position, respectively, by a methyl group.

The difference in the two reactions can perhaps be explained on the basis of greater stability of the mesomeric allylic cation, in the later case due to hyperconjugation of the charge with the methyl group.



$$CH_3CH{=}\underset{\underset{CH_3}{|}}{C}CH_2 \longleftrightarrow CH_3\overset{+}{C}H\underset{\underset{CH_3}{|}}{C}{=}CH_2 \longleftrightarrow \overset{H^+}{CH_2}{=}CH\underset{\underset{CH_3}{|}}{C}{=}CH_2$$

Support for this idea is to be found in the work of Braude and Jones[21] who studied the conversion

$$RCH{=}CHCH(OH)C{\equiv}CH \longrightarrow RCH(OH)CH{=}CHC{\equiv}CH$$

and found that the rate of rearrangement when R was methyl was 3,867 times the rate when R was hydrogen.

Another indication of the relative difficulty in forming a methallyl cation is found in the results of an experiment reported by Vernon.[22] He found that the solvolysis of methallyl (2-methylallyl) chloride in 50% aqueous ethanol was largely bimolecular while the solvolysis of crotyl (3-methylallyl) chloride was largely unimolecular but with the incursion of a bimolecular component, again illustrating that a methyl group in the 3-position tends to favor the formation of an allylic cation.

On the basis of these considerations, one would expect that the conversion of allyl alcohol to propionaldehyde[6] would proceed without rearrangement through a mesomeric allylic cation. However, Nystrom and Leak[23] have shown that a mixture of allyl-1-C^{14} bromide and allyl-3-C^{14} bromide is formed from allyl-1-C^{14} alcohol on treatment with phosphorus tribromide and pyridine at −80°. Reaction through a mesomeric allylic cation is one possible explanation of their results. It would be interesting to study the conversion of allyl-1-C^{14} alcohol to propionaldehyde.

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(19) Another possible path for the reaction may go through a cyclic transition state involving the intramolecular transfer of a proton from the alcohol conjugate acid to the number three carbon, coupled with the other shifts shown here. This mechanism differs from that shown here only in the precise source of the proton which adds to the double bond and has certain attractive features. However, such a mechanism would seem to be unnecessarily complicated in the closely related conversion of isobutylene glycol to isobutyraldehyde.

(20) R. W. Taft, Jr., THIS JOURNAL, **74**, 5372 (1952).

(21) E. A. Braude and E. R. H. Jones, *J. Chem. Soc.*, 122 (1946).

(22) C. A. Vernon, *ibid.*, 423 (1954).

(23) R. F. Nystrom and J. C. Leak, THIS JOURNAL, **75**, 3039 (1953).