[Contribution from the Chemical Laboratories of the Polytechnic Institute of Brooklyn]

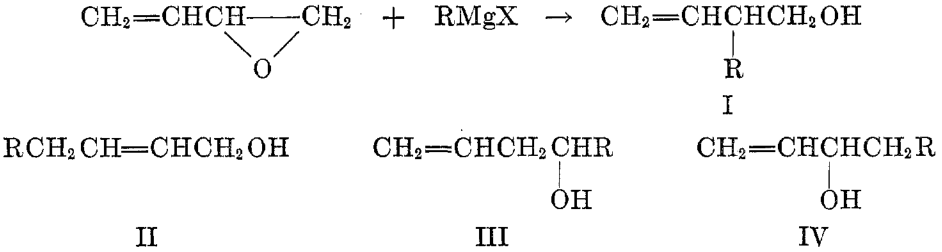
THE REACTION OF GRIGNARD REAGENTS WITH 3,4-EPOXY-1-BUTENE. II. ETHYLMAGNESIUM BROMIDE AND DIETHYLMAGNESIUM[1, 2]

ROBERT W. FREEDMAN[3] and ERNEST I. BECKER

Received June 20, 1951

INTRODUCTION

The conjugation of a vinyl group with an oxirane ring, as in 3,4-epoxy-1-butene, provides a variety of reaction paths with the Grignard reagent. These have been discussed in detail by Gaylord and Becker (1, 2), so that only the pertinent courses and more recent references are given here. The most likely products are those resulting from attack of R^- at the 3-position (I), attack at the 1-position accompanied by rearrangement to a primary allylic alcohol (II), addition of R^- preceded by rearrangement to vinylacetaldehyde (III), and attack at the 4-position with formation of a secondary allylic alcohol (IV).



I

II III IV

Semeniuk and Jenkins (3) obtained only one product which they claim to correspond to II, when R = methyl, cyclohexyl, phenyl, *o*-ethoxyphenyl, and 1-naphthyl. It was later shown, however, that the alcohol which results from the reaction with 1-naphthylmagnesium bromide corresponds to IV (1). More recently, Gmitter and Benton (4) have reported that α-thienylmagnesium bromide gives 25% of the alcohol corresponding to II. In none of these researches was an attempt made to seek out all of the feasible products.

It is the purpose of this investigation to isolate all of the products of the Grignard reaction employing ethylmagnesium bromide in order to evaluate the controlling factors in determining their structures. Reaction with diethylmagnesium was employed first in order to obtain only the products formed without rearrangement of the 3,4-epoxy-1-butene.

---

[1] The material presented here is taken from the Dissertation for the degree of Doctor of Philosophy presented by R. W. F. to the Graduate Faculty of the Polytechnic Institute of Brooklyn, June 1951.

[2] This paper was delivered at the XIIth International Congress of Pure and Applied Chemistry, New York, September 1951.

[3] Frederick Gardner Cottrell Research Fellow, July 1949 to June 1951.

RESULTS

When 3,4-epoxy-1-butene is treated with diethylmagnesium in ether, an exothermic reaction takes place to give a mixture of two unsaturated alcohols in a total yield of about 70%. Distillation separates the mixture into two alcohols, b.p. 86.4° (95 mm.), n_D^{25} 1.4310, and b.p. 100.5–101.5° (95 mm.), n_D^{25} 1.437–1.438, in a 3:1 ratio. Each of the alcohols rapidly decolorizes bromine in carbon tetrachloride. The lower-boiling alcohol gives an allophanate, m.p. 154.5–155° and a 3,5-dinitrobenzoate, m.p. 54.5–55.0°. Quantitative bromination and elemental analysis correspond to the expected empirical formula, $C_6H_{12}O$.

The higher-boiling alcohol gives an allophanate, m.p. 153°, which depresses the melting point of the allophanate of the lower-boiling alcohol. Quantitative bromination shows only 89% unsaturation based upon the formula $C_6H_{12}O$. Redistillation of this fraction through a 54-plate column does not improve the constants of this alcohol.

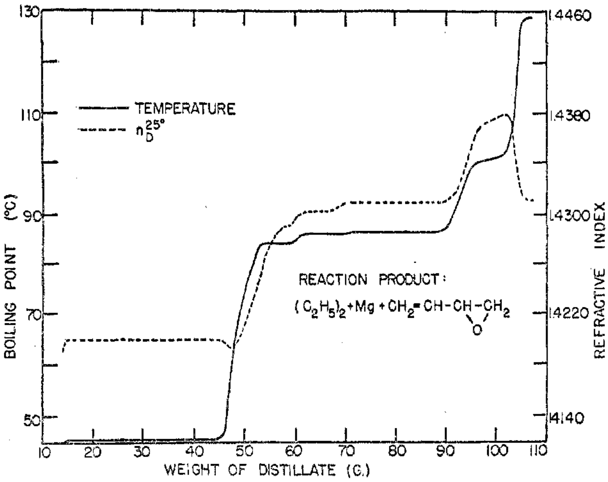
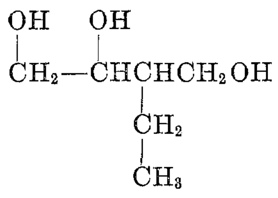


FIG. 1. DISTILLATION OF REACTION PRODUCT: $(C_2H_5)_2Mg + CH_2{=}CH{-}\underbrace{CH{-}CH_2}_{O}$

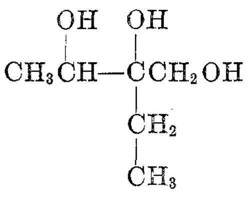
The carbon skeleton and position of the hydroxyl group of the lower-boiling alcohol were established by quantitative hydrogenation to 2-ethylbutanol, whose allophanate, m.p. 161.5–162.0°, and 3,5-dinitrobenzoate, m.p. 50–51°, did not depress the corresponding derivatives of authentic 2-ethyl-1-butanol. The position of the double bond was established in two ways. The infrared spectrum showed strong absorptions at 910 and 990 cm^{-1} which are characteristic of a terminal vinyl group (5, 6). A chemical proof was obtained by nearly quantitative hydroxylation of the double bond to give a trihydroxyhexane whose structure could be only V or VI depending upon whether the double bond was in the expected terminal position or the internal position, respectively.

Titration of the trihydroxy compound with periodic acid indicated that nearly one mole of periodic acid was consumed per mole of compound. Were VI the structure, the compound would have consumed two moles of periodic acid. Therefore, the trihydroxy compound is V, 2-ethyl-1,3,4-trihydroxybutane, and the lower-boiling alcohol is 2-vinyl-1-butanol corresponding to product I (See Chart I).



$\mathrm{CH_2(OH)\text{—}CH(OH)CH(CH_2CH_3)CH_2OH}$

V



$\mathrm{CH_3CH(OH)\text{—}C(OH)(CH_2CH_3)CH_2OH}$

VI

In view of the earlier work of Semeniuk and Jenkins (3) and of Gmitter and Benton (4), 2-hexen-1-ol appears to be a likely structure for the higher-boiling alcohol. Its synthesis was accomplished (7) by reduction of 2-hexenoic acid with lithium aluminum hydride to give an alcohol, b.p. 102° (95 mm.), n_D^{25} 1.4350, from which an allophanate, m.p. 154–155°, was prepared. No depression was observed in a mixed melting point with the allophanate of the higher-boiling alcohol, but there was depression with that of the lower-boiling alcohol. Therefore, the higher-boiling alcohol is 2-hexen-1-ol corresponding to II. (See Chart II for the proof of structure, which also shows additional derivatives of this alcohol obtained from another reaction.)

3,4-Epoxy-1-butene reacts with ethylmagnesium bromide exothermically to give a product mixture in a total yield of about 80%. Three individual alcohols were separated by distillation, a hitherto unobtained one, b.p. 78.0–78.5° (95 mm.), n_D^{25} 1.4300; 2-vinyl-1-butanol (I) and 2-hexen-1-ol (II) in a ratio of 2.7:4.0:3.3.

A search of the literature disclosed that only 1-hexen-3-ol and 1-hexen-4-ol have boiling points close to that of the newly obtained alcohol. Since 1-hexen-3-ol (the product corresponding to IV) was not found in the reaction with diethylmagnesium, 5-hexen-3-ol was chosen as the more likely structure. Accordingly, 5-hexen-3-ol was synthesized from allylmagnesium chloride and propionaldehyde. Comparison of the physical properties of the two alcohols showed no variations, and the allophanates and 3,5-dinitrobenzoates prepared from each exhibited no depression. Further, the infrared absorption spectrum showed the bands typical of the terminal double bond. Therefore, the new alcohol is 5-hexen-3-ol (II) corresponding to preliminary rearrangement of the oxide followed by addition of R^-.

With a larger quantity of 2-hexen-1-ol available from this reaction, the 3,5-dinitrobenzoate, m.p. 58.0–58.5°, was prepared and compared with the 3,5-dinitrobenzoate of the product obtained by reduction of 2-hexenoic acid (7), m.p. 57.0–58.0°, and showed no depression (see Charts II and III).

CHART I

Proof of Structure of 2-Vinyl-1-butanol

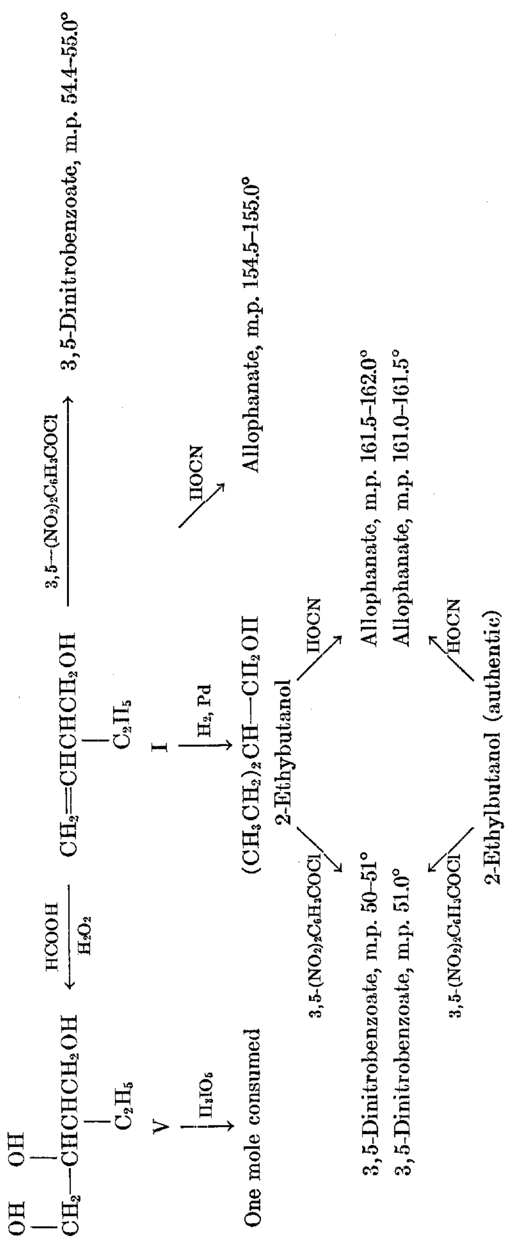
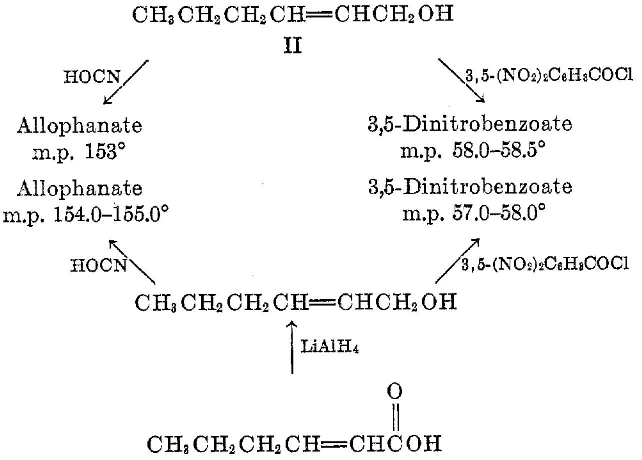


CHART II

PROOF OF STRUCTURE OF 2-HEXEN-1-OL



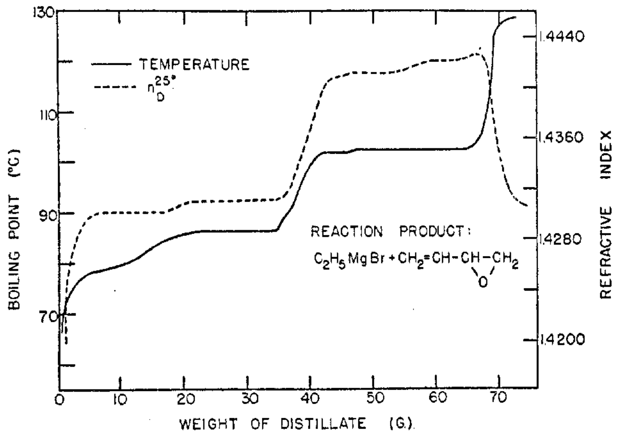
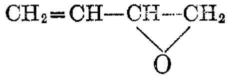


FIG. 2. DISTILLATION OF REACTION PRODUCT: $C_2H_5MgBr + CH_2{=}CH{-}CH{-}CH_2$



$CH_2{=}CH{-}\underbrace{CH{-}CH_2}_{O}$

TABLE I

PHYSICAL CONSTANTS OF 1-HEXEN-3-OL AND 5-HEXEN-3-OL

COMPOUND	B.P., °C., (MM.)	n_D (°C)	REF.
1-Hexen-3-ol	133.5–134	1.4215 (26)	8
	133.5–134.0		9
5-Hexen-3-ol	131.5–132.0	1.4320 (20)	10
	130	1.4330 (20)	11
5-Hexen-3-ol (This investigation)	76.0– 77.8 (95)	1.4294 (25)	

A sample of crude II, also from this reaction, was found by quantitative means to contain 5.6% bromine. The mixture reacted in the cold with alcoholic sodium hydroxide, producing bromide ion and resulting in an odor characteristic of 3,4-epoxy-1-butene. This indicates the presence of a bromohydrin of the empirical formula C_4H_7BrO, probably the α-bromohydrin. It is well-known that in the preparation of dialkylmagnesium by the addition of dioxane to an ethereal solution of alkylmagnesium bromide the precipitation of all halide is incomplete. Reaction of residual $RMgX_2$ or MgX_2 with 3,4-epoxy-1-butene could then account for the formation of bromohydrin. In turn, this bromohydrin may account for the difficulty in purification of the 2-hexen-1-ol obtained in the reaction with diethylmagnesium.

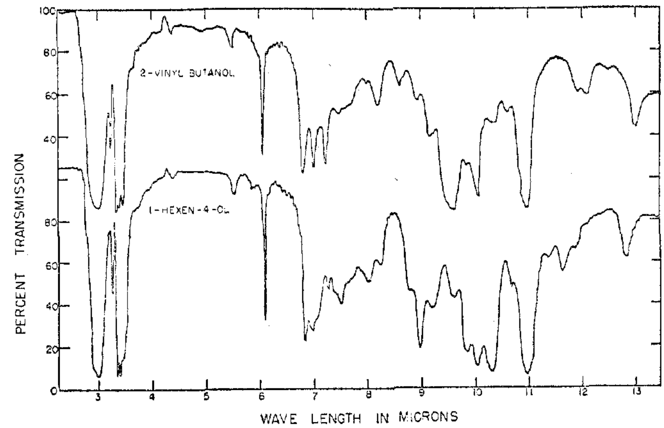
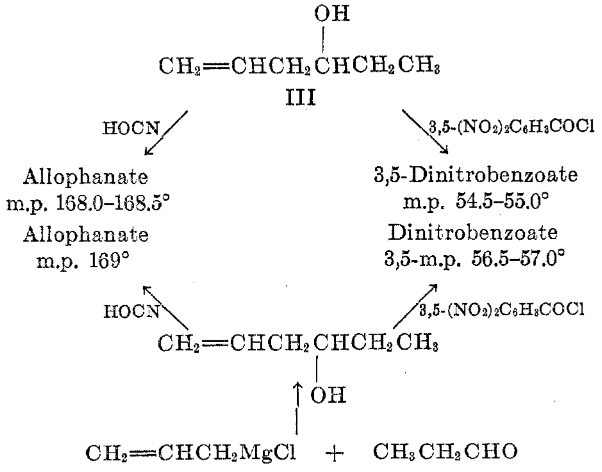


FIG. 3. INFRARED ABSORPTION SPECTRA OF HEXENOLS

CHART III

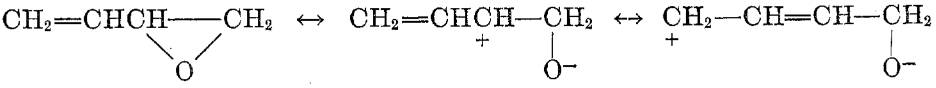
PROOF OF STRUCTURE OF 5-HEXEN-3-OL



$$CH_2{=}CHCH_2\overset{OH}{\overset{|}{C}}HCH_2CH_3$$

DISCUSSION

In general, two factors may be concerned with the opening of the oxide ring in 3,4-epoxy-1-butene; namely, an electronic factor and a steric factor. The electronic factor may be illustrated by the resonance structures a ↔ b ↔ c:



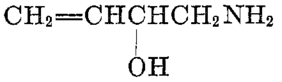
a b c

These structures, whose importance would be increased by coordination of the oxygen atom with Lewis acids, such as the magnesium atom in alkylmagnesium bromide or in dialkylmagnesium, would be expected, in the absence of strong steric factors, to direct the alkyl group to the 1- or 3-position. A larger proportion of 3-attack would be expected because of the proximity to the oxygen atom.

It is pertinent that the infrared spectrum of 3,4-epoxy-1-butene shows a bathochromic shift of the epoxide absorption-band when compared with that for a non-conjugated epoxide in accord with the postulate of interacting electronic forms (12).

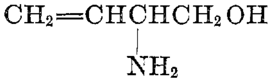
Previous workers have shown that magnesium or zinc halides cause rearrangement of organic oxides to aldehydes or ketones (13–21). Since Stewart and Ubbelohde (22) have shown that the Grignard solution probably contains magnesium ions, rearrangements of the oxirane ring may be expected in the presence of RMgX.

These considerations account satisfactorily for the formation of only two products corresponding to opening of the oxide ring at the 3-position with linking of the C_2H_5- group at the 3- and 1- positions with diethylmagnesium and the formation of an additional product resulting from initial rearrangement of the oxide in the presence of ethylmagnesium bromide. Likewise, the presence of bromohydrin is understood from the consideration that Br^- will compete weakly with $C_2H_5^-$ in the reaction. The fact that α-thienylmagnesium bromide (4) and 1-naphthylmagnesium bromide (1) give products corresponding to opening of the oxide ring at end positions may be due to steric factors, since arylmagnesium halides may actually be colloidal (23). Steric factors may also be operative in the reaction of anions such as $^-OCH_3$ in methanol (24, 25), diethyl malonate anion in ethanol (26), and acetoacetic ester anion in ethanol (27), which may be solvated or of such inherent size as to prevent attack at the 3-position. In this connection, Ettlinger (28) has observed that with the smaller ammonia molecule, both amino alcohols VII and VIII were formed. Thus, a large number of experimental results are now more consistently explained.



$CH_2{=}CHCH(OH)CH_2NH_2$

VII



$CH_2{=}CHCH(NH_2)CH_2OH$

VIII

Acknowledgment. The authors wish to express their sincere appreciation and thanks to Research Corporation for the financial support given throughout the course of this investigation.

EXPERIMENTAL

The addition of 3,4-epoxy-1-butene to diethylmagnesium. All temperatures are corrected except where noted.

Diethylmagnesium. The procedure employed was that of Norton and Hass (29) with the modification that dry dioxane was added dropwise to the Grignard solution under reflux to moderate the reaction which precipitates halide. Subsequently, the mixture was allowed to stir overnight and then was centrifuged. The insoluble cake was suspended in 500 ml. of 40% dioxane in ether and centrifuged. The combined liquid was concentrated at reduced pressure to a total volume of 1.0 liter. Acidimetric titration showed 51% yield of diethylmagnesium.

Addition of 3,4-epoxy-1-butene. 3,4-Epoxy-1-butene[4], b.p. 68° (760 mm.), n_D^{25} 1.4148, (106 g., 1.52 mole) was added dropwise with stirring to a solution of 0.76 mole of diethylmagnesium contained in 1.0 l. of ether-dioxane as obtained from its synthesis. After stirring for an additional hour, 400 ml. of saturated ammonium chloride solution was added dropwise and the mixture was filtered. The precipitate was washed with 100 ml. of iced 10% sulfuric acid and the combined filtrates extracted with four 100-ml. portions of ether. After drying the ethereal solution with two 15-g. portions of freshly ignited potassium carbonate, the ether was distilled using a column 75 x 1.5 cm. i.d. packed with 4.7 mm., single-turn helices, and tested at 12 theoretical plates. One-half of the yellow residue was mixed with 24 g. of 3,5,5-trimethylhexanol, b.p. 191° (760 mm.), n_D^{25} 1.4308, and fractionated at 95 mm. using an externally heated, helix-packed (1.6 mm.) column (50 x 1.2 cm. i.d.) tested at 19 theoretical plates, equipped with a solenoid operated take-off described by Diehl and Hart (30). After removing a forerun consisting mostly of ether the following fractions were obtained: 1. 31.4 g. of dioxane, b.p. 45.8° (95 mm.), n_D^{25} 1.4193–1.4289; 2. 34.6 g. of alcohol (I), b.p. 83.8–86.4° (95 mm.), n_D^{25} 1.4209–1.4310; 3. 8.2 g. of an intermediate fraction, b.p. 80.4–100.5° (95 mm.), n_D^{25} 1.4318–1.4368; and 4. 5.9 g. of alcohol (II), b.p. 100.5–103.4° (95 mm.), n_D^{25} 1.4368–1.4380. The over-all yield of isomeric alcohols ($C_6H_{12}O$) as determined by electrometric bromination (31) was 54.3 g. (0.543 mole, 70.3%). Based upon the distillation curve, this was divided into (I) 41.2 g. (53.4%) and (II) 13.1 g. (16.9%). The dioxane fraction showed no unsaturation, indicating no formation of azeotropes with the unsaturated alcohols which might have been expected.

Isolation of alcohol I. Distillation of 37 g. of the center-cut portion of two combined runs yielded a center cut consisting of 15.6 g., b.p. 86.2–86.4° (95 mm.), n_D^{25} 1.4310, d_4^{25} 0.8424.

Anal. Calc'd for $C_6H_{12}O$: C, 71.93; H, 12.08; R, 30.96.
Found: C, 71.56; H, 12.50; R, 30.78.

The *3,5-dinitrobenzoate* was prepared in the usual manner (32), m.p. 54.5–55.0° after three recrystallizations from petroleum ether (b.p. 28–38°).

Anal. Calc'd for $C_{13}H_{14}N_2O_6$: C, 53.06; H, 4.80; N, 9.54.
Found: C, 52.88; H, 4.61; N, 9.71.

The *allophanate* was prepared as usual (33), m.p. 154.5–155.0° after three crystallizations from acetone.

Anal. Calc'd for $C_8H_{14}N_2O_3$: C, 51.58; H, 7.58; N, 15.00.
Found: C, 51.80; H, 7.60; N, 15.04.

Allophanate of alcohol II. The allophanate of alcohol (II) was prepared, m.p. 153°. It did not depress the melting point of the allophanate of 2-hexen-1-ol, m.p. 154.0–155.0°; synthesized independently (7).

Hydroxylation of alcohol I. The procedure employed was that of Swern *et al.* (34).

---

[4] The preparation was carried out by modifying the procedure of Kadesch (24). Copies of this detailed procedure are available upon request.

Ten grams (0.10 mole) of I in 80 ml. of formic acid was treated with 13.0 g. of 28.8% hydrogen peroxide for 4.5 hours, maintaining the temperature at 40°. The solution was concentrated to a syrup at reduced pressure and below 40°, neutralized to phenolphthalein with alcoholic sodium hydroxide, and finally refluxed with 100 ml. of *N* sodium hydroxide to hydrolyze hydroxy-formoxy compounds. Neutralization with 0.5 ml. of formic acid, dilution to 50 ml. with absolute ethanol, and drying with sodium sulfate was followed by filtration, washing the cake with two 10-ml. portions of ethanol, and combining the filtrates. Concentration at 50° at reduced pressure gave 13.1 g. (0.0977 mole, 97.7%) of crude product. Two distillations gave an almost colorless product in 50% yield, b.p. 148–152° (1.5 mm.), 171.0–172.0° (10 mm.), n_{D}^{25} 1.4743; d_{D}^{25} 1.1050.

Anal. Calc'd for $C_6H_{14}O_3$: C, 53.71; H, 10.51; R, 34.49.

Found: C, 53.95, 54.11; H, 10.56, 10.62; R, 34.14.

According to the procedure of Malaprade (35), 0.1063 g. of V consumed periodic acid equivalent to 15.03 ml. of 0.1000 *N* sodium thiosulfate, corresponding to 94.9% of 1,2-glycol.

Hydrogenation of alcohol I. Using 5% palladium on charcoal as catalyst at 3 atm. overpressure, 10 g. (0.10 mole) of I absorbed 98% of the theoretical quantity of hydrogen. Distillation of 4.5 g. of the filtered product gave 2.55 g. (56%) of an alcohol, b.p. 149° (760 mm.) (uncorr.), n_{D}^{25} 1.4200 [reported for 2-ethyl-1-butanol (36): b.p. 146.27°, n_{D}^{25} 1.4205]. This alcohol did not decolorize a solution of potassium permanganate.

The *3,5-dinitrobenzoate* melted at 50–51° [reported (37): m.p. 51.5°]. It did not depress the melting point of the 3,5-dinitrobenzoate prepared from authentic 2-ethyl-1-butanol.

The *allophanate* melted at 161.5–162.0° [reported (33): m.p. 161.0–161.5°] and did not depress the melting point of the allophanate of the authentic material, m.p. 161.0–161.5°.

The addition of ethylmagnesium bromide. A mixture of 70 ml. of dry ether and 60 g. (0.855 mole) of 3,4-epoxy-1-butene was added dropwise with stirring under reflux to 0.859 mole of ethylmagnesium bromide in 272 ml. of dry ether. The mixture was stirred for two hours, and hydrolyzed with 80 ml. of water followed by a 0° mixture of 90 g. of sulfuric acid in 300 g. of water. The aqueous phase was extracted with three 100-ml. portions of ether, and the combined ether layers were washed with 10% potassium carbonate and dried over potassium carbonate. The ether was removed and the residue distilled under a pressure of 95.0 mm., collecting 40 g. of a forerun, b.p. 46.5–77.5°, n_{D}^{25} 1.4200–1.4290; followed by 12.5 g. of an isomeric hexenol (III), b.p. 77.5–84.0° (95 mm.), n_{D}^{25} 1.4290–1.3000; 4.8 g. of an intermediate fraction, b.p. 84.0–86.0° (95 mm.), n_{D}^{25} 1.4300–1.4308; 13.0 g. of I, b.p. 86.0–87.1° (95 mm.), n_{D}^{25} 1.4308–1.4310; 7.3 g. of an intermediate fraction, b.p. 87.1–101.9° (95 mm.), n_{D}^{25} 1.4310–1.4395; and 24.99 g. of II, b.p. 101.9–105.0° (95 mm.), n_{D}^{25} 1.4393–1.4427. The over-all yield of unsaturated isomeric alcohols ($C_6H_{12}O$) was 63.0 g. (73.8% yield), and on the basis of the distillation curve was subdivided into (III), 16.1 g. (0.161 mole, 18.9%); (I), 20.1 g. (0.201 mole, 23.5%) and impure (II), 26.8 g. (0.268 mole, 31.4%).

Isolation of alcohol III. A 7.29-g. portion, b.p. 78.5–85.0° (95 mm.), n_{D}^{25} 1.4300–1.4304, was redistilled using a concentric-tube column tested at 54 theoretical plates (7) collecting 5.64 g., b.p. 76.0–83.6° (95 mm.), n_{D}^{25} 1.4294–1.4305.

A middle fraction, b.p. 76.0–77.8° (95 mm.), n_{D}^{25} 1.4294–1.4295, was converted to the *3,5-dinitrobenzoate*, m.p. 53.5–54.5°. This did not depress the melting point of the 3,5-dinitrobenzoate prepared from authentic 5-hexen-3-ol, but it depressed the melting points of the 3,5-dinitrobenzoate of 2-vinyl-1-butanol and of 2-hexen-1-ol, respectively.

The *allophanate* was also prepared from this fraction, m.p. 168.0–168.5°. This did not depress the melting point of the allophanate of authentic 5-hexen-3-ol described later; it depressed the melting points of the allophanates of 2-vinyl-1-butanol and of 2-hexen-1-ol, respectively.

Isolation of alcohol II.—A total of 19.91 g. of the material, b.p. 102.3–105.0° (95 mm.), n_{D}^{25} 1.4411–1.4427, was combined with 4.00 g. of distillation pusher and the mixture distilled under 95.0 mm. pressure using the concentric-tube column collecting 10.51 g. of material. The boiling point rose continuously from 96.5–103.6° (95 mm.) and the refractive index dropped steadily from n_{D}^{25} 1.4414 to n_{D}^{25} 1.4406.

A 28.9-g. portion, b.p. 101.0–104.0° (95 mm.), n_D^{25} 1.4400–1.4425, was dissolved in 100 ml. of absolute methanol, 42.0 g. of bromine added at −40° to −20°, and the pale yellow solution carefully neutralized to phenolphthalein with methanolic sodium hydroxide. The mixture was dried with fused potassium carbonate and most of the methanol removed from the filtrate at reduced pressure at 30°. The residue was washed with water, diluted with an equal weight of ether, dried, and distilled using a Vigreux column. After collecting a forerun of ether, a residue (23.0 g.) remained consisting mainly of the dibromide. A small sample gave the boiling point 90–95° (1.5 mm.), n_D^{25} 1.5070.

A 33.0-g. fraction of the residue was treated with 10 g. of zinc shot and 30 ml. of 60% acetic acid under reflux at room temperature, applying external heat toward the end of the reaction, about ninety minutes. The product, weighing 15.4 g., was mixed with 10 g. of 3,3,5-trimethyl-1-hexanol and distilled at 30.0 mm. using the 50-cm. column. After collecting 1.73 g. of forerun, b.p. 50–66° (30 mm.), n_D^{25} 1.4169–4271, and 7.96 g. of alcohol (II), b.p. 66.0–75.5 (30 mm.), n_D^{25} 1.4271–1.4324, the latter fraction was redistilled in the concentric-tube column with 2 ml. of pusher added. A foreun of 0.85 g., b.p. 70.2–98.6° (95 mm.), n_D^{25} 1.4263; an intermediate fraction of 2.53 g., b.p. 98.6–101.8° (95 mm.), n_D^{25} 1.4330–1.4330; and 3.62 g. of alcohol (II), b.p. 102.2–103.6° (95 mm.), n_D^{25} 1.4340–1.4341, were collected.

The *3,5-dinitrobenzoate* was prepared without any difficulty and melted at 58.0–58.5°. It did not depress the melting point of the known 3,5-dinitrobenzoate, m.p. 57.0–58.0° (7) but it did depress the melting points of the 3,5-dinitrobenzoates of 2-vinyl-1-butanol and 5-hexen-3-ol.

Qualitative identification of the impurity in alcohol II. When a few drops of impure II were shaken with a cold 10% aqueous solution of sodium hydroxide, the characteristic odor of 3,4-epoxy-1-butene developed and a test for inorganic bromide became positive. A quantitative estimation of bromine (38) gave 5.6% bromine, corresponding to 7.9% of a bromohydrin, C_4H_7BrO (probably 4-bromo-3-hydroxy-1-butene derived from 3,4-epoxy-1-butene).

5-Hexen-3-ol. A solution of 58 g. (1.00 mole) of propionaldehyde in 75 ml. of ethyl ether was added dropwise to a dry, nitrogen-swept, 500 ml., 3-necked flask containing allylmagnesium chloride (from 40 g. of magnesium) (39) in 450 ml. of ether. Cooling was necessary during the addition; afterwards it was allowed to warm to room temperature with continued stirring under nitrogen. The contents of the flask were slowly added to 800 g. of ice and acidified with the slow addition of ice-cold 20% sulfuric acid. After separating the ether layer, and extracting the aqueous layer with two 100-ml. portions of ether, the combined extracts were washed once with water, dried over potassium carbonate, and distilled at atmospheric pressure to remove ether. The residue was mixed with 27 ml. of 3,3,5-trimethyl-1-hexanol and distilled in the 50-cm. column to give 78.2 g. (0.782 mole, 78%) of 5-hexen-3-ol, b.p. 125–133° (760 mm.). A heart-cut boiled at 132° (760 mm.), n_D^{25} 1.4302; d_4^{25} 0.8397; $R_{obs.}$ 30.83 ($R_{calc.}$ 30.96) (see Table I for reported constants).

The *3,5-dinitrobenzoate* melted at 56.5–57.0°.

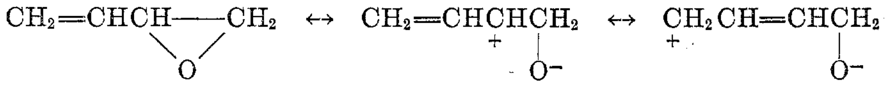
The *allophanate* melted at 169.0°.

SUMMARY

The addition of diethylmagnesium to 3,4-epoxy-1-butene gives only two products in a 3:1 ratio; namely, 2-vinyl-1-butanol and 2-hexen-1-ol. The addition of ethylmagnesium bromide gives about 8% of butadiene monobromohydrin and three major products in a ratio of 4:3.3:2.7; namely, 2-vinylbutanol, 2-hexen-1-ol, and 5-hexen-3-ol.

The structure of 2-vinyl-1-butanol is proved by hydrogenation to 2-ethyl-1-butanol; by conversion to 2-ethylbutan-1,3,4-triol, followed by quantitative cleavage with only one mole of periodic acid, thus distinguishing it from a possible 1,2,3-triol; and by determination of the infrared absorption bands characteristic of a terminal double bond.

These data are consistent with a reaction controlled by resonance structures of 3,4-epoxy-1-butene, such as:



Brooklyn 2, New York

REFERENCES

(1) Gaylord and Becker, *J. Org. Chem.*, **15,** 305 (1950).
(2) Gaylord and Becker, *Chem. Revs.*, in press.
(3) Semeniuk and Jenkins, *J. Am. Pharm. Assoc., Sci. Ed.*, **37,** 118 (1948).
(4) Gmitter and Benton, *J. Am. Chem. Soc.*, **72,** 4587 (1950).
(5) Thompson and Torkington, *Proc. Royal Soc.*, **184** A., 3 (1945).
(6) Thompson and Whiffen, *J. Chem. Soc.*, 1412 (1948).
(7) Freedman and Becker, *J. Am. Chem. Soc.*, **73,** 2366 (1951).
(8) Delaby, *Compt. rend.*, **175,** 967 (1922).
(9) Ginnings, Herring, and Coltrane, *J. Am. Chem. Soc.*, **61,** 807 (1939).
(10) Henze, Allen, and Lesli, *J. Org. Chem.*, **7,** 326 (1942).
(11) Kiun-Houo, *Ann. chim.*, **13,** 175 (1940).
(12) Shreve, Heether, Knight, and Swern, *Anal. Chem.*, **23,** 277 (1951).
(13) Cottle and Hollyday, *J. Org. Chem.*, **12,** 510 (1947).
(14) Tiffeneau and Tchoubar, *Compt. rend.*, **207,** 918 (1938).
(15) Tiffeneau, Weill, and Tchoubar, *Compt. rend.*, **205,** 54 (1937).
(16) Tiffeneau, Weill, and Tchoubar, *Compt. rend.*, **205,** 144 (1937).
(17) Deux, *Compt. rend.*, **211,** 441 (1940).
(18) Tchoubar, *Compt. rend.*, **214,** 117 (1942).
(19) Bedos, *Compt. rend.*, **189,** 255 (1925).
(20) Ritter and Russell, *J. Am. Chem. Soc.*, **58,** 291 (1936).
(21) Arbusov, *J. Gen. Chem.* (U.S.S.R.), **9,** 255 (1939); *Chem. Abstr.*, **33,** 6280 (1939).
(22) Stewart and Ubbelohde, *J. Chem. Soc.*, 2649 (1949).
(23) Evans and Pearson, *J. Am. Chem. Soc.*, **64,** 2868 (1942).
(24) Kadesch, *J. Am. Chem. Soc.*, **68,** 41 (1946).
(25) Bartlett and Ross, *J. Am. Chem. Soc.*, **70,** 926 (1948).
(26) Russell and VanderWerf, *J. Am. Chem. Soc.*, **69,** 11 (1947).
(27) Adams and VanderWerf, *J. Am. Chem. Soc.*, **72,** 4368 (1950).
(28) Ettlinger, *J. Am. Chem. Soc.*, **72,** 4792 (1950).
(29) Norton and Hass, *J. Am. Chem. Soc.*, **58,** 2147 (1936).
(30) Diehl and Hart, *Anal. Chem.*, **21,** 530 (1949).
(31) Brae, *Anal. Chem.*, **21,** 1461 (1949).
(32) Shriner and Fuson, "*Systematic Identification of Organic Compounds*", third edition, John Wiley and Sons, New York, N. Y., 1948, p. 165.
(33) Blohm and Becker, *J. Am. Chem. Soc.*, **72,** 5342 (1950).
(34) Swern, Billen, Findley, and Scanlan, *J. Am. Chem. Soc.*, **67,** 1786 (1945).
(35) Malaprade, *Bull. soc. chim.*, **43,** 683 (1928).
(36) Hovorka, Lankelma, and Smith, *J. Am. Chem. Soc.*, **62,** 2373 (1940).
(37) Sutter, *Helv. Chim. Acta*, **21,** 1266 (1938).
(38) Clarke, "*Semimicro Quantitative Organic Analysis*", Academic Press, Inc., New York, N. Y., 1943, p. 43.
(39) Kharasch and Fuchs, *J. Org. Chem.*, **9,** 359 (1944).